

## Atomistic simulations of H2 and He plasmas modification of thin-films materials for advanced etch processes

Vahagn Martirosyan

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# Communauté UNIVERSITÉ Grenoble Alpes

## THÈSE

Pour obtenir le grade de

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Présentée par

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Modification de matériaux en couches minces par plasmas H2 ou He : Simulations atomistiques pour procédés de gravure innovants

## Atomistic simulations of H2 and He plasmas modification of thin-films materials for advanced etch processes

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## Table of abbreviations

Symbol	Description
ALE	Atomic Layer Etching
ARDE	Aspect Ratio Depending Etching
CCP	Capacitively Coupled Plasma
CMOS	Complementary Metal Oxide Semiconductor
CW	Continuous Waves
FDSOI	Fully Depleted Silicon on Insulator
FET	Field Effect Transistor
ICP	Inductively Coupled Plasma
IEDF	Ion Energy Distribution Function
LTM	Laboratoire des Technologies de la Microélectronique
MD	Molecular Dynamics
MOSFET	Metal Oxide Semiconductor Field Effect Transistor
REBO	Reactive Empirical Bond Order
RF	Radio-Frequency
RFA	Retarding Field Analyzer
RIE	Reactive Ion Etching
TEM	Transmission Electron Microscopy
XPS	X-ray Photoelectron Spectroscopy

## Chapter 1

## **General Introduction**

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We are leaving in the world where microelectronic devices such as smartphones, computers, cameras, sensors and many other ones, became an inseparable part of our life. These devices have evolved for the last 40 years, and will evolve as long as there is a demand. One part of this demand is surely based on the necessity of people to have more and more powerful and less expensive gadgets in their quotidian, since these devices allow to ameliorate their life. In this context, microelectronics has enjoyed an extraordinary success since its birth in the 60's; for example, it is sufficient to say that most part of smartphones released in 2017 are much more powerful and functional than most part of computers only ten years before, and the prices are not comparable neither. However, the production of smartphones, is far from being the only field necessitating the development of MI (Artificial Intelligence) and of numerical simulations, two fields which were born and developed alongside microelectronics, and which are nowadays coexisting as a mutual aid system. Although the performance of computing devices has increased significantly, currently it is highly insufficient for multiple simulations; therefore, the further

evolution of microelectronics should allow us to move faster towards the fundamental understanding of Physics (nature). Although it is easy to see the rise of microelectronics each year, one should know that there is a huge scientific, engineering and computer work behind this progress, and that each year, overcoming new technological problems becomes more and more challenging. In this thesis work, we will deal with one of these specific challenges, but in order to understand the related problems, let's take a short review on micro-components bases and examine the tools used in their fabrication.

#### 1.1. The evolution of Microelectronics

First, let's start with some notions and definitions, which are unavoidable in the world of microelectronics.

A **semiconductor** is a material that has an electrical conductivity value falling between that of a conductor, such as copper, and an insulator, such as glass.

In other words, semiconductors are neither conductors nor insulators; however, as one can guess from the name, in some cases it can behave like a conductor, and this property is at the heart of transistor fabrication and operation.

A **transistor** is a semiconductor device used to amplify or switch electronic signals and electrical power.

The concept of field effect transistor (FET) was patented by Julius Edgar Lilienfeld in 1926 [Lilienfeld 26], but the first practically implemented device was a point-contact transistor, invented in 1947 by William Shockley, John Bardeen and Walter Brattain [Bell Labs]. The transistor is the building block of modern electronic devices and has revolutionized the world; its inventors worthily shared the 1956 Nobel Prize in Physics for their achievement. There are multiple types of transistors but here we focus on the most used in microelectronics: the field effect transistor. As it was mentioned, semiconductors are not conductive, i.e. there is no free charge inside these materials; however, it is possible to add electrical charges into materials via doping (using ion implantation). There are two types of doping, n and p; the first one consists in implanting additional negative charges (electrons), the other one positive charges (holes). Figure 1.1 shows an *npn* transistor, with a metal gate and an insulator between the substrate and the gate. When there is no voltage applied on the gate, some electrons diffuse and cross the *np* border, creating a barrier for the further diffusion of electrons and thus blocking the current. On the

contrary, when a positive voltage is applied on the metal gate, this attracts the electrons and creates a channel allowing electrons to flow through it.



Figure 1.1. Example of a FET (field effect transistor). When there is no voltage applied on the gate, there is no current between the source and the drain: the transistor is OFF. When there is a positive applied voltage, there is a current flowing through the channel: the transistor is ON

Using this property, we can create two states in the transistor, OFF when there is no current, and ON when there is one, which gives a possibility to create a binary system. The magic of the transistor is the invariance regarding to its size. Since transistor operation does not depend on its dimensions, the miniaturization of components could start in the early 60's and continue until today, which played a key role in the successful development of microelectronics. From Figure 1.1, we can understand what advantages the miniaturization brings: by reducing the size of the transistor, we hit 3 targets at a time:

- Smaller transistors are faster, since the electrons must pass a shorter distance (gate length) during the switch (ON/OFF)
- Smaller transistors are less energy consuming, since smaller transistors require lower voltage to switch
- Smaller transistors generate less material waste

The first transistor was the size of a human palm, while in December 2016, **TSMC**, **GlobalFoundries**, **IBM** and **Samsung** separately presented papers on 7nm FinFET technology [IEDM 16]. Figure 1.2 illustrates well this race to miniaturization by showing, on the left, a 5Mb hard drive produced in 1956 by IBM, and on the right, a standard current micro-SD produced in 2017, which can easily have a storage capacity greater than 256 GB. This is an illustration of the famous Moore's law, predicted by Intel co-founder Gordon Moore in 1965, saying that the number of transistors per square inch on integrated circuits will double every year.



Figure 1.2.

(left) IBM 5MB hard drive in 1956, price in 1956 3200\$ ⇔ ~30000\$ in 2017 (right) Micro-SD 256 GB in 2017, price ~100\$

Price per MB is decreased more than 15 million times.

Nevertheless, this race to miniaturization may stop soon since transistors are reaching dimensions where quantic effects are not anymore negligible, which can perturb the expected properties of micro-components.

Given the current size of advanced transistors, we understand they cannot simply be handmade, so let's study the physics/technology allowing the fabrication of such tiny structures. Currently there are two principal ways to fabricate such micro-components, which are known as "bottom-up" and "top-down" methods. The "bottom-up" method consists in assembling the elementary (molecular or even atomic) components into a complex structure, like in the famous video-game "Tetris". However, this approach is not highly adopted by the industry, since it is very time consuming and thus not applicable for massive fabrication. The "top-down" method is a combination of lithographic and plasma etching steps for the construction of complex material stacks. This method has always been used for the fabrication of integrated circuits; all its steps have evolved (and have been ameliorated) with time, allowing the successful miniaturization of micro-components. The role of etching in this procedure is to transfer patterns in the active layers of the transistors. Historically (until the 80's), this step was performed using wet etching processes. They were later replaced by dry (plasma) etching processes, since plasmas allow to achieve anisotropic etching (see Figure 1.3), which is vital for the fabrication of the newest transistors, having sizes of ~10nm.



Figure 1.3. Illustration of wet (isotropic) etching and dry plasma (anisotropic) etching.

#### 1.2. Low-temperature reactive plasmas

Plasma is one of the four fundamental states of matter (plasma, gas, liquid, solid) and represents 99% of the matter in the Universe. Maybe the simplest definition of a plasma is as follows:

#### Plasma is a totally or partially ionized gas.

It is composed of stable molecules, neutral atoms, electrons and ions, but this collection of charged particles is, on average, electrically neutral. Plasmas can be classified according to their charged particle density (ne in cm<sup>-3</sup>) and their electron temperature (Te in eV). One of the most important property of plasmas is known as quasineutrality, i.e. that the density of negative species (electrons and negative ions) is equal to the density of positive species (positive ions). As the quasineutrality suggests, a plasma is globally neutral, but not always, or more precisely, not everywhere: significant charge densities can spontaneously exist only within some distance which is known as the Debye length [Lieberman 05]. The other representative property of a plasma is its tendency to preserve the quasineutrality, which induces various plasma behaviors like the plasma oscillation. If in some region of a plasma, some part of electrons is rolled away, it creates a positive space charge region, which will attract back these electrons. In reality, this is what happens in a plasma permanently: electrons being faster tend to escape from the plasma, but are attracted back, and this process is repeating, which is known as the plasma oscillation. The frequency of this oscillation, called electron plasma frequency, is one of the fundamental characteristic of plasmas [Lieberman 05]. Plasmas can be natural (like the core of the Sun, the interstellar space, the aurorae) or artificial. Among the artificial plasmas, one can distinguish the "hot plasmas" (used for magnetic and inertial confinement fusion), the "thermal plasmas" (widely used in metallurgy) and the "cold (or low-temperature) plasmas", used for material processing in microelectronics and which are further described below.

#### 1.2.1. Structure of radio-frequency (RF) glow discharges

To create artificially a plasma from a gas, one should supply enough energy to ionize it. In the microelectronic industry, glow discharges are obtained by applying an electric field to a gas into a reactor. Since a gas is normally composed of neutral molecules and atoms only, this electric field should cause nothing, but as often in nature, there are some impurities in the system. In this case, there are some randomly and freely moving electrons, which can respond instantaneously to this electric field. These few electrons, which gain energy (i.e. are heated) by absorbing the electrical power, collide with other particles and can ionize them (detach an electron), initiating a chain reaction called electron avalanche.

The generation of a simple RF (radio frequency) glow discharge created in a reactor is illustrated in Figure 1.4(a,b).





The gas is confined in the reactor Figure 1.4(a), where there is an electrode contacted to a RF source, which is able to generate signals of type  $E = E_0 + A * \sin(\omega t)$ . Once the RF is applied, as presented in Figure 1.4(b), free electrons are responding to this electric field, and inelastic collisions between electrons and other plasma species can accomplish any of the following processes:

- Excitation: A + e → A\* + e; A\* → A + hv<sub>A</sub>. The electron impact excitation is responsible for the glow and the color of plasma discharges.
- Dissociation: A<sub>2</sub> + e → A + A + e. This process converts relatively unreactive etch gas molecules into chemically reactive radicals, often used as precursors in deposition or etching mechanisms.
- Ionization: A + e → A<sup>+</sup> + e. This process is indispensable to maintain the plasma and is the most energy-requiring one. It takes place for all type of elements but for different electron energy thresholds. The most resistive gas vis-a-vis to ionization is helium, which needs 24.7eV to release an electron. It is also possible to have a dissociative ionization A<sub>2</sub> + e → A + A<sup>\*</sup> + e.
- Attachment: A + e → A<sup>-</sup>. Although negative ions do not play a direct role in material processing, this process should not be underestimated. Indeed, it is usually favored compared to ionization and the presence of negative ions can modify the plasma properties (sheaths, ion flux, etc.). Often this process occurs alongside with molecule dissociation.

Glow discharges are driven/sustained electrically and can be excited at various frequencies (DC or lowfrequency, RF, microwave). Plasmas used for etching or deposition are often driven at frequencies lying between 1MHz and 200MHz, i.e. within the radiofrequency (RF) domain. In particular, 13.56MHz and its harmonic are standards which have been set aside for industrial applications. Indeed, since the masses of ions and electrons are very different (e.g. H<sup>+</sup> ions are 1836 times heavier than electrons in a hydrogen plasma), in the RF range, these species react very differently to the electric field: electrons being very mobile follow the instantaneous variations of the electric field, meanwhile the ions respond only to its time-average value. For very low frequencies, ions could follow the electric field as well, and vice versa, for very high frequencies, electrons would stop do it. This distinct behavior rises an exceptional property of RF glow discharges: each type of species is in thermal equilibrium with itself, meanwhile they are not in equilibrium with each other. In particular, due to the weak energy coupling between electrons and heavy particles ( $m_e \ll m_{i,n}$ ), the temperature of electrons is much higher than that of ions and neutrals, classically  $T_e \sim 3eV \sim 35000K$ , and  $T_i \sim T_n \sim 300-1000K$ .

#### 1.2.2. Plasma sheath and directional ion bombardment

Since the plasma is enclosed in a reactor chamber, there is a flux of particles towards the walls. This flux is given by the formula  $\Gamma = \frac{1}{4} \cdot n \cdot v_{th}$ , where *n* is the particle density and  $v_{th}$  is the thermal velocity of particles and can be computed as  $v_{th} = \sqrt{\frac{8K_bT}{\pi m}}$ , where T is the temperature of the species and m is its mass. Since  $T_e \gg T_i$  and  $m_e \ll m_i$ , thus  $\Gamma_e \gg \Gamma_i$ . This means that the plasma should lose electrons faster than ions, which is impossible at steady state since in this case the plasma would not remain quasineutral. Thus, the flux equality  $\Gamma_e = \Gamma_i$  must be fulfilled, but how? In the first instants of plasma, when switching the discharge, electrons are favored to go to the walls (see Figure 1.5(a)): after this step, which happens almost instantaneously since electrons are very rapid, a positive space charge region is created between the walls (which get negatively polarized) and the plasma. This positively charged region is called the sheath and is represented in green (the color which corresponds to ions) in Figure 1.5(a). Sheaths, which ensure that the plasma remains guasineutral, are small regions (~100µm-1cm) where substantial electric fields can develop across. Their role is to confine low energy electrons (and negative ions) into the plasma and to accelerate positive ions towards the walls. Since the flux of bombarding ions is anisotropic (parallel to the electric field) and since their energy can be tuned (by controlling the sheath voltage), sheaths are obviously interesting for surface treatment in general and in particular for etching applications. On the contrary, as illustrated in Figure 1.5(b), neutral species (atoms and molecules) are ignoring this effect and tend to diffuse isotropically towards the surfaces where they can - eventually - chemically react.



Figure 1.5. (a) First instants of the plasma, favored loss of electrons on the walls. (b) Creation of sheaths, which equilibrate the ion and electron fluxes on the walls.

The understanding of the sheath formation becomes more coherent when ion and electron fluxes are described quantitatively. To do that, let's use the fact that at steady state,  $\Gamma_e = \Gamma_i$ , and solve it mathematically for an electropositive plasma. This calculation was first done by Bohm in 1949. It was shown that when the sheath is established, on its edge the ions have a velocity  $V_i$  higher than  $U_b = \sqrt{\frac{kT_e}{m_i}}$ , which is known as the Bohm criteria. Often it is also interpreted in reverse: for the sheath to be established, on the edge of the sheath, ions should have a velocity at least equal to  $U_b$ . A more detailed structure of the plasma discharge is given on Figure 1.6.



Figure 1.6. Structure of the discharge: plasma species density (electrons, ions and neutrals) and potential profiles depending on the location. The sheath region is represented in green.

At steady state, the flux of positive ions at the walls is given by the following formula:

$$\Gamma_{\rm i} = 0.6 \cdot n_0 \cdot U_b, \quad (1.1)$$

where the  $n_0$  is the electron density in the center of plasma, this flux being called the Bohm flux. And the plasma potential is given as follows:

$$V_{plasma} = \frac{1}{2}kT_e * \ln\left(\frac{m_i}{2\pi m_e}\right). \quad (1.2)$$

The derivation of these formulas is detailed elsewhere [Lieberman 05], nevertheless we can understand them intuitively. Since the ions are entering the sheath with the Bohm velocity, the linear dependence between this velocity and the ion flux is clear, as well as the dependence on  $n_0$ , since on the sheath edge the ion density is  $n_0$ . The dependence of the plasma potential (V<sub>plasma</sub>) on the electron temperature (Te) is easy to understand: the higher the electron temperature, the more electrons will be lost at the walls, and thus the more positively charged the plasma will be compared to the walls. The dependence on the ion mass can be explained by the following statements. Firstly, the plasma is created and sustained via transformation of the electrical power (RF) into kinetic energy of electrons, a part of which is then converted into potential energy (sheath), which is afterwards dissipated by ions impinging on the walls. The heavier the ions, the smaller the Bohm flux (following the Bohm criteria). Thus, since the ion energy acquired in the sheath does not depend on the ion mass, the smaller the dissipated energy on the walls, and consequently the higher the plasma potential. The electron temperature in his turn depends on the plasma pressure and the reactor geometry. Since classically Te ~3eV, for most gases it gives about ~15eV of plasma potential, which means that the ions impinging on the walls have at least ~15eV.

Note that the nature of sheaths and plasma discharges can be much more complicated, and that here only a simplified model was given. For a more detailed description, the readers are invited to examine other works specifically dedicated to RF plasma discharges [Lieberman 05].

#### 1.3. Low-pressure plasmas for material processing in Microelectronics

Now that the operation of a discharge is more or less understood, we can learn how it can be applied for material processing in microelectronics. The main two properties of discharges exploited in microelectronics are: the isotropic flux of radicals, and the anisotropic flux of energetic ions towards the walls.

#### 1.3.1. Surface reactions and etching mechanisms

The main interest of discharges for surface processing lies in the reactions taking place between reactive radicals or ions present in the plasma, and the substrate atoms. Particularly, reactive radicals can chemically react and create volatile products with substrate atoms (which then move back into the plasma), which is known as **chemical etching**. A classic example of such reaction is the etching of silicon by halogens (CI, F, Br), where the formed volatile products are mainly in form of SiX<sub>4</sub>, where X represents the radical used in the process. These reactive radicals may also allow to etch one material selectively with respect to another one, since they do not react similarly with all type of atoms. With an appropriate choice of plasma chemistry, for example, one can stop the etching of a specific thin layer when the underlying material will be reached. However, chemical etching remains perfectly isotropic, meanwhile one big advantage of dry plasma etching is the ability of anisotropic (directional) etching. This specific ability comes from the plasma ions, which are able to sputter substrate atoms, which is known as **physical etching**. Ions are indeed accelerated towards the surface, and mostly promote the

vertical etching. The role of impacting ions on etching anisotropy is very complex and is very casedependent. Particularly, depending on the ion type, the ion energy or the targeted material, the mechanisms of how ion bombardment promotes the anisotropic etching are very diverse. The most distinguishing property of physical etching is its ability to etch non-volatile products. In some processes, the effects of only one of these two plasma species (radicals or ions) may be wanted. Yet in classical ICP/CCP plasmas (see section 1.4.2 for details), we deal with the combination of these two effects known as **RIE** (Reactive Ion Etching). RIE is not a simple combination of two etching mechanisms, but a synergy between them, which yields quite new properties. Particularly, the resulting etch rate (i.e. the speed of etching) may be much faster than the sum of each mechanism etch rate taken apart [Coburn 79]. Of course, the fundamental interpretation of this ion-neutral synergy is quite complex and casedependent, which is one of the reasons of empirical research in microelectronics.

#### 1.3.2. How to transfer a pattern into a material stack?

It may be a bit sophisticated to enter directly in the application of plasma discharges for the fabrication of new type of transistors, so here we just study some elementary bricks, which are implied in such processes, and only in abstract forms, to preserve the genericity.

**Example 1**. Imagine that we have a substrate of element A, and we want to remove few nanometers of this material from the top (see Figure 1.7(a)). We place the substrate above the electrode in the discharge chamber, and we use a plasma which is able to etch material A.





In this case the material will be etched via RIE, and to remove the given thickness from the top, it is sufficient to estimate the etch rate, and compute the necessary plasma exposure time.

**Example 2.** Now let's imagine that we have a substrate of element A, and we want to add few nanometers of element B upon the first one (see Figure 1.8(a)). In this case, a method named CVD (chemical vapor deposition) is often used, which has numerous variations, like LPCVD (low pressure

CVD), UHVCVD (ultra-high vacuum CVD), etc. But let's consider here a deposition technique which implies a plasma, i.e. the PECVD (plasma enhanced CVD). One should thus take a plasma containing the element B (see Figure 1.8(b)), and place the substrate above the electrode in the discharge chamber.





In this process, the main role is played by radicals (chemically active), which will continuously bind to the dangling bonds of the substrate, allowing element B to progressively grow upon element A.

**Example 3.** Finally, consider a much difficult process implying more steps. Let's try to create a pattern in a substrate (see Figure 1.9(a)). In the first step (Figure 1.9(b)), a photoresist is deposited on material A. A photoresist is a light-sensitive material, which degrades when it is exposed to light emission, and then the degraded part is easily removed using an appropriate chemistry. Then, using a mask, we create a pattern in material B (Figure 1.9(c)). Afterwards we proceed to the etching step, where we choose a plasma chemistry that can etch material A but cannot etch material B (selective etching), in order to etch only the part where A is not protected by B (Figure 1.9(d)). Finally, we remove the photoresist by degrading it via light emission exposure (Figure 1.9(e)). From this simple example, we can evoke a lot of technical problems involved in this process and encountered in real experimental conditions, but let's consider only those that are related to the etching.



Figure 1.9. Creation of a pattern into the substrate, using deposition, photolithography and plasma etching.

As seen in Figure 1.9(e), after the etching step the pattern has a perfect rectangular form, i.e. the etching was faultlessly anisotropic. This is almost impossible in practice, since among the species impinging on the substrate, only ions have a normal incidence (anisotropic flux). Since reactive radicals are coming isotropically, they tend to induce a lateral etching, which in this case can create some undercutting feature like in Figure 1.10(a), which may in turn affect the properties of micro-compounds.



Figure 1.10. Pattern transfer related problems. (a) Isotropic etching (b) ARDE, aspect ratio dependent etching

Another problem, known under the name ARDE (aspect ratio dependent etching), is illustrated in Figure 1.10(b), where the rate of lateral etching decreases with the increase of the aspect ratio (ratio between the depth and width of the pattern). One of the reasons for such a behavior is simply the fact that the

radicals tend to reach more and more difficultly the bottom when the depth increases, since their flux is isotropic.

In this subsection, some simple and generic examples of pattern transfer by etching were shown, to give an idea about the goals in micro-fabrication and the encountered problems. However, in the microelectronics industry, problems are usually less abstract, since each small parameter may change crucially the problem (e.g. gas chemistry, reactor geometry, plasma source, substrate material, temperature, etc.), which turns micro-fabrication processes into a complex combinatory problem.

# 1.4. Technological challenges of advanced plasma etching processes for next-generation transistors

For the development of new type of transistors, like the FinFET or FDSOI (Fully Depleted Silicon on Insulator), there is a necessity to etch complex material stacks with a nanoscale precision and an almost infinite selectivity to preserve the electronic properties of active layers (e.g. silicon channel). To understand this necessity and where it comes from, one should first know the general structure of these advanced transistors.

#### 1.4.1. Structure of advanced transistors (FinFET and FDSOI)

In Figure 1.11(a) is illustrated the structure of a standard MOSFET (Metal Oxide Semiconductor Field Effect Transistor),





which was the main structure of transistors manufactured until 2012. Their dimensions were reduced over 40 years, but these transistors, also known as planar 2D transistors, finally met their limits in the race of miniaturization. Indeed, because of the transistor shrinking, the length of the gate decreased as well. This led to reduce the control the gate exercises over the channel region, and in particular, the leakage current became more and more problematic.

To overcome the discussed issues, numerous researches were launched in the 2000s. One possible technology making possible to solve these problems and allowing to preserve existing manufacturing processes was the FDSOI. It is represented schematically on Figure 1.13(b). The difference compared to a standard planar transistor is simple: firstly, an ultra-thin layer of insulator is placed above the silicon bulk, which is called BOX (buried oxide), and then a very thin layer of silicon film plays the role of the channel. Thanks to its thickness, there is no necessity to dope the channel, thus making the transistor fully depleted.



#### Figure 1.12. (a) Structure of a planar bulk transistor, (b) structure of a FDSOI.

As it is illustrated on the Figure 1.12, this simple modification highly reduces performance-degrading leakage currents [STMicroelectronics], since the current is confined in this case. Even if this technology was used by numerous companies like IBM, TSMC and STMicroelectronics, currently only the last one continues to support it. The other companies have migrated to the development of new 3D FinFET transistors proposed by Intel.

In the 2000s, University of California (Berkeley) researchers proposed a new design of transistors, known as FinFET (Fin Field-Effect Transistor) or 3D transistor, which is presented in Figure 1.11(b) (channel in green) [Chenming 00, Hisamoto 00]. In this case, the gate electrode has an excellent control over the channel because it surrounds the channel, which allows to reduce more the gate length. These transistors are already manufactured and can be found in recent products of various companies, like Intel, AMD, NVIDIA, etc. Figure 1.13(a) shows a simplified version of this modern transistor but does not give its complete structure; indeed, each brick inside is in fact covered by specific thin layers, which

are necessary to preserve the high functionality of the scheme. In Figure 1.13(b), the cross-cut of a FinFET is shown, where we can see the gate, a Poly-Si surrounded laterally by silicon nitride spacers and covered on top by a silicon dioxide mask. Notably, these silicon nitride spacers allow to insulate the leakage current, and their use is very common in the design of advanced transistors (e.g. in FDSOI it is used for the same purpose).





To obtain such a structure, first silicon nitride is deposited all over the surface; then it is etched anisotropically, leaving the silicon nitride spacer only on the vertical sidewalls of the gate, as illustrated in Figure 1.14.



#### Figure 1.14. Scheme of the deposition and etching of silicon nitride spacers

These spacers are only few-nanometers-thick, and their removal should be done very cautiously to avoid any damage on the underlying Si, which could affect the electrical properties of the transistor. This specific etching step is a tough challenge, which is at the heart of this PhD work. It is discussed in the next subsections alongside with the limitations of conventional plasma processes.

#### 1.4.2. Limitation of conventional plasmas processes (CW-ICP and CCP)

Plasma reactors must meet high requirements in terms of etching (high etch rate, anisotropy, selectivity, uniformity, etc.) while supporting increasing substrate sizes. In addition to the chamber geometry and the excitation frequency, it is the coupling mode of the electric power to the plasma which differentiates them most. In the microelectronics industry, two types of RF sources are mainly used: the CCP (Capacitively Coupled Plasma) and the ICP (Inductively Coupled Plasma).

CCP reactors were the first ones used for the RIE in the 1970-1980s. The schematic of a CCP is shown in Figure 1.15(a). It is generally a parallel plate reactor, in which a plasma is confined between two electrodes, where one of them is coupled to a RF power through a capacitor, and the other one is grounded.



Figure 1.15. (a) Structure of a CCP reactor, (b) Evolution of the voltage on the RF electrode when the plasma is switched ON.

As it was discussed above, the minimal ion energy in such plasmas is about 15-20 eV, which corresponds to the plasma potential, but often much higher energies are required in etching procedures. In a CCP when the RF is switched ON, the plasma, aiming to keep the quasineutrality, will respond instantaneously. It will lose a lot of electrons, which will go on the upper plate of the capacitor and will charge it negatively, which in turn will shift down the RF voltage on the powered electrode below the plasma potential Vp (see Figure 1.15(b)). Ions, due to their inertia, will only see the mean voltage, also called the self-bias voltage: -V<sub>bias</sub>. Thus, in order to increase the ion energy on the wafer, one should simply increase the RF power; the voltage on the powered electrode will be shifted down one more time,

and the mean value -V<sub>bias</sub> will be lower (see Figure 1.17). Since the power is coupled capacitively to the plasma, the increase of the RF power will also increase the ion flux. Thus, CCP reactors allow to control the ion energy and the ion flux, but they do not allow to control them independently, which is an important limitation of these plasmas. This problem was overcome in the next generation of dual-frequency CCP reactors, where the RF is applied on both electrodes, but with different frequencies. In this case, the low frequency electrode controls the ion energy by modulating the RF power, while the high frequency electrode controls the plasma density by modulating the RF frequency. Working at moderate pressure (10mTorr to 1 Torr), such reactors however provide relatively low plasma densities (10<sup>9</sup>-10<sup>10</sup> cm<sup>-3</sup>) and high ion energies (100's of eV).



Figure 1.16. Effect of the RF voltage on the self-bias voltage in a CCP.

Much higher density plasmas (HDP) working at very low pressure (<10mTorr) became available thanks to the ICP reactors, in which the power is coupled inductively to the plasma via antennas (see Figure 1.17).





The variation of the RF current in the external coil (separated from the plasma via a dielectric window) induces a varying axial magnetic field, which in turn generates an azimuthal electric field accelerating electrons in the plasma. The excited electromagnetic wave is absorbed in the plasma over a characteristic length called the skin depth, large compared to the sheath size but comparable to that of the discharge. The power transfer is thus efficient and allows to achieve high plasma densities (10<sup>10</sup>- 10<sup>12</sup> cm<sup>-3</sup>). And the higher the power on the RF coil, the higher the plasma density, and thus the higher the ion flux on the walls. A second RF generator is connected to an electrode immersed in the plasma (capacitively coupled to the wafer), which allows to accelerate the ions toward the electrode surface with the desired energy, and to have an independent control of the ion flux and the ion energy. ICP reactors permit to obtain plasma densities/ion fluxes an order of magnitude higher than in CCP reactors.

Nevertheless, these CCP and ICP reactors have a common limitation: they provide ion energies at least equal to ~15eV, which induce surface damages on a few nanometers during and after the etching [Brichon 14]. Mainly this damage is brought by the energetic ions, which can break the covalent bonds of the substrate, leading to the creation of dangling bonds inside the substrate and to the formation of diffusion paths. Often the ion bombardment amorphizes the crystalline structures [Wei 84, Vallier 99, Tuda 01, Vitale 03, Fukasawa 11], which can affect the electrical properties of thin layers. Moreover, chemically reactive plasmas lead to the formation of mixed layers near the surface [Brichon 15], which can compromise the etch precision. Another limitation of CW-ICP plasmas is the high plasma

dissociation rate, which induces high fluxes of radicals on the wafer and thus highly increases the etch rate. As a result, even the control of the etched thickness becomes very challenging. The discussed limitations constitute a serious problem for thin films etching, as illustrated on the following example of SiN spacers etching in FDSOI.

#### FDSOI - Etching of silicon nitride spacers

The fabrication process of FDSOI transistors implies several steps. In particular, the etching of silicon nitride spacers must be achieved with a nanoscale precision, in order to stop precisely on the crystalline silicon channel, as illustrated on Figure 1.18. Indeed, the underlying silicon layer must remain undamaged (structurally and chemically) to preserve its initial electrical properties and be compatible with the upcoming epitaxial steps. The CH<sub>3</sub>F/O<sub>2</sub>/He chemistry, often used in this step, is however not consistent with these requirements.



Figure 1.18. Etching step of silicon nitride spacers for the fabrication of FDSOI transistors.

It was shown that using a CW-ICP, a mixed  $SiO_xF_y$  layer is forming in the silicon channel [Blanc 14], as illustrated on Figure 1.19.





As one can see on Figure 1.19, a mixed SiNO<sub>x</sub>F<sub>y</sub> layer is initially created in the silicon nitride surface. It is then continuously transferred towards the subsequent layers, and finally it is merged with the crystalline silicon channel, forming a few-nanometers-thick (3-5nm dependent on the bias power)  $SiO_xF_y$ mixed layer. Even if this layer can be eliminated using a HF bath, it was shown that this process causes a serious consumption of silicon, also named "silicon recess". From this example we see that continuous-wave ICP or CCP processes are not acceptable for several fabrication procedures, where thin films etching is implied. The next subsection speaks about alternative plasma technologies allowing to overcome these issues.

#### 1.4.3. Alternative plasma technologies for advanced etching processes

The major issue of conventional CCP and ICP plasmas for ultrathin layers etching is the relatively high ion bombardment energy (>15 eV) reaching the substrate. In this subsection, we discuss alternative plasma processes, which allow to decrease the incident ion energy. To achieve such a goal, one solution is to lower the electron temperature (Te) of the plasma, temporally (by pulsing the plasma) or spatially (by segregating the electron heating region far from the wafer).

#### **Pulsed plasmas**

Conventional ICP plasmas are often called CW-ICP (continuous wave ICP), which means that the RF source power is continuous; in pulsed ICP plasmas, the source power can be modulated temporally. The procedure is very simple: the RF power coupled to the coil is switched consecutively ON and OFF, which gives two additional parameters to control the plasma, the frequency  $f = 1/(t_{ON} + t_{OFF})$ , and the duty cycle  $DC = t_{ON}/(t_{ON} + t_{OFF})$ , where  $t_{ON}$  and  $t_{OFF}$  are the periods when the RF power is ON and OFF, respectively. Pulsing the plasma allows to have an augmented control over the incident ion energy distribution, the plasma dissociation, the electron temperature and other parameters. When a frequency of pulsation ~1kHz is chosen ( $t_{ON} + t_{OFF} \approx 1$ ms), since electrons are extremely mobile and the electronic temperature  $T_e$  evolves on timescales of about 10 µs, during most of the OFF period,  $T_e$  is about zero (see Figure 1.20(a)). The decrease of  $T_e$  decreases the plasma potential  $V_p$ , which decreases in average the incident ion energy (< 15 eV), as presented in Figure 1.20(b).



Figure 1.20. (a) Evolution of the ion flux and electron temperature when pulsing the plasma [Lieberman 96]. (b) Measured ion energy distribution functions for different duty cycles in pulsed Cl<sub>2</sub>-based plasmas [Brihoum 13].

Also, since the plasma dissociation is induced by electron inelastic collisions, it mostly takes place during the ON period meanwhile recombination takes place permanently. As a result, the pulsed discharge is on average less dissociated and its chemical reactivity can be controlled with the duty cycle. Like the RF source power, the bias power can be pulsed as well, and synchronized or not with the source power, which yields various combinations of pulsing mode. However, pulsing the bias power only is usually not interesting to minimize the ion energy, because in that case the ion energy will be higher than 15eV anyway.

#### Low-Te plasmas

Since the key parameter to reduce the ion energy is the electron temperature, new plasma reactors were developed in the 2010s to reach this goal, in particular by TEL (Tokyo Electronics Lim.). In these plasmas, the electron temperature is lowered spatially, by segregating the electron heating region far from the wafer. Different types of sources exist. One of them consists in inserting a negatively charged grid (at a constant potential) in a classical ICP, some centimeters above the electrode, which divide the plasma in two regions (see Figure 1.21(a)).



Figure 1.21. (a) Structure of a low-Te plasma [Bai 07]. (b) Electron temperature and density as a function of the grid (inserted in the plasma) polarization [Ikada 04].

The grid, located a few centimeters above the substrate, decreases the electron temperature in Region II. Indeed, Region I remains a classical ICP, meanwhile the electrons generated in Region I and which diffuse in Region II, obtain the energy imposed by the potential difference between the grid and the plasma potential in Region II. There, most electrons lose their energy by inelastic collisions, while those with high energy escape rapidly at the reactor walls. As a result, the electron temperature in Region II is less elevated [Hong 99] and can be modulated (like the electron density) by the polarization of the grid [Ikada 04], as shown in Figure 1.21(b) Electron temperatures lower than 1 eV can be obtained, which is two to three times lower than electron temperatures in conventional ICP plasmas.

#### **Atomic Layer Etching**

Finally, Atomic Layer Etching (ALE) is a third technique (or concept) for removing ultrathin layers of materials using sequential reactions steps that are self-limiting [Kanarik 15]. It consists in alternating several steps (deposition/passivation, purging, etching/desorption, etc.) in order to remove only one atomic layer of a substrate. This sequence of steps (or cycles) is repeated several times to perfectly control the etching of a given material (see Figure 1.22).



#### Figure 1.22. ALE (Atomic Layer Etching) principle [Kim 13].

Although such a concept is promising to etch sub-nm-thick stacked materials, experimentally, it is often impossible to damage only one atomic layer. Moreover, another problem remains in the extremely low etch rate, which can be achieved using several alternating steps. Thus, the ALE concept cannot yet provide sufficient productivity on an industrial scale and requires additional development to become commercially viable.

The two previous discussed techniques (pulsed and low-Te plasmas) propose a way to reduce the incident ion energy (< 15 eV) and to control the plasma reactivity, which is so necessary for ultrathin films etching, but yield other problems limiting their promises. Pulsed plasmas indeed permit to reduce the ion-induced damage (i.e. the mixed layer thickness) but not to eliminate it completely; surface damage of the order of 1nm can still be observed [Petit-Etienne 10], and besides, this method is not self-limited. Low-Te plasmas tend to deposit low-energy ions in polymerizing chemistries and to generate broad ion angular distributions, which affects the directionality and the uniformity of the etching [Kanarik 12]. Of course these limitations do not mean that such plasmas are useless - currently these techniques are used in the industry - but alternative approaches may be needed to overcome the aforementioned issues. As one can also remark, new etching processes aim to reuse the existing plasma technologies, only with tiny modifications to solve a given problem. This is not done haphazardly, because all described plasma sources are very expensive, and a completely new technology would require a replacement of existing reactors. Moreover, each of these reactors (CCP, ICP) were studied during dozens of years due to the complex physics related to their structure and geometry, and any new architecture would require such studies likewise, and consequently would be both time and money consuming. In this context, a new approach was recently proposed by Posseme et al. for silicon nitride spacer etching [Posseme 14, Smart Etch patent 14], that we will call the Smart Etch technique. It implies only conventional plasmas: in a first step, the film is modified in volume by exposition to a  $H_2$  or He CCP or ICP; in a second step, the modified layer is selectively removed by wet cleaning or exposure to gaseous reactants only (downstream plasma). But before detailing this procedure, let's examine why and how hydrogen and helium plasmas are used in microelectronics.

#### 1.5. Light gases (H<sub>2</sub>/He) material modification for nanoscale-precision etching

Hydrogen in its monoatomic form is the lightest and most abundant element in the universe, constituting roughly 75% of all mass; the second one is helium, representing about 24% of all mass. These two ubiquitous elements have plentiful applications in very different branches of Science, from biology to nuclear physics. Their use has not been avoided in Microelectronics either, where they are present in various steps of microfabrication, especially hydrogen. At standard temperature and pressure, hydrogen is a diatomic gas (H<sub>2</sub>) which can be dissociated in chemically reactive H radicals using a plasma source. On the contrary, helium (He) is a monoatomic and inert gas, which cannot form covalent bonds with other atoms. These two elements, which differ mainly by their chemical reactivity, have exceptional properties due to their small size and low weight ( $m_H = 1.008u$ ;  $m_{He} = 4.003u$ ), and can modify materials on a considerable depth with a high precision. One of their first applications in Microelectronics was the Smart Cut<sup>TM</sup> technology.

#### 1.5.1. The Smart Cut<sup>™</sup> technology for SOI substrates preparation

The fact that hydrogen can penetrate deep in a material and transform it was first observed in tokamaks, where H<sub>2</sub> plasmas are used for thermonuclear fusion and where deformations of walls were observed [Das 76]. In 1994, Bruel et al. [Smart Cut patent 94] from CEA-Leti found an excellent application to this phenomenon, named Smart Cut, for the preparation of SOI (silicon on insulator) substrates. The Smart Cut technology, based on light ions implantation and wafer-bonding, is a multistep process which allows to transfer a thin layer of crystalline material from a donor substrate to another substrate (see Figure 1.23). First, hydrogen ions are implanted in a substrate A, inducing the formation of a weakened layer located roughly at the mean ion penetration depth. Afterwards, the implanted wafer A is flipped around and bonded to a stiffener (wafer B). Then a heat treatment phase (or annealing step) results in the cleavage of the weakened layer, allowing to separate the new thin film and the initial bulk material [Smart Cut patent 94]. In the case of SOI, the initial or donor substrate is a thermally grown silicon oxide on silicon, and the stiffener is another wafer of silicon, as shown on Figure 1.23.



#### Figure 1.23. Smart Cut procedure for preparation of SOI substrates.

The Smart Cut procedure is mainly based on hydrogen ion implantation, but the same technique was proposed using helium implantation [Xiang Lu 97]. This technology has a wide range of applications in microelectronics, for example in the fabrication of FDSOI transistors. By enabling any thin-film materials to be transferred on top of any other materials, it could also provide opportunities in emerging fields including sensors, flexibles electronics, 3D applications, display panels and solar cells, etc. Although the full Smart Cut procedure was the subject of various studies in the last twenty years [Aspar 97, Weldon 97, Bedell 01, Moutanabbir 05], there is still a lack of fundamental understanding [Terreault 07]. For instance, as regards the first implantation step, the hydrogen profile in the substrate and the effect of the ion dose or the form in which hydrogen is stored in the substrate remain unclear. Similarly, the annealing step of the Smart Cut and the effect of the heat treatment are not yet entirely understood. In the following section, we will see that this property of light elements (He, H) to cause interior modifications to substrates has recently found another utility in 2014, with the Smart Etch concept.

#### 1.5.2. The Smart Etch concept

As previously discussed, conventional etching methods in CCP or ICP allow to etch materials but tend to generate ion-induced damage and mixed reactive layers of a few nanometers in the underlying substrate, which is not desirable. To solve this problem and overcome limitations of alternative methods like pulsed and low-Te plasmas, an innovative approach was recently proposed, which implies two steps.

#### 1.5.2.1. Principle of the Smart Etch

In the first step, the material to be etched is exposed to a hydrogen or helium plasma in order to modify it by light ion implantation; in the second step, the modified part is removed using wet or dry gaseous etching, as shown on Figure 1.24 for the case of silicon nitride.



#### Figure 1.24. SiN blankets etching using the Smart Etch concept.

From this specific example, the potential of this method may not be fully evident since one should only choose a plasma which can etch selectively SiN with respect to Si. But the Smart Etch concept has many advantages over classical plasma processes when one wants to etch with a nanometric precision. Let's consider that we want to etch only few (2-3) nanometers of a given material. In such a case, conventional CCP or ICP processes, besides damaging the underlayers, may bring another problem, the etch precision, since often etch rates are high which makes it difficult to control the etching. The Smart Etch method makes it possible since light ions are able to modify and weaken the material on a desired depth, without etching it. Because the modified part is much sensible with respect to a given chemistry than the non-modified part, it provides a good selectivity which allows to remove only the modified layer during the second step. Another advantage of this method is the anisotropy provided by the ion implantation, which allows further directional etching. Let's examine this specific ability for the problem of silicon nitride spacers etching in FinFET transistors, which is presented on Figure 1.25.



#### Figure 1.25. Anisotropic etching of silicon nitride spacers using the Smart Etch method [Posseme 14].

The directionality comes from the implantation step, where a standard CCP or ICP plasma is used and where ions are accelerated toward the substrate, which allows to avoid the modification of the walls. The next step indeed uses an isotropic etch method to selectively remove the modified layer, but since the material is modified anisotropically, thus it behaves like an anisotropic one. Now that the Smart Etch concept has been described, we can address its experimental implementation and examine the difficulties encountered in the real processes.

#### 1.5.2.2. Experimental implementation of the Smart Etch concept

#### H<sub>2</sub> or He CCP/ICP exposure followed by a HF bath

One way to perform a Smart Etch is to expose the substrate to a H<sub>2</sub> or He CCP/ICP, followed by a wet etching step in hydrofluoric (HF) acid. In this case, the substrate should be transported from the plasma reactor to the HF bath under vacuum, to avoid oxidation. This technique, normally used for research purposes like in the PhD work of Jerome Dubois [Dubois 16], may give excellent results for thin films etching [Posseme 14, Sherpa 17] but requires a smart and cautious use. Depending on the plasma operating conditions (i.e. pressure, source and bias powers, exposure time, etc.), the ion energy and the ion flux on the substrate may be different, and thus the material modification may be different as well (i.e. the thickness of the modified layer or the rate of modification, which defines the further etch selectivity between the modified and non-modified parts). So, for each plasma condition, these two plasma parameters (ion energy and ion flux) should first be determined. Then, to characterize the material modification after plasma exposure, the substrate should be dipped into a HF bath for different times and the remaining thickness of the substrate should be measured using Ellipsometry (see Figure





#### Figure 1.26. Preliminary measurements of the Smart Etch.

In experimental conditions, to save time, the substrate exposed to the H<sub>2</sub> or He plasma is cleaved in smaller parts, and each part is exposed to different times of HF bath. From these data, the etched layer thickness can be computed, which is represented by the red curve, while the slope of the red curve gives the etch rate (etched thickness/time). This sole measurement allows to determine at a time two important unknowns: the modified layer thickness and the selectivity between the modified and non-modified layers with respect to the HF bath. Once the etch rate (green curve) suddenly decreases to become constant, one can conclude that the modified layer is fully etched. Since the interface between the modified layers corresponds to the etch rate transition point, the modified layer thickness is inferred and the selectivity can be computed as the ratio of etch rates before and after the transition. Once these surface characterization steps are done, the real process can be used. For instance, let's imagine that for a given material and specific plasma conditions (pressure, power, exposure time), preliminary measurements showed that the thickness of the modified layer is 2nm, the etch rate is 12nm/min, and the selectivity is 10. To etch 6nm of this material, one should enchain 3 times the following cycle: plasma exposure + 10 seconds of HF bath.

#### The RADION prototype: H<sub>2</sub> CCP exposure followed by a remote NF<sub>3</sub>/NH<sub>3</sub> plasma

The RADION is a new reactor prototype developed by Applied materials, which is able to work in both CCP and downstream modes. In downstream (remote) mode, energetic plasma ions are filtered so that the wafer, located away from the ionization region, is only exposed to radical impacts. To obtain a downstream plasma, a system of ion-blocking shower is inserted in the plasma above the substrate. The advantage of a downstream plasma over wet etching (e.g. in an HF bath) is the conformity of the

etch; also, it can coexist with other plasmas in the same reactor, like in the RADION prototype. These two modes of operation allow to implement the complete Smart Etch concept in the RADION chamber without removing the substrate from the reactor, which makes the process much faster and eliminates any risk of oxidation. Regarding the process itself, the ion implantation step in a H<sub>2</sub> CCP plasma remains the same. The modified layer removal step is done by reactive radicals generated in a downstream NF<sub>3</sub>/NH<sub>3</sub> plasma; these radicals react with the modified layer to form salts which will be sublimed by heating the substrate.

#### Plasma diagnostics: RFEA and capacitive ion probe

Even if the Smart Etch concept uses only conventional plasmas, it remains a new approach and thus requires a fundamental understanding of all mechanisms involved in the process, especially during the ion implantation step. Particularly, one of the most important part is to study the effect of the ion energy and the ion dose on the substrate modification. To do that, plasma diagnostics should be used to measure both the flux and the energy of ions for given operating conditions. The measure of the ion energy can be obtained with a RFEA (retarding field ion energy analyzer) [Gahan 08, Gahan 09, Gahan 12] like it was done in previous works [Mourey 16, Brihoum 13]. To measure the ion flux, the capacitive probe method proposed by Braithwaite et al. [Braithwaite 96] is often used. These techniques being highly documented in the literature and remaining out of the main interests of the current work are not described here.

#### Surface diagnostics: Ellipsometry, XPS, SIMS

Besides the plasma diagnostics, it is indispensable to perform some surface diagnostics as well, to understand especially the chemico-physical nature of the substrate modification. For this purpose, in various works the following techniques are used: Ellipsometry, XPS, FTIR and SIMS. Like for the plasma diagnostic tools, the operation of these surface diagnostics is not described into details either, and only a brief description of their main capabilities is presented.

**Ellipsometry** is an optical technique for investigating the dielectric properties of thin films, and enables notably to measure the roughness, thickness, composition, or crystalline nature of a given sample [Drevillon 82].
**XPS** (X-ray photoelectron spectroscopy) is a surface-sensitive quantitative spectroscopic technique which measures the elemental composition, empirical formula, chemical state and electronic state of the elements that exist within a material [Briggs 83].

**FTIR** (Fourier transform infrared spectroscopy) is a technique which is used to obtain an infrared spectrum of absorption or emission of a solid. It is commonly used for the chemical analysis of samples with covalent bonds [Tolstoy 03].

**SIMS** (Secondary Ion Mass Spectroscopy) is a technique used to analyze the composition of solid surfaces and thin films by sputtering the surface of the specimen with a focused primary ion beam and by collecting and analyzing ejected secondary ions [Vickerman 13].

To conclude this section, the Smart Etch concept is promising to achieve nanometric-precision etching of materials with both high selectivity and anisotropy, while preserving the integrity of surfaces (stoichiometry and roughness). However, many questions remain. What is the exact role of the ion energy and ion dose on the substrate pre-modification and on the self-limited implantation? How different is the nature (structure, composition) of the modified layer when exposed to a hydrogen or a helium plasma? Although experimental diagnostics can help to provide answers to some of these questions, there is still a lack of fundamental understanding [Dubois 16]. Surface characterization tools are especially limited in the presence of hydrogen, which is difficult to detect and to quantify into materials. Since the empirical approach and the experimental characterization of plasma-material interaction are not sufficient, supplementary methods can help to fulfil the lack of understanding in the Smart Etch concept, and one candidate is Molecular Dynamics (MD) simulation.

#### 1.6. Molecular Dynamics simulation to assist process development

Plasma-surface interaction is extremely complex. In a real etch process, numerous operating conditions have to be set by the experimentalist or the clean room engineer, like the source power, the pressure, the substrate temperature, the gas chemistry, etc. Since each of these parameters can be controlled independently, it gives more than one billion possible combinations to setup this interaction. And since each parameter modification may affect multiple aspects of the interaction (separately or in synergy with others), one can understand why process recipes are often deduced empirically rather than from a full fundamental understanding. Surface diagnostics allow to correlate the operating conditions with a given surface state (chemical composition, structure, damage depth, etc.), while plasma diagnostics allow to

correlate them with a given set of plasma parameters (ion and radical fluxes, ion energy, neutral and ionic composition, etc.). However, none of these experimental diagnostics allow to visualize or understand the reaction mechanisms at the atomic scale, nor to directly investigate the impact of a given plasma parameter on the surface state.

Atomistic simulations like Molecular Dynamics (MD) are a natural tool to study plasma-material interactions since they provide a microscopic overview of the reaction processes at the atomic level. Although MD does not pretend to explain all phenomena quantitatively nor to replace the empirical development, we will see in this work that MD can reveal numerous occurrences hidden from experimentalists and provide a better understanding of the plasma-surface interaction. Moreover, with the continuously decreasing size of microelectronic devices, and the incessantly increasing computing capabilities of the MD community, these two worlds are converging to each other.

During the last 30 years, MD has been used to study plasma-surface interaction in low-pressure discharges for various combinations of plasma chemistries (Ar, Cl, F, H) and substrate materials (Si, C, O) [Garofalini 82, Stillinger 85, Tersoff 88, Beardmore 94, Abrams 99, Brenner 02, Vach 06, Brulin 06, Graves 09]. Nevertheless, the existing literature was far not sufficient to understand the reaction mechanisms involved during the first step of the Smart Etch, i.e. the modification of silicon nitride by exposure to a hydrogen or a helium plasma. We thus decided to develop MD simulations to investigate this specific interaction. Although the main material of interest was silicon nitride (used for spacers in CMOS - Complementary Metal–Oxide–Semiconductor transistors), it was first decided to examine the interaction between Si films and H<sub>2</sub>/He plasmas (a case study), before investigating the SiN-H/He system (a more realistic but also more complicated case). Since in parallel, an extensive experimental work was carried out at LTM and in other groups around this subject, an excellent opportunity was given to compare our MD simulations data with experimental measurements.

#### 1.7. Purpose of the study and organization of the PhD manuscript

The present study focuses on one technological challenge related to the development of advanced transistors (FinFET, FDSOI), in which the etching of silicon nitride spacers cannot be addressed by conventional CW plasmas. The main goal of this study is to support the understanding of the recently developed Smart Etch technology – in particular the first step based on light ion implantation - using

molecular dynamic simulations. For this purpose, MD simulations are performed to study the interaction of silicon and silicon nitride films with hydrogen and helium plasmas. MD is used to investigate how the substrates modification is affected by the ion energy, the ion dose, the ion composition or the radical-toion flux ratio (in the case of a H<sub>2</sub> plasma). Since the present MD studies cover a wider scientific area than that of silicon nitride modification in H<sub>2</sub>/He plasmas, our simulations are used to bring new insights to other technologies exploiting these plasmas, notably to the Smart Cut technology. This work is organized as follows. Chapter 2 presents the basic principles of Molecular Dynamics and various computational details specific to the modeling of plasma-surface interaction in Si-N-H-He systems. Chapter 3 investigates He<sup>+</sup> ion implantation into Si and SiN substrates in He plasmas, while Chapter 4 focuses on the modification of Si by H<sub>x</sub><sup>+</sup> (x=1-3) ions and H radicals in H<sub>2</sub> plasmas. Chapter 5 finally studies the modification of SiN substrates in H<sub>2</sub> plasmas. General conclusions and perspectives for future work are discussed in last chapter 6. Additionally, some supplementary details about the C++ program, the optimization and parallelization algorithms, or the interatomic potentials used for these simulations, are presented in the appendix.

# **Chapter 2**

# Molecular dynamics simulations

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Plasma-surface interaction is a major problem in material processing, in particular in etching processes, which are omnipresent in semiconductors fabrication. To support the understanding of these interactions, often molecular dynamics (MD) is used. MD can be used to study an infinite quantity of interactions, nonetheless it is important to target precise interactions to be simulated, otherwise it may bring an ocean of results, which can somehow be "bothering" rather than really useful. Besides, MD remaining a simulation, it reproduces only a theoretical reality, so MD is most beneficial and valuable when it is systematically compared with experimental data. Particularly, for plasma-surface interaction, MD can be applied to study the influence of the ion energy and the flux of plasma species (ions, molecules, radicals) on the structural and chemical modifications of the bombarded substrate. This chapter describes the fundamental principles of Molecular Dynamics, as well as all hypotheses and assumptions related to the modeling of plasma-surface interaction. Afterwards, numerical parameters

used to study the Si-H-He and SiN-H-He systems are discussed, as well as the specific difficulties encountered to model hydrogen and helium interactions with materials. Finally, in the end, some details about post-processing and data analysis are presented.

## 2.1. MD: General principles

In this section, the basic principles of molecular dynamics are discussed.

#### 2.1.1 Atomic motion

MD refers to a class of simulations that solves Newton's equations of motion for a system of N interacting atoms. This is equivalent to calculate the position and velocity of each atom in the system at any given instant. In this approach, atoms are considered as punctual masses, and point mechanics is applied. From Newton's second law, we have,

$$F_i = -\frac{\partial U}{\partial r_i} = m_i \ddot{r}_i = m_i a_i, \quad (2.1)$$

where  $F_i$  is the force exerted on atom *i* by other atoms in the system,  $m_i$  is the atom's mass, and  $a_i$  is its acceleration, respectively. In this equation, *U* is the interatomic potential, which defines the further trajectories of all atoms for any given initial conditions (positions and velocities). Indeed, *U* defines  $a_i$ , and since we have

$$\dot{v}_i = a_i \quad and \quad \ddot{r}_i = a_i, \qquad (2.2)$$

then one needs to simply integrate these two equations to obtain atomic positions and velocities. At this point, MD refers to the class of deterministic simulations. This means that starting from any given initial conditions, the further evolution of the system is always the same (defined), contrary to Monte-Carlo simulations, which employ a Markov chain procedure to determine a new state from a previous one, according to appropriate Boltzmann probabilities.

In NVE MD simulations, the ensemble of *N* atoms is considered as isolated, so the total energy - which is the sum of kinetic and potential energies - should be conserved:

$$E_{total} = \frac{1}{2} \sum_{i=1}^{N} m_i v_i + U(r_i) = const, \quad (2.3)$$

This equation is not directly used in the simulation of atomic motion, but the conservation of total energy serves as an important control tool in MD.

#### 2.1.2. Interatomic potentials, classical and ab-initio MD

An atom is composed of a nucleus and electrons, which obey the equations of Schrodinger. In many fields of MD modeling, often many thousands of atoms should be simulated. In this case, solving numerically at each timestep Schrodinger's equations would require a tremendous computing capacity, which makes this approach not applicable currently. Instead, the approximation of Born-Oppenheimer is used [Born 27], which assumes that the motion of atomic nuclei and electrons can be decoupled, since the last ones are much faster. The nucleus being relatively heavy, it can be well described by the classical Newton's equations of motion, which is not the case for electrons. At this point, two MD approaches can be followed: ab-initio or first principle MD, and classical MD. The first one calculates both the motion of nuclei and the electronic behavior, which is obtained from first principles by using quantum mechanical methods, such as density functional theory. However, this approach remains computationally very expensive, and often only few tens of atoms can be simulated, which is far not enough to describe plasma-material interactions in etching processes. Classical MD in his turn calculates only the motion of nuclei, while electrons are assumed to form a potential field around the nucleus which can respond almost instantaneously to the nuclear motion. This simplifies the problem enormously and permits to model an important quantity of atoms (even millions of atoms, depending on the problem studied). In this approach, the nuclei (atoms) move according to an interatomic potential function  $U(r_{ii})$ , whose analytical form has been specified beforehand. But classical MD suffers from an important issue: such quantity of assumptions does not allow to have a generic interatomic potential function for all systems. Thus, for each given system (for example Si-H), it requires a specific potential. Moreover, even for a given system, various interatomic potentials can be used, which may describe correctly only some specific properties. For example, for some element one potential can describe perfectly the crystalline structure, meanwhile the representation of the liquid phase will be poor, and vice-versa. Certainly, the abilities/properties of interatomic potentials used in classical MD are not random; these potentials are semi-empirical, and all their properties are pre-designed. To construct a semi-empirical interatomic potential, the following steps are generally needed:

- Choice of a chemical system to be modeled, for example Si-N
- Choice of the main properties to be reproduced, for example bond lengths, bond angles, lattice parameters, atomic coordination, etc.
- Choice of an analytical form which includes the terms to be described, for example

$$U(r) = a * e^{-rc} + b$$

where *r* is the bond length, and *a*, *b*, *c* are constants

• Search for the best ensemble of parameters (*a*, *b*, *c*) to best fit given properties.

The most general form of a semi-empirical interatomic potential is as follows:

$$U = U_0 + \sum_i U_1(r_i) + \sum_{i < j} U_2(r_i, r_j) + \sum_{i < j < k} U_3(r_i, r_j, r_k) + \cdots$$
(2.4)

where the  $U_0$  is a reference potential,  $U_1$  describes the interaction of atoms with an external field,  $U_2$  the bond lengths,  $U_3$  the bond angles and the atomic coordination, and so on. It is evident that the higher N, the more complex is  $U_N$ , and the less computationally efficient is U. Consequently, parameters are also chosen such that  $U_N$  converges to zero rapidly. In this work, 3 different interatomic potentials were used, which are highly detailed in section 2.3 and in the appendix.

#### 2.1.3. Statistical physics

As it was mentioned above, MD provides the position and velocity of each atom in a system at any instant, but this information itself may not be very useful. Indeed, one often needs to have a more macroscopic characterization of the system, which could be compared with experimental data. Therefore, statistical physics is used to convert MD data to structural and thermodynamic data. A good example is the calculation of the system temperature:

$$T = \frac{1}{3Nk_B} \sum_{i=0}^{N} m_i v_i^2.$$
 (2.5)

#### 2.1.4. Numerical integration

MD is ruled by the self-consistent differential equation given by formula 2.1, the numerical integration of which is done using the finite-difference method. To do that, the time space is first discretized, and afterwards Taylor Series are used:

$$r(t+h) \approx r(t) + \dot{r}(t) * h + \frac{1}{2} * \ddot{r}(t) * h^{2}, \quad (2.6)$$
$$v(t+h) = \dot{r}(t+h) \approx \dot{r}(t) + \ddot{r}(t) * h, \quad (2.7)$$

From these equations, a simple scheme can be derived:

$$a_n = \ddot{r_n} = -\frac{1}{m} * \frac{\partial U_n}{\partial r},$$
  
$$r_{n+1} = r_n + v_n * dt + \frac{1}{2} * a_n * dt^2,$$

$$v_{n+1} = v_n + a_n * dt.$$

where  $a_n$ ,  $U_n$ ,  $r_n$  and  $v_n$  correspond to the acceleration, the potential energy, the position and the velocity at time  $t = t_n$  (n-th instant of the discretized time space). But this scheme requires very small timesteps to remain convergent, which is computationally inefficient, so often other schemes are used. Particularly, in this work, the Verlet algorithm [Swope 82] was chosen, which is schematically represented on Figure 2.1. This scheme allows to gain efficiency more than 100 times over the simplest one, but remains at the same time very simple, that is why it is one of the most used in MD. Since in NVE simulations (constant number of atoms N, volume V and energy E), a necessary condition is the conservation of the total energy over the runtime, the timestep dt is chosen as small as needed to satisfy this condition; this choice is detailed in subsection 2.4.1.

Initial configuration	
+	
Update positions	
$r_{n+1} = r_n + v_n * dt + \frac{1}{2} * a_n * dt^2$	7
↓	Fig. 2.1 Variat algorithm for the numerica
	Fig. 2.1. Venet algorithm for the numerical
$v_{n+1} = v_n + \frac{1}{2} * a_n * dt$	Integration of formula (2.2)
<b>↓</b>	
Compute the force and acceleration	
$a_{n+1} = r_{n+1} = \frac{1}{m} * \frac{\partial U_{n+1}}{\partial r}$	
Update velocities (2)	
$v_{n+1} = v_{n+1} + \frac{1}{2} * a_{n+1} * dt$	

Starting from this point, let's define some common terms in MD which will be used in the following chapter:

- Timestep (unit fs) is the size of the discretization of the time space
- Run (unit ps) Numerical integration of the atomic motion over a given time
- Configuration Position and velocities of all atoms in the system

## 2.2. MD for modeling plasma-surface interaction

#### 2.2.1 General concepts of the model

As discussed in the previous chapter, in a plasma discharge, the substrate is bombarded by an isotropic flux of neutral species, which are often at ambient temperature (~300K = 0.026eV), and an anisotropic flux of positively charged ions, which are accelerated in the sheath and have normal incidence (perpendicular to the walls/substrate). Electrons and photons are not discussed here mainly because they often play a secondary role in etching, and because classical MD does not allow to simulate them. Therefore, as a first approximation, modeling plasma-surface interactions can be done by bombarding alternatively and cumulatively the substrate material by both neutral species and positive ions.

#### 2.2.2. Simulation of plasma species impacts

In this work, hydrogen and helium plasmas are studied, where the following species can impinge on the substrate: H<sub>2</sub>, H, He (neutrals), and H<sup>+</sup>, H<sub>2</sub><sup>+</sup>, H<sub>3</sub><sup>+</sup>, He<sup>+</sup> ions. The plasma is considered to be at steady state, i.e. the fluxes of ions and neutrals are constant in time. Thus, a uniform distribution of impacts over time is chosen. The modeling of the plasma species impacts is illustrated on Figure 2.2.



Fig. 2.2. Schematic of the modeling of plasma species impacts. Neutrals are illustrated as blue balls and positive ions as green balls, respectively.

The impinging neutrals are in thermal equilibrium around 300K and have a Maxwell-Boltzmann distribution of velocities; thus, initial random velocities chosen from a Maxwellian distribution are assigned to these species. Certainly, those who are directed away from the substrate are not simulated, since they do not impact the surface. Positive ions, besides their thermal velocity, are accelerated in the sheath, so both components should be taken into account  $\overrightarrow{v_{ion}} = \overrightarrow{v_{th}} + \overrightarrow{v_{\perp}}$ . Since most interatomic potentials used in classical MD do not model the charge effects, ions are treated as fast neutrals. This assumption is justified by Auger neutralization processes [Hagstrum 61, Helmer 98], which show that positive ions rapidly recombine with surface electrons when approaching a conductive surface. All these species, neutrals and ions, are initially located sufficiently above the surface, to be out of any interaction with it. Each added species is then translated towards the surface (in the direction of its velocity) until

its interaction with the surface. In the case of a  $H_2^+$  ion, the configuration of the molecule is chosen such that the initial bond length is in the [0.6-0.9] Å range. In the case of a  $H_3^+$  ion, the 3 H atoms are placed on the vertexes of an equilateral triangle, such that the length of each side is in the [0.85-0.95] Å range. After each plasma species impact, a **run** of the global system is performed for a certain time (**runtime**). This runtime should be sufficiently long to capture the full collision cascade (and the ion kinetic energy dissipation) in the case of ion impacts. For radical impacts, it should be long enough to capture their interaction with the surface (covalent bonding, formation of etch products, diffusion, reflection, etc.). Once this run is finished, the cell is analyzed and statistical data are collected. The same procedure is then repeated on the resultant cell, which allows to obtain the dynamical evolution of the substrate.

#### 2.2.3 Simulation cell and periodic boundary conditions

Since we are limited by the computing cost, and thus by the total number of atoms we can follow simultaneously, it is impossible to simulate a wafer of 300mm in diameter and some millimeters in thickness. Using classical MD, we can only simulate a very small part of the substrate, which we call the simulation cell, and which is presented on Figure 2.3.



static layers at the bottom

#### Fig. 2.3. From the experimental sample to the simulation cell.

The size of this cell should be as small as possible to reduce the simulation time (which can reach several years), but at the same time it should be large enough not to affect the simulation results. For plasma-material interaction, the main reaction processes take place typically near the surface, on the first nanometers of the substrate (dependent on the species type and energy), so there is no big interest to simulate thicker cells. We are limited in the lateral directions as well, but in this case, interactions occur all over the surface, so periodic boundary conditions are applied in lateral directions to mimic a

semi-infinite surface. Nonetheless the cell dimensions in lateral directions should be i) sufficiently large to capture the volume of the collision cascade during the ion bombardment, and ii) greater than the diffusion length of reactive radicals on the surface. Free boundary conditions are used at the top to allow deposition or etching, while one layer of atoms is fixed at the bottom to avoid the translation of the cell during the bombardment. In this thesis work, simulation cells typically have dimensions of 3nm in lateral directions and up to 18nm in vertical direction, which is equivalent to ~1000-20000 atoms for the studied substrates.

#### 2.2.4 Thermalization

After each plasma species impact, the system is simulated as an NVE ensemble, in which the total energy is conserved but the temperature T and pressure P are unregulated. During energetic ion impacts, the ion kinetic energy, which can achieve several hundreds of eV, is distributed among the other atoms during the collisional cascade, which increases the cell temperature following formula 2.5. After the impact, to simulate the dissipation of this excess energy out of the cell, the system is quenched artificially to the desired temperature, when the cell temperature is out of the given range. To perform this action, the eponym algorithm of [Berendsen 84], or Berendsen heat bath, is applied. Since the temperature depends on the atoms velocities, one can scale them to control the temperature. This algorithm suggests to multiply the atoms velocities at every timestep by the following coefficient

$$\lambda = \sqrt{1 + \frac{1}{\tau} (\frac{T_{set}}{T} - 1)}$$
, (2.8)

where *T* is the current temperature of the substrate,  $T_{set}$  is the desired one and  $\tau$  is a parameter which controls the roughness of the heat bath (the higher  $\tau$ , the smoother and slower the thermalization). However, this algorithm is not completely adapted to cool down the simulation cell after energetic ion impacts, since the cell temperature is not homogeneous and is typically greater near the top of the cell (where most of the ion energy is deposited). As a result, this algorithm will quench the cell to the desired global temperature, but the final temperature will be inhomogeneous, with hot top layers and bottom layers continuously cooled down. To avoid such a phenomenon, the cell is discretized vertically in z layers (layer thickness ~3Å) and this algorithm is applied stratum by stratum, i.e. formula 2.8 is applied to each layer, taking *T* as the temperature of the layer. In this way, the cooling/heating coefficient  $\lambda$  is adapted to each layer, and finally all layers are set to the same temperature. After applying the stratified

Berendsen heat bath, atoms velocities are not Maxwellian, so to bring them to their natural state, a small run is simply applied. Here we define two new procedures (or terms) often used in MD:

- Quench  $\Leftrightarrow$  Run + application of Berendsen heat bath every timestep
- Thermalize  $\Leftrightarrow$  Run + application of stratified Berendsen heat bath every timestep

In present simulations, the value of  $\tau$  is chosen in the [50-100] range and the duration of the thermalization varies between 0.1 and 0.2ps; indeed, preliminary studies have shown that with these parameters, the cell is smoothly thermalized to the desired temperature after energetic ion impacts, which is preserved during the further runs.

#### 2.2.5. Timescale related problems

To fully simulate plasma-surface interactions in real etching/deposition processes, one should follow several thousands of atoms during one to several minutes. It is practically impossible to simulate such timescales since it is too time consuming; for example, with a timestep ~0.1fs, simulating 1s of a small molecule like Si<sub>2</sub>H<sub>6</sub> can take about 20.000 of years if no specific accelerating algorithm is used. However, even this problem can be avoided in some cases, especially when one simulates a solid material, since in that case all atoms are oscillating near their equilibrium position and do not change their localization. As a result, no practical changes occur in such systems, if the temperature remains homogeneous. In our simulations, it is the case during the major part of the process, except for the moments when there are plasma species impacts, which have to be simulated properly. Indeed, in classical ICP/CCP plasmas, ion fluxes usually vary between 0.1 and 10 mA/cm<sup>2</sup>. Taking into account the area of our simulation cells (~10nm<sup>2</sup>), it is equivalent to an ion impact every 10<sup>-4</sup>-10<sup>-2</sup> s, and a neutral impact every 10<sup>-6</sup>-10<sup>-4</sup> s, if one considers a neutral-to-ion flux ratio ~100. The simulation of these discrete time intervals should be sufficiently long to capture the full collision cascade of energetic ions and all possible diffusion, desorption, sputtering and etching phenomena occurring after each plasma species impact. Fortunately, calculations show that these intervals are relatively short, between 0.1-100ps, which allows to simulate hundreds of thousands impacts. Thus, for a given plasma-surface interaction, only ~10-7-10-4 % of the real time is simulated, as illustrated on Figure 2.4.



Fig. 2.4. Ignored time intervals in the MD simulations of plasma-surface interaction.

This approach remains valid if there is no long timescale phenomena (e.g. diffusion, reattachment, slow nucleation) occurring between impacts, since during the ignored intervals, the atomic positions are defined with a precision of an angstrom. Concerning the formation of etch products, these processes refer to events that occur within about 1ps [Humbird 05], thus it can be captured correctly as well.

#### 2.2.6. Etch products

After each plasma species impact, it is possible to have the formation of etch products. We distinguish two type of products. The first ones are the sputtered products, which can be obtained only after an energetic ion impact; these products are usually atomic species and unsaturated molecules. The second ones are the chemically etched products, which are typically created after neutral species impacts, but can also occur after low-energy ion impacts; these products are usually volatile or fully saturated molecules. If these two types of products are leaving the surface region at the end of an impact, there is no point to simulate them, so they are erased from the system. The main algorithm to detect these products is very simple: an imaginary barrier is defined some angstroms above the surface (sufficiently high to be out of any interaction with the substrate atoms), and once any molecule/atom is above this barrier and moving in the +z direction, it is erased from the system. However, some saturated or volatile products may take more time than the runtime to overpass this barrier (sometimes the desorption time can achieve few nanoseconds for these slow species). In this study, such behavior was shown for SiH<sub>4</sub> and NH<sub>3</sub> etched molecules, so when such molecules were detected on the surface, they were automatically erased from the system.

#### 2.3. Modeling of Si-H-He and SiN-H-He interactions

As presented in the introduction, the main goal of the present work is to study the modification of silicon and silicon nitride substrates exposed to helium and hydrogen plasmas. Since the "motor" of classical MD is the interatomic potential, the choice of this semi-empirical function is one of the most important parts of the study.

#### 2.3.1. Choice of the Si-H interatomic potential

To model Si-Si, Si-H and H-H interactions, Murty's potential [Murty 95] was used, which is an extended version of the Tersoff potential for silicon [Tersoff 88] (also known as Reactive Empirical Bond Order (REBO) potential) including the hydrogen interactions. This semi-empirical potential was accurately fitted for various hydrogen interstitial configurations, as well as for multiple molecules like SiH<sub>4</sub>, Si<sub>2</sub>H<sub>6</sub>, etc. It was shown to be in good agreement with experimental data and was successfully tested to model some plasma-surface interaction in etching processes [Végh 09]. It should be mentioned that other interatomic potentials were developed to model Si-H interactions for other purposes [Dyson 96, Kohen 98, Hansen 98, Ohira 00]. These potentials were especially used to study the passivation of Si surfaces and hydrogen deposition on Si for photovoltaic and optoelectronic applications [Ramalingam 98, Ohira 00, Pan 04], the deposition of high quality silicon thin films [Ning 09, Le 14a, Le 14b] and even the fabrication of nanometer particles [Hawa 08]. Murty's potential was preferred over this wide choice since it was shown to adequately reproduce etching mechanisms of silicon by atomic hydrogen, as well as the impact of H<sub>2</sub> molecules on Si surfaces. In our study, since energetic ion impacts (5-200eV) are simulated, Murty's potential was splined with the Moliere potential [Molière 47] to better capture the strong atomic repulsions at short interatomic distances [Brichon 15] (see details in the appendix).

#### 2.3.2. Choice of the Si-N-H interatomic potential

Since silicon nitride (Si<sub>3</sub>N<sub>4</sub>) and the Si-N-H system have not been much studied using MD until now, very few interatomic potentials were developed and available in the literature. In this work, the augmented Tersoff potential derived from *ab initio* calculations and recently proposed by Billeter et al. [Billeter 06, 09] was used to model Si-Si, Si-N, Si-H, N-H and N-N interactions. Previously, a commonly used potential to study the Si-N systems was that of Mota et al. [Mota 98], which was also based on Tersoff functional form but with a different parametrization. However, this last potential was shown to

suffer from an issue since it could only model the repulsive part of N-N interactions. As reported in the work of Ippolito et al. [Ippolito 11], this issue can have an important impact on macroscopic parameters like for instance the stoichiometry of the substrate, especially when simulating the amorphous phase of Si<sub>3</sub>N<sub>4</sub>. On the contrary, using the potential of Billeter et al., the presence of N-N bonds in the bulk was observed, which was consistent with experimental data [Misawa 79]. Moreover, the potential of Billeter et al. includes in his functional form a correction term which prevents the over-coordination, i.e. the formation of stable complexes with atoms having more covalent bonds than it is possible naturally (for example SiH<sub>5</sub> molecules). The effect of this correction term is detailed in the appendix.

#### 2.3.3. Choice of the Si/SiN-He interatomic potential

Finally, to model Si-He and N-He interactions, the Moliere potential [Molière 47] was applied. This universal screened Coulomb potential is widely used in classical MD, mainly to model repulsive interactions at very short distances or with inert atoms. Its simple functional form and its universality promote its choice, especially for multicomponent systems like Si-N-He. Its functional form is also detailed in the appendix.

### 2.4. Preparation of the initial Si and SiN substrates

#### 2.4.1. Crystalline Si (100) substrate

To model the silicon substrate, a Si crystal of orientation (100) was generated, as presented on Figure 2.5. Preliminary tests were performed to define and optimize the dimensions of the initial substrate, depending on the simulation conditions (nature and energy of impacting species). These dimensions were chosen such that the MD cell was i) larger than the volume of the collision cascade for the highest ion energy, ii) wider than the diffusion length of H radicals on the surface, and iii) thicker than the maximal ion penetration depth for a given ion energy. Since hydrogen and helium ions are very lightweight, the volume of their collision cascade is relatively small, and ~3nm in lateral directions was highly sufficient (except for 250eV He<sup>+</sup>). For the same reason (low mass), their penetration depth in silicon can be significant, from to 3nm to 16nm for ion energies between 5 and 100eV. Consequently, it was imposed

to have very thick (deep) simulation cells, composed of 1000 to 16000 of atoms, which in turn increased the simulation time expenses.



Lx, Ly ~2.7-4.3nm

#### Fig. 2.5. Si (100) unit cell and initial MD silicon substrate.

Before running any impact simulation, all initial Si cells were quenched during 1ns to 300K; then, they were allowed to relax for another 1ns to ensure that the quenching was sufficiently long to preserve the assigned temperature. Since plasma etching reactions are then simulated, the cell thickness may decrease progressively, as substrate atoms are removed during the process. In such cases, the thickness of the cell may become lower than the ion penetration depth; to avoid this problem, a simple algorithm is applied, which adds new layers to the bottom when the thickness of the substrate is lower than a pre-defined minimal thickness.

#### 2.4.2. Amorphous SiN substrate

The preparation of the initial silicon nitride (Si<sub>3</sub>N<sub>4</sub>) MD cell is a bit more complicated, since in experimental conditions for the Smart Etch process, the layers of silicon nitride are deposited using LPCVD. Thus, they are totally amorphous, and contrary to crystalline structures, it is not possible to numerically generate the natural structure of an amorphous material. Fortunately, there are few methods allowing to amorphize the crystalline structure of a given material. In our work, a crystalline  $\beta$ -Si<sub>3</sub>N<sub>4</sub> [Wang 96] was generated, and afterwards the cell was amorphized using the "melt-quench" procedure proposed by Ippolito et al. [Ippolito 11], as illustrated on Figure 2.6.



Fig. 2.6. Preparation of an amorphous silicon nitride substrate from the crystalline state, using the melting-quench method [Ippolito 11].

The method to choose the initial dimensions of the silicon nitride substrate is analog to that of silicon, and similarly, once the cell was prepared, it was quenched to 300K during 1ns and then allowed to relax for another 1ns. However, the fact that the substrate is amorphous does not allow to perform the addition of new layers at the bottom during the simulation, since it is impossible to generate an amorphous structure. Thus, for processes where etching can occur, one should anticipate the material thickness that can be etched during the simulation, and take an initial substrate having: *initial thickness = minimal thickness + possible etched thickness*. However, this imposes to simulate an important quantity of unnecessary atoms (located near the bottom) during most of the simulation, which increases significantly the simulation time (which was already far not negligible). Thus, an additional algorithm was applied, which keeps the unnecessary atoms inactive (i.e. they are not simulated), until the moment when they are in the interaction zone, as presented on Figure 2.7.



Fig. 2.7. Illustration of atom activation algorithm. All atoms are present in the configuration file, but only active ones (blue) are simulated; inactive atoms (yellow) are activated when the minimal thickness of the active zone is lower than a pre-defined value.

In this section, we explained the general methods for the construction of Si and SiN simulation cells, and for the calculation of their initial size. The specific dimensions of MD cells used for each studied interaction will be precised in each corresponding chapter.

# 2.5. Encountered issues related to H<sub>2</sub> and He interactions with Si and SiN

Modeling and simulating the interaction of H<sub>2</sub> and He plasmas with a substrate is a tough problem, firstly because these simulations are extremely time consuming, and secondly because these plasmas are reacting very differently from classical gas-based plasmas used in Microelectronics (like chlorine or fluorine), which makes impossible any analogy between the observed phenomena.

#### 2.5.1. Timestep and cell size

The simulation cell size depends on the ion energy and its depth can reach up to 18nm, which imposes to simulate a significant quantity of atoms and increases the computation time. Besides, as previously mentioned for the numerical integration, small timesteps are required to keep the Verlet algorithm convergent (Figure 2.1) and to ensure the conservation of total energy (Formula 2.3). Numerically, this convergence can be controlled only by the timestep; however, this timestep depends on the atoms velocities and accelerations, and the higher these quantities, the smaller should be the timestep. Since helium and especially hydrogen are very lightweight, for a given kinetic energy ( $KE = \frac{1}{2}mv^2$ ), they are extremely rapid: for example, the ratio of argon, helium and hydrogen velocities is ~ 1:3:6. Consequently, these species require integration timesteps shorter than for all other elements, which increases the

simulation time, since the last one depends inversely on the timestep. To simulate the interaction of hydrogen ions with a substrate at 300K, a timestep of 0.1fs is sufficient for ion impacts with a kinetic energy smaller than 50eV. But for higher energies, smaller timesteps (0.02-0.05fs) must be taken during the first instants of the impact, until the ion energy is dissipated and becomes lower than 50eV, otherwise all results can be affected at the macroscopic level, especially the penetration depth. So, for high energy ion impacts, the numerical integration is divided in two parts: a first part during which the species is still highly energetic ( $KE \ge 50eV$ ) and a smaller timestep is used, and a second part after the energy was dissipated and during which a timestep equal to 0.1fs is used. It is the same procedure for helium, but in this case the impact is often divided in three parts using the same analogy. For each studied interaction, these numerical parameters will be precised in corresponding chapters.

#### 2.5.2. Adequate runtime and capture of He/H<sub>2</sub> desorption

When simulating low-energy (5-100 eV) ion bombardment in classical etching chemistries (Ar<sup>+</sup>, Cl<sup>+</sup>, F<sup>+</sup>), the MD cell is usually run during about [0.5-1ps] after an impact, which is quiet enough to capture the full collision cascade, as well as the physics of the interaction (reflection, covalent bond formation with the substrate, product desorption, etc.). But in the case of helium and hydrogen, such approach may induce incorrect macroscopic results, since these two gases have different behaviors. Firstly, the H and He species being lightweight compared to the substrate atoms (Si, N), the energy transfer during collisions is very inefficient, and thus for the studied energies (5-100 eV), longer runtimes are needed to capture the ion energy dissipation (at least 1-2ps). Secondly, other errors may arise if the desorption of He atoms and H<sub>2</sub> molecules from the substrate is not correctly treated.

#### He desorption

For helium, 2ps are sufficient to capture the impact of a single helium ion on an undamaged substrate, but this runtime becomes far not satisfactory in the case of a cumulative bombardment. Indeed, often energetic helium ions remain trapped in the substrate, which leads to the accumulation of helium in the material during the cumulative bombardment (see Figure 2.8.).

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Particularly, since the helium atoms trapped in the substrate could possibly desorb on timescales longer than 2ps, this desorption should be captured after each ion impact, otherwise the simulation may not be valid. Numerical tests showed that the time required to capture this desorption was highly dependent on the ion energy, the number of trapped helium atoms and the nature of the substrate. Thus, to estimate this time, the following approach was adopted for all ion energies. Cumulative He<sup>+</sup> bombardments were simulated with different runtimes (between 2 and 100ps) until the steady state was reached, and afterwards, a long run of 10ns was performed (with no ion impact). When the chosen runtime was too short, numerous helium atoms were shown to change their localization and/or desorb during this last long run; when the chosen runtime was long enough, no He desorption phenomenon was observed. The adequate runtime was shown to increase with the ion energy. For example, in the case of 250eV He<sup>+</sup> ion bombardment on silicon, the runtime was fixed to 100ps, which made these simulations very time consuming, requiring more than 6 months to reach the steady state.

#### H<sub>2</sub> desorption

For hydrogen, our first simulations of cumulative H<sup>+</sup> ion bombardment of silicon with Eion > 25eV showed a breaking of the substrate in two parts, starting from a certain ion dose, as illustrated on Figure 2.9.





Even if a similar behavior was observed in studies related to the Smart Cut technology [Moutanabbir 05], it was necessary to check if such a phenomenon was not due to a numerical problem. Particularly, the interatomic potentials used in the present work are short-range REBO potentials, which correctly describe covalent materials but do not take into account long-range interactions. The nature of these potentials could have been the reason for this breaking, like it was the case in the thesis of [Davydova 14] where multilayer graphene was bombarded by hydrogen ions. To verify this possible scenario, a long-range Lennard-Jones potential (cutoff distance - 6Å) was splined to the Murty potential to model Si-Si interactions; the same simulation was then repeated, but the phenomenon was still taking place. It was then decided to check if this breaking could be related to the cell dimensions; much larger cells  $(Lx = Ly \sim 6nm)$  were thus simulated (both with a long-range potential and without) but the same cell breaking was observed. Finally, since H<sub>2</sub> molecules were trapped between the two substrate parts, it was decided to apply a long run of ~ 10ns after a certain ion dose, to let the substrate relax and check if some occurrences could have remained unnoticed because of the ignored time intervals (see section 2.2.5.). This last hypothesis was the right one. All H<sub>2</sub> molecules created in the substrate were shown to diffuse into the material and desorb within a few nanoseconds (see section 4.3.2. for a more detailed description). However, it is practically impossible to simulate the system for a few nanoseconds after each ion impact (for a comparison with the Si-He system, each run would be more than 10 times longer if the same timestep was used). And because the Si-H system requires a minimal timestep of 0.1fs, meanwhile 1fs is sufficient for the Si-He system, the simulation of each hydrogen ion impact would take 100 times longer. Fortunately, it was noticed that besides this H<sub>2</sub> desorption, nothing else happens in the system during these few nanoseconds. Therefore, to take into account this slow desorption process without truly simulating it, after each ion impact, H<sub>2</sub> molecules were detected and erased from the system. The detection algorithm simply searches for H-H bonds remaining in covalent state during more than a predefined time, typically 0.1ps. Indeed, an instantaneous check for these molecules could show fault H<sub>2</sub> molecules, which were in covalent state only at the given instant. With this H<sub>2</sub> desorption procedure, the cell breaking which was caused by an accumulation of H<sub>2</sub> gas in the material was no more observed.

As one can conclude, the modeling and simulation of He and H interactions with materials is very time consuming and requires specific algorithms. In the beginning of this thesis, a pre-existing MD code was available at LTM, successfully used to study plasma etching mechanisms in other chemistries [Brichon 15, Davydova 14, Despiau 10, Végh 09]. However, this program was far not sufficiently fast for the present work (some simulations might have lasted more than 10 years). Therefore, the first year of this thesis was devoted to the development of a new MD program, parallelized and particularly optimized for the simulations of He/H<sub>2</sub> plasmas interaction with Si/SiN substrates. This programming effort allowed to boost the computing speed until 50 times and to accomplish the present work. This program is also highly detailed in the appendix.

#### 2.6. Computational details

Now that major computational difficulties were exposed, we can focus on the simulation parameters of interest for our study of the Smart Etch process. As discussed in chapter 1, the main objectives are to understand the role of the ion energy and the ion dose in the plasma-material interaction, as well as the mechanisms driving the self-limited ion implantation. To determine the relationship between the flux/energy of species (He<sup>+</sup>, H<sub>x</sub><sup>+</sup>, H) bombarding the substrate and the structural/chemical changes induced in the material, the main plasma parameters that should be investigated are the ion energy, the ion dose and the plasma composition (ion type, neutral-to-ion flux ratio). To help us choose proper values for these input parameters, we looked for experimental measurements performed in He and H<sub>2</sub> plasmas used for the Smart Etch process.

#### 2.6.1. Input plasma parameters

In his experimental work on the SmartEtch process [Dubois 16], J. Dubois measured the ion energy (using RFEA) in various helium and hydrogen plasmas generated in a DPS (Decoupled Plasma Source) reactor of AMAT, in both CCP and ICP modes, as shown on Figure 2.10.



Fig. 2.10. Mean ion energies in helium and hydrogen plasmas, dependent on the bias and source power, measured by [Dubois 16] using RFEA.

Theoretically, it could have been possible to simulate all these conditions; however, since an increase of the ion energy drastically increases the simulation time due to multiple parameters (cell dimensions, runtime, timestep, etc.), the ion energies were limited at 250eV for the helium case and 100eV for the hydrogen case, respectively. Indeed, at these energies, the computing time required to be at steady state could already reach between 2 weeks and 8 months. Finally, the following energy ranges were simulated: 5-250eV for Si-He, 5-200eV for SiN-He, and 5-100eV for Si/SiN-H. Although the energies of interest for the Smart Etch process are higher than 15eV (typical values found in CCP/ICP), low-energy ion bombardments (5-10eV) were also simulated, since these energies could be obtained in pulsed mode or in low-Te sources for ALE processes.

The choice of plasma composition, in the case of helium, was easy. Indeed, one should only simulate He<sup>+</sup> ion impacts since there is practically no other ion in the plasma, and because the impacts of neutral He atoms have no effect on the substrate due to their inert nature. For hydrogen, the problem is harder, since among the possible ions we find H<sup>+</sup>, H<sub>2</sub><sup>+</sup> and H<sub>3</sub><sup>+</sup>, and for neutral impacts, atomic H and molecular H<sub>2</sub>. In practice, molecular H<sub>2</sub> impacts did not require to be simulated, since H<sub>2</sub> behaves like an inert species due to its strong chemical bond; various tests showed that it was almost always reflected, or very rarely diffused deep in the substrate (see details in section 4.3.2). Before simulating a real plasma

interaction (i.e. a mixed ion/radical cumulative bombardment of the mentioned species), the substrate was bombarded cumulatively by each type of ion only, as well as by atomic hydrogen. This study was done to investigate the separate effect of each species, which helps to have a better understanding of the results when they are mixed afterwards. This study was also used to bring new insights to the Smart Cut process, where the substrate is only exposed to a pure ion beam. Next, to model the influence of a real CCP or ICP plasma, one should know first its composition. Unfortunately, few plasma diagnostics could be performed in hydrogen plasmas by experimentalists working on the Smart Etch at LTM; thus, the ion composition was based on results found in literature. Experimentally, for a pure hydrogen ICP plasma (5-40mT, alumina walls), Sode et al. report that the major positive ion detected by mass spectrometry is  $H_{3^+}$  [Sode 13]. For comparable plasma parameters but a different reactor configuration (stainless steel walls), Ahmad et al measure 90% of  $H_{3^+}$  at 2 Pa (15mT) while  $H_{2^+}$  progressively dominates when the pressure is reduced to 0.2Pa (1.5mT) [Ahmad 13]. The H<sub>2</sub> plasma composition was also investigated using global (0D) models by [Zorat 00] and [Samuel 15]. Both models provide quite similar results for the plasma parameters of interest. Samuel et al. benchmarked their numerical results with some measurements performed in a helicon plasma in the MAGPIE reactor [Samuel 15]; the plasma composition they report for a low-pressure hydrogen plasma (10mT, 0-1kWs) is presented in table 2.1.

Species	Percentage
Н	99.26 -99.1
H+	0.005-0.1
H <sub>2</sub> +	0.001
H <sub>3</sub> +	0.6-0.8

Table. 2.1. Percentage of each species in the ensemble [H, H<sup>+</sup>, H<sub>2</sub><sup>+</sup>, H<sub>3</sub><sup>+</sup>] in a lowpressure hydrogen plasma, for the following conditions: pressure 10 mTorr, source power 0-1kW [Samuel 15]. H<sub>2</sub> is not presented, since it was not simulated.

However, these are the concentrations of the species in the plasma, meanwhile we want to know the ratio of the fluxes on the substrate. Fortunately, the data provided by [Dubois 16] regarding the ion flux and the plasma dissociation rate in hydrogen ICP plasmas allow to roughly estimate values for the radical-to-ion flux ratio ( $\Gamma$ ) at low source power (<100W) and low pressures (10-25 mTorr). Based on these models and the measured data, the following base case was chosen for our simulations:

radical – to – ion flux ratio : 
$$\Gamma = \frac{\Gamma_{atomic H}}{\Gamma_{ion}} = 10$$
  
ion composition :  $\Gamma_{H^+}$ :  $\Gamma_{H_2^+}$ :  $\Gamma_{H_3^+} = 9$ : 1: 90

ion energy : Eion = 
$$100eV$$
.

Since MD is especially efficient to give qualitative results and draw trends, a wider range of values was simulated to capture more possible scenarios. All combinations of parameters which were simulated are given on Figure 2.11.



# Fig. 2.11. Combinations of parameters tested for mixed ion/radical bombardment simulations in hydrogen. In the center is the base case; the red line studies the effect of ion energy, the blue line the effect of the radical-to-ion flux ratio $\Gamma$ , and the green line the effect of the ion composition.

Firstly, ion energies in the range 5-100eV were simulated for the base-case plasma composition. Secondly, for fixed ion energy (100eV) and radical-to-ion flux ratio (10), the ion composition was varied from 100% H<sup>+</sup> to 100% H<sub>3</sub><sup>+</sup>, while H<sub>2</sub><sup>+</sup> was always kept negligible (1%). Finally, for the base-case ion composition and ion energy, the radical-to-ion flux ratio was varied from 1 to 100, which are typical values that should be found in hydrogen ICP. Certainly, some of these parameters values may not be relevant for the experimental conditions used in the Smart Etch, but they remain realistic for low-pressure hydrogen plasmas. Besides, such a set of simulations can allow to draw trends and understand the effect of each plasma parameter on the substrate modification, and then extrapolate to the desired conditions, if necessary.

#### 2.6.2. Analysis of the substrate modification

It is important to analyze correctly the MD data, since in the end they will be compared with available experimental measurements. To characterize the modified layer, it is impossible to repeat the experimental protocol described in subsection 1.5.2.2, but it is possible to determine it numerically. There are two possible modifications of the substrate due to its interaction with the plasma: a structural and a chemical one. In the case of silicon, which was initially crystalline, one possible structural modification is clearly the amorphization.



Figure. 2.12. Calculation of the amorphization depth using Humbird's method [Humbird 07]. The layer is considered as amorphous if the parameter  $\xi < 0.15$ .

To compute the depth of amorphization, the method proposed by Humbird et al. [Humbird 07] was used, where the parameter  $\xi$  describes the deviation of the atomic configuration from the crystalline structure following the formula:

$$\xi = \frac{1}{3} (\lambda_x + \lambda_y + \lambda_z), \quad \lambda_{x(yz)} = \frac{1}{N} \sum_{atom \, i} \cos(\frac{8\pi}{a} x(yz)_i),$$

where  $a \approx 5.431A^{\circ}$  is the silicon lattice parameter. As illustrated on Figure 2.12, the layer is considered as amorphous if  $\xi \leq 0.15$ . It is more complicated to evaluate the structural modification in silicon nitride since the substrate is initially amorphous; nonetheless, a deeper investigation shows that there is indeed some structural modification in this material, as it will be discussed in the next chapter.

The chemical modification, for both materials, can be evaluated via the presence of mixed layers. In the helium case, it may not be totally correct to speak about a "chemical" modification, since helium atoms

are only trapped in the substrate without formation of chemical bonds with the other atoms. However, for genericity, this term will be used for both plasmas. In the case of Si, a layer is considered as modified/mixed if it contains more than 20% of implanted species (helium/hydrogen) as presented on Figure 2.13.





For silicon nitride, the limit percentage is taken much lower, 10% for hydrogen and 5% for helium respectively, since the SiN atomic density is almost two times higher than that of silicon (20% of foreign atoms is often not even reached).



Figure. 2.14. Analysis of hydrogenated groups in the substrate.

Finally, one may want to know the hydrogen density depth profile, but also in which chemical form hydrogen is stored in the modified material. Thus, an analysis of hydrogenated groups in the substrate was also done systematically, as presented on Figure 2.14.

# **Chapter 3**

# Helium plasma modification of Si/Si<sub>3</sub>N<sub>4</sub> thin films

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In this chapter, molecular dynamics (MD) simulations of low-energy (5-250 eV) He<sup>+</sup> ion bombardment on crystalline Si(100) and amorphous Si<sub>3</sub>N<sub>4</sub> surfaces are performed to investigate the influence of the ion energy and the ion dose on these substrates modification.

# 3.1. Motivation and objectives of the study

As discussed in Chapter 1, due to high ion bombardment energies and significant fragmentation rates, conventional CW plasma processes are not able to selectively etch ultrathin films (e.g. silicon nitride spacers) without damaging the active layers of advanced transistors (e.g. FinFET, FDSOI). To solve this problem, one alternative is to use the Smart Etch process, which consists of two steps: first, the modification of the material to be etched by exposure to a hydrogen or helium ICP or CCP plasma, and secondly, the removal of the modified layer using wet or dry gaseous etching. To investigate the plasma-material interactions occurring during the first step, Molecular Dynamics (MD) simulations of He<sup>+</sup> ion bombardment are performed on both Si and Si<sub>3</sub>N<sub>4</sub> substrates. During the last 30 years, helium implantation in different substrates (Si, SiC, InN) was studied experimentally. These research works were dedicated to understand the formation of helium-filled cavities in implanted crystalline or amorphous silicon [Cerofolini 00], to study the precursors of helium bubbles [Corni 99] and their annealing behavior [Grifficen 87, Gandy 08], or to determine the location of helium atoms in silicon carbide after implantation [Linez 15]. In addition, some studies were devoted to the possible application

of helium implantation in the Smart Cut technology [Lu 97, Daghbouj 16]. However, all these studies were carried out for very high ion energies (2-100keV) and often for a fixed ion dose. In the past years, the Si-He system was also examined using MD, but mostly to understand the formation and stability of helium bubbles in implanted silicon [Pizzagalli 13, Okuniewski 04]. However, no study was carried out to examine the interaction of low energy (5-250eV) He<sup>+</sup> ions with Si substrates, and no data at all were reported for Si<sub>3</sub>N<sub>4</sub> substrates. Few years ago, the interaction of 50-200eV He<sup>+</sup> ions with tungsten was investigated using MD [Henriksson 06]; however, since tungsten is a heavy element (~6.5 times heavier than Si) with properties different from that of silicon or silicon nitride, the modification caused by helium to tungsten may be very different.

Since existing data reported in literature were not sufficient to understand all mechanisms driving the helium ion implantation in the Smart Etch process (and cover the lack of understanding revealed in [Dubois 16]), we applied MD simulations to the Si-He and Si<sub>3</sub>N<sub>4</sub>-He systems with the following goals: (i) investigate the influence of the ion energy and ion dose on the substrate modification, (ii) understand the mechanisms of self-limited implantation and (iii) characterize the structure and composition of the modified layer. In this chapter, Si/Si<sub>3</sub>N<sub>4</sub> substrates are thus bombarded with He<sup>+</sup> ions having energies between 5 and 250eV. The structural modification and composition of the substrates are compared for all studied energies. Both substrates (Si/Si<sub>3</sub>N<sub>4</sub>) are discussed in parallel, and a comparison between them is given at the end of each section.

# 3.2. Computational details

#### 3.2.1. Preliminary statistical studies

Before performing MD simulations of cumulative He<sup>+</sup> bombardment on Si and Si<sub>3</sub>N<sub>4</sub> substrates, preliminary studies were carried out to optimize the numerical parameters (essentially the cell sizes, timestep and runtime) for a given simulation. Ideally one should take a very large cell (e.g. 1mm-wide in each direction), a timestep as small as possible and a runtime on the order of the millisecond, but as discussed in chapter 2, we are limited by the computational cost. Hence, the best set of parameters must satisfy the following two conditions: (1) optimize the computation time, (2) do not affect the simulation results. One example of such optimization is the choice of the sample thickness: if one knows that the maximal penetration depth of a given species is X (nm), there is no point to take a much deeper cell. Figure 3.1. presents the maximal penetration depth of He<sup>+</sup> ions in both crystalline Si and amorphous

Si<sub>3</sub>N<sub>4</sub> as function of the ion energy, based on 500 statistical tests of single ion impacts on the same initial substrate (but with random impact locations).





As expected, the penetration depth increases with the ion energy and is always higher for silicon. This is due to two main reasons: firstly, the atomic density of amorphous silicon nitride is nearly twice that of silicon ( $\rho Si = 0.051 a tom/A^{\circ 3}$ ,  $\rho Si_3 N_4 = 0.093 a tom/A^{\circ 3}$ ), and secondly, the collision energy transfer between He and N is more efficient than between Si and He since masses are more comparable  $(mass_{Si}/mass_{He} = 7; mass_N/mass_{He} = 3.5)$ . Preliminary studies have also shown that ions are able to penetrate deeper in a crystalline structure than in an amorphous one (because of the collisionless penetration of ions in the crystalline structure), nevertheless the penetration depth of ions in amorphous Si remains much deeper than in silicon nitride. The timestep was chosen to be as long as possible, making sure that the total energy of the system was conserved. Numerically such conditions can be satisfied only with some precision. For instance, for the silicon substrate, during a simple run with a timestep dt = 1 f s, we have  $\frac{\Delta E}{E} < 5 \cdot 10^{-6}$ . This incertitude is the result of numerical errors coming from the used integration schemes, as well as from the finite precision of the numerical variables. For energetic ion impacts, the timestep was chosen to obtain the same variation in the total energy:  $\frac{\Delta E}{E}$  <  $10^{-5}$ . Finally, the choice of the adequate runtime had to be done very cautiously for He<sup>+</sup> ions. Indeed, as mentioned in chapter 2, helium ions bombarded cumulatively can demonstrate a collective behavior, therefore the choice of a runtime based on statistical single ion impacts may not provide an adequate value. More precisely, preliminary studies showed that for energies in the 5-250eV range, helium ions impacting Si and Si<sub>3</sub>N<sub>4</sub> substrates dissipate their energy in less than 2 ps and tend to remain trapped in the structure. However, further analysis revealed that such a short runtime is far not sufficient for a cumulative He<sup>+</sup> ion bombardment. Indeed, in this case, helium atoms implanted in the substrate during

previous impacts tend to be in unstable equilibrium and very sensitive to any variation in the system, therefore much bigger runtimes are required to bring all helium atoms to their equilibrium position.

Numerical parameters used for each specific simulation are presented in the next section. But before, let's address another result yielded by the preliminary studies, which does not affect the numerical parameters but reveals an interesting fact. Figure 3.2 presents the percentage of reflected He<sup>+</sup> ions during these statistical impact tests, and shows that the probability of reflection is inversely proportional to the ion energy. This result is important to understand, since it affects the speed at which our substrates are modified, and consequently affects the ion dose required to reach the steady state. To illustrate this idea, let's consider an example: the modification of silicon by He<sup>+</sup> ions having 10eV of energy. Since reflected ions (~80%) usually transfer only a small part of their energy to the substrate, in this case, only 20% of impinging ions will cause the main material modification, which evidently decreases the efficiency or the speed of the modification.



Fig. 3.2. (Color online) Percentage of He<sup>+</sup> ions reflection as a function of their incident energy both for Si (grey) and Si<sub>3</sub>N<sub>4</sub> (blue) substrates.

## 3.2.2. Conditions of simulation

Based on our preliminary studies for various ion energies, different numerical parameters were chosen to simulate cumulative He<sup>+</sup> bombardment on Si and Si<sub>3</sub>N<sub>4</sub> substrates, as presented on table 3.1 for Si-He and on table 3.2 for Si<sub>3</sub>N<sub>4</sub>-He, respectively.

Ion Energy(eV)	Timestep(fs)	Runtime(ps)	Cell sizes (Å)	Thermalization
5	0.5	2	32x32x27	au = 100, time 1ps
10	0.5	2	32x32x37	au = 100, time 1ps
25	0.2 for 1ps 1 for the last 4ps	5	32x32x42	au = 100, time 1ps
50	0.2 for 1ps 1 for the last 19ps	20	32x32x80	au = 100, time 1ps
100	0.2 for 1ps 1 for the last 49ps	50	32x32x108	au = 100, time 1ps
250	0.1 for 0.5ps 0.25 for next 0.5ps 1 for the last 99ps	100	43x43x173	au = 100, time 1ps

Table 3.1. Simulation parameters	s for He+ (5-250eV)	cumulative bom	bardment on Si (100)
substrate.			

Ion Energy(eV)	Timestep(fs)	Runtime(ps)	Cell sizes (Å)	Thermalization
5	0.5	2	30x30x26	$\tau = 100$ , time 0.5ps
10	0.5	2	30x30x26	$\tau = 100$ , time 0.5ps
25	0.5 for 0.5ps 1 for the last 4.5ps	5	30x30x26	au = 100, time 0.5ps
50	0.25 for 0.5ps 1 for 9.5ps	10	30x30x49	$\tau = 100$ , time 0.5ps
100	0.1 for 0.5ps 1 for the last 14.5ps	15	30x30x61	au = 100, time 0.5ps
200	0.1 for 0.5ps 1 for the last 39.5ps	40	30x30x86	au = 100, time 1ps

Table 3.2. Simulation parameters for He<sup>+</sup> (5-200eV) cumulative bombardment on  $Si_3N_4$  (amorphous) substrate.

From these tables, one can see another physical difference between these two substrates. Silicon requires a relatively higher thermalization time compared to silicon nitride, because the last one is much denser and absorbs the ion energy more efficiently and more homogeneously.

Regarding the impact procedure, the interaction range (or the cutoff distance) for Moliere's potential was chosen to be 6Å, because for higher interatomic distances the potential was negligible (for example the 2-body Si-He interaction force at 6Å is  $5.81 \times 10^{-5}$  eV/Å). All ions were thus initially placed 6Å above the surface, to be out of any interaction with the substrate atoms. At 300K, a timestep of 1fs should be sufficient to conserve the total energy of the system, however, smaller timesteps were needed during the collision cascade right after the ion impact. After each ion impact, the cell was thermalized during the time specified in tables 3.1 and 3.2; it was then allowed to relax for another 0.1ps to bring back a Maxwellian distribution of atomic velocities. In all cases, eventual sputtering products were searched for

at the end of each ion impact and then erased from the system. The cells were bombarded cumulatively until they reach some steady state; this required ion doses ranging from 2x10<sup>16</sup> to 1.3x10<sup>18</sup> ion/cm<sup>2</sup>, which is equivalent to 4000-140000 ion impacts. All numerical results reported in the upcoming sections are based on an averaging of two simulations, except for the 200eV and 250eV cases, since these simulations were too time-consuming (> 6 months).

## 3.3. Surface evolution with the ion dose and self-limited ion implantation

In this section, the surface evolution as a function of the ion dose is presented, for a 50 eV He<sup>+</sup> cumulative bombardment of both Si and Si<sub>3</sub>N<sub>4</sub> substrates. We first investigate the case of silicon. Our simulations show a rapid amorphisation of the substrate followed by the formation of stable Si-He modified layer at steady state. Figure 3.3(a) shows the evolution of the modified and amorphous layer thicknesses, as well as the He uptake (i.e. the amount of implanted He atoms), as a function of the ion dose. Figure 3.3(b) presents two snapshots of the surface, in its initial state and after an ion dose of 9.4x10<sup>16</sup> ion/cm<sup>2</sup>, when steady state is reached. We observe two important stages: first, a rapid increase of all 3 curves (between points A and B), and then a slow saturation of the same curves (between B and C) before reaching steady state. The curve of the He uptake shows that we have a self-limited ion implantation; at steady state, the number of He atoms ejected during the bombardment equals the number of He atoms penetrating in the substrate.



Fig. 3.3. (Color online)  $E_{ion} = 50eV$ ,  $He^+pure ion$  cumulative bombardment of silicon: Evolution of the surface with the ion dose.

(a) Modified and amorphous layer thicknesses, and helium uptake (# of implanted He atoms).
(b) Snapshots of the cell before the bombardment, and after an ion dose of 9.4x10<sup>16</sup> ion/cm<sup>2</sup>. The dashed green line shows the initial height of the surface.

As one can see on the snapshots of Figure 3.3(b), the substrate also inflates during this evolution. The reason lies in the fact that the atomic density of the amorphous layer is lower by about 16%, because of the presence of He contaminants, dangling bonds and voids created during the collision cascade. Finally, there is almost no sputtering of Si atoms, due the weak energy transfer of He-Si collisions and the tendency of He atoms to penetrate directly deep into the material (rather than colliding with the atoms on the top surface). This behavior, specific to light gas ions, only induce a transformation of the material while classical etching ions (Cl<sup>+</sup>, F<sup>+</sup>) would sputter it in the same conditions.

Now, let us discuss the same evolution for a 50 eV He+ cumulative bombardment of silicon nitride. Figure 3.4(a) presents the evolution of the modified layer thickness and the He uptake as a function of the ion dose. Figure 3.4(b) shows the snapshots of the cell before bombardment, and after an ion dose of  $8.6 \times 10^{16}$  ion/cm<sup>2</sup>, when steady state is reached.





There is no curve for an amorphous layer here, since the initial  $Si_3N_4$  substrate is already amorphous. As discussed in Chapter 2 (subsection 2.4.2), this choice was done to be coherent with the experimental conditions [Dubois 16, Posseme 14], where silicon nitride substrates are obtained using LPCVD, and are thus amorphous.

The evolution of silicon nitride with the He<sup>+</sup> ion dose is very similar to what was observed for silicon. We observe two important stages: a rapid He implantation followed by a slow saturation and formation of a stable Si-N-He modified layer at steady state. The ion implantation is self-limited and an inflation of the

substrate after bombardment is observed. However, the modified layer thickness is smaller and the inflation weaker than in the case of silicon (see section 3.6). To avoid repetitiveness, the evolution of both substrates with the ion dose for other ion energies are not presented since the trends discussed above are generally reproduced in all cases. Instead, let us focus on the detailed nature of the material modification at steady state.

#### 3.4. Structure and composition of the modified layers at steady state

Once again, we first investigate the case of silicon. Figure 3.5 illustrates the structure and composition of the modified Si substrate after a He<sup>+</sup> dose of  $9.4 \times 10^{16}$  ion/cm<sup>2</sup> with the following subfigures: (a) shows a snapshot of the cell at steady state seen from a side view (45° rotation around z-axis) as it allows to see better where and how the helium is stored into the substrate (because of the Si lattice orientation), (b) presents the corresponding depth density profile, i.e. the number of Si and He atoms in the cell depending on depth, (c) shows the same snapshot where only Si-Si bonds are represented, and finally (d) gives the profile of the amorphization parameter  $\xi$  depending on depth.





We observe that the modified layer is composed of two distinct parts. A first layer, on top, which is thick (38 Å) and amorphous and contains He atoms, and a second layer, below, which is thin (15 Å) and
crystalline but even more enriched in He. The corresponding He/Si ratios in these layers are 0.2 and 0.3, respectively. Here, one could be surprised that He atoms remain stored in the silicon substrate. Indeed, helium atoms being inert species, they are not able to create any covalent bond with silicon and thus should be free to diffuse and to desorb. However, there is another phenomenon which takes place here and keeps these atoms in the material: the trapping.

Our simulations show that helium atoms are trapped either in the voids or cavities generated during the ion implantation, or in the Si crystalline matrix. As one can see, the modified layer is thicker than the amorphous one, due to the presence of a "helium storage layer" located below the amorphous layer. The trapping of helium atoms in silicon and other materials at room temperature was observed in other MD simulations [Pizzagalli 13, Okuniewski 04, Henriksson 06]. Experimentally, the formation and precursors of helium bubbles, as well as the desorption and permeation of helium in silicon were also studied during the last 30 years. These phenomena will be discussed in further details in the next 2 sections. In Figure 3.5(d), the parameter  $\xi$  evaluates the amorphisation rate of the substrate. As explained in chapter 2 (subsection 2.6.2), it is equal to 1 when the layer has a perfect crystalline structure, and goes smoothly to zero when the structure is not maintained. When the value is lower than 0.15, the layer is considered as amorphous [Humbird 07]. On this graph, as well on snapshot 3.5(c), we clearly see the sharp cutoff between the amorphous layer and the subsequent crystalline stack.

It is more difficult to see the structural modification of the substrate in the case of silicon nitride, as it is amorphous initially. Figure 3.6(a) shows the snapshot of a Si<sub>3</sub>N<sub>4</sub> cell at steady state, with the corresponding depth density profile presented in Figure 3.6(b). From this snapshot, the only way to distinguish the modified and non-modified parts, is the presence of helium atoms, represented as red balls. The ratio between the helium and the substrate atoms nHe/(nSi + nN) in the modified layer is about 0.12. However, there are other differences between these two layers, like the total atomic density of the substrate, which is lower by 7% in the modified part. Figure 3.6(c) presents the number of Si-N, Si-Si and N-N bonds depending on depth. In the non-modified part, Si-N bonds represent more than 95% of all bonds; in the modified part, the number of Si-N bonds decreases ( $E_{Si-N} = \sim 3.9eV$ ), meanwhile the number of less strong Si-Si bonds ( $E_{Si-Si} = \sim 2.66eV$ ) increases.

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Fig. 3.6. (Color online)  $E_{ion} = 50 eV$ ,  $He^+ pure ion$  bombardment of Si<sub>3</sub>N<sub>4</sub>, steady state: Structure and composition of the cell after an ion dose of 8.6x10<sup>16</sup> ion/cm<sup>2</sup>. (a) Snapshot of the cell, (b) corresponding density depth profile and (c) bond depth profile.

In other words, there is a rearrangement in chemical bonds caused by the energetic ion bombardment and we believe these modifications can facilitate the subsequent removal of this layer.

# 3.5. Helium trapping and clusters formation in both materials

# 3.5.1. Mechanisms of He implantation and storage

The trapping of gas species in materials was firstly discovered in far 1858 [Scherzer 83], and was since then extensively examined for different chemistries. A brief overview of the evolution of these studies is available in the introduction of [Henriksson 06]. In his turn, [Elliman 83] discovered the formation of helium bubbles in silicon after implanting high energy 80keV ions in silicon. Later, the formation and annealing of these helium bubbles was investigated experimentally [Grifficen 87, Corni 99, Cerofolini 00, Gandy 08, Linez 15] in different materials. Understanding the formation and stability of helium-filled cavities has been of high interest in the scientific world since then; it was in particular investigated by means of molecular dynamics simulations during the last decade. Particularly, [Henriksson 06] have found that in tungsten, He<sup>+</sup> ions having less than 500eV (non-damaging energy for tungsten) can produce helium clusters into the substrate containing up to 100 atoms. Afterwards, [Pizzagalli 13] have modeled as-implanted silicon substrates (with 100keV He<sup>+</sup> at 10<sup>15</sup> ion/cm<sup>2</sup>) using an initial random distribution of helium interstitials and silicon vacancies (at 1400K); they have shown that one cause of

helium clusters coarsening is the migration and coalescence of He atoms at high temperature. In our MD simulations, the formation of helium-filled cavities was also observed. These cavities appear during the ion bombardment and become bigger until the substrate reaches steady state. This phenomenon is illustrated in Figure 3.7 for the case of 50eV He<sup>+</sup> bombardment on Si: the total number of cavities, as well as the mean and maximal number of helium atoms in each cavity, are plotted as a function of the ion dose.





On Figure 3.7 we see that the mean size of cavities (or the mean number of He atoms they contain) seems to be stable at steady state, which is not the case for the maximal size of cavities which keeps oscillating. The reason why cavities fail to grow steadily is the instability of the helium clusters during the bombardment. Indeed, the impinging energetic helium ions can break the existing clusters during their collision cascade (strong momentum transfer), inducing the displacement or the desorption of the cluster atoms on surface. This can be observed on figure 3.7 for an ion dose of  $6.1 \times 10^{16}$  ion/cm<sup>2</sup>, where a large He cavity (~30 atoms) suddenly disappears (following the curve of helium uptake on Figure 3.3(a), the cluster was desorbed). A detailed MD study of helium bubbles stability in amorphous silicon subjected to heavy-ion bombardment is available in [Okuniewski 04]. In their work, the implanted Si sample was irradiated by heavy Xe<sup>+</sup> ions (0.2-2keV) and it was shown that He bubbles with gas pressures equal to or greater than 0.1kbar are stable under isotropic 2 keV Xe<sup>+</sup> bombardment, while bubbles with pressures below this limit collapse completely. In our simulations, the same phenomenon (formation of helium clusters) was observed for silicon nitride as well. In both cases, the helium clusters and cavities created (and then destructed) at steady state become larger with the increase of the ion energy. This is presented on Figure 3.8, where (a) the maximal cavity size ever detected is plotted as a

function of the ion energy for both substrates, and (b) two snapshots corresponding to the highest energies (most distinguishable cases) are presented.



Fig. 3.8. (Color online) (a) Maximal He cavity size detected (#He atoms they contain) as a function of the ion energy for both Si and Si<sub>3</sub>N<sub>4</sub>. (b) Snapshots of the cells at steady state, corresponding to Si-He<sup>+</sup> bombardment at 250eV and Si<sub>3</sub>N<sub>4</sub>-He<sup>+</sup> bombardment at 200eV, respectively.

This behavior is related to the penetration depth of He+ ions depending on their incident energy (see Figure 3.1) and to their desorption probability depending on their implantation depth. Like the ion penetration depth, the location depth of the created He clusters increases with the ion energy, and the deeper the cluster, the more protected it is. Indeed, since the probability of helium atoms to desorb decreases with depth, the created clusters have then more chances to grow into bubbles. Nevertheless, in our low-energy cases (<250eV), the clusters are located close enough to the surface to be broken and to desorb easily during the implantation. This prevents the further coalescences of these clusters into big bubbles of helium, contrary to what is observed experimentally for higher energies (>keV).

#### 3.5.2 Temperature-dependent desorption of helium

In 1987, [Griffioen 87] have experimentally shown that high temperature helium atoms (~1100K) can desorb from helium bubbles in silicon, leaving empty cavities in the substrate. Afterwards, [Corni 98] have studied the effect of various heat treatments on the helium desorption. Particularly, the as-implanted (20keV He<sup>+</sup>, 5x10<sup>15</sup> ion/cm<sup>2</sup>) silicon samples were treated isothermally during long times (~2h), and several temperature windows (~800K) were found, where all helium atoms desorbed from the substrate. Even if the ion energies studied in our MD simulations (5-200 eV) are far from the ones reported in these experiments, we decided to investigate this phenomenon using MD. To model it, our as-implanted silicon cell (which had reached steady state) was consecutively run (allowed to relax)

during several nanoseconds. It was then heated (or quenched) by 100K during 0.5ns (temperature ramp) to check if some He migration or He desorption was induced by the temperature increase. At each new temperature level, if during 5ns no change was detected in the system (i.e. all atoms kept their location), the cell was heated again by 100K following the same procedure. Figure 3.9(a) shows, for an as-implanted Si cell bombarded by He<sup>+</sup> 25eV ions, the number of desorbed He atoms as a function of time, when applying this heating procedure. Figure 3.9(b) presents the snapshots of the corresponding initial and final cells, before and after the treatment. As one can see on Figure 3.9(a), at 300K, there is practically no helium desorption. After the first temperature ramp, some He atoms are shown to desorb at 400K. Finally, at 500K, the desorption becomes important and 70% of all trapped helium atoms have desorbed after about 30 ns.



Fig. 3.9. (Color online) Temperature-dependent He desorption from an implanted Si cell ( $E_{ion} = 50eV, He^+, ion \, dose \, 9 \times 10^{16} \, ion/cm^2$ ). (a) Number of desorbed helium atoms as a function of time (blue) during the heat treatment. The grey dotted-line shows the initial number of He atoms stored in the substrate. (b) Snapshots of the initial and final cells before and after the treatment.

Most probably, the remaining 30% should desorb as well, however this long-timescale process was not followed until the end because of the high simulation time. The same heating simulation was repeated for the 100eV He<sup>+</sup> implanted silicon sample, and in that case, a higher temperature ~800K was required to desorb all helium atoms. Experimentally, [Corni 99] reported that an isothermal treatment of as implanted c-Si (5x10<sup>15</sup> He<sup>+</sup> ion/cm<sup>2</sup> at 20 keV) at 250°C (~500K) produces first a helium redistribution, while the total annealing occurs only after 2h of isothermal treatment at 500°C (~750K). Surprisingly, this phenomenon is reproduced fairly well in our simulations, showing the wide range of Moliere's and Tersoff's potentials applicability. Another interesting result can be seen on Figure 3.9(b), where all He atoms previously trapped in the crystalline silicon matrix have desorbed after the heat treatment,

meanwhile the amorphous part still contains some He atoms. This shows that the trapped helium atoms are more stable in the amorphous structure than in the crystalline one. Our MD simulations show the same desorption behavior for helium implanted in silicon nitride, however to avoid repetition it is not discussed here.

#### 3.6. Influence of the ion energy on the substrate modification

In this section, let us return to the main objective of this thesis and observe the influence of the ion energy on the substrate modification at steady state (thickness of the modified layer, sputtering rate and substrate inflation). On Figure 3.10, the thickness of the modified layer and the substrate inflation (in nm) are plotted as a function of the ion energy for both Si and Si<sub>3</sub>N<sub>4</sub> substrates. In both cases, the modified layer thickness increases with the ion energy, nevertheless it increases faster for Si than for Si<sub>3</sub>N<sub>4</sub>. As mentioned in section 3.2.1, this is explained by the fact that (1) Si<sub>3</sub>N<sub>4</sub> has a higher stopping range (atomic density 1.8 times higher than Si), and (2) the collisional energy transfer between N and He is more efficient than between Si and He (cf. mass difference).





As a direct consequence, the same trend is observed for the substrate inflation, which increases with the ion energy and is always higher for silicon. This inflation comes only from the modified part, and therefore, the thicker the modified layer, the more inflated the substrate. The influence of the ion energy on the sputtering yield of Si and SiN is plotted on Figure 3.11. There is a threshold energy near 50eV, below which no sputtering is observed; it then increases with the ion energy.



Fig. 3.11. (Color online) Sputtering yield of silicon and nitrogen atoms as function of the ion energy, at steady state, for both Si and Si<sub>3</sub>N<sub>4</sub> materials.

An interesting phenomenon is observed in the Si<sub>3</sub>N<sub>4</sub> case for energies between 50eV and 200eV. On Figure 3.11, we see that the sputtering of nitrogen atoms is larger than that of silicon atoms (even at steady state). Consequently, at steady state, the near surface region is depleted in nitrogen and contains more Si atoms than N atoms, as shown in the depth density profile of Figure 3.6(b). This behavior is also due to the more efficient collisional energy transfer between N-He compared to Si-He.

#### 3.7. Comparison with experimental data

In this section, the presented MD results are compared with experimental data provided in the thesis of Jérôme Dubois [Dubois 16]. The plasma source used in these experiments is an ICP+CCP DPS reactor of AMAT, equipped with various diagnostics, allowing the measurements of the ion flux and the ion energy on the wafer (see chapter 2, section 2.6.1). In these experiments, an amorphous Si<sub>3</sub>N<sub>4</sub> substrate was exposed to a 10mTorr He plasma, varying the source power between 0 and 1000Ws, the bias power between 0 and 200Wb and the exposure time between 1 and 10 min. Afterwards, the thickness of the modified layer was measured using TEM images and other techniques, as detailed in chapter 1 (see subsection 1.5.2.2). Figure 3.12 presents the effect of the bias power on the substrate modification (a) experimentally and (b) "using" MD. More precisely, Figure 3.12(a) presents the etched thickness as a function of the HF 1% bath time, for three samples: a pure LPCVD Si<sub>3</sub>N<sub>4</sub> (blue), a Si<sub>3</sub>N<sub>4</sub> exposed to 60s of CCP 100Wb He plasma (black), and a Si<sub>3</sub>N<sub>4</sub> exposed to 60s CCP 200Wb He plasma (red). Figure 3.12(b) presents MD results of the evolution of modified layer thicknesses for He<sup>+</sup> 50eV (black) and He<sup>+</sup> 100eV (red) bombardment of Si<sub>3</sub>N<sub>4</sub>.



Fig. 3.12. (Color online) Effect of the bias power. (a) [EXP] Etched thickness as a function of HF 1% bath time [Dubois 16], for non-modified (blue curve) and modified (black and red curves) silicon nitride. (b) [MD] Evolution of modified layer thicknesses for  $He^+ 50eV$  (black curve) and  $He^+ 100eV$  (red curve) bombardment of Si<sub>3</sub>N<sub>4</sub>.

The last MD conditions are equivalent to experimental conditions [600Ws, 50Wb] and [600Ws, 100Wb] respectively. Understandably, such conditions are chosen since ion energies of 450eV and 800eV (equivalent to the experimental conditions in Figure 3.12(a)) were not accessible in MD because of the huge simulation time required. Nonetheless, on Figure 3.12 we see that MD reproduces well the experimental results – the increase of bias power increases the modified layer thickness (because of the increase of the ion energy).

Figure 3.13 illustrates the effect of the plasma exposure time on the substrate modification (a) experimentally and (b) "using" MD.



Fig. 3.13. (Color online) Effect of plasma exposure time. (a) [EXP] Etched thickness as a function of HF 1% bath time [Dubois 16] for silicon nitride after different plasma exposure times (1, 2, 5 and 10min). (b) [MD] Evolution of the modified layer thickness as function of the ion dose for *He*<sup>+</sup> *100eV* bombardment of Si<sub>3</sub>N<sub>4</sub>.

On Figure 3.13(a), we see that experimentally the modified layer thickness initially increases with the plasma exposure time (i.e. it increases with the ion dose) and saturates after 5min (after a certain ion dose). The same trend is observed in our simulations (see Figure 3.13(b)): the modified layer thickness increases in the fast-transient regime before reaching a constant value at steady state, due to the self-limited implantation. Other interesting similarities between MD and experiments can be observed for the same experience, as presented on Figure 3.14. This time we focus on the experimental etch rates, i.e. the slopes of the curves on Figure 3.14(a).



Fig. 3.14. (Color online) Effect of plasma exposure time. (a) [EXP] Etched thickness as a function of HF 1% bath time [Dubois 16] for silicon nitride after different plasma exposure times (1, 2, 5 and 10min). (b) [MD]  $He^+$  100eV bombardment of Si<sub>3</sub>N<sub>4</sub> – Number of Si-N bonds depending on depth for ion doses equal to 1.5 and 10 x10<sup>16</sup> ion/cm<sup>2</sup> (black and blue curves respectively).

Figure 3.14(a) shows that experimentally the etch rate decreases when the etched thickness increases (for all exposure times or ion doses), suggesting that the deeper layers are less modified. As a result, the etch rate in the top (green region) and in the bottom (red region) of the modified layer are very different. This is also seen numerically on Figure 3.14(b), where the number of Si-N bonds depending on depth (which can quantify the material modification) is given for 2 different ion doses. We observe that the quantity of Si-N bonds increases with the depth, which explains the change of etch rate seen experimentally. Also on Figure 3.14(a), the initial etch rate increases with the exposure time (or the ion dose), as shown by the purple arrow, but becomes stable at steady state (for exposure times  $\geq 5$ min). The same trend is given by MD on Figure 3.14(b): the number of Si-N bonds in the modified layer is much lower at high ion dose (10x10<sup>16</sup> ion/cm<sup>2</sup> - blue curve) when steady state is reached, than at low

ion dose (1.5x10<sup>16</sup> ion/cm<sup>2</sup> - black curve) when the evolution of the modified layer is still in transient regime. The last three comparisons show a good phenomenological (or qualitative) agreement between our MD simulations and experiments; now let us give a quantitative comparison. Figure 3.15(a) shows the effect of the source power on the modified layer thickness [Dubois 16]; the ion energies and doses measured experimentally for each operating condition are given in the legend. Since the lower ion energies (<200eV) were accessible in MD, they were simulated to estimate numerically the modified layer thicknesses. The comparison between MD and experimental data is given on Figure 3.15(b). In this figure statistical MD predictions of the maximal ion penetration depth were also added; for each ion energy, these data were obtained from 1000 tests of He<sup>+</sup> ion bombardment performed on the same initial Si<sub>3</sub>N<sub>4</sub> cell.



Fig. 3.15. (Color online) (a) [EXP] Effect of the source power on the substrate modification [Dubois 16]: etched thickness ( $\Leftrightarrow$  modified layer thickness) of Si<sub>3</sub>N<sub>4</sub> dependent on the ion energy. (b) Comparison between experimental data and MD calculations. The modified layer thickness for E<sub>ion</sub> >200eV can be estimated from statistical MD results of the maximal ion penetration depth.

From the last graph, we see an excellent quantitative agreement between MD simulations and experiments. Moreover, statistical studies of the maximal ion penetration depth (blue curve) are shown to reproduce fairly well the modified layer thickness measured experimentally or truly simulated for energies  $\leq 200$ eV. Following it, for E<sub>ion</sub> = 450eV, the gap between the measured and the statistically estimated data suggests that the steady state was far not reached in these experimental conditions (100Wb, 0Ws, 60s), which is confirmed experimentally on Figure 3.13(a).

In the end, it can be concluded that the present MD simulations are in good agreement with experiments, not only qualitatively but also quantitatively.

# 3.8. Technological potential of helium plasmas for the Smart Etch process

From a technological point of view, our MD simulations show the high applicability of helium plasmas in the Smart Etch technology for both Si and Si<sub>3</sub>N<sub>4</sub> materials. Nonetheless, it shows that much attention must be paid to the deposited ion energy and to the ion dose. In the Smart Etch process, the role of the He plasma modification (step 1) is to ensure a high selectivity between the modified and non-modified material, to then allow the subsequent removal of the modified layer with a good precision (step 2). MD shows that helium plasmas can indeed weaken Si and Si<sub>3</sub>N<sub>4</sub> on a precise depth without etching them, by creating a less dense modified layer, full of He-filled cavities and containing weaker bonds. For 50eV He<sup>+</sup> ions bombarding silicon, the interface between the modified and non-modified parts is sharply defined, preserving the initial crystalline state below (see snapshots on Figure 3.16). If the same behavior is observed for 100eV He<sup>+</sup> ions, this interface tend to become askew (or blurred) for 250 He<sup>+</sup> ions, which in turn may affect the surface roughness after the removal of the modified layer.





For silicon nitride, it is difficult to visualize this interface simply (fully amorphous substrate), nevertheless the structural analysis of the sample depending on depth shows that even for 200eV He<sup>+</sup> bombardment, this interface remains very sharp.

In all cases, the sputtering rate of Si and Si<sub>3</sub>N<sub>4</sub> materials at steady state is relatively weak. However, much attention should be paid to the ion dose, which depends experimentally on both the ion flux and the plasma exposure time. Indeed, following our MD data, sputtering remains relatively weak at 100eV, removing less than 0.2nm before reaching steady state (ion dose  $\sim 1 \times 10^{17}$  ion/cm<sup>2</sup>), but for a dose higher

than ~6x10<sup>17</sup> ion/cm<sup>2</sup>, sputtering could remove more than 1nm, thereby the nanoscale precision of the Smart Etch process may not be ensured.

As mentioned in section 3.2.2, numerical values reported in this study are based on an averaging of two simulations (except for  $E_{ion} \ge 200$ eV). One should note that for energies in the 5-100eV range, all results were reproduced with a high precision; for example, the reported thicknesses of modified layers were duplicated with a precision of 1-3 Å. This may be important from a process point of view, since it suggests that the modifications induced by a low energy helium plasma should be homogeneous, a necessary condition to avoid the development of roughness after the second step.

Finally, contrary to the Smart Etch, low energy He<sup>+</sup> ions bombardment does not show a strong interest for the Smart Cut technology. Indeed, following these simulations, at these energies the top-surface is always amorphous because the collision cascade takes place near the surface. However, experiments [Lu 97] show that helium plasma can be applied for this process at higher energies (> keV), because it is then possible to keep the near-surface region crystalline and to obtain the formation of helium bubbles deep in the material, allowing the further splitting of the substrate during the heat treatment.

#### 3.9. Conclusion

In this chapter, the influence of He<sup>+</sup> ion bombardment on Si and Si<sub>3</sub>N<sub>4</sub> substrates modification was investigated, for ion energies varying in the 5-250eV range. Similar phenomena and tendencies were established for both materials, as well as some distinct behaviors for each one.

In all cases, a self-limited ion implantation takes place with a surface evolution composed of two stages: a rapid modification followed by a slow saturation and the formation of a stable modified layer at steady state. The self-limitation (of ion implantation) is guaranteed thanks to the mechanism of helium trapping. He trap in these materials prevents the diffusion of helium atoms deep in the substrate, and at steady state, the total number of implanted helium atoms is constant in average (the number of penetrating He atoms equals the number of desorbing He atoms). In silicon, the ion implantation induces a strong amorphization and generates He-filled cavities in the bulk. For silicon nitride, besides the presence of He cavities, there is a rearrangement in bonds: the breaking of amorphous Si-N bonds is followed by the creation of less strong Si-Si bonds. In silicon, helium atoms are trapped in the cavities or voids created during the ion implantation and in the Si crystalline matrix, meanwhile in silicon nitride, the trapping occurs mainly in cavities. In both cases, helium atoms can out-diffuse from small cavities and desorb if the substrate is annealed (heated at ~500-800K depending on the ion energy of implantation). The modified layer thickness increases with the ion energy and is always thicker in the case of Si. For the studied energies, the substrates also tend to inflate during the bombardment, this inflation increasing with the ion energy. A threshold value of ion energy ~50eV is found, below which no sputtering occurs; for higher energies, the sputtering yield increases with the ion energy but remains weak (<0.05 atom/ion for  $E_{ion} < 250$ eV). In the case of Si<sub>3</sub>N<sub>4</sub>, preferential sputtering of nitrogen is detected, which makes the near surface region depleted in nitrogen. Another threshold value of ion energy 10eV is established, below which no structural modification appears: He<sup>+</sup> ions with  $E_{ion} < 10$ eV penetrate in silicon on 1-2nm without damaging the crystalline structure and stay trapped into it.

The discussed structural modifications - less dense implanted layer, full of He-filled cavities and containing weaker bonds - can explain the selective removal of the modified part during the second step of the Smart Etch. The simulation results are also compared with experimental data provided by [Dubois 16], showing a both qualitative and quantitative agreement. Present MD simulations shows the high applicability of helium plasma in the Smart Etch process for both Si and Si<sub>3</sub>N<sub>4</sub> substrates, nevertheless the ion energy and the ion dose must be controlled very cautiously, to preserve the nanoscale precision of the process and ensure the homogeneous modification of the substrate.

# Chapter 4

# Hydrogen plasmas modification of Si thin films

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In this chapter, Molecular Dynamics (MD) simulations of both low-energy (5-100 eV)  $H_x^+$  ion implantation and mixed  $H_x^+$  ion/ H radicals bombardment of crystalline (100) Si surfaces are performed, to investigate the influence of the ion energy, ion dose, ion composition and radical-to-ion flux ratio on the substrate modification.

# 4.1. Motivation and objectives of the study

In microelectronics, the eternal challenge of transistors miniaturization gave rise to numerous complex procedures involving both plasma etching and ion implantation steps. Due to its unique physical and chemical properties, hydrogen is almost ubiquitous in all these processes; in particular, it plays a key role in both the Smart-Cut [Smart Cut Patent 94] and the recently developed Smart-Etch [Smart Etch Patent 14] technologies. As detailed in chapter 1, the Smart-Cut technology is a multistep process that makes it possible to transfer a thin layer of crystalline material from a donor substrate to another substrate. As illustrated in Figure 1.22, hydrogen ions are implanted in a substrate A, which is then flipped around and covered with a stiffener B. Afterwards, a heat treatment phase allows to cleave and separate the new thin film and the initial bulk material [Smart Cut Patent 94]. The Smart-Etch is a two-

step process that enables to modify a thin layer of material and then remove it, while avoiding usual dryetching issues. In the first step, a hydrogen plasma is used to modify the substrate by light ion implantation; in a second step, the modified part of the material is removed using an appropriate wet- or dry- etching chemistry, with a high selectivity with respect to the non-modified part [Posseme 14]. This process, which was recently proposed as an alternative way for thin films etching [Kanarik 15], has shown in particular promising results for silicon nitride spacers etching [Posseme 14, Sherpa 17].

Although the Smart Cut technology was extensively used and studied over the last 20 years [Aspar 97, Weldon 97, Lu 97, Bedell 01, Terreault 07], some fundamental mechanisms involved in this process are still poorly understood [Terreault 07], partly because of the hard detectability of hydrogen in materials in experiments. In particular, the chemical form in which hydrogen is stored in the substrate during the ion implantation step remains unclear. In the Smart Etch process, the exact role of the ion energy and ion flux on the substrate pre-modification needs to be clarified. The different nature of the modified layer when exposed to a hydrogen or a helium plasma should also be understood, as well as the reasons why these modifications facilitate the subsequent removal of the layer.

Thus, in this work, molecular dynamics simulations were performed on silicon, first to understand the effect of the ion energy and ion dose on the substrate modification, during a bombardment with lowenergy (5-100 eV)  $H_x^+$  ions only (SmartCut-like conditions). Then, to model a real  $H_2$  plasma exposure (SmartEtch-like conditions), mixed H<sub>x</sub><sup>+</sup> ion/H radical bombardments were simulated, to understand the effect of additional plasma parameters like the ion composition or the radical-to-ion flux ratio. Although the main material of interest is silicon nitride (used for spacers in CMOS transistors), the study of the Si-H system constitutes a first and necessary step to understand the fundamental mechanisms involved in these processes. The more sophisticated case of silicon nitride, which was effectively etched using the SmartEtch technique with H<sub>2</sub> plasmas [Posseme 14, Dubois 16, Sherpa 17, Chambettaz 18], will be investigated in the next chapter. The Si-H system was examined using MD for various purposes: passivation of silicon surfaces and hydrogen deposition on Si for photovoltaic and optoelectronic applications [Ramalingam 98, Ohira 00, Pan 04], deposition of high quality silicon thin films [Ning 09, Le 14a, Le 14b], hydrogen abstraction [Cereda 07], hydrogen diffusion on c-Si surfaces [Bowler 00], and even the fabrication of nanometer particles [Hawa 08, Vach 06]. However, very few studies were carried out to understand the role of energetic ion bombardment on the substrate [Wang 16], and no MD study at all was reported on the interaction between low-temperature H<sub>2</sub> plasmas and Si surfaces.

## 4.2. Computational details

As explained in chapter 3, preliminary studies were carried out to choose the best set of numerical parameters for each performed simulation, depending on the ion energy and the ion type investigated. Basing on these preliminary studies, the following simulation conditions were chosen to simulate various cumulative  $H_{x^+}$  (x=1-3) bombardment on silicon, as presented in table 4.1.

Ion energy (eV)	Timestep (fs)	Runtime (ps)	Cell sizes (Å)	Thermalization
and type				
5eV H <sup>+</sup> , H <sub>2</sub> <sup>+</sup> , H <sub>3</sub> <sup>+</sup> ,	0.1	2	27x27x27	$\tau = 100$ , time 0.2ps
10eV H <sub>2</sub> +, H <sub>3</sub> +				
10eV H+,	0.1	2	27x27x42	$\tau = 100$ , time 0.2ps
25eV H <sub>2</sub> +, H <sub>3</sub> +				
25eV H+	0.1	2	27x27x64	$\tau = 100$ , time 0.2ps
50eV H <sub>2</sub> +, H <sub>3</sub> +				
100eV H <sub>3</sub> +	0.04 for 0.1ps 0.1 for the last 1.9ps	2	27x27x64	$\tau = 100$ , time 0.2ps
50eV H+,	0.04 for 0.1ps	2	27x27x102	$\tau = 100$ , time 0.2ps
100eV H <sub>2</sub> +	0.1 101 110 105 1.305			
100eV H⁺	0.02 for 0.1ps 0.1 for the last 1.9ps	2	27x27x150	au = 100, time 0.2ps

# Table 4.1. Simulation parameters for $H_{x^+}$ (5-100eV) cumulative ion bombardment on crystalline Si (100) substrate.

The ion impact procedure was similar to the one described in chapter 3. Like in the case of the He<sup>+</sup> bombardment, once the  $H_{x^+}$  ion energy exceeds some threshold value (here 50eV), simulating the collision cascade for the first few hundreds of femtoseconds after the ion impact requires a smaller timestep for the numerical integration convergence. For the mixed ion/radical bombardment, the cell depth was chosen according to the most energetic ion present in the mixture (e.g. for 25eV H<sup>+</sup>:H<sub>2</sub><sup>+</sup>:H<sub>3</sub><sup>+</sup>, the cell depth was 64Å, which corresponds to the cell depth of a 25eV H<sup>+</sup>). Regarding the H radical impact procedure, there was no fixed runtime; instead, a sequence of consecutive small runs (or loops) of 0.05ps was performed, until the surface diffusion was finished and the physics of the interaction fully captured (i.e. covalent bonding to the surface, reflection, formation of a volatile etch product, etc.). The H radical impact was then considered as finished.

In both cases (pure ion and mixed ion/radical bombardment), after each ion impact the cell was thermalized at 300 K; then it was run for another 0.1ps to bring back a Maxwellian distribution of atomic velocities. During this additional run, H<sub>2</sub> molecules were also detected and erased from the configuration. Indeed, as further detailed in section 4.3.2, all H<sub>2</sub> molecules created in the substrate should diffuse into the material and desorb within a few nanoseconds, i.e. well before the next ion or radical impact. Besides, after each plasma species impact, the presence of etching and sputtering products was searched for, and when such products were detected on the surface, they were erased from the system. The silicon cells were bombarded cumulatively until reaching steady state; this required ion doses from 0.7x10<sup>16</sup> to 3.5x10<sup>17</sup> ion/cm<sup>2</sup>, which is equivalent to 500-25000 ion impacts. All numerical results reported in the upcoming sections, are based on an averaging of two simulations.

Here, to model the interaction between Si-Si, Si-H and H-H, we used the Murty's potential [Murty 95], which is an extended version of the Tersoff potential for silicon [Tersoff 88] including the hydrogen interactions (see section 2.3.1). Ion and radical bombardment on the substrate was simulated by initially placing the impacting species at random locations in the XY plane, and 3Å above the surface (i.e. out of any interaction with the surface). Then, they were sent towards the surface, isotropically and with a thermal energy of 300K for H radicals, anisotropically and with kinetic energies varying from 5 to 100eV for ions.

#### 4.3. H<sub>x</sub><sup>+</sup> (x=1-3) ion implantation in Si

In this section, the numerical results of a pure bombardment of  $H_{x^+}$  (x=1-3) ions on crystalline Si (100) surfaces are presented; then, possible fundamental mechanisms driving the Smart Cut technique are discussed.

#### 4.3.1. Surface evolution with the ion dose and self-limited ion implantation

In this subsection, the surface evolution with the ion dose is investigated, for a 25eV H<sup>+</sup> ion bombardment of silicon. Simulations show a rapid amorphization of the substrate followed by the formation of stable [a-Si:H] modified layer at steady state. Figure 4.1(a) shows the evolution of the modified and amorphous layer thicknesses, as well as the H uptake (i.e. the amount of implanted H atoms), as a function of the ion dose. On Figure 4.1(b) are presented two snapshots of the surface, in its initial state and after an ion dose of  $14x10^{16}$  ion/cm<sup>2</sup>, when steady state is achieved. In this evolution, there are two important stages: first, a rapid increase of all 3 curves (between points A and B), and then a slow saturation of all curves (between B and C) before reaching steady state.



Fig. 4.1. (Color online) [MD]  $E_{ion} = 25eV$ , pure H<sup>+</sup> ion bombardment of silicon: Evolution of the surface with the ion dose. (a) Modified and amorphous layer thicknesses, and hydrogen uptake, as function of the ion dose. (b) Snapshots of the cell before the bombardment, and after an ion dose of  $14x10^{16}$  ion/cm<sup>2</sup> (steady state). The dashed green line shows the initial height of the surface. [EXP] (c) TEM images of Si samples exposed to 500eV H<sup>+</sup> ion beam at 2 different angles (0° and 60°), ion dose 1x10<sup>17</sup> ion/cm<sup>2</sup> [Ito 12], (d) Corresponding depth profiles of dislocated Si atoms for different ion doses [Ito 13].

As one can see, the modified layer is always thicker than the amorphous one, since some crystalline part of the substrate below the amorphous layer is still hydrogenated. Indeed, like in the helium case, ions are losing their kinetic energy during the collision cascade, and starting from a certain depth, the ion energy is no more sufficient to amorphize the substrate (i.e. break the crystalline Si-Si bonds) but still sufficient to let the ion go deeper and hydrogenate the substrate. Simulations show that a relatively high ion dose, dependent on ion energy, is needed to observe a significant amorphization. These results are in agreement with experimental data obtained from ion beam experiments in Japan [Ito 11, 12, 13]. In their study, Ito et al. report 2 TEM images of Si samples exposed to 500eV H<sup>+</sup> ion beam at 2 different

angles, in which the dark spots represent regions of dislocated Si (defects) caused by the bombardment (see Figure 4.1c)). Since H ions are much lighter than Si, they observe that H ions penetrate into the material in nearly all directions. As shown in Figure 4.1d), Ito et al. also report the depth profiles of dislocated Si atoms for different ion doses obtained from Rutherford backscattering spectroscopy; they show that the modified layer thickness increases with the ion dose before saturating. On Figure 4.1(a), the curve of the H uptake shows that we have a self-limited ion implantation; at steady state, the number of desorbing H<sub>2</sub> molecules (created in the bulk during the implantation) is balanced by the number of H<sup>+</sup> ions penetrating in the substrate. Finally, as one can see on the snapshots of Figure 4.1(b), our simulations also show that the substrate inflates during this evolution. This happens because the atomic density of Si in the modified part is lower by 15-30% than in the crystalline one, and because of the absence of etching or sputtering. Indeed, due the weak energy transfer of H-Si collisions and the tendency of H atoms to penetrate deep into the material, the hydrogen ion implantation only induces a transformation of the material.

#### 4.3.2 Structure of the H-implanted Si layer at steady state

For the same simulation conditions, let us zoom on the steady state and give a more detailed description of the modified layer. Figure 4.2 illustrates the structure and composition of the H-implanted Si layer after a 25eV H<sup>+</sup> dose of 13x10<sup>16</sup> ion/cm<sup>2</sup>.



Fig. 4.2. (Color online)

 $E_{ion} = 25eV$ , pure H<sup>+</sup> ion bombardment of silicon, ion dose ~13x10<sup>16</sup> ion/cm<sup>2</sup>. Structure and composition of the cell at steady state.

(a) Snapshot of the cell, (b) corresponding density depth profile, (c) bond depth profile, and (d) snapshot of the cell with Si-Si bonds only.

Figure 4.2(a) shows a snapshot of the cell at steady state and Figure 4.2(b) presents the corresponding depth density profile, i.e. the number of Si and H atoms in the cell depending on depth. Finally, Figure

4.2(c) gives the depth profile of covalent bonds in the material. First on Figure 4.2(b), we observe a Gaussian-like distribution of the hydrogen profile in the material, which is in agreement with various experiments [Bedell 01, Moutanabbir 05, Lu 97]. Such behavior takes place thanks to the absence of Si etching/sputtering during the ion bombardment (for this 25eV energy), and thanks to the high reactivity of atomic hydrogen with silicon, which prevents its diffusion. As hydrogen is chemically reactive (contrary to helium), ion implantation leads to the rupture of Si-Si bonds and to the formation of SiH, SiH<sub>2</sub>, SiH<sub>3</sub> groups in the modified material (Figure 4.2c)). Near the peak of hydrogenation (depth ~3.5nm), the ratio H/Si is almost equal to 1, and one can observe the presence of SiH<sub>3</sub> groups, as well as an extremely low concentration of non-hydrogenated Si atoms. Since Si atoms are tetrahedrally coordinated (initially having 4 covalent silicon bonds), most of them in this modified layer have now x covalent hydrogen bonds, and 4 - x covalent silicon bonds. On the contrary, hydrogen atoms can only form 1 single covalent bond, which means that Si atoms bound to 3 H atoms have only one possible covalent bond remaining with the bulk. This shows that the material is extremely weakened in this region, and we believe that this fracture of the substrate is at the origin of the Smart Cut mechanism. On Figure 4.2(c), one can notice the absence of H<sub>2</sub> molecules in the material. As mentioned above, these H<sub>2</sub> molecules are artificially erased from the system after each ion impact, since it was seen that during the nonsimulated long timescales (few nanoseconds) between ion impacts, these H<sub>2</sub> molecules diffuse and leave the surface region. To prove this assumption, for all studied energies (5-100eV), simulations were made without erasing the  $H_2$  molecules; when the silicon cells were hydrogenated and full of  $H_2$ molecules, long runs of few nanoseconds were performed, during which all H<sub>2</sub> molecules were shown to desorb. The results of this procedure, applied to the case { *E*<sub>ion</sub>=100eV, pure H<sup>+</sup> ion bombardment, dose 5x10<sup>16</sup> ion/cm<sup>2</sup>}, are illustrated on Figure 4.3, where (a) gives the hydrogen bonds depth profile right after the H<sup>+</sup> bombardment, (b) shows the total number of H<sub>2</sub> molecules in the cell as function of time, and (c) gives the same hydrogen bonds depth profile but after 5ns. This assembly of graphs shows that after 5ns, all H<sub>2</sub> molecules are released from the cell.



Fig. 4.3. (Color online)  $E_{ion} = 100eV$ , pure H<sup>+</sup> ion bombardment of silicon, ion dose ~5x10<sup>16</sup> ion/cm<sup>2</sup>. H2 molecules desorption in a few nanoseconds following the last ion impact. (a) Hydrogen bonds depth profile of the cell right after the ion bombardment (b) Number of H<sub>2</sub> molecules present in the cell as a function of time (c) Hydrogen bonds depth profile of the cell after 5 nanoseconds.

Nevertheless, this is not sufficient as a proof since some part (~35%) of all H<sub>2</sub> molecules were released through the cell's bottom, and unfortunately, the further trajectories of these molecules were lost, because it is computationally too expensive to simulate a cell with a depth of some microns. Further investigation of this phenomenon showed that H<sub>2</sub> molecules are unbreakable in this system due to their strong covalent bond (4.76eV), and as a result, they are repulsed by all other atoms, doing a random walk. To estimate the probability of a H<sub>2</sub> molecule displacement in the silicon lattice, a H<sub>2</sub> molecule was randomly placed in the middle of a crystalline Si bulk, and its trajectory was then tracked until it eventually leaves the cell. An example of such a H<sub>2</sub> molecule random displacement is shown on the snapshots of Figure 4.4(a), which are taken each 10ps. The same test was repeated 200 times. The vertical trajectories of the H<sub>2</sub> molecule (i.e. the variation of its z coordinate) during the first two tests are plotted on Figure 4.4(b). Based on these statistical tests, the vertical displacement probability of a H<sub>2</sub> molecule in 10ps is given in the inset graph, which was used to simulate the random walk of H<sub>2</sub> in the next step. A H<sub>2</sub> molecule was then placed at initial depths of 0,10,100,1000 and 10000nm, and its random walk was simulated during 1 millisecond, a duration equivalent to the time between two

consecutive ion impacts. After 1000 tests for each depth, the probability of a  $H_2$  molecule to desorb in 1 ms depending on its initial depth was estimated, as shown on Figure 4.4(c).



Fig. 4.4. (Color online) H<sub>2</sub> molecules random walk in the silicon lattice and H<sub>2</sub> desorption probability at 300K.

(a) Snapshots of the Si cell with a  $H_2$  molecule inside (in red circles), taken each 10 picoseconds (b)  $H_2$  random walk trajectories (variation of its z coordinate) and vertical displacement probability in the inset graph

(c) H<sub>2</sub> molecule desorption probability in 1 ms depending on its initial depth

As expected, the desorption probability decreases with the increase of the initial depth of the H<sub>2</sub> molecules. For an initial depth of 10nm, which is the maximal depth of H<sub>2</sub> molecules in our 100eV H<sup>+</sup> bombardment simulations, 99.98% of H<sub>2</sub> should desorb. Moreover, following the experiments of [Moutanabbir 05], no H<sub>2</sub> accumulation was reported even for an ion implantation at 5keV. From this study, we can conclude that for ion energies studied in the present work (5-100eV), all H<sub>2</sub> molecules created in the silicon bulk should desorb before the next ion impact. Since no H<sub>2</sub> accumulation can occur, thus a self-limited ion implantation is observed, which is maintained by the fact that, at steady state, the number of penetrating hydrogen atoms (in form of H<sub>x</sub><sup>+</sup> ions) is balanced by the number of desorbing H<sub>2</sub> molecules.

#### 4.3.3 Influence of ion type and ion energy on the substrate modification

Now that one specific simulation and its results were highly detailed, we can study the effect of the ion type and ion energy on the substrate modification. The same simulation (corresponding to Figure 4.1) was performed for energies in the 5-100eV range, with  $H^+$ ,  $H_2^+$  and  $H_3^+$  ions. On Figure 4.5, the thickness of the modified layer at steady state is plotted as a function of the ion energy for different ion types. As

expected, the modified layer thickness increases with the ion energy but decreases with the ion size, since more energetic and smaller  $H_x^+$  ions penetrate deeper in the substrate. The thickness increases linearly with the ion energy, for all types of ions, nevertheless this tendency is not provided for  $H_2^+$  ions having an energy  $\leq 5eV$ . Indeed, since the bond energy of  $H_2$  molecules is 4.76eV, impinging  $H_2^+$  ions with  $E_{ion} \leq 5eV$  are either reflected or broken, and bind to the first layers of the substrate (H fragment atoms do not penetrate deep into the substrate, since almost all kinetic energy was spent on the bond breaking), causing principally no modification.





Figure 4.6 represents the etch yield at steady state as a function of the ion energy, for different hydrogen ions.





A non-standard behavior is observed: the etch rate decreases when the ion energy increases and is zero for energies  $\geq$  50eV. Hydrogen being very lightweight, it is not able to sputter Si atoms which are 28 times heavier, so the main way to etch silicon remains chemical etching. This explains why the etch yield is higher for molecular ions: low-energy H<sub>3</sub><sup>+</sup> and H<sub>2</sub><sup>+</sup> ions tend to break apart and to lose kinetic energy upon impact, acting then almost as H radicals on the surface. This can be seen on the inset graph, where the distribution of etch products for a  $10eV H_3^+$  bombardment is given, and where we see that the major part of etch products are saturated molecules (70% SiH<sub>4</sub>, 6% Si<sub>2</sub>H<sub>6</sub>, 4% Si<sub>3</sub>H<sub>8</sub>). Above a threshold energy of ~25eV, all ions penetrate deep into the bulk, leaving the near surface region almost not hydrogenated. As a consequence, they cannot form any volatile product on the surface, and thus do not initiate any chemical etching.

#### 4.3.4. Effect of the surface temperature and application to the SmartCut technology

Finally, let's conclude this section by a contribution to the fundamental understanding of the Smart Cut technology, which was briefly detailed in the introduction, and is schematically represented on Figure 4.7. The first step of this process, i.e. the hydrogen ion implantation and the formation of a modified [a-Si:H] layer (in red on Fig 4.7), was discussed in the previous sections. Then, the implanted wafer is bonded to a stiffener and a heat treatment results in the cleavage of the weakened layer, which enables to separate the new thin film and the bulk material.





In this section, the heat treatment phase is simulated using MD. The temperature control we apply is given on Figure 4.8(a), where the substrate is heated with successive ramps of 100K. Each time the cell is heated (quenched) by 100K during 10ns; then the new temperature is maintained during 50ns and we observe the evolution. The snapshots on Figure 4.8(b) present the evolution of the H-implanted Si cell (after a 50eV  $H_2^+$  dose of  $11 \times 10^{16}$  ion/cm<sup>2</sup>) during the heat treatment at 300K, 600K and 1000K. On these snapshots, only Si-Si bonds are plotted, to see intrinsically what happens with the substrate structure. As one can see, until 1000K there is no clear visual effect, but the fracture between the modified and non-modified parts increases when heating the substrate.



Fig.4 8. (Color online)  $E_{ion} = 50 \text{eV}$ , pure  $H_2^+$  ion bombardment of silicon, dose ~11x10<sup>16</sup> ion/cm<sup>2</sup>. Evolution of the hydrogen-implanted Si crystal when increasing its temperature.

At 1000K, because of the strong thermal vibrations, the remaining Si-Si bonds located in the most hydrogenated region are breaking, which induces an in-depth micro-slicing of the cell. However, this simulation may show some limitations, since some experiments reported a recombination and desorption of H<sub>2</sub> molecules during heating [Weldon 97, Moutanabbir 05], which are not captured here. Nevertheless, based on the aforementioned facts relative to molecular hydrogen desorption, all recombined H<sub>2</sub> molecules should be formed and desorb one by one. Thus, H<sub>2</sub> molecules should not affect the cell breaking, unless a significant quantity of H<sub>2</sub> molecules was desorbing simultaneously, which is unlikely, especially if one compares the heat treatment duration (~20 minutes) with the reported implantation ion doses ~6x10<sup>16</sup> ion/cm<sup>2</sup>. Indeed, these ion doses are equivalent to ~4000 H<sup>+</sup> ion impact on our MD cell, and even if we assume that all implanted ions could recombine and desorb in form of  $H_2$  molecules during the annealing, it would give a mean desorption rate ~1.66  $H_2$  per second. It is also worth reminding that these MD simulations were performed for relatively low energies ( $\leq 100 eV$ ) compared to experiments, where often the hydrogen is implanted with energies ~100keV [Bedell 01]. Since the hydrogen penetration depth increases linearly with the ion energy, the formation of  $H_2$ molecules should occur deeper for higher energies. For example, for energies ~100keV, it is highly probable to form H<sub>2</sub> molecules at a depth of a few dozens of microns, where the desorption time of H<sub>2</sub> molecules may be sufficiently long to bring its contribution to the full process (ion implantation and heat

treatment). Unfortunately, such bombardment energies are far not accessible with MD, because of the computational time.

#### 4.4. Mixed H<sub>x</sub><sup>+</sup> ion/H radical bombardment of silicon (H<sub>2</sub> plasma exposure)

In this section, the results of a mixed bombardment of  $H_x^+$  ions and atomic H on Si are presented, to investigate the effect of real H<sub>2</sub> plasmas on silicon substrates. In the end, some fundamental issues related to the Smart Etch process are discussed. The input parameters related to the plasma composition were deduced from the works of [Samuel 15, Zorat 00, Dubois 16], as presented in chapter 2 (in subsection 2.6.1). As already mentioned, thermal H<sub>2</sub> molecules behave like inert species in this interaction due to their strong chemical bond. Since H<sub>2</sub> impacts do not require to be simulated, we focus on two other parameters: the radical-to-ion flux ratio ( $\Gamma = \Gamma_H / \Gamma_{Hx+}$ ) and the ion composition (H<sup>+</sup>:H<sub>2</sub><sup>+</sup>:H<sub>3</sub><sup>+</sup> ratio). The disregard of impacting H<sub>2</sub> molecules may lead to miss two phenomena, the etching of Si by H<sub>2</sub>, and its diffusion into the substrate. The first one was shown to be impossible at ambient temperature in the experimental work of [Uchida 01], in total agreement with the present simulations. The second one may be possible, however, these diffusing molecules should either go deep in the substrate or desorb, as it was shown in previous sections.

#### 4.4.1. Surface evolution with the ion dose and etching

In this subsection, the evolution of the silicon surface with the ion dose for a mixed ion/radical bombardment is discussed. To avoid repetition, we first investigate the following base case:  $\{E_{ion}=100eV, mixed H_x^* ion/H radical, \Gamma=10, 90\% H_3^*\}$  (see section 2.6.1. for details). The influence of each parameter (ion energy, radical-to-ion flux ratio, ion composition) will be discussed independently in the next subsections. Upon bombardment, simulations show the rapid formation of an H-rich modified layer, the thickness of which initially increases with the ion dose. On Figure 4.9(a), the modified layer and etched thicknesses are given as a function of the ion dose. Despite the presence of H radicals, the evolution is similar to the pure ion implantation case. The rapid modification of the substrate is followed by a slow saturation, nevertheless there are new effects here: the modified layer is simultaneously etched during the bombardment with a constant etch rate. This graph is in good agreement with the experimental study of [Fontcuberta 02], in which a [a-Si:H] thin film was exposed to a RF H<sub>2</sub> plasma (18W, 133Pa) and was then characterized using in-situ ellipsometry coupled to secondary ion mass

spectrometry (SIMS). Fontcuberta et al. report the evolution of both the total film thickness and the Hrich modified layer thickness when increasing the plasma time, and as shown in Figure 4.9c), it is in agreement with our numerical results. On Figure 4.9(b), MD snapshots of the cell before bombardment and after an ion dose of 6x10<sup>16</sup> ion/cm<sup>2</sup> are shown. One can see that the substrate was both etched during the bombardment and simultaneously modified/hydrogenated. The etch rate is almost stable during all plasma exposure; it is lower only for very low ion doses (<0.1x10<sup>16</sup> ion/cm<sup>2</sup>), where the mixed [a:Si-H] layer starts establishing.



Fig. 4.9. (Color online) [MD]  $E_{ion} = 100eV$ , mixed  $H_x^+$  ion/H radical bombardment of Si,  $\Gamma = 10$ , 90%  $H_3^+$ . Evolution of the surface with the ion dose.

(a) Modified layer and etched thicknesses depending on the ion dose.

(b) Snapshots of the cell (seen from a side view) before bombardment and after an ion dose of  $6x10^{16}$  ion/cm<sup>2</sup>. The dashed green line shows the initial height of the surface.

[EXP] (c) a-Si:H sample exposed to a RF H2 plasma (18W, 133 Pa). Evolution of the total thickness of the film and of the hydrogen-rich sub-surface layer [Fontcuberta 12].

Because of this competition between modification and etching mechanisms, the thickness of the modified layer is not as stable as it was for a pure ion bombardment. It is oscillating near a mean value at steady state, and this phenomenon could be responsible for a non-homogeneous (or non-reproducible) hydrogenation of the substrate after the plasma exposure.

#### 4.4.2. Structure and composition of the [a:Si-H] modified layer at steady state

In this subsection, the detailed nature of the modified layer is investigated for the same simulation conditions. On Figure 4.10(a), a snapshot of the cell at steady state is presented, and next to it, the corresponding density depth profile (Figure 4.10(b)). Here, a big difference compared to the pure ion bombardment case is observed: the hydrogen distribution in the material is not Gaussian-like anymore. The H density is homogeneous near the surface and then decreases with the depth. Such a difference may be due to the concurrent etching of Si during the bombardment. Indeed, the Gaussian-like hydrogenation can only be reached at high ion doses, and only if ions are always impinging on the "same" surface, which is not the case here since the etching is relatively fast compared to the hydrogenation.



The corresponding bond depth profile is given on Figure 4.10(c). Here again, we observe the presence of highly hydrogenated Si atoms in form of SiH<sub>3</sub> groups; however, they are less numerous than in the pure ion implantation case (and thus cannot induce a cell breaking-like phenomenon). As previously explained, all H<sub>2</sub> molecules created in the bulk during the bombardment were automatically erased from the system, since they should desorb in a few nanoseconds, i.e. well before the next ion or radical impact.

#### 4.4.3. Influence of the ion energy (Eion)

In this subsection, we investigate the effect of the ion energy on the modification and etching of silicon, for a mixed ion/radical bombardment with  $\Gamma = 10$  and 90% H<sub>3</sub><sup>+</sup>. Figure 4.11 shows the dynamical evolution of the modified layer thickness as a function of the ion dose, for ion energies equal to 5, 25 and 100eV. All cases show the same type of evolution, i.e. a rapid modification of the substrate followed by a slow saturation. However, the ion dose required to reach steady state increases with the ion energy.



Fluence (x10<sup>16</sup> lon/cm<sup>2</sup>)



One should notice the behavior of the modified layer thicknesses at steady state, which oscillates at 100eV near a mean value (variations > 1nm) and is more stable for lower energies. The ion dose required to reach steady state conditions, as well as this oscillation, are key parameters for the Smart Etch technology and will be discussed in the end of this chapter. In Figure 4.12, the thickness of the modified layer and the Si etch yield, at steady state, are plotted as a function of the ion energy. The distribution of etch products for two extreme energies (5eV and 100eV) are given in the inset graph. As expected, the thickness of the modified layer increases with the ion energy, but when we look at the error bars, we see that the uncertainty in estimating this thickness also increases with the ion energy. On the other hand, the etch yield is highly stable and almost the same for all energies, showing that the etching is mainly driven by hydrogen radicals. The same conclusion comes out when one observes the distribution of etch products: more than 90% of silicon was etched in form of SiH<sub>4</sub> volatile molecules. It should also be underlined that in the case of a pure ion bombardment, there was practically no sputtering at 100eV.



Fig. 4.12. (Color online) *Mixed*  $H_x^+$  *ion/H radical bombardment of silicon,*  $\Gamma = 10$ , 90%  $H_3^+$ . (a) Modified layer thickness and etch yield, at steady state, as a function of the ion energy. (b) Snapshots of the cells corresponding to 25eV and 100eV at ion dose 2.2x10<sup>16</sup> ion/cm<sup>2</sup>.

Here, the presence of non-fully-saturated SiH<sub>x</sub> products shows that hydrogenated Si atoms on surface can be sputtered more easily than non-hydrogenated ones. The fact that silicon, independent from its form, is easily etched by atomic H, was also shown in numerous experimental works [Ito 13, Chang 82, Gates 89, Bianco 09, Thedjoisworo 12, Veprek 08, Wanka 97, Wei 95]. In particular, the work of [Wei 95] proposed that silicon is etched via the formation of SiH<sub>4</sub> molecules, and [Veprek 08] showed that the contribution of physical sputtering of Si is negligible in hydrogen plasmas.

## 4.4.4. Influence of the radical-to-ion flux ratio ( $\Gamma = \Gamma_H / \Gamma_{Hx+}$ )

This subsection illustrates the effect of the radical-to-ion flux ratio  $\Gamma$  on the modification and etching of silicon, for a mixed ion/radical bombardment with  $E_{ion}=100$ eV and 90%  $H_{3}^{+}$ . Figure 4.13 shows the dynamical evolution of the modified layer thickness as function of the ion dose, for  $\Gamma = 1$ , 10 and 100. In this case, the ion dose required to reach steady state increases when the radical-to-ion flux ratio decreases. The instability (or the oscillations) of the modified layer thickness, observed for  $\Gamma=10$ , disappears in the two other cases.



Fig. 4.13. (Color online)  $E_{ion} = 100eV$ , mixed  $H_x^+$  ion/H radical bombardment of silicon, 90%  $H_3^+$ . Modified layer thickness depending on the ion dose for  $\Gamma = 1$ , 10 and 100. Green crosses denote the beginning of steady state.

For  $\Gamma$ =1, it disappears since we are converging to the case of pure ion bombardment, where Si etching is extremely low and principally volume transformation takes place. For  $\Gamma$ =100, Si etching happens so fast that ions do not have time to hydrogenate the material, and as a consequence there is almost no modified layer and thus no instability.

On Figure 4.14, the modified layer thickness and the etch yield, at steady state, are given as a function of the radical-to-ion flux ratio. The case  $\Gamma = 0$  (corresponding to a pure ion bombardment) is also plotted, and the etch products distribution is presented in the inset graph.



Fig. 4.14. (Color online) *E<sub>ion</sub>* = 100eV, mixed H<sub>x</sub><sup>+</sup> ion/H radical bombardment of silicon, 90% H<sub>3</sub><sup>+</sup>.
(a) Modified layer thickness and etch yield at steady state depending on the radical-to-ion flux ratio.
(b) Snapshots of the cells corresponding to Γ = 1 and 10 at ion dose 6x10<sup>16</sup> ion/cm<sup>2</sup>.

An increase of  $\Gamma$  induces both a decrease of the modified layer thickness and a linear increase of the etch yield, since the etching is mainly driven by H radicals. Thus, for high  $\Gamma$  values, the "volume transformation only" that is sought in the Smart-Etch technology cannot be achieved in the case of silicon. The inset graph shows that when  $\Gamma$  increases, the etching becomes more and more chemical, and for  $\Gamma$  = 100, more than 99% of Si was etched in form of saturated products (mainly SiH<sub>4</sub>). In terms of plasma parameters, one could make an analogy between the plasma dissociation and  $\Gamma$ , since an increase of the plasma dissociation should increase the concentration of atomic H in the gas phase. However, this analogy should be done very cautiously, since often an increase of the dissociation (e.g. by increasing the source power in an ICP) is accompanied by a change in the ion flux as well.

#### 4.4.5. Influence of the ion composition

The last effect related to the plasma composition presented here, is the influence of the ion composition. This time, all previously discussed parameters are fixed ( $E_{ion}=100eV$ , mixed  $H_{x^+}$  ion/H radical bombardment,  $\Gamma=10$ ), and the ion composition is varied from a case with 100%  $H_{3^+}$  ions to a case with 100%  $H^+$  ions. The influence of the ion composition on the modification and etching of silicon is shown on Figure 4.15.



Fig. 4.15. (Color online)  $E_{ion} = 100eV$ , mixed  $H_x^+$  ion/H radical bombardment of Si,  $\Gamma = 10$ . (a) Modified layer thickness and etch yield at steady state as a function of the ion composition. (b) Snapshots of the cells corresponding to two ion compositions (H<sub>3</sub><sup>+</sup> only and H<sup>+</sup> only) at ion dose  $3.5x10^{16}$  ion/cm<sup>2</sup>.

As expected, with the increase of the H<sup>+</sup> concentration, the thickness of the modified layer increases, since for a given energy, H<sup>+</sup> ions are much faster than H<sub>3</sub><sup>+</sup> ion fragments and are thus able to penetrate deeper in the substrate. The maximal instability of the modified layer is observed for 90% H<sup>+</sup>, where the uncertainty on its thickness reaches 3nm. Similarly, as in previous cases, the etching is again driven by H radicals. However, an interesting fact appears in the distribution of etch products presented in the inset graph of figure 4.15. The increase of H<sub>3</sub><sup>+</sup> concentration slightly increases the proportion of non-saturated products, i.e. the probability of sputtering events, since sputtering is favored only when the top-surface is highly hydrogenated.

#### 4.4.6. Limitations of hydrogen plasmas for the Smart Etch of silicon substrates

The main objective of the Smart Etch technology is the anisotropic etching of thin film layers, which should be reached in two steps: an anisotropic modification of the substrate, followed by a selective removal of the modified layer. The reason why silicon (contrary to silicon nitride) cannot be etched using this method in hydrogen plasmas, is the isotropic etching of the substrate during the modification. This spontaneous and simultaneous etching induced by hydrogen radicals is not desirable, especially in the presence of patterns.

In this chapter, two other possible issues were revealed regarding the first step of this procedure. First, the modification of the substrate must be the most homogeneous possible, to avoid the development of surface roughness after the second step (removal of the modified layer). As previously observed, the modification of the substrate occurs in two stages. In the first stage, a rapid hydrogenation and amorphisation of silicon takes place, during which the modified layer is extremely dependent on the ion dose. Thus, a non-homogenous modification is highly probable for low ion doses (i.e. for short plasma exposure times), since the received ion dose might not be homogeneous on the wafer. In addition, in some cases the thickness of the modified layer varies with time (even at steady state) and can be determined only with some uncertainty, the minimization of which is highly dependent on a trade-off between ion energy and etch rate (which depends on the plasma composition). If this phenomenon cannot be controlled, the substrate modification could be non-reproducible (or non-homogeneous) from one process to another.

#### 4.5. Conclusion

In this chapter, using molecular dynamics, the influence of both low-energy  $H_{x^+}$  ion implantation and mixed  $H_{x^+}$  ion/H radical bombardment on the modification of Si (100) crystalline substrates was investigated, for various ion energies ( $E_{ion} = 5-100$ eV), radical-to-ion flux ratios ( $\Gamma$ =1-100) and ion compositions (from 100% H<sup>+</sup> to 100% H<sub>3</sub><sup>+</sup>).

Simulations of pure  $H_{x^+}$  (x=1-3) ion bombardment of silicon showed that the implantation leads to a surface evolution composed of two stages: a rapid modification followed by a slow saturation and the formation of a stable modified layer at steady state. During the ion bombardment, there is a formation and desorption of H<sub>2</sub> molecules, which balances the number of penetrating ions at steady state and enables the self-limited ion implantation. At steady state, Gaussian-like density profiles of hydrogen in the substrate are observed. Near the peak of hydrogenation, the substrate is extremely weakened because of broken Si-Si crystalline bonds and a high density of SiHx (x=1-3) groups. As a result, the modified layer is weakly bound to the underlying material, which is at the origin of the Smart Cut mechanism. The thickness of the modified layer increases with the ion energy and is higher for smaller ions. A non-standard behavior is observed for the etching: the etch yield decreases with the ion energy and disappears for  $E_{ion} \ge 25 \text{eV}$ . Finally, simulation of the annealing step of the Smart Cut process showed that the fracture between the modified and non-modified parts increases when heating the substrate (~1000K). This in-depth micro-cutting of silicon happens due to the breaking of remaining Si-Si bonds in the most hydrogenated layer, caused by the thermal vibrations of atoms (increasing with the temperature). At these low energies, molecular hydrogen does not seem responsible for this process, since it desorbs in relatively short timescales compared to the annealing time.

Simulations of mixed ion/radical bombardment showed that there is a simultaneous modification and etching of the Si substrate during the plasma exposure, where the modification is principally governed by ions and the etching by atomic H. Because of these concurrent mechanisms, the hydrogen density depth profile is less Gaussian-like and the modified layer less saturated in hydrogen compared to the pure ion implantation case. Nevertheless, SiH<sub>x</sub> groups (x=1-3) are still detected in the modified layer. The modified layer thickness and the ion dose required to be at steady state both increase with the ion energy, but decrease with the increase of the radical-to-ion flux ratio, respectively. An increase of the H<sup>+</sup> population in the ion composition also increases the modified layer thickness. Finally, some possible issues for the Smart Etch were revealed, related to the non-homogeneous or unstable modification

obtained at low ion doses or even at steady state, which could be responsible for the development of surface roughness after the second removal step. It was also shown that silicon etching cannot be achieved in H<sub>2</sub> plasmas using the Smart Etch process (because H radicals readily etch silicon). In parallel, the numerical results were compared with experimental data reported in the literature and a general phenomenological agreement was seen, showing the applicability of [Murty 95] Si-H potential for modeling plasma-surface interactions.

# Chapter 5

# Hydrogen plasmas modification of SiN thin films

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# 5.1. Motivation and objectives of the study

As mentioned in chapter 1 (subsection 1.4.2), silicon nitride spacers were historically etched in ICP plasmas with  $CH_3F/O_2/He$  chemistry, which leads to silicon recess [Kastenmeier 99, Blanc 13]. In  $CH_3F/O_2/He$  chemistry, the Si recess can be reduced by optimizing the gas concentration ratio  $[CH_3F]/[O_2]$ , nevertheless such optimizations often produce other problems, like the generation of Si-C bonds below the oxidized layer in carbon-rich mixtures [Blanc 14]. As discussed in the previous chapters, the recently developed Smart Etch technology showed very promising results for silicon nitride spacers etching using hydrogen plasmas [Posseme 14, Sherpa 17]. The etching of Si<sub>3</sub>N<sub>4</sub> in a downstream H<sub>2</sub> plasma was highly investigated by [Thedjoisworo 12], who gives a huge vision about the Si<sub>3</sub>N<sub>4</sub> etch rate depending on operating conditions. However, some fundamental mechanisms involved in the Si<sub>3</sub>N<sub>4</sub> modification by H<sub>2</sub> ICP or CCP plasmas remain misunderstood, especially because the presence of hydrogen into materials is rather difficult to detect and quantify experimentally [Dubois 16]. In the past 10 years, Molecular Dynamics simulations were performed to study the stoichiometry of amorphous Si<sub>3</sub>N<sub>4</sub> [Ippolito 11], the growth of Si<sub>3</sub>N<sub>4</sub> upon crystalline Si [Gou 09, Houska 10], and the interface between c-Si and amorphous Si<sub>3</sub>N<sub>4</sub> [Butler 11, Lamers 13]. However, no study was carried out to examine the interaction of hydrogen with this material.
In this chapter, the modification of silicon nitride by hydrogen plasmas is thus investigated by means of Molecular Dynamics. This study is necessary to understand the chemico-physical mechanisms responsible for the modification of SiN in the Smart Etch process, and to determine the key plasma parameters (or operating conditions) controlling this modification (or weakening) step. In particular, one purpose of this study is to clarify the effect of the ion dose, the ion energy, and the radical-to-ion flux ratio during the plasma exposure. From an experimental point of view, this allows to study indirectly the effect of various plasma parameters (exposure time, bias power, pressure, source power) on the substrate modification. In this chapter, the aforementioned effects will be explored using MD simulations and the numerical results will be compared with experimental measurements. Finally, some plasma conditions (or range of parameters) will be proposed to optimize this first step of the Smart Etch process. This study being similar to the one described in chapter 4, with the sole difference being the substrate nature (SiN instead of Si), it may seem repetitive. However, we will see that there is a package of differences in the interactions of these two materials with hydrogen plasmas, and to underline these differences, both cases will be discussed in parallel.

## 5.2. Computational details

All simulations performed for the study of the Si-N-H system are in analogy with the Si-H case (presented in chapter 4), i.e. the same numerical parameters were chosen and the same set of simulations was kept. Firstly, pure ion bombardments were investigated for ion energies in the 5-100eV range and for all type of H<sub>x</sub><sup>+</sup> ions (x=1-3). Afterwards, mixed H<sub>x</sub><sup>+</sup> ion/H radical bombardments were performed for the same ion energies, for radical-to-ion flux ratios  $\Gamma = [1, 10, 100]$ , and for ion compositions varying from 100% H<sub>3</sub><sup>+</sup> to 100% H<sup>+</sup>. The numerical parameters chosen to simulate pure ion bombardments of SiN are presented in table 5.1.

lon energy and ion	Timestep (fs)	Runtime	Cell sizes (Å)	Thermalization
type		(ps)		
5eV H <sup>+</sup> , H <sub>2</sub> <sup>+</sup> , H <sub>3</sub> <sup>+</sup> ,	0.1	1	30.4x30.4x26	$\tau = 100$ , time 0.1ps
10eV H <sub>2</sub> +, H <sub>3</sub> +				
10eV H⁺,	0.1	1	30.4x30.4x40	$\tau = 100$ , time 0.1ps
25eV H <sub>2</sub> +, H <sub>3</sub> +				
25eV H+	0.1	1	30.4x30.4x50	au = 100, time 0.1ps

50eV H <sub>2</sub> +, H <sub>3</sub> +				
100eV H₃⁺	0.05 for 0.05ps 0.1 for the last 0.95ps	1	30.4x30.4x50	$\tau = 100$ , time 0.1ps
50eV H+,	0.05 for 0.05ps 0.1 for the last 0.95ps	1	30.4x30.4x60	au = 100, time 0.1ps
100eV H <sub>2</sub> +				
100eV H⁺	0.02 for 0.05ps 0.1 for the last 0.95ps	1	30.4x30.4x86	$\tau = 100$ , time 0.1ps

#### Table 5.1. Simulation parameters for $H_{x^+}$ (5-100eV) cumulative ion bombardment on SiN.

For mixed ion/radical bombardment simulations, the initial SiN cell was chosen with the following size: length x width x height =  $3.04 \times 3.04 \times 15.5 \text{ nm}^3$ . The atom activation algorithm (described in chapter 2, subsection 2.4.2) was then used to simulate only the minimal thickness required for the substrate. Like in the case of silicon, it was observed that during the bombardment of silicon nitride by hydrogen ions, H<sub>2</sub> molecules are created in the substrate but desorb in a few nanoseconds. Thus, one more time, H<sub>2</sub> molecules were searched for and erased from the system after each ion impact. The simulation of radical impacts was less time-consuming. Each radical impact (in our case atomic hydrogen) was run for a maximum of 5ps, but the system was checked each 0.05ps to see if the radical-surface interaction (H diffusion, bonding, reflection, etc.) was fully captured, in which case the integration was stopped. At the end of both ion and radical impacts, the cell temperature was checked, and if the mean temperature was out of the range [285K, 315K], a thermalization at 300K was applied. To reach steady state, especially for pure ion bombardments, extremely high ion doses were needed, in some cases reaching 9x10<sup>17</sup> ion/cm<sup>2</sup>. As a result, 20.000 to 100.000 plasma species impacts were needed depending on the simulation, which is why these simulations were immensely time-consuming and took between 1 and 8 months.

## 5.3. Pure $H_{x^+}$ (x=1-3) ion implantation in SiN.

In this section, a pure  $H_{x^+}$  (x=1-3) ion bombardment of amorphous silicon nitride substrate is studied, for ion energies in the 5-100 eV range. As seen in previous chapters, such a study is necessary to understand basic phenomena on ion implantation before investigating a mixed ion/radical bombardment. We will discuss the effect of the ion energy, ion type and ion dose on the substrate modification, as well as the nature of the modification (structure and chemical composition of the modified layer).

## 5.3.1. Evolution of the surface with the ion dose

In this subsection, the evolution of the SiN substrate with the ion dose is investigated for a cumulative  $H_{3^+}$  ion bombardment at 100eV. The evolution of the modified layer thickness and of the H uptake as a function of the ion dose are presented on Figure 5.1(a).





On Figure 5.1(b) are given the snapshots of the initial and final cells, before the bombardment and after an ion dose of 80x10<sup>16</sup> ion/cm<sup>2</sup>, where steady state was achieved. This evolution is composed of two main stages. The first one is lying between points A and B, where there is a rapid increase of both the modified layer thickness and the H uptake, and the second one between points B and C, where both curves saturate slowly before reaching steady state. The hydrogen uptake shows that a self-limited ion implantation takes place: at steady state, the number of desorbing H<sub>2</sub> molecules (created in the bulk during the implantation) is balanced by the number of penetrating ions in the substrate. Also, as one can see on the snapshots of Figure 5.1(b), the substrate slightly inflates during this bombardment. The atomic density of SiN in the modified part is indeed lower than in the non-modified part, due to the presence of implanted hydrogen and because almost no etching or sputtering occurs during the implantation.

### 5.3.2 Structure of the H-implanted material at steady state

In this subsection, for the same simulation conditions, we focus on the cell at steady state. Figure 5.2 illustrates the structure and composition of the H-implanted SiN layer after a  $100 \text{eV} \text{H}_3^+$  dose of  $80 \times 10^{16}$  ion/cm<sup>2</sup>. Figure 5.2(a) shows a snapshot of the cell at steady state and Figure 5.2(b) presents the corresponding depth density profile. Finally, the depth profile of SiH<sub>x</sub> and NH<sub>y</sub> bonds in the substrate is presented on Figure 5.2(c), which shows in what form hydrogen is stored in the substrate depending on depth.



Fig. 5.2. (Color online)  $E_{ion} = 100 \text{eV}$ , pure  $H_3^+$  ion bombardment of SiN, dose ~80x10<sup>16</sup> ion/cm<sup>2</sup>. Structure and chemical composition of the cell at steady state. (a) Snapshot of the cell, (b) Corresponding density depth profile and c) H-bond depth profile.

First on Figure 5.2(b), a Gaussian-like distribution of hydrogen is observed in the material. This is due to an extremely low sputtering rate and to the high reactivity of atomic hydrogen with silicon and nitrogen atoms, which prevents its diffusion. One can note that the near-surface region is depleted in nitrogen, which can even be seen on the snapshot; we will see in section 5.3.3 that this is due to the preferential sputtering of N atoms by high energy ions. Such behavior is also observed near the peak of the hydrogenation (at a depth of ~2.5 nm), where ~30% of nitrogen have migrated downward and ~70% upward. Near this peak, the ratio  $nH/(nSi + nN) \sim 1$ , and one can see the presence of SiH<sub>3</sub> and NH<sub>2</sub> groups, as well as a very low concentration of non-hydrogenated atoms. The SiN material is thus strongly weakened in this region. From Figure 5.2(c), we can better understand what may facilitate the selective removal of the modified layer by wet cleaning (HF bath) or exposure to gaseous reactants (NF<sub>3</sub>/NH<sub>3</sub> downstream plasma). The modified layer is filled with SiH<sub>x</sub> (x=1-3) and NH<sub>y</sub> (y=1,2) groups, and since Si and N atoms are respectively tetra- and tri-valent, one can intuitively understand the reason

of this removal. The mechanisms of silicon nitride etching in HF bath were proposed by [Knotter 11], with the following reaction

$$Si_3N_4 + 12HF \rightarrow 3SiF_4 + 4NH_3$$
 (5.1)

Formula 5.1 suggests that a F atom substitutes a NH<sub>2</sub> group on the surface, and after successive breaking of Si-N bonds, a SiF<sub>4</sub> volatile molecule is finally formed. Now let us consider a modified or hydrogenated SiN layer, in which the initial structure is already perturbed. In this case the reaction described by formula 5.1 requires less steps, since some Si-N bonds are already broken and some nitrogen atoms are already hydrogenated. Hence, the more hydrogenated the layer, the easier it can be etched (using an appropriate chemistry evidently).

## 5.3.3 Influence of the ion energy and ion type on the substrate modification

As seen in the case of silicon, the ion type and especially the ion energy have a huge effect on the substrate modification; they can even induce a different material modification, from a volume transformation + etching to a pure volume transformation. Here, the simulations of pure ion bombardment by  $H^+$ ,  $H_2^+$  and  $H_3^+$  ions having energies in the 5-100eV range, are compared at steady state. On Figure 5.3, the thickness of the modified layer is presented as a function of the ion energy for different ion types.



Fig. 5.3. (Color online)  $E_{ion} = 5-100eV$ , pure  $H_x^+$  ion bombardment of SiN, steady state. Modified layer thickness as a function of the ion energy for different ion types. For the cases of  $H_2^+$  and  $H_3^+$ , the modified layer thickness is  $\approx 0.4 \div \sqrt{E_{1-1}}$  which is

layer thickness is  $\approx 0.4 \cdot \sqrt{E_{ion}},$  which is given by the dashed black line.

Like for silicon, the thickness of the modification increases with the ion energy but decreases with the ion size, since more energetic and smaller  $H_{x^+}$  species penetrate deeper in the substrate. For  $H_{2^+}$  and  $H_{3^+}$  ions, the modified layer thickness increases proportionally to the square root of the ion energy  $(e_{modified} \sim \sqrt{E_{ion}})$  but this tendency is not provided for ions with energies < 10eV. Indeed, chemical

etching occurs at low energy, because molecular ions break apart and lose kinetic energy upon impact, acting then almost as H radicals on the surface. On the contrary, for higher energies, only volume transformation takes place. As also observed in chapter 4, impinging H<sub>2</sub><sup>+</sup> ions having  $E_{ion} \leq 5eV$  are causing practically no modification due to their high bond energy (4.76eV). Finally, for the case of H<sup>+</sup> bombardment, the dependence of the modified layer thickness on the ion energy seems to be more linear.

In Figure 5.4(a), the ratios nH/(nSi + nN) in the modified layer at steady state are compared for all studied ions.





(d)  $H_2$  molecules creation/desorption rate in the substrate as function of the ion energy.

This sole graph contains a vast quantity of information relative to the fundamental processes taking place during the ion implantation, and to understand them, we need to observe at a time all graphs

presented on Figure 5.4. In particular, we see that the nH/(nSi + nN) ratio reaches a peak (~1) for lowenergy ion cases and then decreases with the increase of the ion energy. We also observe that for a given ion energy, the H/SiN ratio is always lower for smaller ions. We also calculated the volume density of hydrogen in the modified layer (see Figure 5.5(b)), which again shows that the higher the ion energy, the lower the hydrogenation rate. The reason for these phenomena is the fact that energetic ions are more able to detach hydrogen atoms bound to the substrate atoms, which in turn increases the production/desorption of  $H_2$  molecules. This is illustrated on Figure 5.4(c), where the number of created/desorbed  $H_2$  molecules in the substrate is given as function of the H<sup>+</sup> ion dose (5, 25, 100eV). As one can see from the 5eV H<sup>+</sup> bombardment case (green line), the creation/desorption rate of H<sub>2</sub> molecules (slope of the curve) increases with the ion dose and reaches steady state after ~45.000 ion impacts, because the H<sub>2</sub> creation/desorption depends on the cell hydrogenation as well. It is the same for other energy cases, however it happens too fast (during the first 1000 impacts) to be visible on the graphs. Finally, the H<sub>2</sub> creation/desorption rate (i.e. the number of created/desorbed H<sub>2</sub> per ion impact) is given on Figure 5.4(d) for all studied energies and ion types. This last graph explains the trends observed on Figures 5.4(a, b). We observe that for energies >25eV,  $H_{3^+}$  ions produce [1.2-1.4] times more H<sub>2</sub> molecules per impacted ion compared to H<sup>+</sup> ions. However, during a H<sub>3</sub><sup>+</sup> bombardment there are 3 hydrogen atoms impinging at a time on the substrate (vs 1 for  $H^+$ ), and thus the production of  $H_2$ per impacting H atom is in fact higher for H<sup>+</sup> ions. Impacting molecular ions (H<sub>2</sub><sup>+</sup>, H<sub>3</sub><sup>+</sup>) tend to share their kinetic energy among fragment ions, which explains why, for a given ion energy, the H/SiN ratio at steady state is lower for H<sup>+</sup> ions compared to H<sub>3</sub><sup>+</sup> ions (Figure 5.4a). In other words, the faster the H<sub>x</sub><sup>+</sup> ion, the less hydrogenated the substrate at steady state. This last fact can be seen on Figure 5.5, where cell snapshots and corresponding density depth profiles at steady state are presented for 25eV H<sub>3</sub><sup>+</sup>, 100eV H<sub>3</sub><sup>+</sup> and 100eV H<sup>+</sup> bombardment. We clearly observe a difference and decrease of the hydrogenation rate in the modified layer when the ion energy increases. As one can see, in the first 25eV H<sub>3</sub><sup>+</sup> case, the cell is so hydrogenated (and consequently weakened) that it breaks into two pieces. Such highly weakened cells were observed for the following cases: 5eV H<sup>+</sup>, 10eV (H<sup>+</sup>, H<sub>2</sub><sup>+</sup>), 25eV (H<sub>2</sub><sup>+</sup>,  $H_{3^+}$ ) and 50eV  $H_{3^+}$  bombardment.



Fig. 5.5. (Color online) **25eV H<sub>3</sub><sup>+</sup>, 100eV H<sub>3</sub><sup>+</sup>, 100eV H<sup>+</sup>, pure ion bombardment of SiN, steady** *state.* 

Density depth profiles and corresponding snapshots, demonstrating the decrease of the hydrogenation rate with the increase of the ion energy. In the first case, the cell is so hydrogenated on a small depth that it breaks into two pieces.

In these specific cases, the creation rate of H<sub>2</sub> molecules is too low and consequently a high accumulation of hydrogen becomes possible into the material. However, the "cell-breaking" phenomenon may be due or enhanced by a numerical issue. Indeed, since a short-range interatomic potential is used to model all interactions, no long-range interaction (like Van der Waals) is taken into account while such forces could eventually hold the cell together. Such phenomena were observed in MD simulations of multilayer graphene bombardment by hydrogen ions [Davydova 14], and prevented by adding a Lennard-Jones potential for long-range C-C interactions. Unfortunately, such an approach would have required a simulation time exceeding two years, hence it was not applied here. Nevertheless, since a similar "cell-breaking" phenomenon was observed experimentally for very

energetic ions (~5keV) bombarding silicon [Moutanabbir 05], any experience of low energy (5-50eV) pure hydrogen ion bombardment on SiN would be extremely interesting.

Finally, Figure 5.6 gives the etch yield at steady state as a function of the ion energy, for different ion types. Once again, for  $E_{ion} < 25$ eV, the etch rate decreases with the increase of the ion energy and it disappears at 25eV. However, contrary to the silicon case, a small etch rate is observed for  $E_{ion} > 25$ eV, which increases with the ion energy. This behavior is specific to light ion implantation and reveals two different types of etching mechanisms. The etch products for two extreme cases (5eV H<sub>3</sub><sup>+</sup> and 100eV H<sup>+</sup>) are presented in the inset graph of Figure 5.6. One can see that at very low energy, the etching is purely chemical (~100% of products are SiH<sub>4</sub> or NH<sub>3</sub> saturated molecules), while at high energy, the etching is physical (~100% of products are sputtered atoms).



Fig. 5.6. (Color online)  $E_{ion} = 5-100eV$ , *pure H<sub>x</sub>*<sup>+</sup> *ion bombardment of SiN, steady state.* Etch yield (# substrate atom/ion) as a function of the ion energy for different ion types. Etch products for 5eV H<sub>3</sub><sup>+</sup> and 100eV H<sup>+</sup> bombardments are shown in the inset graph.

As we see, 95% of sputtering products (100eV H<sup>+</sup> case) are nitrogen atom, showing that contrary to silicon, nitrogen can be sputtered. This is due to the lower mass of nitrogen and the higher energy transfer efficiency of H-N collisions compared to H-Si collisions. It explains why the near surface region is often depleted in nitrogen (see subsection 5.3.2.), as also showed experimentally [Dubois16]. However, in all cases the etch yield remains very weak, and extremely high ion doses (> 10<sup>19</sup> ion/cm<sup>2</sup>) are required to etch just one nanometer of SiN.

### 5.3.4. Conclusive remarks

In this section, the cumulative bombardment of 5-100eV  $H_{x^+}$  (x=1-3) ions on amorphous silicon nitride was studied. Simulations showed a self-limited ion implantation characterized by the formation of a stable [a-SiN:H] modified layer at steady state. The thickness of the modified layer increases proportionally to the square root of the ion energy (for  $H_{2^+}$  and  $H_{3^+}$  ions), while the ratio nH/(nSi + nN)

in the modified layer decreases with the ion energy. A Gaussian-like distribution of hydrogen is shown depending on depth, with the presence of SiH<sub>3</sub> and NH<sub>2</sub> groups and a very low concentration of non-hydrogenated atoms near the hydrogenation peak. The average hydrogenation rate in the modified layer reaches a maximal value for 5eV H<sup>+</sup>, 10eV H<sub>2</sub><sup>+</sup>, 25eV H<sub>3</sub><sup>+</sup> and 50eV H<sub>3</sub><sup>+</sup> bombardments. In these specific cases, the modified layer is so hydrogenated on a small depth that the cell almost breaks into two pieces. This behavior might be due or enhanced by a simulation issue (cf. short-range interatomic potential), nonetheless it would be extremely interesting to explore this phenomenon experimentally. Finally, few chemical etching is observed for very low energy ions (<10eV), while for higher energies (> 25eV), a very weak sputtering of nitrogen atoms is observed, which shows the particularity of hydrogen ions to cause mostly a volume transformation of SiN substrates.

# 5.4. Mixed H<sub>x</sub><sup>+</sup> ion/H radical bombardment of SiN

Now that the effect of each impacting ion species is known, it is time to study the effect of a mixed ion/radical bombardment on SiN, in order to observe the effect of a real hydrogen plasma on the substrate modification. Certainly, the impact of neutrals on SiN (atomic H and molecular hydrogen H<sub>2</sub>) was not studied independently but there is no necessity to do it. Indeed, MD simulations show that molecular hydrogen (H<sub>2</sub>) is reflected in 99.999% of cases, otherwise it penetrates deep (>micron) into the substrate, so there is no necessity to simulate it. On the contrary, atomic hydrogen is chemically reactive with Si and N atoms and passivates the substrate instantaneously. It even etches it by forming SiH<sub>4</sub> and NH<sub>3</sub> volatile products, however silicon nitride is etched ~10 times slower than silicon. These numerical results are in qualitative agreement with experiments. [Chang 82] have shown that in a hydrogen plasma (quartz discharge tube), the ratio between the etch rates of silicon and silicon nitride varies in [17-50]. More recently, [Thedjoisworo 12] reported that this ratio in a downstream H<sub>2</sub> plasma is much higher; it varies in [25-520] and is mainly dependent on the substrate temperature.

For the simulation of mixed ion/radical bombardments, all chosen numerical parameters corresponding to a given plasma composition (ion type, ion energy, radical-to-ion flux ratio) were discussed in section 5.2. In the following, the surface evolution with the ion dose and the nature of the modification at steady state are detailed for the base case { $E_{ion}=100eV$ , mixed  $H_x^+$  ion/H radical,  $\Gamma=10$ , 90%  $H_3^+$ } (see section 2.6.1. for details). Afterwards, the effect of each plasma parameter on the surface modification is discussed independently.

#### 5.4.1. Evolution of the surface with the ion dose

In this subsection, the evolution of the surface with the ion dose for a mixed  $H_x^+$  ion/H radical bombardment of SiN is discussed for the base case { $E_{ion} = 100eV, H_3^+ 90\%, \Gamma = 10$ }. Figure 5.7(a) presents the modified layer and etch thicknesses, as well as the hydrogen uptake, as a function of the ion dose. In chapter 4, the main effect of H radicals during the mixed bombardment of silicon was to initiate a simultaneous etching of the substrate during its modification. In this study, this effect is much less significant, because silicon nitride is etched by atomic H about 10 times slower than Si. Figure 5.7(a) shows that the substrate evolution is preserved compared to the pure ion implantation case: the rapid hydrogenation of SiN is followed by a slow saturation and the formation of a stable [a-SiN:H] layer at steady state. Even if the effect of atomic H radicals is not as important as it was for silicon, it brings significant effects which must be studied and taken into account very cautiously, especially when the goal is to modify the substrate with a nanoscale precision.





(a) Hydrogen uptake, modified and etched layer thicknesses as a function of the ion dose.

(b) Snapshots of the cell before the bombardment, and after an ion dose of 7.8x10<sup>16</sup> ion/cm<sup>2</sup>. The dashed green line shows the initial height of the surface.

The snapshots of the cell before the bombardment and after an ion dose of  $7.8 \times 10^{16}$  ion/cm<sup>2</sup> are shown on Figure 5.7(b). One can see the modified/hydrogenated layer, as well as the etched thickness, the evolution of which is given by the green curve on Figure 5.7(a). If we estimate the etched thickness on the snapshots, we will get ~ 0.1nm less than presented on Figure 5.7(a), due to the inflation of the modified layer. It means that the *x* nm of the modified material do not correspond to the *x* nm of the initial non-modified material; thus, in experimental measurements, it is important to estimate the inflated thickness to control more precisely the process. For example, if one must etch 10nm of SiN, and measurements shows that after the plasma exposure the modified layer thickness is 1nm (considering that there is no etching), intuitively 10 consecutive cycles of Smart Etch are needed to remove these 10nm. But in reality, each 1 nm may correspond to 0.9nm of non-modified layer due to the inflation, and thus 11 cycles may be necessary to remove the whole desired thickness. In chapter 4, we have seen that because of the concurrent modification/etching of silicon, the thickness of the modified layer might not be stable in time, but in the case of SiN, this problem is less relevant. Nevertheless, in further sections the magnitude of this thickness variations will always be measured, since in the current measurements each angstrom is important.

## 5.4.2. Structure and composition of the modified layer at steady state

This subsection continues the examination of the same simulation (base case); it details the nature of the modified layer at steady state and compares it with the case of a pure ion bombardment. Figure 5.8 presents: (a) a snapshot of the cell at steady state, its corresponding (b) density depth profile, and (c) H-bonds depth profile.



Fig. 5.8. (Color online)  $E_{ion} = 100 \text{eV}$ , mixed  $H_x^+$  ion/H radical bombardment of SiN,  $\Gamma = 10$ , 90%  $H_3^+$ , ion dose

7.8x10<sup>16</sup> ion/cm<sup>2</sup>. Structure and composition of the cell at steady state.
(a) snapshot of the cell
(b) corresponding density depth profile

(c) corresponding H-bonds depth profile

Compared to the pure ion bombardment case, the Gaussian-like hydrogenation profile is well perturbed. One can clearly observe a passivation of the surface, caused by the exposure of the substrate to a strong flux of H radicals. As one can see on Figure 5.8(b), the near-surface region is no more depleted in nitrogen (contrary to the pure ion bombardment case), which will be explained in the next section. The corresponding H-bond depth profile shows the presence of many SiH<sub>x</sub> (x=1-3) and NH<sub>y</sub> (y=1-2) bonds in the modified layer, which are principally located near the peak of the hydrogenation. Although silicon and nitrogen atoms are less saturated in hydrogen compared to the pure ion implantation case, the substrate remains strongly hydrogenated and weakened in this part, which indicates why it can be etched selectively with respect to the non-modified part in a second step (using an appropriate chemistry).

## 5.4.3. Influence of the ion energy (Eion)

In this subsection, we investigate the effect of the ion energy on the modification and etching of SiN, for a mixed ion/radical bombardment with  $\Gamma = 10,90\% H_3^+$ . Figure 5.9(a) shows the evolution of the modified layer thickness as a function of the ion dose for energies in the 5-100eV range. Figure 5.9(b) gives the cell snapshots corresponding to two extreme cases,  $E_{ion} = 5eV$  and 100eV, for an ion dose ~2.5x10<sup>16</sup> ion/cm<sup>2</sup>. All cases show the same type of evolution, i.e. a rapid modification of the substrate followed by a slow saturation. Figure 5.9(a) also shows the ion dose required to be at steady state, which are denoted by black crosses on each curve, and one can clearly see it increases with the ion energy.



Fig. 5.9. (Color online)  $E_{ion} = 5-100eV$ , mixed  $H_x^+$  ion/ H radical bombardment of SiN,  $\Gamma = 10$ , 90%  $H_3^+$ . (a) Modified layer thickness as a function of the ion dose. The black crosses are denoting the beginning of steady state. (b) Snapshots of the cells corresponding to  $E_{ion} = 5eV$  and 100eV, at ion dose  $2.5 \times 10^{16}$  ion/cm<sup>2</sup>.

The same graph shows that the modified layer thickness is very stable at steady state for all energies, being defined with a precision of some angstroms. The importance of these two parameters, i.e. the ion dose required to be at steady state and the stability of the modified layer, for the Smart Etch process was emphasized in chapter 4.

Figure 5.10 shows the effect of the ion energy on the modified layer thickness, the etch yield and the nH/(nSi + nN) ratio in the modified layer at steady state.



Fig. 5.10. (Color online)  $E_{ion} = 5-100 \text{eV}$ , mixed  $H_x^+$  ion/H radical bombardment of SiN,  $\Gamma = 10$ , 90%  $H_3^+$ .

a) Modified layer thickness, etch yield and ratio nH/(nSi + nN) as a function of the ion energy. b) Percentage of saturated Si- and N- containing etch products as a function of ion energy, and etch products for the case of  $E_{ion} = 100 eV$  in the inset graph.

As observed in previous cases, the thickness of the modified layer increases with the ion energy, contrary to the etch yield, which is almost the same for all ion energies since the etching is mostly induced by H radicals. The nH/(nSi + nN) ratio in the modified layer (blue curve) decreases with the ion energy. The reason for this behavior is related to the production/desorption of H<sub>2</sub> molecules in the substrate and was explained in detail in subsection 5.3.3. This hydrogenation rate is extremely important for the second step of the Smart Etch, since the more modified the material, the easier (or faster) it will then be removed, with a higher selectivity with respect to the non-modified part. Another interesting behavior is noted in the distribution of etch products. Figure 5.10(b) gives the percentage of silicon- and nitrogen- containing saturated etch products as a function of the ion energy. The increase of ion energy favors the sputtering of Si atoms, but even for the highest studied energy (100eV here), more than 95% of all Si is etched chemically (mostly in form of SiH<sub>4</sub>). It is very different for nitrogen atoms, where the percentage of saturated products (mostly NH<sub>3</sub>) decreases linearly with the increase of ion energy; at 100eV, ~46% of products containing N atoms were sputtered rather than chemically etched. This difference between Si and N atoms sputtering comes from the more efficient energy transfer in N-H collisions compared to Si-H collisions. The inset graph of Figure 5.10(b) shows the etch products distribution corresponding to the case  $E_{ion} = 100 \text{eV}$ , where we see that ~45% of all products were etched as SiH<sub>4</sub> molecules. Since the initial material contains more N atoms than Si atoms (nSi: nN = 3:4), we conclude that a preferential chemical etching of Si balances/overbalances the preferential sputtering of N atoms during the bombardment, that's why the near-surface region is not depleted in nitrogen (see Figure 5.8(b)).

## 5.4.4. Influence of the radical-to-ion flux ratio ( $\Gamma = \Gamma_H / \Gamma_{Hx+}$ )

In this subsection, we examine the effect of  $\Gamma$  (flux ratio of atomic H/H<sub>x</sub><sup>+</sup> ions) on the modification and etching of the surface, for a mixed ion/radical bombardment of SiN. In this study,  $\Gamma$  was varied between 1-100, while the ion energy (100eV) and the ion composition (90% H<sub>3</sub><sup>+</sup>) were kept constant. Let us start with the evolution of the modified layer thickness as function of the ion dose, which is presented on Figure 5.11(a), for  $\Gamma = 1, 10, 100$ .



Fig. 5.11. (Color online)

 $E_{ion}$  = 100eV, mixed  $H_x^+$  ion/H radical bombardment of SiN, Γ = 1-100, 90%  $H_3^+$ . (a) Modified layer thickness as a function of the ion dose for various radical-to-ion flux ratios. The red crosses are denoting the beginning of steady state. (b) Snapshots of the cells corresponding to  $\Gamma = 10$  and 1 at ion dose 7.8x10<sup>16</sup> ion/cm<sup>2</sup>.

Figure 5.11(b) gives the cell snapshots corresponding to  $\Gamma = 10$  and  $\Gamma = 1$ , for an ion dose ~7.8x10<sup>16</sup> ion/cm<sup>2</sup>. Like in other cases, the evolution of the modified layer is conserved, but this graph brings a package of other important information. It shows that the ion dose required to be at steady state increases when  $\Gamma$  decreases, and that the modified layer thickness is more stable for the lowest values of  $\Gamma$  (due to the decreasing etch rate induced by H radicals). Figure 5.12(a) shows the modified layer thickness, the etch yield and the ratio nH/(nSi + nN) in the modified part as a function of  $\Gamma$ , at steady state. The modified layer thickness when  $\Gamma$  increases when  $\Gamma$  because a certain ion

dose (or exposure time) is required to form a modified layer meanwhile the etching starts instantaneously. Thus, the modified layer cannot grow as much as it would without H radicals, since it is etched permanently. In the case of SiN, the etch rate remains small even for  $\Gamma = 100$ , meanwhile in the case of silicon, there is almost no more modified layer since the etch rate is very high compared to the modification rate (see figure 4.14).



Fig. 5.12. (Color online) *E<sub>ion</sub>* = 100eV, mixed H<sub>x</sub><sup>+</sup> ion/H radical bombardment of SiN, Γ = 1-100, 90% H<sub>3</sub><sup>+</sup>.
(a) Modified layer thickness, etch yield and ratio nH/(nSi + nN) as a function of Γ, at steady state.
(b) Percentage of saturated Si- and N- containing etch products as a function of Γ.

This figure also suggests that the hydrogenation rate increases slightly with  $\Gamma$ , but this trend is not very significant, especially if we take into account the error bars. Finally, on Figure 5.12(b) we see that the percentage of saturated Si- and N- containing products increases with  $\Gamma$ , because H radicals favor the chemical etching. As in the previous subsection, these saturated products are mostly (~95-100%) in form of SiH<sub>4</sub> and NH<sub>3</sub>, while unsaturated ones are mainly in form of SiH<sub>4</sub> (x=2,3), atomic N and NH<sub>y</sub> (y=1,2).

## 5.4.5. Influence of the ion composition

In this subsection, all previously discussed parameters are fixed ( $E_{ion}=100eV$ , mixed  $H_x^+$  ion/H radical bombardment,  $\Gamma = 10$ ), and the ion composition is varied from 100%  $H_3^+$  to 100%  $H^+$  (the  $H_2^+$  proportion is always 1% in intermediary cases), to observe the influence of the ion composition on the modification and etching of SiN. This is summarized on Figure 5.13, where the modified layer thickness, the etch yield and the ratio nH/(nSi + nN) are plotted as a function of the ion composition, at steady state. Here the evolutions with the ion dose are not discussed, since there are no significant effects.



Fig. 5.13. (Color online)  $E_{ion} = 100eV$ , mixed  $H_x^+$  ion/H radical bombardment of SiN,  $\Gamma = 10$ . Modified layer thickness, etch yield and ratio nH/(nSi + nN) as a function of the ion composition, at steady state.

As in the case of silicon (see figure 4.15), an increase of the H<sup>+</sup> concentration increases the modified layer thickness, but at the same time decreases the ratio nH/(nSi + nN). Contrary to the other discussed parameters, the etch rate seems invariant with respect to the ion composition. And among all the studied cases, the modified layer is less stable for the 100% H<sup>+</sup> case. The ion composition has no significant effect on the etching/sputtering products, so it is not described here.

### 5.4.6. Comparison with experiments

In his thesis, [Dubois 16] has studied experimentally the effect of various hydrogen plasmas on the modification of silicon nitride. As detailed in chapter 2 (see section 2.6.1), the measurements were done in a DPS reactor which works in both CCP and ICP modes, and where it is theoretically possible to control the ion energy and the ion flux independently. In particular, [Dubois 16] has measured the modified layer thickness of silicon nitride substrates exposed to different hydrogen plasma conditions, and their removal rate in a HF bath (see section 1.5.2.2 for details). The etched thickness of a premodified SiN substrate as a function of the HF bath time is reported on Figure 5.14(a), for two different H<sub>2</sub> plasma conditions (the source power is varied between 0Ws and 1000Ws while the pressure, exposure time and bias power are fixed).



Fig. 5.14. (Color online) (a) Experiment: Etched thickness of a pre-modified SiN substrate as a function of the HF bath time [Dubois 16]. (b) MD simulations { $E_{ion} = 100eV$ , mixed  $H_x^+$  ion/H radical bombardment of SiN,  $\Gamma = 1$ , 90%  $H_3^+$ , ion dose  $6x10^{16}$  ion/cm<sup>2</sup>}: density depth profile and corresponding snapshot of the cell.

We see that in the beginning, the etch rate (i.e. the slope of the etched thickness) is low (green region); it then increases (red region) before going down again at the end of the removal step (blue region). In these experimental conditions, the ion energy was equal to 180eV and 600eV, respectively, and following [Dubois 16], in both cases the etching of SiN during the H<sub>2</sub> plasma exposure was negligible. Since such high energies were not accessible in MD simulations, our highest studied energy (100eV) was chosen for a comparison. Similarly, since in experimental conditions the etching was negligible, the numerical case  $\Gamma = 1$  was chosen, for which the etching is negligible as well. As one can see on Figure 5.15(b), where the density depth profile and the snapshot of the MD cell are presented for an ion dose  $\sim 6x10^{16}$  ion/cm<sup>2</sup>, in such conditions, the hydrogenation profile is Gaussian-like, which can explain the etch rate variations observed experimentally. Indeed, as suggested in section 5.3.2, the more hydrogenated the substrate, the easier it will be etched during the removal step. Thus, the green region should be etched slowly, then the red one faster, and finally the blue region slowly again, as in experiments. At this point, our MD simulations are in qualitative agreement with the experiments. Later, [Dubois 16] has measured the modified layer thickness of silicon nitride after 60s exposure to a

H<sub>2</sub> plasma for various source power (Ws) and bias power (Wb), as presented on Figure 5.15.



Fig. 5.15. (Color online) Measured thickness of the SiN modified layer as a function of the bias power for different source powers [Dubois 16]. Blue symbols give MD predictions of the SiN modified layer thickness in similar conditions.

To better understand this graph, let us remind the following approximation:

$$P_{RF \ bias} = V_{bias} \times I_{ion}, \quad where \ V_{bias} \approx E_{ion}$$
(5.1)

where  $I_{ian}$  is the ion flux and  $P_{RF bias}$  is the bias power. As mentioned in chapter 1, in an ICP plasma, the increase of the RF source power (Ws) increases the ion flux, but following formula 5.1, it simultaneously decreases the ion energy at constant RF bias power (Wb). Figure 5.15 shows one expected tendency: for a given source power, the increase of the bias power induces an increase of the modified layer thickness, which is logical since it increases the ion energy. However, it also shows that for a given bias power, the source power has practically no effect on the SiN modification. This behavior raises questions, since at constant bias power, different source powers normally induce different ion energies, which makes think here that different ion energies can bring the same modification. For a clear understanding, one must know how the operating conditions affect quantitatively the ion energy and the ion flux. Fortunately, in his work [Dubois 16] has measured both the ion energy and the ion flux for different operating conditions, as presented on Figure 5.16(a, b). To compare these experimental results with our MD data, let us take the case of a bias power equal to 50Wb, for which the measured ion energies are comparable to the one simulated in this chapter. And let us focalize on two relatively different energies, for example 50eV and 200eV, which correspond to source powers equal to 1000Ws and 200Ws, respectively. Indeed, the increase of the source power (5 times) decreases the ion energy (4 times), but also increases the ion flux (9 times).



Fig. 5.16. (Color online) Experimental measurements of (a) Ion energy, (b) ion flux as a function of the bias power for different source powers in a DPS H<sub>2</sub> plasma [Dubois 16].

This means that for the same time of plasma exposure, the ion dose was increased as well (9 times). Now let us compare the same ratio of ion energies and ion doses in MD. Instead of 200eV and 50eV, 100eV (highest simulated ion energy) and 25eV are chosen to keep the experimental ratio between ion energies. On Figure 5.17, the evolution of the modified layer thicknesses for these two MD cases are shown as function of the ion dose. Two specific ion doses are denoted by black crosses, with a ratio equal to 9 (as in experimental conditions); they clearly show that despite the huge difference between the ion energies, the thicknesses of the modified layers are the same, because the measurement were done for two different ion doses in the transient regime (out-of-steady-state).



Fig. 5.17. (Color online) MD simulations { $E_{ion}$  = 25 and 100eV, mixed  $H_x^+$  ion/H radical bombardment of SiN,  $\Gamma = 10$ , 90%  $H_3^+$ }. Modified layer thicknesses as a function of the ion dose. The 2 black crosses demonstrate that the modified layer thickness for very different ion energies out-of-steady-state can give the same value.

In the present work, it was shown several times that the modification of Si/SiN by a hydrogen plasma necessitates a significant ion dose to reach steady state, and that this dose increases with the ion energy. Following experimental and MD data, for a source power equal to 1000Ws (high ion flux ~0.85-0.88 mA/cm<sup>2</sup> and low ion energy < 250eV), even 30 seconds of plasma exposure will provide ion doses

>15x10<sup>16</sup> ion/cm<sup>2</sup>, which is sufficient to reach steady state, meanwhile for low source powers, much more time is required (because of lower ion fluxes and higher ion energies). Thus, to examine the effect of the source power (or other plasma parameters) on the SiN modification, one must be sure that the measurements were done at steady state.

If we return to Figure 5.15, only two experimental data points (measured at steady state) can be quantitatively compared to our MD predictions: [50Wb; 1000Ws]  $\Leftrightarrow$  E<sub>ion</sub> = 50eV, ion dose ~31.8x10<sup>16</sup> ion/cm<sup>2</sup> and [100Wb 1000Ws]  $\Leftrightarrow$  E<sub>ion</sub> = 100eV, ion dose ~32.2x10<sup>16</sup> ion/cm<sup>2</sup>. Since plasma diagnostics could only provide information on the mean ion energy and ion flux, we compared the measured thicknesses with all available simulations performed at these energies. In the case of pure H<sup>+</sup> bombardment, MD and experiments are in excellent quantitative agreement. In other cases, MD simulations seem to underestimate the modified layer thickness, which could be due to a too high etch rate of SiN in MD or to the bimodal nature of the IEDF in experiments. However, it is difficult to make a judgement about quantitative MD predictions, since in this case more plasma diagnostics are needed to fully characterize the plasma (especially the ion composition or the radical-to-ion-flux ratio) for the given operating conditions. Besides, let us remind that we are comparing MD and experimental results with a nanoscale precision, while experimental measurements were performed using ex-situ ellipsometry, where such precisions are hardly provided.

Following our estimation, in experimental measurements at 1000Ws, steady state is reached in all cases, and following the measurements of the modified layer thickness on Figure 5.15 (green curve), the estimation

# Modified thickness ~ $\sqrt{E_{ion}}$ (5.2)

seems to be valid even for higher energies. As mentioned in chapter 2, MD is especially powerful for the qualitative description of plasma-surface interaction phenomena, nevertheless it may also be used for quantitative predictions.

## 5.4.7. Stochastic effects of ion implantation at low doses

The previous subsection showed the importance of the ion dose in the Smart Etch, and it appears that this parameter is as important as the ion energy, if not more. In section 5.4, we saw that the modified layer is well defined at steady state (with ~0.5nm of precision), but also that extremely high ion doses are required to reach this state (or in other words, extremely long plasma exposure times), which is not

always desirable in industry. Thus, let us study what happens if one uses the same DPS reactor as [Dubois 16] to modify a SiN substrate with a hydrogen plasma, but with a short exposure time (~10 seconds) at [50Wb, 200Ws]. For this study, new simulations were performed with the following parameters { $E_{ion} = 200$ eV,  $\Gamma = 10,90\%$   $H_3^+$ }, which are – at least for the ion energy – equivalent to the [50Wb, 200Ws] case. This high energy becomes available in MD since only a small ion dose must be simulated. In these conditions the ion flux is ~0.1 mA/cm<sup>2</sup>, which gives an ion dose ~0.62x10<sup>16</sup> ion/cm<sup>2</sup> for 10s of exposure time, equivalent to ~600 ion impacts on our ~10 nm<sup>2</sup> MD cell (that is to say ~6.600 impacts in total since H radical impacts are also included). The same simulation was done on two SiN cells separately, which are presented on Figure 5.18(a, b) with their corresponding nH/(nSi + nN) ratio depending on depth (Figure 5.18(c)). As one can see, the main modification occurs near the first 4nm of the surface, however if one looks more carefully, some ions (especially H<sup>+</sup>) can penetrate deeper, until 12nm of depth. Finally, Figure 5.18(d) gives the evolution of the nH/(nSi + nN) ratio, averaged on the first 4nm, with the ion dose.



Fig. 5.18. (Color online)  $E_{ion} = 200eV$ , mixed  $H_x^+$  ion/H radical bombardment of SiN,  $\Gamma = 10$ , 90%  $H_3^+$ . (a) Snapshots of two 10 nm<sup>2</sup> cells corresponding to two separate but identical simulations after an ion dose ~0.62x10<sup>16</sup> ion/cm<sup>2</sup> (~600 ion impacts or 10s of exposure time), and corresponding ratios nH/(nSi + nN) depending on depth. (b) Evolution of ratios nH/(nSi + nN), averaged on the first 4nm near the surface, with the ion dose.

Now let us imagine that the experimental substrate is divided into such small (~10 nm<sup>2</sup>) MD cells, and we want to observe the homogeneity of modification. From Figure 5.18(c) the difference between the modifications in the two cells seems negligible; however, Figure 5.18(d) shows that the difference between the averaged hydrogenation ratios can overpass 20% (in the region marked by a green circle) for a slightly lower ion dose. Moreover, we are doing this comparison for exactly the same number of ion impacts on each cell, which is practically impossible to achieve in reality. Certainly, it is assumed that the flux of ion species is homogeneous on the substrate, but for a short plasma exposure time, the received ion dose on each 10nm<sup>2</sup> (MD cell) can be significantly different. To illustrate this effect, a surface ~100x100 nm<sup>2</sup> composed of 1089 simulation cells was randomly bombarded with an ion dose ~0.62x10<sup>16</sup> ion/cm<sup>2</sup> (~10s of plasma exposure). Figure 5.19(a) shows the number of ion impacts received by each 10 nm<sup>2</sup> simulation cell. As we see, the maximal difference can achieve 34%, which cannot be neglected since the surface is still in the transient regime (rapid modification stage) for such a low exposure time. Now if we merge these data with the data of Figure 5.18(d), we get Figure 5.19(b), where the averaged ratio nH/(nSi + nN) in the first 4nm, is plotted for all cells. As one can see, the difference between the hydrogenation ratios can achieve 25%; this means that the H<sub>2</sub> plasma-induced modification of SiN is far not homogeneous on the given surface, which may lead to surface roughness after the subsequent removal of the modified layer in the second step.



Fig. 5.19. (Color online) Simulation of the exposure of a 100x100 nm<sup>2</sup> substrate to a [50Wb, 200Ws] hydrogen plasma during 10s. (a) Received ion doses for each individual MD cell (3x3 nm<sup>2</sup>). (b) Ratios nH/(nSi + nN), averaged on the first 4nm near the surface, for each individual MD cell (3x3 nm<sup>2</sup>).

In other words, the difference of hydrogenation ratios given on Figure 5.19(b) is equivalent to the nonhomogeneity of the modification at low ion doses (or short exposure times). Finally, Figure 5.20 illustrates this non-homogeneity by showing the maximal difference of hydrogenation ratios (averaged on the first 4nm of the modified substrate), as a function of the ion dose.





As one can see, the modification is extremely non-homogeneous at low ion doses; with the increase of the ion dose, the modification becomes more and more homogeneous. To avoid this stochastic effect, one should thus increase the ion dose, which can be done in two different ways:

- Simply increase the plasma exposure time, which preserves all other plasma parameters (ion flux, ion energy, etc.) but increases significantly the process time.
- Change the operating conditions to increase the ion flux while preserving the other plasma parameters, especially the ion energy. For example, the discussed operating conditions [50Wb, 200Ws] and [200Wb, 1000Ws] provide barely the same ion energy (~200eV), but the ion flux is 9 times higher in the second case.

For the Smart Etch process, this subsection underlines the importance of the plasma diagnostics, which enable to determine the plasma composition, ion energy and ion flux, depending on the operating conditions (source and bias power, pressure, etc.).

## 5.4.8. Key parameters for the Smart Etch of SiN in hydrogen plasmas

In this chapter, MD simulations enabled to address issues encountered in the experimental investigation of the Smart Etch of SiN. Since MD data were shown to be predictive qualitatively, in this subsection, they are used to propose a range of plasma parameters to optimize the first step of the Smart Etch process. To do that, let us clarify one more time the goals and the requirements for this process. The goal here is the directional etching of silicon nitride with a nanoscale precision, without damaging the underlayers. Thus, the following requirements are imposed to the first step:

- To etch with a nanoscale precision, the modified layer thickness must always be controlled with the same exactness.
- 2. To provide a high selectivity between the modified and non-modified parts, which allows to stop the etching on the non-modified part, a high modification/hydrogenation rate is needed. This high rate is also needed to increase the etch rate of the modified part, which will accelerate the second step of the Smart Etch and minimize the loss on the sidewalls (isotropic etching).
- 3. To avoid any stochastic effects during the ion implantation, which may induce surface roughness after the second step, the modification must be as homogeneous as possible. For that, one should always provide ion doses sufficiently large to be out of the fast transient regime (rapid modification), i.e. in the saturation stage.
- 4. To not affect the directionality of the Smart-Etch, the isotropic etching of the substrate during the plasma exposure must be negligible compared to its volume modification.

Since the influence of many plasma parameters (ion dose, ion energy, radical-to-ion flux ratio, etc.) was studied in this chapter, it may be easier to find a best range of parameters by exclusion. Figure 5.21 shows again the evolution of the modified and etched layers thicknesses (as well as the H uptake) as function of the ion dose for our MD base case. In this graph, the red and blue regions denote the ion dose ranges which must be avoided.



Fig. 5.21. (Color online)  $E_{ion} = 100eV$ , mixed  $H_x^+$  ion/H radical bombardment of SiN,  $\Gamma = 10$ , 90%  $H_3^+$ . Hydrogen uptake, modified and etched layer thicknesses as a function of the ion dose. Red and blue regions demonstrate the ion dose ranges which must be avoided in Smart Etch. The red region must be avoided because it is not compatible with the 2<sup>nd</sup> and 3<sup>rd</sup> conditions (low hydrogenation rate and in the fast transient regime); the 4<sup>th</sup> condition is not compatible with the blue region either since the etching starts to be non-negligible. The determination of these regions depends on the plasma parameters and can be done experimentally, by analyzing the evolution of the modified layer thickness, as presented in chapter 1 on Figure 1.25. For hydrogen plasmas, such an experimental analysis of the modified layer was done in the thesis of [Chambettaz 18]. In the present MD work, the determination of these regions was done for all studied simulations, and we will now focus on the white region only (i.e. in the saturation stage).

Among all tested cases, the worst case can be considered as  $\{E_{ion} = 100 \text{eV}, \Gamma = 100, 90\% H_3^+\}$ , which should be eliminated because it does not satisfy the 1<sup>st</sup>, 2<sup>nd</sup> and 4<sup>th</sup> conditions; in particular, the high value of  $\Gamma$  induces a too high etch rate during the plasma exposure, which must be minimized. Then, the 1<sup>st</sup> condition is not satisfied in the cases presented on Figure 5.22.



Fig. 5.22. (Color online) Density depth profiles for the following simulation cases: (a)  $E_{ion} = 100 \text{eV}$ ,  $\Gamma = 1$ , 90%  $H_3^+$ , ion dose 2.5x10<sup>16</sup> ion/cm<sup>2</sup>. (b)  $E_{ion} = 100 \text{eV}$ ,  $\Gamma = 10$ , 100%  $H^+$ , ion dose 2.2x10<sup>16</sup> ion/cm<sup>2</sup>. (c)  $E_{ion} = 100 \text{eV}$ ,  $\Gamma = 10$ , 50%  $H_3^+$ , ion dose 3.5x10<sup>16</sup> ion/cm<sup>2</sup>.

The green region denotes the etched part, the red region the modified one, and the gray region the weakly hydrogenated part, which cannot be considered as modified but may affect the nanoscale precision of the modification.

In these cases, the etched layer (green region) is negligible compared to the modified layer (red region); however, a thick but weakly hydrogenated layer is formed below the modified layer, which cannot be considered as modified but may affect the properties of underlying layers. Besides, in these cases, the  $2^{nd}$  condition is not fully satisfied either, since the nH/(nSi + nN) ratio in the modified part is ~0.2 only. On the contrary, the other cases presented on Figure 5.23 can be considered as satisfactory.



Fig. 5.23. (Color online) Density depth profiles for the following simulation cases: (a)  $E_{ion} = 100 \text{eV}$ ,  $\Gamma = 10$ , 90% H<sub>3</sub><sup>+</sup>, ion dose 2.2x10<sup>16</sup> ion/cm<sup>2</sup>. (b)  $E_{ion} = 100 \text{eV}, \Gamma = 10, 100\% \text{ H}_3^+$ , ion dose  $2.2 \times 10^{16} \text{ ion/cm}^2$ .

(c)  $E_{ion} = 50 \text{eV}$ ,  $\Gamma = 10$ , 90%  $H_{3^+}$ , ion dose 2.2x10<sup>16</sup> ion/cm<sup>2</sup>.

(d)  $E_{ion} = 25 \text{eV}$ ,  $\Gamma = 10$ , 90%  $H_{3^+}$ , ion dose  $1.5 \times 10^{16}$  ion/cm<sup>2</sup>.

The green region denotes the etched part, the red region the modified one, and the gray region the weakly hydrogenated part, which cannot be considered as modified but may affect the nanoscale precision of the modification.

On Figures 5.23(a, b), one can see that the modification is more accurate (thinner weakly hydrogenated underlayers) and more saturated in hydrogen when the ion composition is mono-species; this is logical since as shown previously, H<sup>+</sup> and H<sub>3</sub><sup>+</sup> ions are modifying Si/SiN on significantly different depths. The same trend is observed when the ion energy decreases: in last case (d), there is no weakly hydrogenated underlayers and  $nH(nSi + nN) \sim 0.4$  (but the modified layer is only 1nm-deep).

Based on this analysis, the following conclusion can be established. To optimize the implantation step of the Smart Etch process, the following plasma conditions must be fulfilled:

(a) High ion fluxes, to avoid stochastic effects of implantation

(b) Low radical-to-ion flux ratios, to minimize the etch rate of SiN during the hydrogen plasma exposure

(c) Low ion energies, because the higher the ion energy, the less homogeneously-distributed the hydrogen in the modified substrate (with a more and more Gaussian-like hydrogen depth profile)

(d) Ion composition should be as mono-species as possible, for the higher precision of the modified layer thickness, and be preferably composed of molecular ions (e.g.  $H_{3}$ ) since the hydrogenation rate is higher.

# 5.5 Conclusion

In this chapter, the influence of low-energy  $H_{x^{+}}$  ion implantation and mixed  $H_{x^{+}}$  ion/H radical bombardment on amorphous silicon nitride modification was investigated, for various ion energies ( $E_{ion} = 5-100$ eV), radical-to-ion flux ratios ( $\Gamma$ =1-100) and ion compositions (from 100% H<sup>+</sup> to 100% H<sub>3</sub><sup>+</sup>).

The study of pure  $H_{x^+}$  (x=1-3) ion bombardment of silicon nitride showed that the ion implantation leads to a surface evolution composed of two stages: a rapid volume modification followed by a slow saturation, with the formation of a stable [a-SiN:H] modified layer at steady state. During the ion bombardment, there is a formation and desorption of  $H_2$  molecules into the substrate, which balances the number of penetrating ions at steady state and enables a self-limited ion implantation. At steady state, Gaussian-like profiles of hydrogen in the substrate are observed. Near the peak of hydrogenation, the substrate is extremely weakened, with H/SiN ratios ~ 1 and a high density of SiH<sub>3</sub> and NH<sub>2</sub> groups. The modified layer thickness increases with the ion energy and is higher for smaller ions, while the hydrogenation ratio nH/(nSi + nN) shows exactly the inverse trend. A non-standard behavior, specific to the implantation of light ions, is observed for the etching. For very low ion energies, some weak chemically etching of SiN is observed, which disappears for ion energies ~25eV; for ion energies  $\geq$ 50eV, a preferential sputtering of nitrogen appears, which increases with the ion energy and explains why the near-surface region is depleted in nitrogen.

The study of mixed ion/radical bombardment on silicon nitride showed a simultaneous modification and etching of the substrate, where the modification is principally governed by ions and the etching by atomic H. For the same plasma conditions, Si is etched 10 times faster than  $Si_3N_4$ , which is in qualitative agreement with experiments but remains quantitatively far from the few measurements reported in literature. Because of the etching, the hydrogen density depth profile is less Gaussian-like and the modified layer is less saturated in hydrogen compared to the pure ion bombardment case. Nonetheless,  $SiH_x$  (x=1-3) and NH<sub>y</sub> (y=1-2) groups are still detected in the modified layer. The modified layer thickness and the ion dose required to be at steady state increase with the ion energy, meanwhile the nH/(nSi + nN) ratio decreases and the etch rate remains constant. The increase of the radical-to-ion flux ratio

increases the etch rate, which decreases the modified layer thickness and the ion dose required to be at steady state. An increase of the H<sup>+</sup> population in the ion composition increases the modified layer thickness but decreases the nH/(nSi + nN) ratio. Comparison of the present MD simulations with experiments shows an excellent qualitative agreement but experimental data are missing to conclude quantitatively. MD also enabled to answer some open questions encountered in experiments, related to the nature of the modification or the influence of the ion dose. In particular, the unexplained effect of the source power on the substrate modification reported in [Dubois 16] was clarified. Some other possible issues were revealed, like the stochastic effects of implantation at low ion doses, which can induce a non-homogeneous modification and be responsible for the development of surface roughness after the second removal step. Finally, key plasma parameters were proposed to optimize the implantation step of the Smart Etch. In this chapter, the Si-N-H interatomic potential from [Billeter 06] showed a good agreement with experiments on macroscopic data; however, it should be mentioned that it presents some issues at the microscopic level (cf. overcoordination of atoms for high degrees of hydrogenation), showing that the modeling of SiN interactions with hydrogen must still be improved.

# Chapter 6 General conclusion

This PhD thesis focuses on one technological challenge related to the development of advanced transistors (FinFET, FDSOI), where the etching of thin films reveals several issues. In particular, the etching of silicon nitride spacers, which should be achieved with a nanoscale precision without damaging the underlayers, is considered as one of the most challenging steps. In classical continuous-wave ICP and CCP plasmas, the ion-neutral synergy induces the creation of few-nm-thick reactive layers and significant etch rates (ion energies >15-20eV), which can compromise the etch precision; their applicability in such advanced processes is thus limited. To overpass this limitation, an innovative approach was recently developed (often called Smart Etch), which is based on light ion implantation and composed of two steps. First, the material to be etched is modified by exposure to a hydrogen (H<sub>2</sub>) or helium (He) ICP or CCP plasma; in a second step, the modified layer is selectively removed using wet etching (e.g. HF bath) or gaseous reactants only (e.g. in downstream plasmas).

In this work, to assist the development of the SmartEtch technology and support the fundamental understanding of its first step, the interaction between silicon or silicon nitride films and hydrogen or helium plasmas was studied by means of molecular dynamics (MD) simulations. In particular, MD was used to investigate how the Si and Si<sub>3</sub>N<sub>4</sub> substrates modification is affected by the ion energy, the ion dose, the ion composition or the radical-to-ion flux ratio (in the case of a H<sub>2</sub> plasma). Since the present MD studies cover a wider scientific area than that of silicon nitride modification in H<sub>2</sub>/He plasmas, our simulations were also used to bring new insights to other technologies exploiting these plasmas, notably to the Smart Cut technology.

Firstly, the influence of He<sup>+</sup> ion bombardment on both Si/Si<sub>3</sub>N<sub>4</sub> substrates modification was investigated, for ion energies varying in the 5-250eV range (chapter 3). Afterwards, the effect of pure H<sub>x</sub><sup>+</sup> (x=1-3) ion bombardment and mixed H<sub>x</sub><sup>+</sup> ion/H radical bombardment on Si (chapter 4) and Si<sub>3</sub>N<sub>4</sub> (chapter 5) were investigated, for various ion energies (E<sub>ion</sub> = 5-100eV), radical-to-ion flux ratios ( $\Gamma$ =1-100) and ion compositions (from 100% H<sup>+</sup> to 100% H<sub>3</sub><sup>+</sup>). In all studied cases, simulations showed that a self-limited ion implantation takes place with a surface evolution composed of two principal stages: a rapid volume modification followed by a slow saturation and the formation of a He- or H- implanted layer of constant thickness at steady state. The modified layer thickness increases with the ion energy, and is always higher for silicon compared to silicon nitride (due to the higher stopping range of SiN). Finally, in all cases, the ion implantation in Si and SiN leads to a small inflation of the substrate. Beyond this general behavior, specific mechanisms of ion-induced damage were observed for each studied case, with various structure/composition of the substrate at steady state.

In the case of He<sup>+</sup> bombardment on Si/Si<sub>3</sub>N<sub>4</sub> substrates (chapter 3), the self-limited ion implantation is guaranteed thanks to the mechanism of helium trapping. The He storage prevents the diffusion of helium atoms deep into the substrate, and at steady state, the number of penetrating He atoms equals the number of desorbing/ejected He atoms. In silicon, the ion implantation induces a strong amorphisation of the substrate and generates He cavities (or clusters) in the bulk. For silicon nitride, besides the presence of He-filled cavities, there is a rearrangement in bonds characterized by the breaking of amorphous Si-N bonds and the creation of less strong Si-Si bonds. In silicon, helium atoms are trapped in the cavities/voids created during the ion implantation and in the Si crystalline matrix, meanwhile in silicon nitride, the trapping occurs mainly in cavities. In agreement with experiments, He implanted at room temperature (300K) does not spontaneously desorb. However, in both cases, MD shows that substrate annealing (~500-800K depending on the energy of ion implantation) leads to helium outdiffusion from small cavities and desorption. Regarding the ion energy, a threshold value ~50eV is found, below which no sputtering occurs; for energies higher than 50eV, the sputtering yield increases with the ion energy but remaining very weak (<0.05 atom/ion for Eion < 250eV). In the case of Si<sub>3</sub>N<sub>4</sub>, preferential sputtering of nitrogen is detected, which makes the near-surface region depleted in nitrogen, as observed experimentally. For ion energies lower than 10eV, no structural modification of the substrate appears (ions are reflected or penetrate on 1-2nm without damage). Some simulation results are compared with experimental data provided by [Dubois 16]: a qualitative and quantitative agreement is found regarding the impact of the ion dose and ion energy on the modified layer thickness. This study confirms that He plasmas can transform Si and SiN materials on a precise depth without etching them. The discussed structural modifications (creation of a less dense modified layer, full of He-filled cavities and containing weaker bonds) may explain the selective removal of the modified part during the second step of the Smart Etch process.

In the case of a pure  $H_{x^+}$  (x=1-3) ion bombardment of Si (section 4.3) and Si<sub>3</sub>N<sub>4</sub> (section 5.3), the ion implantation is self-limited due to the formation and desorption of  $H_2$  molecules during the ion bombardment.  $H_2$  molecules created in the bulk during the ion collision cascade desorb in a few

nanoseconds, which balances the number of penetrating H<sub>x</sub><sup>+</sup> ions at steady state. Also, since hydrogen (atomic H) is chemically reactive with both silicon and nitrogen, it tends to create covalent bonds with the substrate atoms rather than diffusing deep into the substrate. To reach steady state, relatively high ion doses are needed. At steady state, Gaussian-like hydrogen density depth profiles are observed in the material. Near the peak of hydrogenation, the substrates are extremely weakened, with H/Si and H/SiN ratios ~ 1 and a high density of SiH<sub>3</sub> or NH<sub>2</sub> groups. As a result, the modified layers are weakly bound to the underlying material, which is at the origin of the Smart Cut mechanism. In the case of silicon, annealing simulations show that the fracture between the modified and non-modified parts increases when heating the substrate (~1000K), which induces an in-depth micro-slicing of the cell. With the increase of the ion energy, the hydrogen concentration in the modified layer decreases. A non-standard behavior, specific to the implantation of light ions, is observed for the etching. For E<sub>ion</sub> < 25eV, the etch yield decreases when the ion energy increases, and disappears for E<sub>ion</sub> ~25eV (pure chemical etching at very low energy with ~100% SiH<sub>4</sub> or NH<sub>3</sub> saturated products). In the case of Si<sub>3</sub>N<sub>4</sub>, a small etch rate is observed for E<sub>ion</sub> ≥ 50eV, with a preferential sputtering of nitrogen atoms (pure physical etching at high energy).

Finally, the simulations of mixed  $H_x^+$  ion/ H radical bombardment (H<sub>2</sub> plasma exposure) on Si (section 4.4) and SiN (section 5.4) show a simultaneous modification and etching of the substrates, where the modification is principally governed by ions and the etching by atomic H radicals. For the same plasma conditions, Si is etched 10 times faster than Si<sub>3</sub>N<sub>4</sub>, which is in qualitative agreement with experiments but remains quantitatively far from the few measurements reported in literature. Because of the concurrent modification/etching of the substrate, the hydrogen density depth profile is less Gaussian-like and the modified layer less saturated in hydrogen compared to the pure ion implantation case. Nevertheless, a high density of SiH<sub>x</sub> (x=1-3) and NH<sub>y</sub> (y=1-2) groups is still detected in the modified layer, which weakens the substrate and suggests why it can then be etched selectively with respect to the non-modified part. The modified layer thickness, as well as the ion dose required to reach steady state, increase with the ion energy but decrease with the increase of the radical-to-ion flux ratio. An increase of the H<sup>+</sup> population in the ion composition also increases the modified layer thickness, since more energetic and smaller ions penetrate deeper in the substrate.

From a technological point-of-view, our simulations brought new insights to both the Smart-Cut and Smart-Etch technologies. In particular, simulations showed that low energy helium ion implantation (E<sub>ion</sub>

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 $\leq$  250eV) in c-Si leads to a near-surface amorphisation but that further annealing (or substrate heating) do not induce any cutting phenomenon in silicon, contrary to what is reported experimentally at high energy (tens of keV). By contrast, low energy hydrogen ion implantation (E<sub>ion</sub> < 100 eV) can induce a micro-slicing of silicon, even if the near-surface region is highly damaged (amorphisation and hydrogenation). These simulations suggest that at low energy, the micro-cutting of silicon during the heat treatment step is driven by the hydrogenated amorphous Si bonds and the formed SiHx groups (which weaken the structure), rather than by the desorption of  $H_2$  molecules. For implantation at high energy (tens of keV), since H<sub>2</sub> molecules should be formed much deeper in the substrate (several microns), their desorption may take sufficient time to bring a contribution to both ion implantation and heat treatment steps. As for the Smart-Etch, simulations showed that the ion energy and the ion flux must be controlled very cautiously, both to preserve the nanoscale precision of the process and to ensure a homogeneous modification of the substrate. In particular, low ion doses must be avoided since the substrate evolution cannot be precisely controlled in the fast transient regime. The applicability of helium plasmas in the Smart Etch process was confirmed for both Si and SiN substrates. In hydrogen plasmas, on the other hand, the radical-to-ion flux ratio  $\Gamma$  must also be considered since the etch rate of both materials increases with  $\Gamma$ . In agreement with experiments, simulations thus showed that silicon etching cannot be achieved in hydrogen plasmas using the Smart-Etch, because H radicals readily etch silicon. As for silicon nitride, simulations confirmed the high potential of this process and reproduced fairly well some experimental measurements reported in literature. MD also enabled to answer some open questions encountered in experiments, related to the nature of the modification or the influence of the ion dose. In particular, the unexplained effect of the source power on the substrate modification reported in [Dubois 16] was clarified. Some other possible issues were revealed, like the stochastic effects of implantation at low ion doses, which can induce a non-homogeneous modification and be responsible for the development of surface roughness after the second removal step. Finally, key plasma parameters were proposed to optimize the implantation step of the Smart Etch.

This PhD work provides interesting perspectives for both MD calculations and experimental work related to the Smart Etch topic. During this PhD work, a new MD parallelized and highly optimized code was developed, which allows to work with a considerable number of atoms and thus makes possible the study of patterns. In the future, it would be extremely interesting to examine the effect of H<sub>2</sub> and He plasmas on silicon nitride spacers form, and notably analyze how different the modification can be on

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the top and sidewalls. The Si-N-H interatomic potential [Billeter 06] included in this MD code was also developed for the Si-O-N-H system, which makes possible the study of the Smart Etch of other materials (especially SiO<sub>2</sub>) using H<sub>2</sub>/He plasmas, as well as the Smart Etch of silicon nitride in oxygen plasmas. The last gas being much heavier than H<sub>2</sub> and He, it could modify the substrate on lower depths, which may be interesting for ALE applications. Finally, it would be interesting to simulate the second step of the Smart Etch, i.e. the removal of the modified layer, in a NH<sub>3</sub>/NF<sub>3</sub> downstream plasma. However, if interatomic potentials were developed to model the Si-H-F system, none of them unfortunately includes the interaction with nitrogen, which currently makes impossible this last MD study.

# Appendix

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This appendix will detail the used interatomic potentials, the encountered problems in the coding of these potentials, and some ruses permitting to increase the coding efficiency of the force. Afterwards, it presents the developed MD code, dedicated to simulating the interactions of a substrate with helium and hydrogen.

## 7.1.1. Tersoff's potential

It is reasonable to start with Tersoff's [Tersoff 88] interatomic potential, since two other potentials are modified versions of this one. The mathematical form is as follows

$$E = \sum_{i} E_{i} = \frac{1}{2} \sum_{i \neq j} V_{ij}, \quad (7.1)$$

$$V_{ij} = f_{c}(r_{ij}) [a_{ij}f_{R}(r_{ij}) + b_{ij}f_{A}(r_{ij})], \quad (7.2)$$

$$f_{R} = Ae^{-\lambda_{ij}r_{ij}}, \quad (7.3)$$

$$f_{A} = -Be^{-\mu_{ij}r_{ij}}, \quad (7.4)$$

$$r < R - D$$

$$f_{c}(r) = \begin{cases} 1, & r < R - D \\ \frac{1}{2} - \frac{1}{2} \sin\left(\frac{\pi(r - R)}{2D}\right), & R - D < r < R + D, \\ 0, & r > R + D \end{cases}$$

$$b_{ij} = (1 + \beta^{n}\xi_{ij}^{n})^{-\frac{1}{2n}}, \quad (7.6)$$

$$\xi_{ij} = \sum_{k \neq i,j} f_{c}(r_{ik})g(\theta_{ijk}) \exp\left[\gamma^{3}(r_{ij} - r_{ik})^{3}\right], \quad (7.7)$$

$$g(\theta_{ijk}) = 1 + \frac{c^{2}}{d^{2}} - \frac{c^{2}}{d^{2} + (h - \cos(\theta_{ijk}))^{2}}, \quad (7.8)$$

$$a_{ij} = (1 + a^{n}\eta_{ij}^{n})^{-\frac{1}{2n}}, \quad (7.9)$$

$$\eta_{ij} = \sum_{k \neq i,j} f_c(r_{ik}) \exp\left[\gamma^3 (r_{ij} - r_{ik})^3\right].$$
(7.10)

The functional form is quite complicated, so let's consider each term separately. Consider a simple example of 3 Si atoms, as illustrated on Figure 7.1.



Figure 7.1. Three Si atoms in interaction.

Eq. 7.1 says that the total potential energy of the system is the sum of potential energies of each atom, or the sum of pair interactions potentials, described by  $V_{ij}$ , which is given by formula 7.2. In its turn, each pair potential  $V_{ij}$  is composed of attractive and repulsive parts given by formulas 7.3 and 7.4 respectively, and if one assumes that the other terms ( $f_c(r)$ ,  $a_{ij}$ ,  $b_{ij}$ ) are just constants, then the  $V_{ij}$  has the following shape, given on Figure 7.2.





On Figure 7.2, one can see that this pair interaction decreases rapidly from a certain interatomic distance, and converges to zero. This fact is smartly used to accelerate the computing efficiency, by using a simple cutoff function given by formula 7.5, which goes smoothly to zero from the given distance, and so does  $V_{ij}$ , as presented on Figure 7.3. This assumption allows to dramatically decrease the
computing costs, since it descreases the number of pair interactions ( $V_{ij}$ ) to be computed. At this point, this potential is referred to the class of short range interatomic potentials, since it does not simulate the long range interactions.



Figure 7.3. (a) Cutoff function f<sub>c</sub>, passing smoothly from 1 to zero, starting from the point where the bond is no more considered as covalent, and (b) its effect on the pair interaction shown by the red curve.

Usually  $f_c$  equals to one, when two atoms are in covalent bond (i.e. for interatomic distances where it is in covalent state), and then it passes to zero. The discussed functions/parameters are responsible only for the reproduction of interatomic distances, and in some cases, like for the rare gases, this is sufficient to correctly describe the system, but not for the solid-state structures, where the atoms are bound to each other, and the angle between the bonds is as important as the interatomic distances. Moreover, the influence of atom k on the pair i - j must be taken into account as well, which are done via the complicated terms  $a_{ij}$  and  $b_{ij}$ , which are often called three body terms, since they are modeling the three-body interaction.

#### 7.1.2. Murty's Si-H potential

Murty's potential generally has the same shape as the previous one, with some additional terms.

$$E = \frac{1}{2} \sum_{i \neq j} V_{ij}, \quad (7.11)$$

$$V_{ij} = f_c(r_{ij}) [f_R(r_{ij}) + b_{ij} f_A(r_{ij})], \quad (7.12)$$

$$f_R = AF_1(N) e^{-\lambda_{ij} r_{ij}}, \quad (7.13)$$

$$f_A = -BF_2(N) e^{-\mu_{ij} r_{ij}}, \quad (7.14)$$

$$f_{c}(r) = \begin{cases} 1, & r < R - D \\ \frac{1}{2} - \frac{9}{16} \sin\left(\frac{\pi(r-R)}{2D}\right) - \frac{1}{16} \sin\left(\frac{3\pi(r-R)}{2D}\right), & R - D < r < R + D, \\ 0, & r > R + D \end{cases}$$
(7.15)  

$$b_{ij} = \left(1 + \xi_{ij}^{n}\right)^{-\delta}, & (7.16) \end{cases}$$
  

$$\xi_{ij} = \sum_{k \neq i,j} f_{c}(r_{ik})g(\theta_{ijk}) \exp\left[\alpha\left[\left(r_{ij} - R_{ij}^{e}\right) - \left(r_{ik} - R_{ik}^{e}\right)\right]^{\beta}, & (7.17) \end{cases}$$
  

$$g(\theta_{ijk}) = \left[c + d(H(N) - \cos(\theta_{ijk}))\right]^{2}, & (7.18) \end{cases}$$
  

$$N_{H}^{i=(Si)} = \sum_{j=(H)} f_{c}\left(r_{ij}\right), & N_{Si}^{i=(Si)} = \sum_{j=(Si)} f_{c}\left(r_{ij}\right), & (7.19) \end{cases}$$
  

$$N = N_{H}^{i=(Si)} + N_{Si}^{i=(Si)}. & (7.20)$$

Here the values of  $F_1(N)$ ,  $F_2(N)$  and H(N) are computed using the cubic interpolation. For the force computing, one should compute the derivative of the potential, formula 2.1, and special attention must be paid on the derivative of H(N). In the standard Tersoff's potential, and generally in most three-body potentials, each part of three-body term (each term in the sum of 7.17) depends only on atoms *i*, *j*, *k*,

$$\xi_{ij} = \sum_{k \neq i,j} \Omega, \quad \Omega = \Omega(r_i, r_j, r_k), \quad (7.21)$$

while in this potential  $\Omega$  depends also on each atom p, which is in interaction with atom i, since it depends on N, and N depends on p. This means, that compared to the standard three-body potentials, where  $\Omega$ has a contribution to the forces of atoms i, j, k, in this case it contributes to the force of the atom p, and particularly the angle  $\theta_{ijk}$  depends on atoms p as well. As we see, due to terms  $F_1(N), F_2(N)$  and H(N)the derivative of the potential energy becomes much more complicated, which besides increases the computation time, especially because of the cubic spline interpolation. The cubic spline interpolation, and the corresponding algorithm are well described in "Numerical Recipes in C" [Press 96], but in this work, this algorithm was extremely simplified and accelerated. The goal of the cubic spline interpolation is to get an interpolation formula that is smooth in the first derivative, and continuous in the second derivative, both within an interval and at its boundaries, as it is illustrated on Figure 7.4.



Figure 7.4. Cubic spline interpolation for the parameter  $F_1(N)$  in the Murty's potential, and its 1<sup>st</sup> and 2<sup>nd</sup> order derivatives.

The spline function is given by the following formulas

$$y(x) = Ay_{j} + By_{j+1} + Cy_{j}'' + Dy_{j+1}'', \quad (7.22)$$

$$A = \frac{x_{j+1} - x}{x_{j+1} - x_{j}}, \quad B = 1 - A, \quad (7.23)$$

$$C = \frac{1}{6}(A^{3} - A)(x_{j+1} - x_{j})^{2}, \quad C = \frac{1}{6}(B^{3} - B)(x_{j+1} - x_{j})^{2}, \quad (7.24)$$

$$y' = \frac{dy}{dx} = \frac{y_{j+1} - y_{j}}{x_{j+1} - x_{j}} - \frac{3A^{2} - 1}{6}(x_{j+1} - x_{j})y_{j}'' + \frac{3B^{2} - 1}{6}(x_{j+1} - x_{j})y_{j+1}'', \quad (7.25)$$

and the corresponding algorithm for example for the case of  $F_1(N)$ , is given by the following pseudocode

- function  $[F_1, dF_1] = cubic_Spline(N)$
- Declare x points x[4] = {1.0, 2.0, 3.0, 4.0}
- Declare known values y[4] = {1.005, 1.109, 0.953, 1.000}
- Reserve a vector for y"
- · Declare some variables for the y" computing
- Compute y" //18 lines of code
- Using y", compute the values of  $F_1$  and  $dF_1$  at the point x = N //2 lines
- Free all reserved variables

However, imagine taht this algorithm/function is called multiple times, which is the case for the Murty's potential, where this function will be called for each  $V_{ij}$  at each timestep, then the most part of this algorithm, dedicated to compute the values of  $y''_{j}$ , will be the same in all cases, so this algorithm can be used externally to compute these values, and the spline function could be done as follows

function [F<sub>1</sub>, dF<sub>1</sub>] = cubic\_Spline(N)
Declare x points - static x[4] = {1.0, 2.0, 3.0, 4.0}
Declare known values - static y[4] = {1.005, 1.109, 0.953, 1.000}
Declare pre-calculated y" - static y2 = {0.6636, -0.7032, 0.5892, -0.4356}
Using y", compute the values of F<sub>1</sub> and dF<sub>1</sub> at the point x = N //2 lines

It is thus better to declare the variables of x, y, and y2 as static, to avoid their initialization and destruction during each call of this function, and in this way this function is  $\sim$ 6 times faster than the original form.

## 7.1.3. ZRL Si-O-N-H potential

In term of analytical form, the most complicated potential was that of Billeter et al. [Billeter 06, 09] for modeling the Si-N-H system (it models as well the oxygen), which is given by the following formulas

$$\begin{split} E &= \frac{1}{2} \sum_{i \neq j} V_{ij} + N_I \sum_{I} E_I^0 + \sum_{I} E_I^c, \quad (7.26) \\ V_{ij} &= f_{ij}^{IJ}(r_{ij}) [f_R(r_{ij}) + b_{ij}f_A(r_{ij})], \quad (7.27) \\ f_R &= A_{IJ} e^{-\lambda_{IJ}r_{ij}}, \quad (7.28) \\ f_A &= -B_{IJ} e^{-\mu_{IJ}r_{ij}}, \quad (7.29) \\ f_{ij}^{IJ}(r) &= \begin{cases} 1, & r < R_{IJ} \\ \frac{1}{2} - \frac{1}{2} \sin\left(\frac{\pi(r - R_{IJ})}{2D}\right), & R_{IJ} < r < S_{IJ}, \quad (7.30) \\ 0, & r > S_{IJ} \end{cases} \\ A_{IJ} &= (A_I A_J)^{\frac{1}{2}}, B_{IJ} = (B_I B_J)^{\frac{1}{2}}, R_{IJ} = (R_I R_J)^{\frac{1}{2}}, S_{IJ} = (S_I S_J)^{\frac{1}{2}}, \quad (7.31) \\ \lambda_{IJ} &= \frac{\lambda_I + \lambda_J}{2}, \quad \mu_{IJ} = \frac{\mu_I + \mu_J}{2}, \quad (7.32) \\ b_{ij}^{IJ} &= \chi_{IJ} (1 + (\beta_I \xi_{ij}^{IJK})^{n_I})^{-\frac{1}{2n_I}}, \quad (7.33) \\ \xi_{ij} &= \sum_{k \neq i,j} f_{ik}^{IK}(r_{ik}) g(\theta_{ijk}) \exp[\mu_{IJ}^{m_I}(r_{ij} - r_{ik})^{m_I}], \quad (7.34) \\ g(\theta_{ijk}) &= 1 + \frac{c_I^2}{d_I^2} - \frac{c_I^2}{d_I^2 + (h_I - \cos(\theta_{ijk}))^2}, \quad (7.35) \\ E_I^c &= c_{I,1} \Delta z_i + c_{I,2} \Delta z_i^2, \quad (7.36) \\ z_i &= \sum_{J \neq i} f_{iJ}^{IJ} b_{iJ}^{IJ}, \quad (7.37) \end{cases}$$

$$f_{s,ij}^{II}(z) = int(|z - z_0^I|) + \begin{cases} 0, & z < z_T - z_B \\ \frac{1}{2} + \frac{1}{2} \sin\left(\frac{\pi(z - z_T)}{2z_B}\right), & z_T - z_B < z < z_T + z_B, \\ 1, & z > z_T - z_B \end{cases}$$

$$z = |z_I - z_I^0| - int(|z_I - z_I^0|), \quad (7.39)$$

Among all these terms, the following ones are just constants

 $N_{I}, E_{I}^{0}, A_{I}, B_{I}, R_{I}, S_{I}, \lambda_{I}, \mu_{I}, A_{II}, B_{II}, R_{II}, S_{II}, \lambda_{II}, \mu_{II}, n_{I}, m_{I}, \chi_{II}, c_{I}, d_{I}, h_{I}, c_{I,2}, z_{T}, z_{B}, z_{I}^{0}.$ 

This potential comes with an Erratum, where formula 7.26, and terms  $A_i$ ,  $h_i$  where corrected (here the corrected version is presented). Besides, during this PhD work, other errors were found in the original form of  $f_{s,ij}^{IJ}$ , and after contacting the authors, the form described in formula 7.38 was chosen, which was used in the similar potential Ge-Te [Zipoli 13]. Afterwards, there was a small error of parameter  $z_i^0$  (table IV [Billeter 06]), where its values for oxygen and nitrogen should be swapped. Besides these corrections, in this work, it was necessary to make one more change in the parameters. The bombardment of the  $\beta$ Si<sub>3</sub>N<sub>4</sub> substrate by H<sub>x</sub><sup>+</sup> ions, was begetting a huge overcoordination in the substrate, like presence of Si atoms having till 8 covalent bonds. One possible cause of this behavior, might have been the correction term *Ec*, which might be not sufficiently repulsive. The second one is the value cutoff of H-H bond = ~0.89Å (which is too short), because of which hydrogen atoms in an overcoordinated molecules like SiH<sub>6</sub> are not seeing each other, and thus the three-body potential does not prevent the stability of this molecule (for comparison in other MD potentials describing H-H interaction [Brenner 02, Murty 95, Ohira 00] this value is 1.7Å).

The dependence of correction term Ec from the effective coordination  $z_i$  (7.37), is given on Figure 7.5.



Figure 7.5. Correction term Ec as a function of effective coordination (formulas 7.37-7.39), for the ZRL potential.

To amplify the effect of this correction term, it was decided to multiply it by a constant  $\alpha > 1$ . But even so, the problem of overcoordination persists, which is not surprising, since as we see, this term is constant for example for the values of the effective coordination [4.5-5], or [5.5-6], etc., and consequently its derivative will be zero, thus it won't affect the force, and if one multiplies this term by a constant there will be no big difference. Sure, one can choose another form of this correction function for the overcoordinated cases, like  $Ec = (z_i - z_i^0)^2$ , if  $z_i > z_i^0$ , but this modification is far from being negligible, and finally it was decided to not touch this term.

In its turn, the change of the H-H cutoff distance has significantly improved the problem of the overcoordination. To find the best cutoff distance of H-H interaction, firstly multiple small overcoordinated molecules like SiH<sub>5</sub> were simulated, to check if the potential still admits the overcoordinated molecules (if they remain stable during the time, typically during 100ps). Afterwards the simulation of a mixed ion/radical bombardment of  $H_x^+/H$  on Si was done, and compared with the same simulation carried with the Murty's potential. Finally, the best choice was fallen on the H-H cutoff distance 1.5Å. This simple replacement, at a time has significantly increased the simulation speed, since in this case, for the convergent numerical integration of a hydrogenated substrate, a timestep 0.1fs (which is typical for the hydrogen) is sufficient. With the original value of ZRL potential ~0.89Å timestep should be about 0.02fs, otherwise the integration is not convergent, and let's understand why. In a hydrogenated substrate, often configurations, similar to the presented on Figure 7.6, are present.



Figure 7.6. (a) H atom k, approaching to the H atom i, which is bound to Si atom j, and which is reflected du the three-body term (b).

In the first configuration (a), hydrogen atom k is approaching to hydrogen atom i, which is bound to silicon atom j. The hydrogen atom i, which is already fully saturated is trying to reflect the atom k, which brings the configuration in the state (b). Between these two configurations, the main difference is the small displacement of hydrogen atom k, which enhances a significant difference of the potential energy.

The force being computed by the formula (2.1.), gives a magnitude of the force ~100eV/Å (in a real hydrogenated bulk this force can be even ~150eV/Å), which is very high (for comparison in a non-hydrogenated Si bulk this magnitude is about 1eV/Å). Since accelerations are proportional to forces and inversely proportional to atom masses, it gives huge acceleration to hydrogen atom k, about 100-150Å/ps<sup>2</sup>, and because of that the integration of the atomic motion with dt = 0.1 fs leads to the divergence of the schema. So, how the short H-H cutoff distance is related to all that? On Figure 7.7(a), is given the original H-H pair ZRL potential, where the red zone corresponds to the part where the bond is no more considered as covalent (cutoff function goes from 1 to 0).



Figure 7.7. (a) Original form of the H-H pair interaction given by the ZRL potential, and (b) the modified (in this work) version, which was used in all simulations, which gives smoother switch of the interaction, and prevents significantly the overcoordination.

In this "red region" there is a drastic change in potential energy with the change of distance, which affects the three-body term, and which enhances the mentioned phenomenon. Thus, we suggest to change the H-H cutoff distance by 1.5Å, which gives the shape of the pair potential as in Figure 7.7(b).

## 7.1.4. Modeling of the repulsiveness for short interatomic distances

The described interatomic potentials are not designed to model the interaction of atoms at very short ranges, where atoms are immensely repulsed from each other, meanwhile in the simulations of plasma surface interaction there are such interactions after each energetic specie impact, and to model this part correctly, these potentials are splined with the Moliere potential for the short interatomic distances, using the following formula

$$V_{R}(r_{ij}) = \begin{cases} V_{R}^{Moliere}(r_{ij}) + s_{ij}, & r_{ij} < r_{ij}^{min} \\ V_{R}^{Spline}(r_{ij}) + s_{ij}, & r_{ij}^{min} < r_{ij} < r_{ij}^{max} , \\ V_{R}^{Morse}(r_{ij}) + s_{ij}, & r_{ij} > r_{ij}^{max} \end{cases}$$
(7.40)

The idea is to have a continuous and smooth spline between two potentials, which has a continuous derivative (force), as presented on Figure 7.8 for the case of Si-H interaction using Murty's potential.



Figure 7.8. Spline between Murty's and Moliere's potential for Si-H interaction. Green zone Murty's potential, blue zone Spline, red zone Moliere's potential.

The same spline was done for all atom pairs, like Si-Si, N-Si, N-H, etc. Even if there were no impact of energetic Si, N atoms, these splines are necessary, since after an energetic ion impact, in the volume of collision cascade, it is possible to have energized atoms approaching the other ones.

#### 7.2. Straightforward way to debug the force field

As was seen above, the analytical forms of the potentials are quite involved, and this form is much heavier when it is derived, for the direct computing of the force field. The potential derivative's analytical form can be obtained even via different softs, like MATLAB or Octave, however the coding of the force, which sometimes exceeds 1000 line in C, often implies small errors, which are extremely hard to detect and debug. Sometimes the full coding of the force field (followed by the optimization), may take more than 2 months, and below is proposed a simple way to overcome this difficulty. Compared to the force field, the coding of the interatomic potential itself is much easier, and so for each given configuration one can compute the potential energy. Once this is done, and the force field is coded as well, one way to check if the last one is coded 100% correctly, is to compare atomic motions/trajectories using the direct force field, and using the non-direct force field, derived from the potential energy using the finite difference scheme, as it is presented on the scheme on Figure 7.9.



Figure 7.9. Compute of the atom forces without derivation of the potential energy, using the finite difference scheme.

Using this method, it is practically impossible to not detect the bugs in the force field, if there is one. The only case where it is possible to leave an error, it is to have exactly the same errors both in the force field and in the potential, which is "not easy" to do. This method imposes to find a *h*, for the given *dt*, for which the scheme will remain convergent, which takes some minutes to do. Particularly, only after using this method it was found the missing term in the Murty's potential, and a package of bugs during the coding of the ZRL force field. Besides, this method can be readily used to simulate small systems, particularly to test some new potentials, without coding the full force field.

## 7.3. Optimization and parallelization of the MD code

VPMD is a Parallel Molecular Dynamics simulator, which was developed during this work, to study the H<sub>2</sub>/He plasmas interaction with Si/SiN substrates.

## 7.3.1. Re-neighboring algorithm – Smart Linked Cell

One of the most time-consuming parts in MD is the re-neighboring, which searches all neighbors/bonds of all atoms in the system, and computes the corresponding bond lengths. The easiest algorithm for this job is the checking of all possible pairs in the system, as on the pseudocode below



However, this simple algorithm will check N(N - 1)/2 pairs, and the time spent on this algorithm has a quadratic growth with the number of atoms. If the interatomic potential is a short range like one, as

REBO, there is an excellent algorithm, which allows to significantly boost the re-neighboring. For these potentials there is an interaction only within a certain range (given by the potential), let's name it max\_c. The Linked cell algorithm suggests to construct an imaginary grid in the simulation box, where each atom will belong to a cell (of the grid), which is illustrated on Figure 7.10 for the 2D case.



Figure 7.10. Linked cell algorithm in two dimensions.

Now, for example to check the neighbors of the atom in the blue cell (2,3), one should check only the atoms placed in the neighbor cells of the blue cell (red region, including the blue cell as well). In the 2D case, it suggests checking only atoms of these 9 cells, and in the 3D case, it becomes 27 cells. Using this algorithm, the time spent on the re-neighboring increases linearly with the number of atoms. There are multiple other versions of this algorithm [Welling 11], however this one is one of the most used due to its simplicity and universality. In this work, this algorithm was improved, by keeping all its advantages, with one simple modification. In the original algorithm all pairs are checked twice, since all cell pairs are checked twice: for example firstly is checked the cell-pair (cell(2,3), cell(3,4)), and then (cell(3,4), cell(2,3)). The improved version suggests using this algorithm as follows, for each cell, check only the cells which are placed on its right and above it, as presented on Figure 7.11(a). In the case of the 2D instead of checking 9 cells, one should check only 5 cells, and 14 instead of 27 in the 3D case. This simple modification, allows to eliminate the double check of each atom pair, therefore it increases the computing efficiency by ~2 times. Afterwards, another modification was introduced for the study of inert species (in present case helium) interaction with the substrate.



Figure 7.11. Smart-Linked cell algorithm in two dimensions (a) standard case, (b) for a system containing inert atoms.

For inert species, often the range of interaction is much longer than that of other species, for example in the Murty's potential the range of Si-Si is 3Å, meanwhile that of helium (which is described via the Moliere's potential) is 6Å. In such cases there is an approach, to perform the re-neighboring in two steps, firstly construct the grid with  $\max_{c} = 3\text{\AA}$ , re-neighbor only silicon atoms, then construct another grid with  $\max_c = 6\text{Å}$ , and search neighbors only of helium atoms. This method is much faster, than if one made the re-neighboring in one step directly with max\_c = 6Å, since in the last case each Si atom will search neighbor Si atoms in the volume  $V = (3 \max_c)^3 \approx 51 * V_{min}$ , where  $V_{min} = \frac{4}{3}\pi R_{Si\_cutoff}^3$  is the volume of the sphere, where all possible Si neighbors of the atom are located. Consequently, for each Si atom only ~2% of all checked atoms will be its neighbor, meanwhile using the two-step algorithm  $V \approx$ 6 \* V<sub>min</sub>. However, this two-step algorithm can be optimized as well. Consider the atom in the blue cell is helium (see Figure 7.11(b)), and now instead of constructing a new grid with max\_c = 6Å, one can use the existing one with  $\max_c = 3\text{\AA}$ , and check some supplementary cells - neighbors of the neighbor cells, as it is presented on Figure 7.11(b). In this way, instead of checking a volume  $V = (3 \cdot 6A^{\circ})^{3} =$  $5.832nm^3$ , one should check only  $V = (5 \cdot 3A^\circ)^3 nm^3$ , optimizing ~1.7 times the computing time spent on the re-neighboring of inert atoms. This method, coupled with the Smart-Linked cell algorithm, for example for Si bulk of 2000 atoms containing 300 helium atoms, can accelerate the computing time of the total re-neighboring till ~2.8 times, and this factor increases with the increase of the number of helium atoms. In simulations of helium bombardment on Si/SiN substrates, which are extremely time

consuming, this algorithm has played an important role in this work, particularly allowing to decrease the simulation time to 6 months.

#### 7.3.2. Atomic order optimization

Besides algorithmic optimizations, the computing performance of MD can be accelerated only by changing the order of atoms in the configuration, i.e. increase the performance without touching the source code. In the code atoms are stocked in vectors, and they are loaded from the configuration file in the order that they are placed in this file. Now assume that atoms are configured totally arbitrarily, as presented on Figure 7.12(a), where each atom's index in the vector is written on it.





In this case, there is a package of deceleration of the computing, because of the memory access. For example, during the re-neighboring, the atom-pair (19,1) will be checked to see if they are in interaction, and in this case, there will be some time spent on the reaching the memory corresponding to atom 1, and this time will be as big as the distance between these two atoms in the atom's vector. Besides, after the check of the atom 19, the re-neighboring algorithm is passing through all cells in the order, and the next atom that will be loaded is the atom 11, and one more time the same problem will be encountered, if these two atoms are placed far in the configuration. The same problem is occurring in the force computing. Multiple orderings were tested, and among them, the simplest one, where atoms are placed in the order of the cells, as given in Figure 7.12(b), was the most efficient. One may wonder, how a disordered configuration in the modeling of interaction of solids with a plasma can be obtained? Such

configurations are highly probable after a several number of plasma species impacts, since firstly the ions, which were added in the end of atom's vector, can penetrate deep in the substrate, and be placed "anywhere" in the simulation box, and besides the substrate may be etched, and new added layers will be placed in the end of the configuration, breaking the order. So, to be sure that atoms are well ordered, after each plasma specie impact the atoms can be reordered, (the time spent on this operation is negligible compared to the time spent on the simulation of the impact). This simple ordering can speed up the computing up to 20%.

Besides the mentioned optimizations, other small ones were applied as well, and their integrity allowed to boost the performance by 2-4 times as a sequential code. On the other side, MD being a highly parallelizable problem, it was decided to use the OpenMP method to parallelize the new code, to boost more these heavy calculations.

#### 7.3.3. Principles of the OpenMP parallelization in MD

Nowadays, almost all computers (even smartphones) are equipped with processors having multiple cores, which can work separately, moreover, recent processors are hyper-threaded, i.e. each physical core is considered as two logical ones, which roughly means that each core can perform two actions in parallel. Alongside this tendency, the tools for parallel computing were developed in multiple languages. In C++, there are different methods of parallelization, however maybe the easiest and the most intuitive one, is the OpenMP, which allows to parallelize the code simply by using some preprocessors; an easy example is given below.

#pragma omp parallel for num\_threads(n)
for(int i=0; i<N; i++) sendmail(recipient[i], "Hello");</pre>

In this example, the mail *"Hello"* should be sent to *N* recipients, and OpenMP allows to do it using *n* threads, using one simple line. An excellent tutorial of OpenMP is available on the following reference [OpenMP]. There is no need to repeat all possible properties of the OpenMP, so only those which are unavoidable are emphasized below.

The main advantage of the OpenMP is the simple parallelization of the loops, which divides the loop to n parts, where the n is the number of threads requested by the user (which is surely limited by the number of threads available on your machine), and each part is executed by a single thread. The main rule that has always to be preserved, is the following.

All threads can read the same memory (shared memory) simultaneously, but they can't write at the same place at a time.

If two or more threads are trying to operate with the same memory at a time, for example

int a = 0; #pragma omp parallel num\_threads(4) a += omp\_get\_thread\_num();

then, sometimes it can work as expected and sometimes not. A simple analogy to understand this rule is the human conversation: 10 people can listen one person (read from the shared memory) and acquire the information, meanwhile if 10 people speak to one person (write to the same memory) simultaneously, it is not sure that the last one will get any information from that conversation.

Now, when we know this rule, we can understand the problem of the parallelization of the force computing. One more time consider Figure 7.12(b), and imagine that the atomic motion is described using a two-body potential, for example by Lennard Jones [Verlet 67]. In this case one should compute all derivatives of  $V_{ii}(r_{ii})$ , for all pairs i < j, which can readily be done in parallel, but afterwards the computed forces should be added to corresponding atoms. Now assume that the atom pair (2,5) is treated by the thread #0, and the atom pair (5,8) by the thread #1 respectively. If they try to write the force on the atom 5 simultaneously, it might run into an error. Thus, some additional tricks are needed to avoid such problems. Firstly, a geometry dependent solution was used to prevent this problem. Since in present simulations the simulation cells were very deep, it was possible to stratify it, in such a way that no atom of the layer interacts with an atom of a layer which is two layers above, and perform the parallel computing in two steps, as presented on Figure 7.13. In the first step the thread #0 will treat all atoms in layer 1, that are not interacting with atoms in layer 3 treated by the thread #1 at the same time. Once this step is done, the threads are synchronized, and the next layers are treated. This stratification is a bit complex for the three-body potentials, but it remains very feasible. This method being easy and efficient, remain geometry dependent, and if one will use another sized structure, the parallelization will be highly affected.

Step 2 Thread 1 Layer 4	
Step 1 Thread 1 Layer 3	
Step 2 Thread 0 Layer 2	
Step 1 Thread 0 Layer 1	

Figure 7.13. Geometry dependent stratified parallelization.

To overcome this problem, and have a generic parallelization, a simple solution was given. If the simulation should be carried using for example 4 threads, then instead of having a single value for the atom force, now each atom will have a vector of forces having 4 components *F[4]*, and each thread *i* will write only in the *F[i]*, and once all forces are computed, they are summed in *F[0]*. Certainly, this method is more time and memory consuming, and is not highly interesting if one wants to use 100 threads, but for small number of threads (<12) it remains very efficient, and the thread-safety will be easily assured for each type of interatomic potential and each type of geometry.

All these optimizations, the OpenMP parallelization and the discussed method of force field debugging, were indispensable for accomplishment of the results presented in this PhD work.

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