Synthesis and characterization of refractory oxides doped with transition metal ions
Suyeon Cho

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Université Paris XI – Faculté des Sciences d'Orsay

THÈSE

présentée par

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pour l’obtention du grade de

Docteur en Sciences de l’Université Paris Sud XI
Spécialité : Chimie des Matériaux

Synthesis and Characterization of Refractory Oxides Doped with Transition Metal Ions

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Soutenue le 1er septembre 2011 devant le jury composé de :

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Abstract

In this study, the oxygen-deficient TiO$_2$, SrTiO$_3$ systems and transition metal ion (Cr or V) doped TiO$_2$, SrTiO$_3$ and SrZrO$_3$ systems have been investigated. We prepare samples as polycrystals, single crystals and thin films for various desires. Their structural, physical and electronic properties are measured by bulk-sensitive techniques (X-Ray Diffraction, SQUID and Electro Paramagnetic Resonance) or surface-sensitive techniques (Photoemission spectroscopy and X-ray absorption spectroscopy). The measurement of SQUID and EPR shows not only their magnetic properties but also the valence state of Cr dopant. We verify the valence state of Cr ions in Cr:TiO$_2$, Cr: SrTiO$_3$ and Cr: SrZrO$_3$ with three forms of samples, polycrystals, single crystals or films. We try to find the key parameters of sample synthesis which control the valence state of Cr ions. The cluster containing various valence state of Cr or the segregated phases such as CrO$_3$ or SrCrO$_4$ can be formed when the sample was synthesized under O$_2$ rich environment. Cr ions in those systems tend to be oxidized easily under O$_2$ rich environment. The surface properties of Cr doped SrZrO$_3$ films are also discussed. We find the synthesis conditions which influence on not only the behavior of Cr ions but also the resistive-switching behaviors. Various resistive-switching behaviors seem to depend on the surface chemistry of films. We found that the accumulation of Cr $^{3+}$ on film surface provides a clean interface without any non-stoichiometric oxides and this sharp interface termination resulted in a good performance of resistive-switching.

**Key words:** refractory oxide, Cr doping system, TiO$_2$, SrTiO$_3$, SrZrO$_3$, SQUID, electron paramagnetic resonance, photoemission, X-ray absorption spectroscopy, Diluted magnetic semiconductor, resistive-switching random access memory
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Refractory oxide: Synthesis, Characterization and their Applications

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1. Introduction

The American Society for Testing and Materials (ASTM) defines refractories as "non-metallic materials having those chemical and physical properties that make them applicable for structures, or as components of systems, that are exposed to environments above 1,000 °F (811 K; 538 °C)". They must be chemically and physically stable at high temperatures. Among them, TiO_2, SrTiO_3 and SrZrO_3 are refractory materials with high melting points and they are important materials that have found many applications.

TiO_2 and SrTiO_3 have been known to possess photocatalytic activity. Since photo-assisted water splitting into hydrogen and oxygen on TiO_2 was discovered [1], photocatalytic reaction has attracted extensive interests as a potential way to solve the energy and environmental issues. Moreover, room temperature ferromagnetism of the so-called ‘diluted magnetic semiconductors (DMS)’ has been reported in TiO_2 and SrTiO_3 with transition metal dopants [2-4]. Defective refractory oxides have many advantages for industrial application from the easy control of charge carrier concentrations The oxygen-deficient TiO_2, SrTiO_3 and SrZrO_3 have been known as Resistive-switching Random Access Memory (RRAM) materials [5-7]. Transition metal doped SrTiO_3 and SrZrO_3 also exhibit resistive-switching phenomena [8-10].

In our study, transition metal doped refractory oxides (Cr doped TiO_2, V doped TiO_2, Cr doped SrTiO_3 and Cr doped SrZrO_3) and oxygen-deficient TiO_2 were investigated. We focused on how we utilize refractory oxides in the field of photocatalyst, DMS and RRAM in application point of view.
2. Applications

2.1. Photocatalyst

After first discovery of the photocatalytic splitting of water on TiO$_2$ [1], much efforts have been focused on understanding the fundamental photocatalyst processes. Figure 1 shows the excitation of an electron from the valence band to the conduction band by light absorption. This photo-induced electron transfers to the adsorbate A (the acceptor species) on the surface (pathway C) while the hole migrates to the surface region to obtain an electron from D (the donor species) (pathway D). The electron/hole recombination also happens on the surface (pathway A) and the bulk region (pathway B).

Among various materials, TiO$_2$ and SrTiO$_3$ are known to be a good photocatalyst. They possess high driving force for the reduction and oxidation processes. For the decomposition of H$_2$O into H$_2$ and O$_2$, the potential level of A is required to be below the conduction band and the potential level of D needs to be above the valence band (see figure 2). However, there are many obstacles to overcome. First, the electrons in the conduction band combine the holes in the valence band very quickly. Second, decomposition of water into hydrogen and oxygen is an energy increasing process, thus the recombination of hydrogen and oxygen into water easily proceeds. Third, only ultraviolet light can be utilized for hydrogen production because of the large band gap.
To enhance the photocatalytic efficiency and overcome the fast recombination of electron/hole pairs, many researchers have suggested alternatives. Anatase TiO₂ generally exhibits superior photocatalytic activity because of higher surface area. The mixed-phase (anatase TiO₂ – rutile TiO₂) exhibits enhanced photocatalytic activity. The electrons can be trapped in conduction band of rutile TiO₂ after electron/hole creation [13].

It has been reported that noble metals such as Pt, Au and Ag, are very effective for enhancement of TiO₂ photocatalysis. For example, if the metal has a higher work function(\(\phi_m\)) than the semiconductor(\(\phi_s\)), a potential energy diagram such as figure 3 is obtained when the two materials are connected. The electron will migrate from the semiconductor to the metal.
until the two Fermi levels are aligned. Therefore, the surface of the metal has negative charges while the semiconductor has positive charges as a result of electron migration. This can inhibit the recombination of electron-hole.

TiO$_2$ doped with transition metal ions has the benefit to inhibit the recombination of electron/hole pair by trapping of electrons at the site of transition metal ions. Moreover, TiO$_2$ and SrTiO$_3$ doped with transition metal ions show visible light responses. UV-Vis absorption spectra of V-, Cr-, Fe- and N-doped TiO$_2$ are shown in figure 4. In comparison to TiO$_2$, the absorption edge of V-, Cr-, Fe- and N-doped TiO$_2$ appeared in the visible light region at about 500–600 nm. Figure 4 shows the yield conversion of p-xylene over 0.7 wt % V-, Cr- and Fe-doped TiO$_2$ catalysts using UV light (λ of 365 nm) and visible light (λ of 470 nm). The yield conversion under visible light is more enhanced than that under UV light.

FIGURE 4. UV-Vis absorption spectra of samples V-, Cr-, Fe- and N-doped TiO$_2$ and yield conversion of p-xylene over different catalysts [14]
2.2. Diluted Magnetic semiconductors

The development of ferromagnetic semiconductors is a key to the development of spintronics because the charge carrier with spin information can be obtained. Recently many researchers have reported the possibility of room temperature ferromagnetism in many oxides including TiO$_2$ with transition metal dopant. After the first discovery of room temperature ferromagnetism in Co doped TiO$_2$ [15], many TiO$_2$ films doped with transition metal ions have been reported about their unusual enhanced effective magnetic moment and high Curie temperatures above room temperature.[16-19] They are called ‘Diluted Magnetic Semiconductors (DMS)’. They combine these two interesting properties, semiconducting and ferromagnetic. Substitution of transition metal ions in semiconductor shows room temperature ferromagnetic. Interestingly large doping concentration is not required to possess the ferromagnetism. If so, the distance between magnetic ions is not small enough to induce conventional ferromagnetic ordering.

Several models have been proposed to explain ferromagnetic ordering in DMS materials. Toyosaki et al reported that the ferromagnetism can be caused by spin-polarized charge carriers that mediate ferromagnetic exchange interaction between distant localized spins of magnetic impurities [20]. The exchange through bound magnetic polarons has also

FIGURE 5. Schematics for extrinsic and intrinsic ferromagnetic sources in semiconductors doped with magnetic impurities. [20]
been proposed to explain the ferromagnetic ordering [21].

A number of experimental works have been reported. Zhang et al reported that the ferromagnetism of 5.0 % Cr doped TiO₂ film can be enhanced when they are deposited at lower oxygen pressures as seen in figure 6 [22]. It means that the oxygen vacancies play an important role in the ferromagnetic origin of Cr doped TiO₂. On the other hand, Kim et al reported that Co cluster in Co doped TiO₂ film can induce the ferromagnetic behavior by X-ray magnetic circular dichroism measurement [23]. Some of reports says that the dopant is not important to show the ferromagnetism [24].
3.3. Resistive-Random Acess Memory

In recent year the resistive-switching mechanism has been concerned in the field of non-volatile memory. The resistive-switching phenomena have been observed in many transition metal oxides since 1960’s. But the resistive-switching mechanism is still not understood clearly. Lots of models for the resistance switching were proposed and various research groups have tried to prove them experimentally.

One of the explanations for the resistive-switching is formation/rupture of conducting filamentary path [25-27]. Figure 7 shows the AFM image of ON and OFF state in NiO thin film after removing the top electrode [28]. They observed that the density of the conducting filaments changes drastically between the ON and OFF state. The filaments in the OFF state are mainly located at the grain boundaries of the NiO film.

FIGURE 7. (a) The Contact AFM image of the NiO thin film for the $R_{\text{off}}$ state (b) The Contact AFM image of the NiO thin film for the $R_{\text{on}}$ state [28]

FIGURE 8. The filament model as a resistive switching mechanism. (a) Filaments are disconnected ($R_{\text{off}}$ state). (b) Filaments are formed ($R_{\text{on}}$ state) [28]
If there are numerous defects, the voltage may gather them to form conducting filaments. It can result in a sudden increase of the current. These conducting filaments may be disconnected because of some reasons, Mott transition [29], Joule heating [30], or some interfacial effects [31-32]. Then, it can result in a sudden decrease of the current. Inoue et al proposed that the resistive-switching may take place at the interface of conducting filaments [33]. Chae et al introduced the percolation behavior of resistive-switching process [34]. Then, this percolation model has been developed and modified. Lee et al subsequently suggested an interface-modified percolation behavior which is called ‘interface-modified random circuit breaker network model’ [35]. However, the microscopic origin of the formation and the rupture of filaments have not been well understood.

Other explanation of resistive-switching is trapped charges at interface states between the electrode and the oxide. In metal/oxide junctions, we can see a Schottky-like barrier at the interface. As seen in figure 9, the Ti/PCMO junction has a Schottky-like barrier [36]. The electrochemical migration of oxygen vacancies can influence on the Schottky-like barrier. The density of the charges at the interface may modify the barrier width and height [37-38].

FIGURE 9. Capacitance–Voltage curves under reverse bias for a Ti/PCMO/SRO cell show hysteric behavior [36]
FIGURE 14. (left) The image of spatially resolved X-ray fluorescence microscopy after voltage has been applied but without current flowing and (right) The image of spatially resolved X-ray fluorescence microscopy on the fully formed sample. In these maps the darker regions represent Cr\(^{4+}\) and the brighter regions correspond to Cr\(^{3+}\). [39]

X-ray absorption spectroscopy has been used to study the resistive-switching in Cr:SrTiO\(_3\) single crystals. Andreasson et al shows that the Cr\(^{3+}\) ions change to Cr\(^{4+}\) in the anode region during electro-forming process [39]. However, the valence of Cr changes back to Cr\(^{3+}\) when a small current is flowing. They concluded that the switching state is not due to a valence change of Cr but caused by changes of oxygen vacancies at the interface. On the other hands, Alvarado et al shows that the resistive-switching process involves trapping/detrapping of electrons at the Cr site [40]. The role of Cr dopant is still under debate.
2. Thesis Outline

In this study, transition metal doped refractory oxides (Cr doped TiO$_2$, V doped TiO$_2$, Cr doped SrTiO$_3$ and Cr doped SrZrO$_3$) and oxygen-deficient TiO$_2$ were investigated. The bulk properties of Cr and V doped TiO$_2$, Cr doped SrTiO$_3$ are discussed in Chapter 3, Chapter 4 and Chapter 5, respectively. We made samples as precursors (or powder) and sometimes as single crystals. Their structural, physical and electronic properties are mainly measured by bulk-sensitive techniques: X-Ray Diffraction, SQUID and Electro Paramagnetic Resonance (EPR). The measurements of SQUID and EPR show not only their magnetic properties but also the valence state of Cr dopant. We verify the valence state of Cr ions in oxides and find the key parameters of sample synthesis which control the valence state of Cr ions (Chapter 4 and Chapter 5).

After the bulk study, the surface properties modified by Cr dopant are discussed in chapter 6. Among Cr doped refractory oxides, we select Cr doped SrZrO$_3$ films for this study because the surface state of 0.2mol% Cr doped SrZrO$_3$ film have been intensively studied in the field of RRAM. The film properties were measured by X-ray diffraction, Photoemission spectroscopy and X-ray absorption spectroscopy. Photoemission spectroscopy is very sensitive to the surface chemistry. Therefore, we made thin films in vacuum and measured photoemission spectroscopy without breaking the vacuum to prevent the presence of charged adsorbed species. We try to find the synthesis conditions which control the behavior of Cr ions. Then, the RRAM properties of Cr doped SrZrO$_3$ films are discussed in chapter 7. Various resistive-switching behaviors on 0.2mol% Cr doped SrZrO$_3$ films will be shown depending on the surface chemistry of films. We find the synthesis conditions to show an appreciable resistive-switching. In the last chapter, we study the surface chemistry of 0.2mol% Cr doped SrZrO$_3$ films modified by an electric-field. We find that there is a certain correlation between I-V characteristics and the surface chemistry, which means the interface properties play a crucial role on resistive-switching mechanism.
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CHAPTER 2

Experimental Techniques and Methods

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Bibliography
1. Sample Synthesis Methods

Refractory oxides are well-crystallized at high temperature being chemically and physically stable. They can be prepared in the form of single crystals, polycrystalline or thin films. Polycrystalline samples are prepared because we can easily fabricate the sample in large scale. However, the physical properties of polycrystalline samples may vary because the morphology, the composition, and the structure of the surface region vary depending on the preparation procedure. Therefore, for studies where the surface properties are important, single crystals or thin films are prepared. For various purposes of the experiment, we prepared three forms of refractory oxides with methods described below.

1.1. Solid State Reaction for ceramics

Solid state reaction method is a well-known way to synthesize ceramics. Many transition oxide materials such as SrTiO$_3$ and SrZrO$_3$, were synthesized by solid state reaction. Figure 1 shows the procedure to synthesize Cr doped SrTiO$_3$ as ceramics. Polycrystalline x mol\% Cr doped SrTiO$_3$ samples were synthesized from the stoichiometric mixtures of 99.9 \% pure SrCO$_3$, TiO$_2$ and Cr$_2$O$_3$ (process 1). They were ground in an agate mortar and molded into pellets (diameter is 12 mm, thickness is 5 mm). They were calcined at 950 °C for 8-12 hours (process 2). They were again ground for long time and molded into pellets (process 3). They are sintered at 1350-1450 °C for 24 to 36 hours (process 4). Then, we check their crystallographic property with x-ray diffraction (process 5). To get a single phase, more than three additional sintering processes were required with a long-time intermediate grinding (process 6). After the sintering processes, we get a single phase of Cr doped SrTiO$_3$ ceramics using solid state reaction method.
1.2. Floating Zone Method to grow single-crystals

The most common method for the single crystal growth is slow solidification from the melt. The heat source to make the melt is required. We used an image furnace equipped with high power halogen lamps. Figure 2 shows the picture of the image furnace. For the single crystal growth, we first prepare long-bar shaped feedrods with the composition which we desire to grow. The stoichiometric mixture of powders was well-ground and shaped into long-bar with a rubber tube. Subsequently sintering was accomplished. With the long-bar shaped feedrods, single crystals have been prepared using floating zone methods. An image furnace with two mirrors was used to elevate the temperature for melting the feedrods (see figure 2). The thermal energy can be focused at one point where the end of the feedrod is located. Then, the end of feedrod starts melting when the lamp power is sufficient to reach the melting temperatures. When its size is sufficient, we attach the melted zone onto the seed. The newly crystallized material can be obtained as the solidified part moves down slowly.
1.3. Pulsed Laser Deposition for Thin Film

Pulsed Laser Deposition (PLD) is probably the simplest technique among all thin film growth techniques. Figure 3 shows a schematic diagram of an experimental setup. It consists of a target holder and a substrate holder in the vacuum chamber. A pulsed laser is used as an external energy source to vaporize the target such as bulk SrTiO$_3$. When the laser radiation is absorbed by a target surface, the energy is converted first into electronic excitation and then into thermal, chemical and even mechanical energy to cause evaporation, ablation, excitation, plasma formation [2]. Vaporized materials form a plume consisting of a mixture of atoms, molecules, electron, ions, clusters and micron-sized solid particulates. After the laser irradiation the plume rapidly expands into the vacuum from the target surface to the substrate.
2. Experimental Techniques

2.1. Refinement of crystallographic structure

The structures of samples were verified by X-ray diffraction (XRD). The phase analysis has been done by the Rietveld method [3]. In the Rietveld method, the least-squares refinements are carried out until the best fit is obtained between the entire observed diffraction pattern and the entire calculated pattern based on the models for the crystal structure, diffraction optics effects and instrumental factors. The refinement was carried out in the sequence: background, scale factor, lattice parameters, profile parameters, site occupancies and thermal parameters. The Rietveld refinement has been carried out using GSAS-EXPGUI software [4]. The often-used numerical criteria of fit are $R_p$, $R_{wp}$, $\chi^2$ and DW. $R_{wp}$ is the most meaningful because the values are the residual being minimized. Another useful numerical criterion is the ‘goodness of fit’ $\chi$. A $\chi$ value of 1.3 or less is usually considered to be quite satisfactory. A statistic strongly recommended by Hill and Flack [5] is the Durbin-Watson statistics, DW. It is intended to reveal serial correlation between the successive observed intensity. The ideal value for it is 2.00.
2.2. Photoemission spectroscopy (PES) : XPS and UPS

The analysis of surfaces and interfaces mainly consists of composition, crystallographic structure and electronic structure. Among these analyses, the composition of samples can be solved most easily using techniques such as photoemission spectroscopy, especially x-ray photoelectron spectroscopy (XPS). For many systems photoemission spectra, angle-resolved ultra-violet photoelectron spectroscopy (ARPES), have provided detailed information on electronic structure.

The measurement of photoemission spectroscopy base on the photoelectric effect which was first discovered by Heinrich Hertz in 1887. The photoelectric effect happens when electrons are emitted from the solid surface by light irradiation. The photoelectric effect is often decomposed into three steps. First, the electrons can be excited from an initial state to a final state. Second, the electrons travel to the surface. Third, they escape from the surface (see figure 4).

The outgoing electrons excited by incident photons are analyzed to probe the electronic structure of the sample in consideration. Chemical analysis such as element identification, chemical environment change and relative ratio of compositions has been a
popular usage of photoemission spectroscopy. In general XPS is used for species identification, and core level shifts can give chemical state identification. UPS uses ultraviolet radiation as the probe, and collects electrons directly from the valence band, whereas XPS excites a core hole with X-rays. Especially ARPES is the main technique for determining band structure and can also identify surface states.

2.3. X-ray Absorption Spectroscopy (XAS)

The electronic structure of samples can be obtained from the analysis of the absorption spectra around the absorption edge of a given element. X-ray absorption spectra are obtained by measuring the attenuation versus wavelength (or energy) of electromagnetic radiation as it passes through a sample. The absorption spectra represent transitions between energy levels of an element of the samples. Therefore with the obtained spectra and some guidance from theory, we may construct an energy diagram.

![FIGURE 5. The schematics of x-ray absorption spectroscopy][7]

X-ray absorption spectroscopy (XAS) with soft x-ray regime focuses on the surface properties. This measurement requires an ultrahigh-vacuum environment. The photon induces excitations of an electron from a core state to an empty state above the Fermi energy (see figure 5). Therefore XAS measurement can probe the unoccupied states. The dipole transition between 1s to 2p will be allowed in XAS measurement because of the selection rule. Therefore the O 1s XAS will reflect the oxygen p-projected density of states. The core hole effects can usually be neglected in O 1s XAS because the O 2p orbital are quite extended. Therefore, O 1s XAS can be directly compared with the unoccupied O 2p density of states.
from the band structure calculations. Moreover, there is the hybridization between O 2p and transition metal 3d state. Therefore, we can obtain the information of transition metal 3d states from O 1s XAS spectra. In the case of the dipole transition between 2p to 3d of transition metal ions, the charge transfer and multiplet effect are important. In general 2p XAS spectra is not simple because the transition between 2p to 3d states cause the Coulomb interaction between electrons in d orbital ($U_{dd}$) or between the hole in p orbital and the electron in d orbital ($U_{cd}$: core hole effects).

Figure 6. (a) Photoabsorption and electron production in a sample consisting of substrate atoms B and an adsorbate layer A. (b) Electron mean free path in solids as a function of the electron kinetic energy above the Fermi level. The shaded area represents the distribution typically found for different materials. [8]

Figure 6 shows that photons penetrate into the sample by 500Å. Photoelectrons excited by x-ray can contribute to the XAS measurement. When the electron energy above Fermi level is 1000 eV, the electron mean free path is of the order of 10Å as seen in figure 6 (b). Absorption of X-ray creates photoelectrons and Auger electrons. In particular, absorption of x-ray in the range $250 \text{ eV} \leq h\nu \leq 600 \text{ eV}$ (for example, O 1s XAS) creates photoelectrons and Auger electrons within the electron mean free paths less than 10 Å. However, on their way to the surface, these electrons are scattered inelastically by electron-electron and electron-plasmon interactions. Therefore, these electrons results in an electron cascade as shown in figure 6 (a). When the cascade reaches the surface, those electrons will escape into
vacuum which have sufficient energy to overcome the surface potential barrier. This is the origin of the total electron yield (TEY) signal with the electron escape depth L (~50 Å).

2.4. Electron Paramagnetic Resonance (EPR)

Electron Paramagnetic Resonance (EPR) is an outstanding technique for studying chemical species possessing transition metal ions. EPR spectroscopy usually deals with the interaction of electromagnetic radiation with electron magnetic dipole which arises from spin angular momentum. EPR spectroscopy also takes account of the contribution of orbital as well as spin angular momentum. EPR spectroscopy is a technique applicable to systems in a paramagnetic state. Systems with various point defects or localized imperfections have been widely studied by EPR techniques. Deficiency of an electron (a positive hole) may also give rise to a paramagnetic entity.

![Energy-level splitting by applied magnetic field B₀ (Zeeman effect)](image)

EPR spectroscopy is based on ‘Zeeman effect’ (see figure 7). Every electron has a magnetic moment and spin quantum number \( s = 1/2 \), with magnetic components \( m_s = +1/2 \) and \( m_s = -1/2 \). In the presence of an external magnetic field, \( B_0 \), the magnetic moment of electron aligns itself either parallel (\( m_s = -1/2 \)) or antiparallel (\( m_s = +1/2 \)) to the field. The parallel alignment corresponds to the lower energy state, and the separation between it and the upper state is \( \Delta E = g_e \mu_B B_0 \), where \( g_e \) is the \( g \) factor of electron and \( \mu_B \) is the Bohr magneton. The splitting of the energy level is directly proportional to the strength of
magnetic field. An unpaired electron can move between the two energy levels by either absorbing or emitting electromagnetic radiation of energy \( E = h \nu = g_e \mu_B B_0 \).

Table 2 shows the various EPR wave bands. EPR measurements are often made with microwaves of 9.5 GHz (X-band) because electromagnets can generate fields up to about 1 T (10^4 G). Usually the frequency is kept fixed and the magnetic field varies. By increasing an external magnetic field, the energy difference between the \( m_s = +1/2 \) and \( m_s = -1/2 \) is widened. When the energy difference matches the energy of the microwaves, the unpaired electrons can move between their two spin states. For a simple system with one unpaired electron, the resonance occurs at a field of about 0.34 T with microwaves of 9.5 GHz.

<table>
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<th>L</th>
<th>S</th>
<th>C</th>
<th>X</th>
<th>K</th>
<th>Q</th>
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<td>36</td>
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<td>0.34</td>
<td>0.82</td>
<td>1.3</td>
<td>1.8</td>
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</tr>
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</table>

**TABLE 2.** Traditional microwave frequency bands and magnetic fields for the cases, \( g_e=2 \) [9]

Electron paramagnetic resonance of TiO\(_2\) is not simple. TiO\(_2\) is a crystal with tetragonal symmetry. There are two lattice sites at which the Ti\(^{4+}\) ions are located. These sites are identical except for a 90° rotation around the tetragonal axis (see figure 8). Many di-, tri- and tetravalent ions have been observed to occupy the substitutional sites, S1 and S2 in figure 8. The interstitial sites in TiO\(_2\), I1, I2, I3 and I4, are occupied by only several ions such as Ti\(^{3+}\), Ni\(^{3+}\) and Ni\(^{2+}\) [10]. Ti\(^{3+}\) was the first ion in rutile known to be in the interstitial position with somewhat distortion in reduced TiO\(_2\). The spectrum of interstitial Ti\(^{3+}\) has been simultaneously observed with the spectrum of substitutional Ti\(^{3+}\) with comparable strength. V\(^{4+}\) occupies the substitutional site. At 77K the spin-lattice relaxations [11] starts visibly broaden the paramagnetic resonance lines. Cr\(^{3+}\) also occupies the substitutional site. The spin-lattice relaxations occur at higher temperature than the case of V\(^{4+}\). Therefore the spectra are quite sharp up to 350K.
FIGURE 8. Substitutional and interstitial lattice position in TiO$_2$ [12]
Bibliography


[11] Spin-lattice relaxation: The spin system is irradiated by a photon source, usually a microwave oscillator, at the frequency $\nu$. The absorbed radiation is lost by energy diffusion to the lattice at an exponential rate, which allows continuing absorption of photons to occur. Energy ultimately passes from the sample to the surroundings which are commonly referred to the lattice.

CHAPTER 3

Synthesis and Characterization of Polycrystalline Cr and V doped rutile TiO₂

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1. Introduction
2. Results
   2.1. Crystallographic properties
   2.2. Paramagnetic behavior of Cr and V doped TiO₂
   2.3. Mixed valence state of Cr ions in TiO₂
3. Summary
Bibliography
1. Introduction

As presented in chapter 1, several authors [1-10] have reported that transition metal (TM) doped TiO\(_2\) exhibits some unexpected ferromagnetism and, therefore, appears as diluted magnetic semiconductors (DMS). However, some reported results are contradictory. In particular, Cr and V doped TiO\(_2\) films do not exhibit ferromagnetism according to Matsumoto et al [4] whereas Hong et al [6] report that V doped TiO\(_2\) films have a stronger ferromagnetism than Co-doped ones. This V doped TiO\(_2\) film has a large magnetic moment per V ion (4.2 \(\mu_B/V\)). It is worth noting that the structure of thin films depends on their preparation conditions. They can exhibit both the rutile and anatase structures [11, 12] with different solubility limits of the dopants (fig.1).

![FIGURE 1. The solubility limits of TM ions when they are substituted into anatase or rutile TiO\(_2\) films](image)

In this context, we choose to investigate the properties of bulk polycrystalline Cr doped TiO\(_2\) (Cr:TiO\(_2\)) and V doped TiO\(_2\) (V:TiO\(_2\)) materials with doping concentration reaching 10%. In the doped materials Cr, V and even Ti are expected to be found under various valencies. Therefore, we summarized some of their properties in table 1. Crystalline TiO\(_2\) is found under several modifications such as rutile, anatase, and brookite which differ mainly by the kind of linking of the TiO\(_6\) octahedra. In usual conditions, anatase and brookite are metastable phases which are converted to the rutile form when heated above 820°C.
Therefore it is expected that the preparation of doped TiO$_2$ by solid state reaction leads to rutile structure.

<table>
<thead>
<tr>
<th>ions</th>
<th>Ti$^{3+}$</th>
<th>Ti$^{4+}$</th>
<th>Cr$^{3+}$</th>
<th>Cr$^{4+}$</th>
<th>Cr$^{5+}$</th>
<th>Cr$^{6+}$</th>
<th>V$^{3+}$</th>
<th>V$^{4+}$</th>
<th>V$^{5+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_6$ / Å</td>
<td>0.67</td>
<td>0.605</td>
<td>0.615</td>
<td>0.55</td>
<td>0.49</td>
<td>0.44</td>
<td>0.64</td>
<td>0.58</td>
<td>0.54</td>
</tr>
<tr>
<td>$r_4$ / Å</td>
<td>-</td>
<td>0.42</td>
<td>-</td>
<td>0.41</td>
<td>0.345</td>
<td>0.26</td>
<td>-</td>
<td>-</td>
<td>0.355</td>
</tr>
<tr>
<td>$\mu_{\text{eff}}$ / $\mu_B$</td>
<td>1.73</td>
<td>0</td>
<td>3.87</td>
<td>2.83</td>
<td>1.73</td>
<td>0</td>
<td>2.83</td>
<td>1.73</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 1. Structural and magnetic characteristics of the main Ti, Cr and V ions. $r_6$ and $r_4$ are the ionic radius of the ions in coordination 6 and 4 respectively according to Shannon tables ($r_{O^{2-}} = 1.40$ Å, Acta Cryst.1976). The effective magnetic moments are those calculated for high spin states with quenched orbital momentum.

To synthesize TM doped rutile TiO$_2$, we mix and grind the anatase TiO$_2$ powder (99 %, anatase) with transition metal oxide, Cr$_2$O$_3$ powder (99 %) for Cr:TiO$_2$ and V$_2$O$_5$ (99.5 %) for V:TiO$_2$, quantitatively. Subsequently the sintering at high temperature should be required to remove other structures, anatase and brookite which are unstable above 820 °C and to substitute Ti ions by Cr or V ions. Samples were usually sintered at 1100 °C for 12 hours in air. The component V$_2$O$_5$ could be evaporated at high temperature. So prior to sintering at 1100 °C an intermediate thermal treatment at 900 °C for 12 hours is accomplished in the case of V doped TiO$_2$. The rate of elevating and decreasing the temperature is around 200 °C per 1 hour.

2. Results

2.1. Crystallographic properties

X-ray diffraction patterns indicate that Cr$_2$O$_3$ and V$_2$O$_5$ are no more detectable after solid state reaction and that, except for 5.0 % and 10.0 % Cr doping, only one phase is present. The Cr:TiO$_2$ and V:TiO$_2$ solid solutions have the rutile structure (P4$_2$/mm). The
lattice constants in doped TiO$_2$ show a certain tendency according to the doping concentration. If Ti$^{4+}$ ion is well replaced by a dopant ion which has a different ionic radius, the volume of unit cell could be modified. As seen in table 2, X-ray diffraction result shows somewhat increasing in lattice constant of Cr:TiO$_2$ and decreasing in that of V:TiO$_2$. Therefore we could guess that Cr ions are likely found as Cr$^{3+}$ ions which have a bigger radius than that of Ti$^{4+}$ (table 1). Both V$^{4+}$ and V$^{5+}$ ion could be possible in V doped TiO$_2$.

<table>
<thead>
<tr>
<th>samples</th>
<th>a</th>
<th>c</th>
<th>V</th>
<th>comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>4.5943</td>
<td>2.9594</td>
<td>62.466</td>
<td>DW=1.31 ; chi$^2$=1.89 ; Rwp=0.22 ; Rp=0.16</td>
</tr>
<tr>
<td>TiO$_2$-Cr1.0%</td>
<td>4.5942</td>
<td>2.9593</td>
<td>62.462</td>
<td>DW=1.70 ; chi$^2$=1.44 ; Rwp=0.20 ; Rp=0.13</td>
</tr>
<tr>
<td>TiO$_2$-Cr2.0%</td>
<td>4.5949</td>
<td>2.9591</td>
<td>62.478</td>
<td>DW=1.63 ; chi$^2$=1.44 ; Rwp=0.20 ; Rp=0.13</td>
</tr>
<tr>
<td>TiO$_2$-Cr5.0%</td>
<td>4.5959</td>
<td>2.9594</td>
<td>62.510</td>
<td>DW=0.74 ; chi$^2$=3.90 ; Rwp=0.32 ; Rp=0.22</td>
</tr>
<tr>
<td>TiO$_2$-Cr10.0%</td>
<td>4.5881</td>
<td>2.9589</td>
<td>62.287</td>
<td>DW=1.54 ; chi$^2$=1.59 ; Rwp=0.20 ; Rp=0.14</td>
</tr>
<tr>
<td>TiO$_2$-V0.5%</td>
<td>4.5945</td>
<td>2.9597</td>
<td>62.478</td>
<td>DW=1.20 ; chi$^2$=2.05 ; Rwp=0.23 ; Rp=0.17</td>
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<tr>
<td>TiO$_2$-V1.0%</td>
<td>4.5937</td>
<td>2.9593</td>
<td>62.447</td>
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<td>4.5915</td>
<td>2.9594</td>
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<tr>
<td>TiO$_2$-V10.0%</td>
<td>4.5881</td>
<td>2.9589</td>
<td>62.287</td>
<td>DW=1.54 ; chi$^2$=1.59 ; Rwp=0.20 ; Rp=0.14</td>
</tr>
</tbody>
</table>

**TABLE 2. X-ray diffraction of Cr and V doped TiO$_2$ polycrystalline samples**

The Cr:TiO$_2$ at 5.0 % and 10.0 % show another phase, identified as Ti$_{0.78}$Cr$_{0.12}$O$_{1.74}$ [13], it is interesting to notice that Cr ions are found as Cr$^{3+}$ in this compound. Peaks from TiO$_2$ modified by Cr substitution diminished and peaks from the other phase are growing as seen in figure 2. We tried to do additional heat treatments of 5.0 % and 10.0 % Cr:TiO$_2$ at 1100 °C in air. We found that peaks of another structure were growing after several heat treatments when peaks of Cr:TiO$_2$ are continuously decreasing (see figure 2). There would be a limitation of solvency lower than 5.0 mol% of chromium. The peak positions of 5.0 mol% Cr:TiO$_2$ were dramatically changed by thermal treatments as seen in table.3. But there was no tendency for the shift of peak positions. In the case of V:TiO$_2$, the samples don't show any other structures.
FIGURE 2. X-ray diffraction patterns of (a) x% Cr:TiO$_2$ ;(b) 5% and (c) 10% Cr:TiO$_2$ with several heat treatments at 1100 °C. Peaks labeled with a triangle are characteristics of the Ti$_{0.78}$Cr$_{0.12}$O$_{1.74}$ compound.

<table>
<thead>
<tr>
<th>Heat treatment</th>
<th>a</th>
<th>b</th>
<th>V</th>
<th>DW</th>
<th>chisq</th>
<th>Rwp</th>
<th>Rp</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st</td>
<td>4.5959</td>
<td>2.9594</td>
<td>62.510</td>
<td>0.74</td>
<td>3.90</td>
<td>0.32</td>
<td>0.22</td>
</tr>
<tr>
<td>2nd</td>
<td>4.5973</td>
<td>2.9599</td>
<td>62.556</td>
<td>0.57</td>
<td>4.32</td>
<td>0.32</td>
<td>0.21</td>
</tr>
<tr>
<td>3rd</td>
<td>4.5939</td>
<td>2.9576</td>
<td>62.418</td>
<td>0.61</td>
<td>4.05</td>
<td>0.30</td>
<td>0.20</td>
</tr>
</tbody>
</table>

TABLE 3. Cell parameters of 5% Cr:TiO$_2$ after thermal treatments at 1100 °C

2.2. Paramagnetic behavior of Cr and V doped TiO$_2$

The $\chi$ and $1/\chi$ vs T curves plotted in figure 3 for both Cr:TiO$_2$ and V:TiO$_2$ were calculated from the magnetic moment measurements recorded with a SQUID magnetometer between 5 and 300K. The non linear shape of the $1/\chi$ vs T suggests that they don’t follow simple Curie-Weiss paramagnetism and that a temperature independent contribution is present. As temperature independent paramagnetism is rarely found for Cr and V ions, this contribution may have its origin in some ferromagnetism.
To separate both contributions of ferro- and paramagnetism, we recorded magnetization (M) vs field (H) curves of Cr and V doped TiO\textsubscript{2}. They show almost linear curves as increasing magnetic field up to 40000 Oe. In the region of weak magnetic field, there was small contribution of ferromagnetism which saturated under 2000 Oe as a small value in both Cr:TiO\textsubscript{2} and V:TiO\textsubscript{2}. We couldn’t distinguish this small contribution of ferromagnetism with the naked eye. Therefore, we separated the ferromagnetic contribution from M vs H curves by extracting a linear part of M vs H curve which corresponds to the paramagnetic contribution (figure 4). The linear part of M vs H curve has been plotted in figure 4 (b). The saturated values under 2000 Oe in M vs H curves have been plotted in figure 4 (c).
Figure 4. (a) Raw data of SQUID measurements in 5.0% Cr:TiO$_2$ and 5.0% V:TiO$_2$, (b) The linear part of raw data, M vs H curve, which corresponds to the paramagnetic contribution, (c) The saturated values after extracting a linear part of M vs H curve, which corresponds to the ferromagnetic contribution.

FIGURE 5. $\chi$ vs T curves fitting with Curie-Weiss equation in Cr:TiO$_2$ and V:TiO$_2$; the values of $\chi$ are obtained from M vs H curve in various temperatures.

To elucidate the temperature dependency of paramagnetism, we made susceptibility (dividing the paramagnetic contribution by field, $\chi = M/H$) vs temperature curves (figure 5).
The Curie-Weiss equation is modified by adding a temperature-independent parameter to fit the complex behavior of magnetization. By fitting this curve with modified Curie-Weiss equation [15] we calculate the effective magnetic momentum from the Curie constant. The calculated values are shown in table 4. The effective magnetic moments are not well-matched with those of Cr\(^{3+}\) and V\(^{4+}\) ions. We have first to remind that the nominal doping concentrations have certain uncertainty because of measuring the small quantity of Cr\(_2\)O\(_3\) or V\(_2\)O\(_5\) powder when we synthesis the samples but this weight error remains small. We also consider the loss of Cr or V ions during the sample synthesis. Therefore, the effective magnetic moments can be underestimated than expected values. As the effective magnetic moments are smaller than that of Cr\(^{3+}\) or V\(^{4+}\) (except 5.0% Cr), Cr:TiO\(_2\) samples possibly have higher valence state of Cr ions (such as Cr\(^{4+}\), Cr\(^{5+}\) and Cr\(^{6+}\)). In the case of V:TiO\(_2\), the possible explanations for underestimated effective magnetic moments are that V ions are carried away during sample synthesis or remained as V\(^{5+}\) ions. The presence of V\(^{5+}\) ions requires cationic vacancies such as Ti vacancies for electroneutrality.

<table>
<thead>
<tr>
<th>C / (emu K/mol)</th>
<th>θ / K</th>
<th>(\chi_0) / (emu/mol)</th>
<th>(\mu_{\text{eff}}) ((\mu_B)/Cr or V)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cr : TiO(_2)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5% Cr</td>
<td>9.25×10^{-3}</td>
<td>-0.72</td>
<td>4.75×10^{-5}</td>
</tr>
<tr>
<td>1.0% Cr</td>
<td>1.63×10^{-2}</td>
<td>-0.45</td>
<td>2.62×10^{-5}</td>
</tr>
<tr>
<td>2.0% Cr</td>
<td>3.63×10^{-2}</td>
<td>-3.33</td>
<td>5.11×10^{-5}</td>
</tr>
<tr>
<td>5.0% Cr</td>
<td>9.68×10^{-2}</td>
<td>-7.39</td>
<td>1.66×10^{-5}</td>
</tr>
<tr>
<td><strong>V : TiO(_2)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5% V</td>
<td>1.16×10^{-3}</td>
<td>-0.85</td>
<td>3.27×10^{-5}</td>
</tr>
<tr>
<td>1.0% V</td>
<td>2.71×10^{-3}</td>
<td>-0.80</td>
<td>2.77×10^{-5}</td>
</tr>
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<td>2.54×10^{-5}</td>
</tr>
<tr>
<td>10.0% V</td>
<td>2.46×10^{-2}</td>
<td>-3.21</td>
<td>3.81×10^{-5}</td>
</tr>
</tbody>
</table>

**TABLE 4. Calculated parameters of the paramagnetic contributions of doped TiO\(_2\) polycrystals**

The origin of the temperature independent parameter, \(\chi_0\), is not clear. It could from some uncertainty in the removal of the ferromagnetic contribution or from a true paramagnetic contribution.
FIGURE 6. Ferromagnetic contribution of Cr:TiO$_2$ and V:TiO$_2$ at 100K

We get a small value of ferromagnetism (see figure 6) in both Cr:TiO$_2$ and V:TiO$_2$ from M vs H curves. As seen in table 5, there is a little increasing in saturated ferromagnetic contribution as doping concentration is increasing. The saturated value in Cr:TiO$_2$ is roughly 2 times bigger than that in V:TiO$_2$. To calculate the magnetic moment for each dopant, we used the equation below,

$$M_{s} = \frac{M_{s}}{N_{A} \times x \times 9.274 \times 10^{-21} \times \text{emu} / \mu_{B}}$$

where $M_{s}$ is saturated value in M(H), $N_{A}$ is Avogadro number ($6.023 \times 10^{23}$ mol$^{-1}$) and x is the doping concentration. The magnetic moments for each dopant were in table 5.

The magnetic moment per dopant in the ferromagnetic contribution are incredibly small and can only come from a small minority of doping ions. As suggested in the case of Co-doped SrTiO$_3$ ceramics [15], the ferromagnetic contribution may come from some defective regions in the grain boundary regions. However, the presence of a ferromagnetic impurity cannot be discarded.
Cr doped TiO₂

<table>
<thead>
<tr>
<th>(emu/mol)</th>
<th>15K</th>
<th>100K</th>
<th>200K</th>
</tr>
</thead>
<tbody>
<tr>
<td>(μB/1 dopant)</td>
<td>~0.040</td>
<td>~0.040</td>
<td>~0.020</td>
</tr>
<tr>
<td>0.5%</td>
<td>1.43 x 10⁻³</td>
<td>1.43 x 10⁻³</td>
<td>7.16 x 10⁻⁴</td>
</tr>
<tr>
<td>1.0%</td>
<td>0.050</td>
<td>0.040</td>
<td>0.035</td>
</tr>
<tr>
<td></td>
<td>8.95 x 10⁻⁴</td>
<td>7.16 x 10⁻⁴</td>
<td>6.27 x 10⁻⁴</td>
</tr>
<tr>
<td>2.0%</td>
<td>0.030</td>
<td>0.030</td>
<td>0.028</td>
</tr>
<tr>
<td></td>
<td>2.69 x 10⁻⁴</td>
<td>2.69 x 10⁻⁴</td>
<td>2.51 x 10⁻⁴</td>
</tr>
<tr>
<td>5.0%</td>
<td>0.100</td>
<td>0.040</td>
<td>0.040</td>
</tr>
<tr>
<td></td>
<td>3.58 x 10⁻⁴</td>
<td>1.43 x 10⁻⁴</td>
<td>1.43 x 10⁻⁴</td>
</tr>
</tbody>
</table>

V doped TiO₂

<table>
<thead>
<tr>
<th>(emu/mol)</th>
<th>15K</th>
<th>100K</th>
<th>200K</th>
</tr>
</thead>
<tbody>
<tr>
<td>(μB/dopant)</td>
<td>~0.008</td>
<td>0.011</td>
<td>0.012</td>
</tr>
<tr>
<td>0.5%</td>
<td>2.86 x 10⁻⁴</td>
<td>3.94 x 10⁻⁴</td>
<td>4.3 x 10⁻⁴</td>
</tr>
<tr>
<td>1.0%</td>
<td>0.020</td>
<td>0.017</td>
<td>0.016</td>
</tr>
<tr>
<td></td>
<td>3.58 x 10⁻⁴</td>
<td>3.04 x 10⁻⁴</td>
<td>2.86 x 10⁻⁴</td>
</tr>
<tr>
<td>5.0%</td>
<td>~0.014</td>
<td>0.015</td>
<td>0.014</td>
</tr>
<tr>
<td></td>
<td>5.01 x 10⁻⁵</td>
<td>5.37 x 10⁻⁵</td>
<td>5.01 x 10⁻⁵</td>
</tr>
<tr>
<td>10.0%</td>
<td>0.045</td>
<td>0.026</td>
<td>0.027</td>
</tr>
<tr>
<td></td>
<td>8.06 x 10⁻⁵</td>
<td>4.65 x 10⁻⁵</td>
<td>4.83 x 10⁻⁵</td>
</tr>
</tbody>
</table>

TABLE 5. Saturated ferromagnetic contribution as a function of doping concentrations and temperatures

2.3. Mixed valence state of Cr ions in TiO₂

In order to investigate with more accuracy the paramagnetic contribution we recorded electron paramagnetic resonance (EPR) spectra of Cr:TiO₂ samples. The EPR spectra of Cr:TiO₂ are presented in figure 7. They show 5 resonances, among them B, C, D, E and F which are in close agreement with Cr³⁺ occupying a substitutional site in TiO₂ [16]. Depending on the synthesis method, the presence of resonance A is reported by some authors [17]. It seems typical of more oxidized samples. This resonance is located at a position which is close to that typical of a free electron, therefore the presence of some Cr⁵⁺ ions in interstitial positions seems possible. This signal was also considered as a signature of some mixed valence trimers Cr⁶⁺-Cr³⁺-Cr⁶⁺ whose average valence is 5⁺ at the surface of doped TiO₂ films. In polycrystalline materials such trimers might be located in grain boundaries. Another
resonance typical of Cr$^{3+}$ aggregates has been observed by Kohler et al [18]. As it was not observed in our samples we can conclude that Cr ions are well distributed in them.

![FIGURE 7. EPR spectrum of Cr:TiO$_2$ at 100K](image)

3. Summary

We study polycrystalline Cr doped TiO$_2$ and V doped TiO$_2$ system. It seems that Cr$^{3+}$ ions substitute Ti$^{4+}$ ions in Cr:TiO$_2$ and V$^{4+}$ and some V$^{5+}$ substitute Ti$^{4+}$ ions in V:TiO$_2$. In both polycrystalline samples, Cr:TiO$_2$ and V:TiO$_2$, a weak ferromagnetic contribution is found even at room temperature with every small magnetic moment per doping ion. Its origin remains uncertain. These Cr:TiO$_2$ and V:TiO$_2$ systems show strong paramagnetic behaviors. In the case of Cr:TiO$_2$, EPR spectra suggest the presence of some ions with a higher valency than 3+.
Bibliography


CHAPTER 4

Synthesis and Characterization of TiO$_2$ and Cr doped TiO$_2$ Single Crystals

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1. Introduction
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   3.1 Crystallographic properties
   3.2 Optical properties
   3.3 Magnetic properties
   3.4 Valence states of Cr ions in doped TiO$_2$ single crystals
4. Discussion
5. Summary
Bibliography
1. Introduction

In the previous chapter, the synthesis and characterization of polycrystalline TiO$_2$ doped with Cr or V ions were presented. We have shown that, in both polycrystalline samples, Cr:TiO$_2$ and V:TiO$_2$, a weak ferromagnetic signal is detected with a very small magnetic moments per doping ions although large values of the magnetic moment were reported by other authors for Cr:TiO$_2$ and V:TiO$_2$ films. In the case of polycrystalline samples, we could not extract the effect of grain boundaries in which a lot of defects exist [1-2]. Therefore, we tried to grow single crystals of Cr doped TiO$_2$ by the floating zone method to determine their intrinsic magnetic properties.

2. Sample preparation

For the single crystal growth, long-bar shaped feedrods with 0.0 mol%, 0.3 mol%, 0.65 mol%, and 1.0 mol% Cr doping concentrations were prepared with TiO$_2$ (99.99 %, rutile, Alfa Aesar) and Cr$_2$O$_3$ (99.7 %, Alfa Aesar) powder. They were well-ground and shaped within a rubber tube (diameter=5 mm, length=100 mm) with pressure, 2500 bar. Subsequently sintering was accomplished at 1100 °C for 12 hours. The rate of elevating and decreasing the temperature was around 200 °C per hour. Then, the Cr:TiO$_2$ single crystals have been prepared using the floating zone method in an image furnace. The growth rate of single crystals was set to 5 mm/hr and two kinds of gas, oxygen and argon, were used to determine the influence of different oxygen partial pressures on the as-grown crystals.
3. Results

3.1. Crystallographic properties

X-ray diffraction carried out on powder obtained by grinding a small part of the Cr:TiO$_2$ single crystals shows that they have the rutile structure (P4$_2$/mm). Their lattice constants obtained by Rietveld analysis didn’t change too much overall this doping region. However we can notice that we did not observe an increase of the parameters similar to that presented by the polycrystalline samples (chapter 3, table 2). This is a first indication that the valence state of chromium is probably different. The LAUE X-ray diffraction patterns show that the growth axis of all Cr:TiO$_2$ single crystals grown under O$_2$ flow was the [001] direction. Only one domain perpendicular to the growth axis was shown under a polarized light microscope, which confirms that we got a single crystal of Cr:TiO$_2$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Air flow</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>V (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr0.00%</td>
<td>O$_2$</td>
<td>4.5937</td>
<td>2.9588</td>
<td>62.438</td>
</tr>
<tr>
<td>Cr0.30%</td>
<td>O$_2$</td>
<td>4.5933</td>
<td>2.9584</td>
<td>62.417</td>
</tr>
<tr>
<td>Cr0.65%</td>
<td>O$_2$</td>
<td>4.5919</td>
<td>2.9572</td>
<td>62.354</td>
</tr>
<tr>
<td>Cr1.00%</td>
<td>O$_2$</td>
<td>4.5941</td>
<td>2.9583</td>
<td>62.439</td>
</tr>
<tr>
<td>Cr0.30%</td>
<td>Ar</td>
<td>4.5925</td>
<td>2.9576</td>
<td>62.380</td>
</tr>
<tr>
<td>Cr0.65%</td>
<td>Ar</td>
<td>4.5929</td>
<td>2.9578</td>
<td>62.393</td>
</tr>
</tbody>
</table>

TABLE 1. X-ray diffraction result of Cr:TiO$_2$ single crystal

3.2. Optical properties

Pure TiO$_2$ single crystal grown under O$_2$ flow (Cr0.00%(O$_2$) from now) looks similar to a fully oxidized single crystal whose coloration is transparent yellow whereas TiO$_2$ single crystal grown under Ar flow (Cr0.00%(Ar) from now) has blue coloration in its body similar to the reduced TiO$_2$ in certain condition [3]. There is a certain tendency of coloration according to the kind of gas flow during crystal growth. Cr:TiO$_2$ single crystal grown under
O₂ flow (Cr:TiO₂(O₂) from now), are black in body and opaque. But those grown under Ar flow (Cr:TiO₂(Ar) from now) have transparent red coloration in their bodies (see Figure 1).

![Cr:TiO₂ single crystals](image1)

FIGURE 1. The appearance of Cr:TiO₂ single crystals;

The optical absorption spectra of transparent single crystals, Cr0.00%(O₂), Cr0.30%(Ar) and Cr0.65%(Ar) were taken in the visible region (400-800 nm) by transmittance mode. Both sides of single crystals were polished to reduce scattering by surface roughness. To calculate the absorption coefficient α, we use the equation,

\[ \alpha = \frac{1}{z} \ln \frac{I_0}{I} [cm^{-1}] \]

where z is the thickness of the sample, I₀ is the intensity of incident light which is measured without sample and I is the transmittance of light through a sample.
FIGURE 2. Absorption edge of transparent single crystals

In figure 2, the main absorption edge of Cr0.00% (O2) was estimated to be about 415 nm. Both Cr0.30% (Ar) and Cr0.65% (Ar) exhibit larger absorption in the wavelength range of 400-600 nm and 650-800 nm. Through optical absorption, we can estimate the band gap because low absorption for photons with energies smaller than the bandgap and high absorption for photons with energies greater than the bandgap were shown. Cr0.00% (O2) has a sharp absorption edge at 415 nm corresponding to the energy of 3.1 eV, which is close to the bandgap of TiO2. Therefore Cr0.00% (O2) appears as a fully oxidized TiO2 single crystal. Cr0.30% (Ar) and Cr0.65% (Ar) have an absorption edge at 530 nm which corresponds to the energy of 2.6 ~ 2.7 eV.

3.3. Magnetic properties

The magnetic moments of Cr:TiO2 single crystals were measured with a SQUID magnetometer from 10K to 300K with a 1000 Oe field. Their magnetic susceptibilities (χ) and their inverse (1/χ) were then calculated and are plotted in figure 3. Cr:TiO2 (Ar) have almost linear 1/χ curves which represent mainly a Curie’s paramagnetic behavior. But in the case of Cr:TiO2 (O2), only Cr1.00% (O2) shows an almost linear curve while others show non-linear curves which include a ferromagnetic component. However the ferromagnetic signals of Cr:TiO2 are much smaller than the paramagnetic signal at low temperature region.
FIGURE 3. $\chi$ and $1/\chi$ vs T at 1000Oe in (a) Cr:TiO$_2$ (O$_2$) and (b) Cr:TiO$_2$ (Ar)

Figure 4. (a) Raw data of M(H) curves of Cr0.65% (O$_2$) and Cr0.65% (Ar) at 300K.

To confirm the presence of a ferromagnetic contribution, we recorded M (Magnetization) vs H (magnetic field) at different temperatures. Both types of Cr doped TiO$_2$
crystal (grown under Ar and O₂ flow) show almost linear curves in M vs H which are dominated by paramagnetic ordering. But in the region of small field and high temperature, we can see non-linear curve which represents ferromagnetic contribution (figure 4). We separate the ferromagnetic contribution which has a non-linear shape from M vs H curves. The detailed methods to obtain the ferromagnetic contribution and paramagnetic contribution are described in chapter 3. Ferromagnetic ordering is saturated around 2000 Oe in both types of Cr doped TiO₂ single crystals as shown in figure 5. The saturated values of ferromagnetic contribution (Mₛ) are described in table 2. Both Cr0.65%(O₂) and Cr0.65%(Ar) have the biggest value and both Cr1.0%(O₂) and Cr1.0%(Ar) has the smallest value in their group. The intensity of Mₛ in Cr:TiO₂(O₂) is bigger than that in Cr:TiO₂(Ar).

The ferromagnetic signal is observed at all temperatures. It means that the Curie temperature can be higher than 300K as for the polycrystalline samples presented in chapter 3. We observe different behaviors of temperature-dependency of Mₛ in two types of single crystal. Table 2 shows the variation of Mₛ (saturated value in M(H)) between 15K and 300K (or 200K) in both types of single crystals. Mₛ in Cr:TiO₂(Ar) gradually decreases as the temperature increases (figure 5(a)). However, Mₛ of Cr:TiO₂(O₂) remains almost constant except at 15K where it takes a slightly higher value (figure 5(b)).
In Figure 6 (a) and (b), we can see only paramagnetic contribution which is proportional to H after removal of the ferromagnetic contribution from the raw data of M vs H curve. Their susceptibilities depend on the temperature as seen in figure 6 (c) and (d).

<table>
<thead>
<tr>
<th>Sample</th>
<th>C / (emu K/mol)</th>
<th>θ / K</th>
<th>χ₀ / (emu/mol)</th>
<th>μₐeff (µB/Cr)</th>
<th>Mₛ / (emu/mol)</th>
<th>Mₛ (µB/Cr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.30%Cr(Ar)</td>
<td>4.30 × 10⁻⁴</td>
<td>-1.02</td>
<td>1.02 × 10⁻⁵</td>
<td>3.377</td>
<td>0.012</td>
<td>0.009</td>
</tr>
<tr>
<td>0.65%Cr(Ar)</td>
<td>9.43 × 10⁻⁴</td>
<td>-1.27</td>
<td>3.35 × 10⁻⁵</td>
<td>3.397</td>
<td>0.038</td>
<td>0.030</td>
</tr>
<tr>
<td>1.00%Cr(Ar)</td>
<td>1.24 × 10⁻²</td>
<td>-0.80</td>
<td>2.95 × 10⁻⁵</td>
<td>3.141</td>
<td>0.020</td>
<td>0.010</td>
</tr>
<tr>
<td>0.30%Cr(O₂)</td>
<td>1.63 × 10⁻³</td>
<td>-1.53</td>
<td>4.72 × 10⁻⁵</td>
<td>2.076</td>
<td>0.080</td>
<td>0.070</td>
</tr>
<tr>
<td>0.65%Cr(O₂)</td>
<td>3.19 × 10⁻⁴</td>
<td>-1.20</td>
<td>6.49 × 10⁻⁵</td>
<td>1.976</td>
<td>0.100</td>
<td>0.090</td>
</tr>
<tr>
<td>1.00%Cr(O₂)</td>
<td>8.93 × 10⁻⁵</td>
<td>-1.22</td>
<td>1.32 × 10⁻⁵</td>
<td>2.665</td>
<td>0.009</td>
<td>0.008 (at 200K)</td>
</tr>
</tbody>
</table>

TABLE 2. Fitting results of SQUID measurement in Cr:TiO₂

With a modified Curie-Weiss law [4], we calculate θ, χ₀, and μₐeff from susceptibility vs temperature curves (figure 6 (c) and (d)). As shown in table 2, the values of the effective moment (μₐeff) of Cr:TiO₂(Ar) are between Cr³⁺ (3.87 µB) and Cr⁴⁺ (2.83 µB) while the values of μₐeff of Cr:TiO₂(O₂) are between Cr⁴⁺ (2.83 µB) and Cr⁵⁺ (1.73 µB). Despite the possible loss of Cr ions during the crystal synthesis, the obtained μₐeff in table 2 can give some insight into
the valence state of Cr ions in Cr:TiO$_2$ single crystals. Cr:TiO$_2$(Ar) mainly have Cr$^{3+}$ ions. There could be some amount of Cr$^{4+}$, Cr$^{5+}$, and Cr$^{6+}$ ions in Cr:TiO$_2$(Ar). On the other hand, main valence state of Cr ions in Cr:TiO$_2$(O$_2$) can’t be Cr$^{3+}$. There could be a mixture of various valence states of Cr ions such as Cr$^{3+}$, Cr$^{4+}$, Cr$^{5+}$, and Cr$^{6+}$ in Cr:TiO$_2$(Ar).

As in the case of polycrystalline samples (chapter 3), the origin of $\chi_0$ is not clear. It could come from some uncertainty in the removal of the ferromagnetic contribution or from true temperature independent paramagnetism.

3.4. Valence states of Cr ions in doped TiO$_2$ single crystals

We recorded the electron paramagnetic resonance (EPR) spectra of the Cr:TiO$_2$ single crystal. Since Cr$^{3+}$ is a $d^3$ transition metal ion, it has three unpaired electrons ($S = 3/2$) and exhibits a zero field splitting very sensitive to small variations of the local crystal field. In Cr:TiO$_2$ single crystals, 5 resonances are dominant : B, C, D, E and F (Figure 7). We already discussed EPR spectra of Cr$^{3+}$ doped TiO$_2$ in chapter 3.

The main difference of the two types of single crystals is the absence of resonance A for the lowest doped Cr:TiO$_2$(Ar) crystals. In chapter 3, we mentioned that this resonance is associated with the presence of chromium valencies higher than 3+. The resonance A in Cr:TiO$_2$(O$_2$) looks similar with that in polycrystalline Cr:TiO$_2$. Therefore we guess that there are mixed valence states of Cr ions in Cr:TiO$_2$(O$_2$) single crystal. But the resonance A in Cr:TiO$_2$(Ar) has different shape. The linewidth is wider and smoother. Similar resonance is observed in reduced TiO$_2$ powder. The EPR spectra of reduced TiO$_2$ has broad and smooth curve which comes from Ti$^{3+}$ ions. After creating oxygen vacancies, electrons can be trapped at the site of Ti$^{4+}$. Therefore Cr:TiO$_2$(Ar) single crystals have oxygen vacancies with releasing two electrons. And they are trapped at certain sites. In reported article [5] they explain that interstitial Ti$^{3+}$ on the surface can produce the peak intensity located at 3400 G. In the case of Cr:TiO$_2$(Ar), 0.30 mol% and 0.65 mol% Cr:TiO$_2$(Ar) do not have resonance A. but 1.0 mol% Cr:TiO$_2$(Ar) has small peak at this site of resonance A. We address this resonance as Ti$^{3+}$. But in the case of Cr:TiO$_2$(O$_2$) all crystals have resonance A which means that there are valence states of Cr higher than 3+.
FIGURE 7. Electron paramagnetic resonance spectra of Cr doped TiO$_2$ single crystals, recorded at 100K

FIGURE 8. Full range of electron paramagnetic resonance (a) and resonance A region (b) in 1.0 mol% Cr:TiO$_2$(O$_2$), 1.0 mol%Cr:TiO$_2$(Ar) and reduced TiO$_2$ powder at 100K
4. Discussion

It looks clear that both types of Cr:TiO$_2$ single crystals have different physical properties. The main cause can be the difference of valence state of Cr ions. Cr:TiO$_2$(Ar) mainly contains Cr$^{3+}$ ions which show paramagnetic behavior. There may be other valence state of Cr ions and also Ti$^{3+}$ ions because of charge neutrality. They can contribute to the ferromagnetic behavior overall temperatures. However, the ferromagnetic contribution of Cr:TiO$_2$(Ar) decreases as the temperature increases. It is scarcely possible to say that they contribute to the room temperature ferromagnetism. In the case of Cr:TiO$_2$(O$_2$), Cr ions don’t seem to replace Ti atoms with a valence state of 3+ because they have somewhat degraded paramagnetic signal with small effective momentum values.

Since the values of the effective momentum are much smaller than the value of 3+ and a little bigger than the value of 5+, we can suppose that Cr:TiO$_2$(O$_2$) has the valency mixture with Cr$^{3+}$ (3 electrons in d orbital) and Cr$^{6+}$ (0 electrons in d orbital). Corresponding to an hypothetical mixture Cr$^{3+}$ and Cr$^{6+}$, fraction of Cr$^{6+}$ can be calculated by $f$(Cr$^{6+}$) = 1-$\mu_{\text{eff}}$/3.87 (3.87 $\mu_B$: Cr$^{3+}$). We deduce the partial ratio of doping concentration in both groups of Cr:TiO$_2$ as seen in table 3.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Partial ratio of Cr$^{3+}$ or Cr$^{6+}$</th>
<th>[Cr$^{3+}$ or Cr$^{6+}$]/[total Cr ions]x100 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr0.30% (Ar)</td>
<td>0.26</td>
<td>0.04, 87.3</td>
</tr>
<tr>
<td>Cr0.65% (Ar)</td>
<td>0.57</td>
<td>0.08, 87.8</td>
</tr>
<tr>
<td>Cr1.00% (Ar)</td>
<td>0.81</td>
<td>0.19, 81.2</td>
</tr>
<tr>
<td>Cr0.30% (O$_2$)</td>
<td>0.16</td>
<td>0.14, 53.6</td>
</tr>
<tr>
<td>Cr0.65% (O$_2$)</td>
<td>0.33</td>
<td>0.32, 51.1</td>
</tr>
<tr>
<td>Cr1.00% (O$_2$)</td>
<td>0.69</td>
<td>0.31, 68.9</td>
</tr>
</tbody>
</table>

TABLE 3. Deduced partial ratio of Cr$^{3+}$ and Cr$^{6+}$ in Cr:TiO$_2$.

The fractions of Cr$^{6+}$ in Cr:TiO$_2$(O$_2$) are much larger than those in Cr:TiO$_2$(Ar). Cr:TiO$_2$(Ar) have small amount of Cr$^{6+}$ ions which can also be regarded as the amount of lost Cr ions during the crystal growth. Almost half of Cr ions exist as a form of Cr$^{6+}$ in Cr0.3%(O$_2$) and Cr0.65%(O$_2$) following the hypothesis above. Especially Cr0.65%(O$_2$)
which exhibits the largest saturated value of ferromagnetic ordering has the biggest value of partial ratio of Cr$^{6+}$ ions. It tells that the mixture of Cr valence state can be responsible for the ferromagnetic ordering. Many articles have been reported that the mixture of Cr$^{3+}$ and Cr$^{4+}$ favor ferromagnetic ordering to share one electron hopping from one site to another [6]. If comparable amount of Cr$^{3+}$ and Cr$^{4+}$ exists in a short distance, the double exchange interaction between Cr$^{3+}$ and Cr$^{4+}$ can occur. Moreover, close pairs of Cr$^{4+}$ are also known with ferromagnetic interactions as in CrO$_2$. Clusters of Cr ions can cause the strong ferromagnetic signal which was reported in the field of DMS [7].
5. Summary

We study Cr doped TiO$_2$ system by growing single crystals under different gas flows. It looks clear that the type of atmosphere is important to decide the magnetic properties of Cr doped TiO$_2$. The optical absorption spectra suggested that Cr:TiO$_2$(Ar) can have a shallow impurity band located about 0.4 eV under the bottom of the conduction band. This Cr$^{3+}$ doped TiO$_2$ system shows strong paramagnetic behavior. However Cr$^{3+}$ ions alone don’t seem to replace Ti atoms in Cr:TiO$_2$(O$_2$). These single crystals contain a mixture of Cr valence states which can exist in the form of clusters within the crystal. It can enhance the ferromagnetic signals several times in comparison to those of Cr:TiO$_2$(Ar). The ferromagnetic signal of Cr:TiO$_2$(O$_2$) is stronger than that of polycrystalline samples prepared in air. But in all cases, Cr:TiO$_2$ single crystals exhibit a very weak ferromagnetic contribution.
Bibliography


CHAPTER 5

Synthesis and Characterization of Cr doped SrTiO₃ polycrystals and thin films

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   3.3 Mixed valence state of Cr dopant in Cr: SrTiO₃
   3.4 Controlling the valence state of Cr dopant in Cr: SrTiO₃ films
4. Summary
Bibliography
1. Introduction

Transition-metal doped perovskite oxides have shown many interesting phenomena in the field of condensed matter physics for several decades, for examples, photochromism [1], colossal magneto-resistance (CMR) [2], solid oxide fuel cells (SOFC) [3], diluted magnetic semiconductor (DMS) [4], transparent conducting oxide (TCO) [5], and non-volatile memory (Resistive random access memory, RRAM) [6]. Among a high variety of ABO$_3$ perovskites, ATiO$_3$ (A = Ca, Sr, Ba) compositions are particularly interesting: they all show a high chemical stability, CaTiO$_3$ is the mineral which gave its name to this family, SrTiO$_3$ exhibits a perfect cubic structure and BaTiO$_3$ is well known for its ferroelectric properties. Among them, SrTiO$_3$ is an important material that has found many applications. The characteristics of SrTiO$_3$ can be modified by supplying excess electrons of transition metal ions in empty Ti 3d band by doping with heterovalent ions. One way to achieve this doping is to substitute Ti$^{4+}$ by an other transition metal (TM) ion with a different valency in preparing various solid solutions SrTM$_x$Ti$_{1-x}$O$_3$ (TM = Cr, Mn, Fe, and Co). As TM ions generally exist under various valency states, this found in solid solutions, which may be a mixture of valencies, often depends on preparation conditions in particular of the oxygen partial pressure. To achieve their charge neutrality, the resulting compositions often contain oxygen or metallic vacancies and therefore appear as defective perovskites.

SrTiO$_3$ doped with Cr ions has been intensively studied in the field of photochromism (PC). The charge transfer processes between the Cr ions and the host lattice plays an important role in PC. Therefore the valence state of Cr ions is important to identify the characteristics of Cr: SrTiO$_3$ system. The optical absorption spectra have a typical luminescence R line when Ti$^{4+}$ ions are substituted by Cr$^{3+}$ ions [7]. In some reports, the Cr$^{4+}$ dopant substitutes Ti$^{4+}$ with perfect oxygen stoichiometry of SrTiO$_3$ [8] and then charge transfer excitation has been occurred with the subsequent illumination with a photon energy above 1.5 eV. Cr$^{5+}$ and Cr$^{6+}$ also exist as a form of Cr oxides, Cr$_2$O$_3$ and CrO$_3$, but they are usually found in a lower coordination.

For technological applications, this kind of system is often prepared in the form of thin films which may exhibit properties different from those of the bulk material. As film preparation by pulse laser deposition (PLD) required the use of a ceramic target, the properties of the former and of the later may be compared. We reported a limitation of the Cr$^{3+}$ solubility in the film samples depending on the synthesis atmosphere.
2. Experimental details

Polycrystalline x mol% Cr doped SrTiO$_3$ (x=0, 0.5, 1.0, 2.0, 5.0 and 10.0) samples were synthesized by a standard solid-state reaction from stoichiometric mixtures of 99.9 % pure SrCO$_3$, TiO$_2$ and Cr$_2$O$_3$ which were molded into pellets (diameter is 12 mm, thickness is 5 mm). They were calcined at 950 °C for 8-12 hours and sintered at 1350-1450 °C for 24 to 36 hours. To get a single phase, more than 3 additional heat treatments were accomplished with a long-time intermediate grinding.

Cr doped SrTiO$_3$ films (100–200 nm thick) were grown in a preparation-chamber (~10$^{-8}$ Torr) on SrRuO$_3$(20 nm thick)/SrTiO$_3$ substrates by pulsed laser deposition (PLD) using polycrystalline Cr-doped SrTiO$_3$ pellets. The films were grown at 700 °C under P$_{o2}$ = 2.0 × 10$^{-1}$ Torr and post-annealed at 400 °C under P$_{o2}$ = 5.0 × 10$^{-6}$ Torr. A Nd:YAG laser (λ = 266 nm) was used to ablate the Cr:SiTiO$_3$ pellets. The energy and repetition rates of the laser pulses were 0.75 J/cm$^2$ and 10 Hz, respectively.

For PES measurement, main chamber has the base pressure of 1×10$^{-10}$ Torr and is equipped with VG CLAM 4 spectrometer (R=150mm, resolution: ~0.89eV). The binding energy of core level was calibrated with C 1s (285eV). XAS measurements were performed in the total electron yield mode with synchrotron radiation in 2A EPU-beamline, Pohang Accelerator Laboratory, Korea. The resolving power (E/ΔE) in our energy range was 5000~10000 and the intensity was 10$^{10}$~10$^{12}$ photons/sec. The incident beam has an elliptical shape with a size as small as 10μm × 1mm.
3. Results

3.1. Crystallographic properties of polycrystalline Cr: SrTiO₃

X-ray diffraction patterns of polycrystalline Cr: SrTiO₃ are reported in figure 1. Main peaks of Cr: SrTiO₃ are well matched with SrTiO₃ structure (space group: Pm3m). Although Cr³⁺ ions are expected to substitute Ti⁴⁺ ions in SrTiO₃, the 10.0 mol% Cr: SrTiO₃ pattern shows small additional peaks revealing the presence of a second phase identified as SrCrO₄ (space group: P2₁/n, JCPDS No: 15-365).

As seen in table 1, it is found that the lattice constant of Cr: SrTiO₃ shows relatively small decrease as Cr doping increases. Considering the ionic radius of Ti⁴⁺ (0.605 Å) and Cr³⁺ (0.615 Å) (table 1 in chapter 3), the lattice constant should increase with Cr³⁺ doping. It is unlikely that Ti⁴⁺ ions are replaced by Cr³⁺ ions in our samples contrary to the reported articles [9]. It is possible that Ti⁴⁺ ions can be replaced mainly by Cr⁴⁺ ions. It should be noted that the cell parameter for 5.0 mol% is even almost equal to that for 2.0 mol%. There are probably secondary phases which may include higher valence states of Cr ions. It should
be noticed that, due to their small sizes, Cr\(^{5+}\) and Cr\(^{6+}\) ions are hardly found in Cr: SrTiO\(_3\) as substitutes for Ti\(^{4+}\) ions. The XRD measurements suggest that Ti\(^{4+}\) ions may be replaced by Cr\(^{3+}\) ions and also by Cr\(^{4+}\) ions, and secondary phases can be formed with higher valencies. We observe the secondary phase, SrCrO\(_4\) which contains Cr\(^{6+}\) ions in 10.0 mol\% doped SrTiO\(_3\) (inset of figure 1). If some Cr\(^{5+}\) or Cr\(^{6+}\) ions are found in interstitial positions in doped SrTiO\(_3\), oxygen vacancies or Ti\(^{3+}\) ions can be created to compensate their high valencies and can play a part in some defects in the system. In general charge compensation plays an important role in transition metal doped system, since it permits the existence of different valence states of dopant.

<table>
<thead>
<tr>
<th>Cr: SrTiO(_3) ceramic</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Doping rate(mol%)</td>
<td>a</td>
</tr>
<tr>
<td>SrTiO(_3)</td>
<td>3.9088</td>
</tr>
<tr>
<td>0.5</td>
<td>3.9088</td>
</tr>
<tr>
<td>1.0</td>
<td>3.9072</td>
</tr>
<tr>
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<td>3.9067</td>
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<td>5.0</td>
<td>3.9068</td>
</tr>
<tr>
<td>10.0</td>
<td>3.9055</td>
</tr>
</tbody>
</table>

TABLE 1. Refinement results of X-ray diffraction in polycrystalline Cr doped SrTiO\(_3\)

3.2. Magnetic properties of polycrystalline Cr: SrTiO\(_3\)

The magnetic moments of polycrystalline Cr: SrTiO\(_3\) were measured from 5 K to 300 K using a SQUID magnetometer with a magnetic field of 0.1 T. The magnetic susceptibilities were then calculated from these data. Figure 2 shows that SrTiO\(_3\) without Cr dopant has a clear diamagnetic behavior with a small paramagnetic signal coming from some defects. Then additional paramagnetic contribution of Cr ions gradually increases with Cr doping. The magnetic susceptibility of the sample may be fitted by a Curie-Weiss paramagnetic equation including a temperature independent term [10]. The calculated values of $\theta$, $\chi_0$ and $\mu_{\text{eff}}$ are shown in table 2.
Polycrystalline Cr:SrTiO$_3$ samples except 5mol% Cr:SrTiO$_3$ have negative values of $\chi_0$ which represent the diamagnetic contribution of the SrTiO$_3$ matrix. The positive value of $\chi_0$ is probably due to an impurity. All samples have negative values of $\theta$ which are usually related to antiferromagnetic interactions. Interactions between dopants are expected for the highest concentrations of dopants in which the mean distance between Cr ions is sufficiently small, they are more surprising for the lowest concentrations. However the nature of the interactions may vary: It is well-known that LaCrO$_3$ is antiferromagnetic, whereas it has been reported that SrCr$^{4+}$O$_3$ exhibit Pauli paramagnetic behavior [11].

<table>
<thead>
<tr>
<th>Doping rate (mol%)</th>
<th>C / (emu·K/mol)</th>
<th>$\theta$ / K</th>
<th>$\chi_0$ / (emu/mol)</th>
<th>$\mu_{\text{eff}}$ ((\mu_B)/Cr)</th>
<th>f(Cr$^{6+}$) (%)</th>
</tr>
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<td>7.224×10$^{-3}$</td>
<td>-8.280</td>
<td>-6.165×10$^{-5}$</td>
<td>3.390</td>
<td>12.4*</td>
</tr>
<tr>
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<td>7.1</td>
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<td>2.316</td>
<td>18.2</td>
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<td>-7.376</td>
<td>-5.172×10$^{-6}$</td>
<td>1.158</td>
<td>59.1</td>
</tr>
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</table>

TABLE 2. Fitting results of SQUID measurement in polycrystalline Cr doped SrTiO$_3$
As a result of fitting, polycrystalline Cr:SrTiO$_3$ has an effective moment much lower than 3.87 $\mu_B$, an expected value of Cr$^{3+}$ containing 3 electrons in d-orbital. This suggests that a part of the Cr ions ions are found in higher valence states. To set the range of possible fraction for Cr$^{6+}$ in the samples, we assume that Cr ions are only found in the 4+ and the 6+ states for the minimum fraction of Cr$^{6+}$ and in the 3+ and the 6+ states for the maximum fraction of Cr$^{6+}$. Corresponding to an hypothetical mixture Cr$^{3+}$ and Cr$^{6+}$, $f(\text{Cr}^{6+})=1-\frac{\mu_{\text{eff}}}{\mu_{\text{eff}}}$ $(3.87 \mu_B$ for Cr$^{3+}$ or 2.83$\mu_B$ for Cr$^{4+}$) is obtain as seen in table 3. In the case of 0.5 mol% Cr: SrTiO$_3$, we cannot speculate the presence of a mixture of Cr$^{4+}$ and Cr$^{6+}$ because $\mu_{\text{eff}}$ is bigger than 2.83$\mu_B$. The asterisks in table 2 and table 3 mean that we just obtain the maximum fraction of Cr$^{6+}$. The fraction of Cr$^{6+}$ rapidly increases as doping increase. The half of Cr ions can exist as a form of Cr$^{6+}$ in 5.0 mol% and 10.0 mol% Cr: SrTiO$_3$ but seem mainly present in the SrCrO$_4$ secondary phase. X-ray diffraction results show that the lattice parameter of Cr: SrTiO$_3$ has a relatively small decrease overall or an inappropriate increase between 2.0 mol% and 5.0 mol% of Cr doping. Therefore it is clear that Cr ions can exist as mixture of Cr valence states. This indicates that it is hard to obtain the single valency (Cr$^{3+}$) doped SrTiO$_3$ solid solution as doping increase in our conditions of synthesis.

<table>
<thead>
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<th>Doping of Cr (%)</th>
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<th>fraction maximum</th>
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<tr>
<td>10.0%</td>
<td>0.591</td>
<td>0.701</td>
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</table>

TABLE 3. Estimated fraction of Cr$^{6+}$ in Cr doped SrTiO$_3$

3.3 Mixed valence states of Cr dopant in Cr: SrTiO$_3$

X-ray Absorption Spectroscopy (XAS) confirms that polycrystalline Cr: SrTiO$_3$ contain various valence states of Cr. Cr L-edge (L$_{III}$ and L$_{II}$ for 2p-3d transition) of polycrystalline 5.0 mol% and 10.0 mol% Cr: SrTiO$_3$ shows the mixture of valence states, Cr$^{3+}$, Cr$^{4+}$ and Cr$^{6+}$. Comparing with references of Cr L-edge in figure 3, we can address peaks (1, 2, 3, 7, and 8) to Cr$^{3+}$, peaks (1, 2, 3, 5, 7, and 8) to Cr$^{4+}$ and peaks (4, 6, 8, and 9) to Cr$^{6+}$. Polycrystalline 10.0 mol% Cr: SrTiO$_3$ has bigger signal of Cr$^{6+}$ than that of 5.0 mol% Cr: SrTiO$_3$. Both polycrystalline Cr: SrTiO$_3$ have certain amount of Cr$^{4+}$ ions in the system. If we assume that these Cr L-edge spectra is the superposition of each spectrum of different Cr
valence states, we can be sure that Cr$^{3+}$ and Cr$^{4+}$ have 6-fold coordination with oxygen ions because the shape of spectrum is sensitive to the surrounding environment. Because of empty 3d orbitals of Cr$^{6+}$ a relatively simple spectrum was observed. Main peaks represent $e_g$ and $t_{2g}$ orbital split by crystal field. However, we could not prove the presence of Cr$^{5+}$ ions with XAS spectra of Cr L-edge.

![Cr L-edge](image)

FIGURE 3. Cr L-edge (2p-3d transition) of polycrystalline (a) 10.0 mol%, and (b) 5.0 mol% Cr: SrTiO$_3$; Cr L-edge (2p-3d transition) of references, (c) K$_2$CrO$_4$ with Cr$^{6+}$ [12], (d) CrO$_2$ film with Cr$^{4+}$, and (e) Cr$_2$O$_3$ film with Cr$^{3+}$

3.4. Controlling the valence state of Cr dopant in Cr: SrTiO$_3$ films

In polycrystalline materials, instead of Cr$^{3+}$ doped SrTiO$_3$, unintentional compositions were also produced with various valence states, mainly SrCrO$_4$ phase with Cr$^{6+}$ ions in high doping region of Cr: SrTiO$_3$. The results obtained on the ceramics clearly show that the formation of the highly oxidized phase SrCrO$_4$ has to be inhibited in high doping region of Cr: SrTiO$_3$ solid solutions. Miyoshi et al reported the phase diagram of SrCrO$_4$ according to temperature and oxygen pressure during synthesis in La$_{1-x}$Sr$_x$CrO$_3$ system [13]. They suggested that SrCrO$_4$ phase tended to disappear at high temperature and low oxygen pressure. Therefore we tried to prepare Cr: SrTiO$_3$ films in a vacuum system to get an
atmosphere of low oxygen pressure (~10^{-6} Torr). We deposited 10.0 mol% Cr:SrTiO\textsubscript{3} films with polycrystalline 10.0 mol% Cr:SrTiO\textsubscript{3} which contained various Cr valencies. The films were grown at 700 °C under P\textsubscript{O2} = 2.0 \times 10^{-1} Torr. Then one was post-annealed at 400 °C under P\textsubscript{O2} = 5 \times 10^{-6} Torr and the other was post-annealed at 400 °C under P\textsubscript{O2} = 2 \times 10^{2} Torr. XPS and XAS results were obtained with two 10.0 mol% Cr:SrTiO\textsubscript{3} films as shown in figure 4. Cr 2p spectra reveal that the film post-annealed under P\textsubscript{O2} = 2 \times 10^{2} Torr has both valencies, Cr\textsuperscript{3+} and Cr\textsuperscript{6+} whereas the film post-annealed under P\textsubscript{O2} = 5 \times 10^{-6} Torr shows only Cr\textsuperscript{3+}. Likewise Cr L-edge spectra of XAS implies that only Cr\textsuperscript{3+} exists in the film post-annealed under P\textsubscript{O2} = 5 \times 10^{-6} Torr regardless the polycrystalline target of 10.0 mol% Cr:SrTiO\textsubscript{3} has various Cr valencies. It does not show any other valence state of Cr ions such as Cr\textsuperscript{4+} and Cr\textsuperscript{5+} different form the results of polycrystalline samples. There should be some other valence states of Cr ions. But they may be hard to detect by XAS measurements because of small quantity of Cr ions. O K-edge spectra shows an enhanced prominence around 529 eV in the film post-annealed under P\textsubscript{O2} = 2 \times 10^{2} Torr which indicates the second phase, SrCrO\textsubscript{4}, containing Cr\textsuperscript{6+}. This emerged peak can originate from empty 3d-orbital of Cr\textsuperscript{6+} ions. Therefore the lack of O\textsubscript{2} gas during synthesis can help to remove the second phase and to construct Cr\textsuperscript{3+} doped SrTiO\textsubscript{3} system.

![FIGURE 4. XPS and XAS results of 10.0 mol% Cr:SrTiO\textsubscript{3} films post-annealed (a) under P\textsubscript{O2} = 5 \times 10^{-6} and (b) under P\textsubscript{O2} = 2 \times 10^{2} Torr](image-url)
4. Summary

Polycrystalline Cr: SrTiO$_3$ samples were synthesized by a standard solid state reaction in air. The structures of the perovskite phases were revealed to be cubic (Pm$\overline{3}$m) with Cr doping from 0.5 mol% to 10.0 mol%. However, polycrystalline 10.0 mol% Cr: SrTiO$_3$ has unintentional compositions with valence mixture of Cr ions, for example, SrCrO$_4$ with Cr$^{6+}$. The polycrystalline 10.0 mol% Cr: SrTiO$_3$ was used as a target for film growth. Cr: SrTiO$_3$ films were grown by pulsed laser deposition method and subsequently post-annealed under O$_2$ poor (~$10^{-6}$ Torr) and O$_2$ rich (2.0 x $10^{-1}$ Torr) atmospheres. Unintentionally formed second phases with various valence states of Cr were removed when Cr: SrTiO$_3$ films were post-annealed under O$_2$ poor environment. Therefore we can obtain the single valence state, Cr$^{3+}$, doped SrTiO$_3$ under O$_2$ poor environment.
Bibliography


CHAPTER 6

Synthesis and Characterization of Cr doped SrZrO$_3$ films

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5. Summary
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1. Introduction

Transition-metal oxides have been widely used for many applications. Some of the oxide materials are suitable for the high voltage and the high reliability devices with several characteristics such as high dielectric constant and high breakdown strength [1-4]. In the field of transition-metal oxides, the impurities and defects play an important role for modifying the electronic structure of oxides. Generally the basic properties of oxides are mainly determined during the sample synthesis. Therefore we studied the behavior of impurities and defects by changing the growth parameters of the sample synthesis.

For the goal Cr doped SrZrO$_3$ has been selected because it is widely studied as a RRAM material with a good performance [5-7]. A few mol% trivalent ions doped SrZrO$_3$ shows a high chemical stability [8]. Generally substitutional ions can cause oxygen deficiency or local distortion when they substitute Zr$^{4+}$ ions in SrZrO$_3$. Therefore small number of dopants can modify the oxide properties. The role of Cr dopant in Cr: SrZrO$_3$ film is not clearly understood. In chapter 6, we study the chemical state of Cr ions and the Cr doping effects on electronic structures of Cr: SrZrO$_3$ films by changing growth conditions such as growth temperatures during deposition and oxygen pressures during post-annealing process.
2. Experimental details

The SrTiO$_3$(100) single crystal substrates were treated with buffered-HF before bringing into the preparation chamber (~10^-8 Torr) in order to obtain an almost perfect TiO$_2$ termination. Cr:CrSrZrO$_3$ films (100-200 nm thick) on SrRuO$_3$/SrTiO$_3$(100) were epitaxially grown with various growth conditions by PLD technique. A Nd:YAG laser (I = 266nm) was used to ablate the targets. The energy and the repetition rate of the laser pulse were 0.75 J/cm$^2$ and 10 Hz, respectively. The range of substrate temperature was 400-700 °C, in the oxygen pressure of 2×10^{-1} Torr and then the films were post-annealed for 30 minutes long at 400 °C under oxygen pressures, 5.0 × 10^{-6}, 2 × 10^{-1} and 3.3 × 10^2 (or 2.0× 10^2) Torr. SrRuO$_3$ (about 20 nm thick) layer was used as a bottom electrode for I-V measurement (SrRuO$_3$ films were deposited by Pulsed Laser Deposition (PLD) on SrTiO$_3$(100) substrates at 700 °C in the oxygen pressure of 10^{-1} Torr).

The electronic structure of the films was in-situ measured by x-ray photoelectron spectroscopy (XPS) in home lab. In home lab, the main chamber has the base pressure of 5 × 10^{-10} Torr and is equipped with VG CLAM 4 spectrometer (R=150 mm, resolution: ~0.89 eV). The binding energy of core level was calibrated with C 1s (285 eV). The resistances were collected using 4-probe I-V measurement. XAS measurements were performed in the total electron yield mode in 8A1 beam line at Pohang Accelerator Laboratory, Korea. The beam size of X-ray was around 400 μm.
3. Results

3.1. Epitaxial film growth

X-ray diffraction pattern of 0.2 mol% Cr: SrZrO$_3$/SrRuO$_3$/SrTiO$_3$ was shown in figure 1. SrZrO$_3$ was known as an orthorhombic structure whose lattice constants are $a = 8.204$, $b = 5.797$, and $c = 5.818$. When Cr: SrZrO$_3$ film was grown on SrRuO$_3$/SrTiO$_3$, only (200) and (400) direction were selected following the cubic structure of SrTiO$_3$. Therefore it seems that Cr: SrZrO$_3$ films were grown epitaxially on SrRuO$_3$/SrTiO$_3$.

![X-ray diffraction pattern of Cr: SrZrO$_3$ target and 0.2 mol% Cr: SrZrO$_3$/SrRuO$_3$/SrTiO$_3$(100)](image)

FIGURE 1. X-ray diffraction pattern of Cr: SrZrO$_3$ target and 0.2 mol% Cr: SrZrO$_3$/SrRuO$_3$/SrTiO$_3$(100)

It was reported that Cr: SrZrO$_3$ films prepared by PLD method were grown epitaxially above the substrate temperature, 500 °C [9]. Figure 2 shows the surface morphology of as-grown 0.1 mol% and 0.2 mol% Cr: SrZrO$_3$ films as the substrate temperature varies from 600 to 700 °C. Epi-Cr: SrZrO$_3$ films shows different surface morphology depending on the substrate temperature. The nucleation on the surface was observed below the substrate temperature 700 °C.
3.2. Migration of Cr ions on the surface region

It is well known in surface science that some atomic species may migrate to the surface during film growth. To verify this possibility in our case, we have compared the core-level peak intensities in the XPS spectra for films grown at different substrate temperatures. The spectra will give the stoichiometry near the surface region since the probing depth of XPS measurements is limited to only a few atomic layers from the surface. Figure 3 shows the (a) O 1s, (b) Zr 3d (c) Sr 3d, and (d) Cr 2p XPS spectra of the 0.2 mol% Cr: SrZrO$_3$ films that were deposited at three different growth temperatures of 400, 550, and 700 °C under $P_{O_2}$ of $2.0 \times 10^{-1}$ Torr. The films were subsequently annealed for 30 minutes at 400 °C under $P_{O_2}$ of $5.0 \times 10^{-6}$ Torr. The features at the higher BE in O 1s and Sr 3d spectra of the film grown at 400 °C [Fig.3(a) and 3(c)] indicate that phases such as SrO$_x$ were formed because of the low substrate temperature. Those phases gradually disappeared as the growth temperature increased. Moreover, a substantial increase in the Cr 2p peak intensities was observed in Fig. 3(d) at high-temperature growth. The peaks of the Cr 2p$_{3/2}$ (2p$_{1/2}$) core level were clearly observed at 576.8 (586.6) eV when the growth temperature was 700 °C, whereas both peaks were not detected in the other films grown at $T < 600$ °C. The high temperature helps the mobile Cr ions to diffuse into the surface region during the deposition.

As shown in Fig. 3(a)-(c), BEs of O 1s, Zr 3d, and Sr 3d related to the SrZrO$_3$ phase increase uniformly by 0.2 eV as the growth temperature is increased from 400 °C to 550 °C,
which probably means that the Fermi energy (EF) is shifted toward the conduction band minimum by 0.2 eV because of oxygen vacancy creation. On the other hand, the film grown at 700 °C has higher BEs of O 1s and Zr 3d than the film grown at 550 °C by 0.6 eV, whereas BE of Sr 3d is shifted by only 0.2 eV. This suggests that Zr, O, and migrated Cr ions participate in the change of surface chemistry, which leads to the chemical shift in the spectra of Zr 3d and O 1s.

![X-ray photoemission spectra of Cr:СrSrZrO3/SrRuO3/SrTiO3(100) films deposited at the substrate temperature of 400 °C, 550 °C and 700 °C](image)

**FIGURE 3.** X-ray photoemission spectra of Cr:CrSrZrO3/SrRuO3/SrTiO3(100) films deposited at the substrate temperature of 400 °C, 550 °C and 700 °C

### 3.3. Chemical state of migrated Cr ions

We can see the similar results from post-annealed films with different oxygen pressures. Deposited films were post-annealed to promote the incorporation into a proper site for Cr dopant and to recover the oxygen vacancies during deposition. One was just cooled down under the oxygen pressure of $4.0 \times 10^2$ Torr without post-annealing process. Others were post-annealed for 30 min at 400 °C with the oxygen pressure of $5.0 \times 10^6$, $2 \times 10^{-1}$ and $3.3 \times 10^2$ Torr.
FIGURE 4. O 1s and Cr 2p spectra of 0.2mol% Cr: SrZrO$_3$ films which were post-annealed under various oxygen pressures: (a) the film without post-annealing process, (b) $5.0 \times 10^{-6}$, (c) $2 \times 10^{-1}$ and (d) $3.3 \times 10^{2}$ Torr. (All peak intensities were normalized with the area of Zr 3d spectra and fitting results were shown below. The intensity of O 1s peak denoted as an asterisk was diminished as time goes by).

As shown in figure 4 (c) and (d), the BEs of O 1s related to the SrZrO$_3$ phase (main peak) increase by 0.2 eV as the oxygen pressure is decreased from $3.3 \times 10^{2}$ to $2 \times 10^{-1}$ Torr. Figure 4 (b) and (c) show that the BEs of O 1s related to the SrZrO$_3$ phase (main peak) increase by 0.3 eV as the oxygen pressure is decreased from $2 \times 10^{-1}$ to $5.0 \times 10^{-6}$ Torr. It probably means that the Fermi energy (EF) is shifted toward the conduction band minimum because of oxygen vacancy creation. On the other hand, O 1s BE of the film without post-annealing process (Figure 4 (a)) is same with that of the film post-annealed under $5.0 \times 10^{-6}$ Torr.
Therefore the film without post-annealing process contains oxygen vacancies as much as the film post-annealed under $5.0 \times 10^{-6}$ Torr.

Another peak in O 1s spectra at high BE is shown. We suggest that sub-oxides can be created during the film synthesis. The film without post-annealing process has large sub-oxide peak in O 1s spectra. The post-annealing process under suitable oxygen pressure can help to reduce sub-oxides effectively. The sample post-annealed under $2 \times 10^{-1}$ Torr has an unstable SrZrO$_3$ phase (Figure 4 (c)). O 1s, Sr 3d and Zr 3d spectra has another large peak which located at high BE (Sr 3d and Zr 3d spectra were not shown here). This phase was diminished as time goes by.

3.4. Depth profile of Cr accumulated films surface

FIGURE 5. (a) The depth-profile XPS of Cr: SrZrO$_3$ films with successive Ar$^+$- sputtering (The broad humps denoted as asterisks originate from the O 1s plasmon sidebands so they are not relevant to the Cr concentration) and (b) the angle-dependent Cr 2p spectra of 0.2 mol% Cr: SrZrO$_3$ film taken with three different detection geometries

To determine the distribution of Cr ions on the surface region, we performed depth-profile XPS of Cr: SrZrO$_3$ films with successive Ar$^+$- sputtering. Figure 5 (a) shows that the peaks at BEs of 576.8 and 586.6 eV, which correspond to Cr 3+, disappeared when the film...
was etched by 2 nm. This indicates that most of the Cr ions exist within a 2 nm range from the surface. This fact is also confirmed by the angle-dependent XPS shown in Figure 5 (b), which displays three Cr 2p spectra of 0.2 mol% Cr: SrZrO$_3$ film taken with three different detection geometries, i.e. the angle $\theta$ between the sample normal and the electron energy analyzer. The surface sensitivity of XPS increases drastically with increasing $\theta$ because of the limited electron mean free path. The Cr 2p peaks from both Cr$^{3+}$ and Cr$^{6+}$ are clearly seen at a large angle ($\theta = 50^\circ$), while those are barely observable at the sample normal direction ($\theta = 0^\circ$). This confirms that a substantial amount of Cr ions exists only at the film surface to form the Cr-rich surface.

3.5. Segregation of Cr ions with the valence state, Cr$^{6+}$

We took x-ray absorption spectroscopy in Pohang Acceleration laboratory (PAL). We found that a pre-peak located below conduction band of SrZrO$_3$ increases as the ratio of Cr$^{6+}$/Cr$^{3+}$ increases as seen in figure 6. A peak at about 528 eV in O K-edge spectra indicates the segregation phases which contain Cr$^{6+}$ ions. In Cr L-edge spectra, peaks which may correspond to the Cr$^{6+}$-related phases are located at 579 and 586 eV. We could not identify the existence of other valence state of Cr ions because the intensity of Cr L-edge is very small. If Cr ions exist as a form of CrO$_2$, we can detect the ferromagnetic signal because CrO$_2$ is room temperature ferromagnet. However, XMCD of Cr L-edge does not show any ferromagnetism (see figure 6).

Figure 7 shows N 1s XAS spectra of GaN and Ga$_{0.94}$Cr$_{0.06}$N [10]. The peaks in the band gap of GaN corresponds to the $e_g$ and $t_{2g}$ split up-spin ($e^\uparrow$ and $t^\uparrow$) and down spin ($e^\downarrow$ and $t^\downarrow$) states of Cr 3d states hybridized with the N 2p states. Therefore, in the case of Cr: SrZrO$_3$ films post-annealed under $3.3 \times 10^2$ Torr (HP), a pre-edge peak around 528 eV can correspond to the empty 3d state of Cr$^{6+}$ ions.
FIGURE 6. O K-edge spectra (a) and Cr L-edge spectra (b) of 0.2 mol% Cr: SrZrO$_3$ films whose oxygen pressures during post-annealing process are $5.0 \times 10^{-6}$ (LP) and $3.3 \times 10^2$ (HP) Torr, respectively. (c) XMCD results of HP and LP with Cr L-edge.

FIGURE 7. (a) Calculated N 2p partial DOS spectra for Ga$_{0.94}$Cr$_{0.06}$N and GaN. (b) N1s excited SXES (Soft X-ray Emission Spectroscopy) and XAS spectra for Ga$_{0.94}$Cr$_{0.06}$N and GaN [10].
5. Summary

Cr doped SrZrO₃ films were deposited by PLD and analyzed by in-situ XPS. During the deposition and the post-annealing process, behavior of Cr dopants in SrZrO₃ film was quite different. When growth temperature is up to 700 °C, Cr ions are migrated to the surface area of Cr: SrZrO₃ film. These migrated Cr ions have different valence states depending on the oxygen pressure during the post-annealing process. The Cr ions exist with forms of Cr³⁺ or Cr⁶⁺ in the film surface. The exposure of oxygen gas can produce Cr related oxides such as CrO₃ or SrCrO₄ in the film surface. The formation of Cr related oxides can be harmful for the performance of memory devices. In chapter 7, we study the correlation between the surface chemistry of deposited films and I-V characteristics by changing the deposition conditions.
Bibliography


CHAPTER 7

Various I-V Characteristics on Cr:SrZrO$_3$ films

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3. Discussion
4. Summary
Bibliography
1. Introduction

Recently, Cr-doped perovskite (Cr: SrZrO$_3$, Cr: SrTiO$_3$) systems have been actively investigated because they show promising behaviors as a resistive random access memory (RRAM) material with several advantages such as low operational power, capability of high-density integration, and high-speed write-erase operations [1–3]. However, despite numerous phenomenological studies on resistance switching (RS), the origin of RS in Cr: SrZrO$_3$ films is not fully understood yet. Their RS behavior can be classified by the polarity dependence, unipolar RS and bipolar RS (see figure 1) [4]. In unipolar RS, reversible changes between bistable resistance states occur when a bias voltage of the same polarity is applied. In bipolar RS, however, the resistance changes can be made by applying an opposite polarity bias voltage. It has been reported that binary oxides (TiO$_2$ [5], NiO [6] and Ta$_2$O$_5$ [7]) usually possess unipolar RS whether complex oxides (Pr$_{1-x}$Ca$_x$MnO$_3$ [8], PbZr$_{0.2}$Ti$_{0.8}$O$_3$ [9], Cr doped SrZrO$_3$ [10] and Cr doped SrTiO$_3$ [11]) possess bipolar RS.

It was believed that two types of RS mechanism have different origins. However, some materials, TiO$_2$ [12], NiO [13] and SrTiO$_3$ [14] are recently reported that unipolar and bipolar RS are intimately related. Figure 2 shows reversible-type changes between unipolar and bipolar RS in Pt/SrTiO$_{3-x}$/Pt cells [14]. Many approaches to unify two forms of the resistive-switching behavior have been proposed. Kim et al reported that Pt/TiO$_2$/Pt memory cell which possesses unipolar RS can show bipolar RS by varying the electro-forming methods with different $I_{\text{comp}}$ (compliance current) or URS set/reset bias polarity [12].
FIGURE 2. Experimental I-V curves of reversible RS-type changes between BRS and URS. (a) BRS after the forming process from pristine state. (b) RS-type change from BRS to URS. (c) RS type change from URS to BRS. (d) Endurance properties measured at a readout voltage of 0.4V [14].

They adopted the concept of the ‘switching layer’ which transforms between the formation and rupture of conducting filaments. As shown in figure 3, the left and right schematics show the electro-formed conducting filament and ruptured conducting filament, respectively. The shaded yellow circle in figure 3 (right) corresponds to the point where the highest temperature was achieved. The squares in figure 3 (right) mean the switching layer at the tip of the conducting filaments. The change in filament shape caused by a variation in the compliance current resulted in different I-V curves.

FIGURE 3. (Left) bipolar RS I–V curves (a) Icomp = 5 mA (process 1 in inset), (b) Icomp = 20 mA (process 1) and unipolar RS reset (process 2), (c) Icomp = 40 mA (process 1) and unipolar RS reset (process 2), (d) Icomp = 20 mA (process 1), unipolar RS reset(process 2), negative switching with Icomp = 20 mA (process 3) and unipolar RS reset (process 4).
(Right) The schematic filament shapes where (a)–(d) correspond to the bipolar RS I–V (a)–(d). [12]
Lee et al observed reversible type changes between bipolar and unipolar RS in Pt/SrTiO$_x$/Pt memory cell [14]. They proposed the ‘interface-modified random circuit breaker network model’ in which the bulk medium is represented by a percolating network of circuit breakers. They introduced the high resistance state $r^h_{\text{int}}$ for the interface region which can switch to low resistance state for the interface region, $r^l_{\text{int}}$ or low resistance state for bulk region, $r^l_{\text{film}}$. By simulating with these resistance states, they achieved the reversible type changes in terms of connectivity changes in the circuit breakers.

The main key to unifying both types of resistive switching could be the interface properties between the electrode and oxide films [12-14]. The diverse experimental findings report that RS mechanism is closely related to the interface properties. In the previous chapter, we found the growth conditions which have a strong influence on the valence state of migrated Cr ions. Therefore in chapter 7, we change the surface chemistry of Cr ions on 0.2mol% Cr: SrZrO$_3$ films and measure I-V characteristics of each samples.
2. Results

2.1. Surface chemistry and I-V Characteristics

The growth processes of Cr:SrZrO₃ films are composed with 3 processes: deposition, cooling down and post-annealing process. The deposition process has been done by PLD method at 700 °C under oxygen pressure of 2.5 × 10⁻¹ Torr. After deposition, the samples are cooled under oxygen environment (~2 × 10² Torr) down to 400 °C or down to room temperature. Then, they are annealed at 400 °C in almost atmospheric pressure (~5.0 × 10² Torr) or a vacuum (roughly 5.0 × 10⁻⁶ Torr).

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Table 1. Growth conditions of four 0.2mol% Cr doped SrZrO₃ films

We measured I-V curves with various growth conditions. For the I-V measurements, a metal electrode (Pt or Au) was deposited on the Cr:SrZrO₃ films by the sputtering method. The metal electrode and the SrRuO₃ layer were used as a top electrode and a bottom electrode, respectively. The current was measured at room temperature at the probe station with a current meter (HP4155A) in the Inter-university Semiconductor Research Center (ISRC). The SrRuO₃ layer was grounded during I-V measurements. We checked the valence state of Cr ions by XPS measurement (Table 1). Every film grown at 700 °C shows the Cr 2p spectra whose binding energies are well-matched with Cr³⁺ and sometimes Cr⁶⁺. The shape of I-V curve of Cr:SrZrO₃ film strongly depended on the growth conditions. Figure 5 shows four different I-V hysteresis curves of Pt/0.2mol%Cr:SrZrO₃/SrRuO₃/SrTiO₃ films. A voltage was applied across electrodes until the threshold voltage was generated, of which process is
usually called ‘forming’. In general, the threshold voltages of Cr: SrZrO\textsubscript{3} films were sensitive to the film thickness and quality. Here, different behaviors were shown, either the threshold voltages or the shapes of hysteresis curve.

The sample 1 and 2 are deposited with same growth conditions except the deposition time. Therefore they have different thicknesses of roughly 100 nm and 200 nm, respectively. In spite of the different thickness the threshold voltages of sample 1 and 2 are almost similar. The sample 1 has the SET voltage (SET: the resistive-switching voltage from HRS (high resistance state) to LRS (low resistance state)) is around 3.5 V whereas that of sample 2 is around -3.5 V. The RESET voltage (RESET: the resistive-switching voltage from LRS to HRS) is -4 V for sample 1 and that of sample 2 is +4 V for sample 2. Despite of the different thickness of films, the amount of leakage current is almost same. It means that the interface properties could be more dominant than bulk properties such as film thickness.

For sample 3, the post-annealing process has been done under 5 \times 10^2 Torr of oxygen pressure. It shows a small ratio between HRS and LRS and large SET and RESET voltages on resistive switching. The LRS of sample 3 is similar with LRS of sample 1 and 2. However the current in HRS is bigger than the others. The SET voltage is not well-defined but RESET

![Image of I-V characteristics of Cr: SrZrO\textsubscript{3} films grown under four different deposition conditions.](image)

FIGURE 5. I-V characteristics of 0.2 mol\% Cr: SrZrO\textsubscript{3} films grown under four different deposition conditions.
voltage is distinct at -4 or -6 V. The XPS spectra of sample 3 show the coexistence of Cr$^{3+}$ and Cr$^{6+}$ ions on the film surface. Therefore the I-V hysteresis curve could be influenced by Cr related oxides on the film surface.

In the case of sample 4, we observed as-prepared interface mixing state by x-ray absorption spectroscopy (not shown here). Ru ions in SrRuO$_3$ bottom electrode may substitute for Zr ions in Cr:SrZrO$_3$ film. Therefore the interface mixing area between SrZrO$_3$ and SrRuO$_3$ has been broadened with a form of Sr(Ru,Zr)O$_3$. It shows the significant smearing effect in the resistive-switching because of ill-formed interface area. Its current was somewhat small and high voltages, +20 V and -20 V are needed for resistive switching.

### 2.2. Nominal Cr concentrations and resistive-switching

Cr:SrZrO$_3$ films were grown on SrRuO$_3$ (20nm thick)/SrTiO$_3$(100) substrates by PLD method using Cr:SrZrO$_3$ targets (Cr : 0, 0.1, 0.2 and 0.3 mol%).

![Figure 6. I-V curves of the Cr:SrZrO$_3$ films (Cr: 0, 0.1, 0.2, and 0.3 mol%). Schematic diagram shows the sample structure used for applying an electric field across the film. All the films were grown at a substrate temperature of 700 °C (P$_{O_2}$ = 2.0 × 10$^{-1}$ Torr) and post-annealed at 400 °C (P$_{O_2}$ = 5.0 × 10$^{-6}$ Torr).](image-url)

Figure 6 shows the I-V characteristics of Cr:SrZrO$_3$ films that have different Cr-concentrations in the targets (0, 0.1, 0.2, and 0.3 mol%). The films were grown at 700 °C
under $P_{O_2} = 2.0 \times 10^{-1}$ Torr and post-annealed at 400 °C under $P_{O_2} = 5.0 \times 10^{-6}$ Torr. In undoped SrZrO$_3$ films, no leakage current (<1 pA) was observed. The leakage current gradually increased with the Cr concentration and is proportional to the Cr concentration in LRS. This suggests that the Cr ions in the films supply charge carriers to form the LRS. In particular, the SrZrO$_3$ films doped with 0.1 mol% and 0.2 mol% Cr show RS hysteresis between the LRS and HRS, but the film doped with 0.3 mol% Cr only shows an Ohmic dependence without RS hysteresis. The resistance of this 0.3 mol% film can be considered as LRS judging from its magnitude, and the absence of HRS in this film probably indicates that large Cr concentrations give rise to too many charge carriers to sustain HRS. The fact that Cr ions provide charge carriers in this system is also supported by previous reports that the ratio of resistance change increases with the dopant concentration [15,16]. We reported the surface accumulation of Cr ions at high temperature growth of films in chapter 6. We estimated the Cr concentration at the film surface by using the XPS peak intensity and the empirical atomic sensitivity factor of the Cr 2p core level. The [Cr]/[Sr] concentration ratios of the films were considerably higher than the nominal values of the targets: ~4%, ~6%, and ~9% for 0.1 mol%, 0.2 mol%, and 0.3 mol%-Cr-doped SrZrO$_3$ targets, respectively.

2.3. Cr accumulations and resistive-switching

Figure 7 shows the Cr 2p XPS spectra of the 0.2 mol% Cr:SrZrO$_3$ films that were deposited at three different growth temperatures of 400, 550, and 700 °C under $P_{O_2}$ of 2.0 $\times$ $10^{-1}$ Torr. The films were subsequently annealed for 30 minutes at 400 °C under $P_{O_2}$ of 5.0 $\times$ $10^{-6}$ Torr. A substantial increase in the Cr 2p peak intensities was observed in figure 7 at high-temperature growth. The high temperature helps the mobile Cr ions to diffuse into the surface region during the deposition. Figures 7 shows the I–V curves of Cr:SrZrO$_3$ films grown at 550 °C and 700 °C, respectively. The film grown at 550 °C has a huge initial resistance and its RS was not observed even after the forming process with high voltage. In contrast, the I–V curve of the film grown at 700 °C clearly shows RS behavior with two resistance states, LRS and HRS. We believe the main cause of this change of I–V characteristics is the migrated Cr ions. We could conceive other factors such as the difference of crystal structure or the amount of oxygen vacancies as the possible cause. However, both films grown at 550 °C and 700 °C were epitaxial overall. We already discussed in chapter 6 that the Fermi energy (EF) is shifted toward the conduction band minimum because of
oxygen vacancy creation as the growth temperature increases. Although the RS mechanism may also be closely related to oxygen vacancies as reported on the study of undoped SrTiO$_3$ single crystal [17], it should be noted that the amount of Cr ions (roughly $10^{21}$ cm$^{-3}$) at the surface of our samples was even larger than the amount of oxygen vacancies which lead to metal-insulator transition in SrTiO$_3$ single crystal (roughly $10^{14}$~$10^{20}$ cm$^{-3}$).

**2.4. Cr valence state and resistive-switching**

We further investigated the influence of valence state of Cr ions on I-V characteristics using the XPS technique. Figure 8 (a) shows the Cr 2p XPS spectra of the Cr: SrZrO$_3$ films deposited under $P_{O_2} = 2.0 \times 10^{-1}$ Torr at 700 °C and post-annealed for 30 min at 400 °C under different $P_{O_2}$ of $5.0 \times 10^{-6}$ Torr, $2.0 \times 10^{-1}$ Torr, and $3.3 \times 10^{2}$ Torr. When the film was annealed under $P_{O_2} = 5.0 \times 10^{-6}$ Torr, the XPS spectrum showed a doublet near the BEs of 576.8 and 586.6 eV corresponding to the Cr ion valence of +3. When $P_{O_2}$ of the post-annealing process was increased, two peaks near the BEs of 579.8 eV and 589.3 eV grew.

![Figure 7](image_url)  
**FIGURE 7.** XPS spectra of Cr 2p core levels in Cr: SrZrO$_3$ (Cr: 0.2 mol%) films. The I-V characteristics of the samples at growth temperatures of 700 °C and 550 °C are appended in (b) and (c), respectively.
significantly, which indicates the formation of Cr$^{6+}$ states. The surface chemistry strongly influences the electrical properties of the film samples. Although the I–V curves of the low $P_{O_2}$ (=5.0 × 10^{-6} Torr) sample exhibit well-defined RS and threshold voltage (figure 8(c)), those of the high $P_{O_2}$ (= 3.3 × 10^2 Torr) sample exhibit ill-formed non-Ohmic characteristics (figure 8(b)). Therefore, we speculate that Cr$^{3+}$ ions, and not Cr$^{6+}$ ions, at the surface improve the RS behaviors of the Cr: SrZrO$_3$ films.

**FIGURE 8.** XPS spectra of Cr: SrZrO$_3$ (Cr: 0.2 mol%) films. The I-V characteristics of the samples in the case of $P_{O_2} = 3.3 \times 10^2$ Torr and $5.0 \times 10^{-6}$ Torr are appended in (b) and (c), respectively.
3. Discussion

We studied the correlation between I-V hysteresis curves and growth condition of 0.2mol% Cr: SrZrO₃ film. The resistive-switching strongly depends on growth condition of films. In previous chapter, we showed that the surface properties strongly depend on the growth condition of Cr: SrZrO₃ films. The surface chemistry caused by migrated Cr ions to the surface might play a key role of resistive switching phenomena. We studied that the valence state of Cr ion can be determined by the growth conditions. Sample 3 and 4 might have ill-formed interface: Sample 3 has segregated phases which contain Cr⁶⁺ ions underneath Pt top electrode and sample 4 has inter-mixing phases such as Sr(Ru,Zr)O₃ over SrRuO₃ bottom electrode. Both samples have ill-formed I-V hysteresis curves. However sample 1 and 2 show superior I-V hysteresis curves. The accumulation of Cr³⁺ on film surface provides a clean interface without any non-stoichiometric oxides. They provide the sharp interface termination with substitutinal Cr³⁺ ions and also higher doping concentrations at the surface region than nominal doping concentrations: ~4%, ~6%, and ~9% for 0.1 mol%, 0.2 mol%, and 0.3 mol%-Cr-doped SrZrO₃ targets, respectively. This sharp interface termination to the electrodes can result good performance of resistive-switching. The increase in the ratio of Cr⁶⁺/Cr³⁺ might indicate the emergence of segregated phases such as CrO₃ or SrCrO₄ [15]. These unstable phases are known to be easily removed by thermal treatments in vacuum. However, annealing under high oxygen pressure allows the existence of an oxygen-rich phase, such that the Cr ions lose more electrons to the oxygen atoms near the surface. Subsequent strong electric fields might release the electrons and create too many electrical leakage paths to sustain the high resistant state, which may be the reason for the absence of RS behavior in this film. On the other hand, Cr³⁺ ions seem to play an important role for the emergence of RS. If Cr³⁺ ions form a charge reservoir and act as charge traps in insulating SrZrO₃ films, an appreciable RS can be caused by the storage (HRS) and release (LRS) of charges through changing Cr valences underneath the top electrode. The charge transfer process caused by valence change of Cr ions has been reported elsewhere [19, 20]. In our Cr: SrZrO₃ films, most of Cr³⁺ ions were distributed underneath the top electrode. Therefore this can help the process of trapping and releasing charges more efficiently in response to the electric field.
4. Summary

In chapter 7, it has been experimentally shown that the RS behavior of Cr: SrZrO₃ depends strongly on the surface chemistry and the valence state of Cr ions. We determined the factors controlling RS behavior in Cr: SrZrO₃ films by measuring the electrical properties of samples grown from targets with various Cr concentrations (0, 0.1, 0.2 and 0.3 mol% in the target), grown at different substrate temperatures (T = 400 °C, 550 °C, and 700 °C), and post-annealed under various oxygen partial pressures (Pₒ₂ = 5.0 × 10⁻⁶ Torr, 2.0 × 10⁻¹ Torr, and 3.3 × 10² Torr). We found that the electrical properties of these films were different. The optimum RS behavior was observed in the films that were grown at high substrate temperature (~700 °C) which induces Cr migration to the surface region and post-annealed at low oxygen partial pressures (Pₒ₂ < 10⁻⁵ Torr) which maintains the valence of Cr ions as 3+. The abundance of the stable Cr^{3+} appears to be prerequisite for appreciable RS behavior in Cr-doped SrZrO₃.
Bibliography


CHAPTER 8

Surface Chemistry of Cr doped SrZrO$_3$ films Modified by an Electric-Field

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1. Introduction

A great number of transition metal oxides have been concerned in the field of non-volatile resistive random access memory (RRAM), which is a potential candidate for future memories and has various advantages such as low power operation, high density integration and high-speed write-erase operation [1-5]. Most of RRAM materials are known as insulators. But after applying high voltage, so called ‘electro-forming’, the resistance of an insulating oxide separates into two stable resistance states, low(LRS) and high resistance state(HRS). People believe that electro-forming process can create the conducting path through films or the itinerant charge carriers in the films [5-8].

![Figure 1](image)

**FIGURE 1.** (a) Unipolar resistive switching behavior. (b) Schematics of the initial state (as-prepared sample) and (1) electro-forming, (2) reset, and (3) set processes [5]

Figure 1 shows a possible driving mechanism for filament-type resistive switching that shows unipolar switching behavior. People believed that filamentary conducting paths form as a soft breakdown in the dielectric material. Then, rupture or formation of the filaments takes place during the reset or set process. The interface problem between insulating oxide and metal electrode has attracted attentions to explain the resistive-switching phenomenon. Epitaxially grown ternary oxides such as transition-metal doped SrTiO$_3$ and SrZrO$_3$ were believed that the interface effects were involved rather than the bulk effects [9,10]. But experimental techniques have been restricted because of laboriousness of detecting the behavior of ions in the interface.
Here, we studied the change of the surface chemistry on Cr doped SrZrO$_3$ films caused by an electric-field using photoemission spectroscopy (PES) and x-ray absorption spectroscopy (XAS). Moreover the valence state of Cr ion was also under the investigation to figure out the correlation between Cr ions and oxygen ions.

2. Experimental details

2.1. Memory cell preparation

Cr: SrZrO$_3$ films were deposited by Pulsed Laser Deposition (PLD) on SrRuO$_3$/SrTiO$_3$(100) or Nb doped SrTiO$_3$(100) single crystal. To investigate the spatial distribution of Cr dopant or oxygen vacancies on the surface, we prepared Cr: SrZrO$_3$ films patterned with Pt pads (D:1mm) (see Figure 2). The bottom electrodes, SrRuO$_3$ or Nb: SrTiO$_3$(100) were grounded. The I-V characteristics were collected using 4-probe station with a current meter (HP4155A).

FIGURE 2. (Up) The diagram of memory cell, Pt/Cr: SrZrO$_3$/ SrRuO$_3$/SrTiO$_3$(100) substrate or Pt/Cr: SrZrO$_3$/ Nb: SrTiO$_3$(100) substrate. (Down) SPEM image of the memory cell mapping with the intensity of O K-edge.
2.2. SPEM (Scanning Photo-Electron Microscopy)

SPEM (scanning photoelectron microscopy) performs x-ray photoelectron spectroscopy and x-ray absorption spectroscopy with a space resolution better than one micrometer. SPEM uses Fresnel zone plate (ZP) to focus x-rays onto a sample (see Figure 3).

![Figure 3: Fresnel zone plate to focus x-rays onto a sample](image)

The photoelectrons from the sample are analyzed using an electron energy analyzer with 16 channels. We get the spectra of XPS from the focused spot and simultaneously get the sample image mapping with the intensity of the spectra of XPS. Therefore, it provides the chemical state distribution (see Figure 4).

![Figure 4: The schematics of SPEM (scanning photoelectron microscopy)](image)

The sample current is also detected, so that one obtains x-ray absorption spectra of the sample in total electron yield mode. Therefore, we also get the spectra of XAS from the
focused spot and simultaneously get the sample image mapping with the intensity of the spectra of XAS.

The SPEM was performed in 8A1 beam line at Pohang Acceleration Laboratory (PAL) in Korea. The Photon flux at the focus was $10^8$ - $10^9$ photons/s and the best space resolution was 0.5 micrometer. A round-shaped beam has 15, 50 or 500 μm diameter. We used 50μm-sized beam for SPEM measurements and 500 μm-sized beam for XPS and XAS measurements.

3. Results

3.1. Gap state induced by an electric-field

We took the position-dependent XAS of Pt/0.3mol%Cr:SrZrO$_3$/Nb:SrTiO$_3$(100) memory cell before and after applying an electric-field. The voltage across the films was applied up to 5V. Figure 5 shows the I-V characteristics of Pt/0.3mol%Cr:SrZrO$_3$/Nb:SrTiO$_3$(100) memory cell. The leakage current is somewhat degraded comparing to the leakage current of Pt/Cr:SrZrO$_3$/SrRuO$_3$/SrTiO$_3$ memory cell. However, two resistance states are clearly observed.

![FIGURE 5. I-V characteristics of Pt/0.3mol%Cr:SrZrO$_3$/Nb:SrTiO$_3$](image-url)
To verify the change of electronic structure of Pt/Cr:SrZrO$_3$/Nb:SrTiO$_3$ before and after applying an electric-field, we took O K-edge XAS spectra (1s→2p) before and after applying an electric-field. Figure 6 shows O K-XAS spectra of 0.3mol% Cr:SrZrO$_3$ films before (dot line) and after (solid lines) applying an electric-field. To see the effects of the electric-field, we took O K-XAS spectra moving the beam position toward Pt electrode (beam size : 500 μm, one step distance : 500μm).

FIGURE 6. O K-XAS spectra of Pt/0.3mol%Cr:SrZrO$_3$/Nb:SrTiO$_3$ memory cell before applying an electric-field (dot line) and O K-XAS spectra of Pt/0.3mol%Cr:SrZrO$_3$/Nb:SrTiO$_3$ memory cell after applying an electric-field up to 5V (solid line). We move a beam position toward to the Pt top electrode by 500μm
According to calculated band structures of SrZrO$_3$, the lower conduction bands show Zr 4$d_{t2g}$ states hybridized with O 2$p$ states. Zr 4$d_{eg}$ states are apart from Zr 4$d_{t2g}$ by crystal field (10Dq was estimated as 4.7eV) [12]. But peaks with the Sr 4$d$ character couldn’t be distinguished from Zr 4$d_{eg}$ feature in the region between 534 eV to 540 eV because Zr 4$d_{eg}$ states are located near Sr 4$d$ state in band structure calculation of SrZrO$_3$ different from O K-edge XAS of SrRuO$_3$ and SrTiO$_3$[13]. Interestingly, new peak is growing at 530.5 eV as being close to Pt electrode after applying an electric-field. In previous chapter, we reported that a prominence below the conduction minimum can come from empty t$_{2g}$ orbital of Cr$^{6+}$ ions. Moreover two Zr 4$d$ peaks corresponding to t$_{2g}$ (532 eV) and e$_g$ (537 eV) orbitals were getting diminished nearby Pt electrode. In the vicinity of Pt electrode, hidden Sr 4$d$ peaks were appeared because of degradation of Zr 4$d$ peaks. Broaden peaks in the region between 538 eV and 545 eV and an arising peak at 530.5 eV seem to appear a new structure on the region of Pt electrode. We observed the film surface containing Cr$^{3+}$ ions before applying an electric-field in chapter 6. There is a possibility that some of Cr$^{3+}$ ions are changed as other valence state such as Cr$^{4+}$, Cr$^{5+}$ or Cr$^{6+}$ underneath the Pt electrode by applying an electric-field.

3.2. SPEM measurements after applying an electric-field

Figure 7 shows the SPEM image of Pt/0.2mol%Cr:SrZrO$_3$/SrRuO$_3$/SrTiO$_3$ memory cell with the photon energy fixed at 529.2eV where new peak was shown in O K-edge spectra. Before taking x-ray absorption spectroscopy, we applied the electric-field except one Pt top electrode (6th pad) for the reference. It shows that spatial distribution of new peak according to strength. All peaks were normalized with peak intensity of Zr 4$d$ t$_{2g}$ orbital in O K-edge spectra. The region with more enhanced new peak has a charging effect which means that this region has a high resistance comparing to the other region. In figure 7, the region A with yellow color has an enhanced new peak comparing to the region C which has the smallest new peak in O K-edge spectra.
Spatial distribution of new pre-edge peak was well agreed with electronic transport properties. We measured I-V characteristic at each pad. As seen in figure 8, I-V curves on Pad A, B and D show the conducting behavior with Ohmic-behavior. However, I-V curves on Pad E and F show the insulating behavior with extremely small leakage current (<nA). Therefore, we can divide the surface region into the conducting area and the insulating area (see figure 8). O 1s, Zr 3d and Sr 3d spectra in photoemission spectroscopy show different behaviors according to the surface areas. In area 1 (the middle area of pad A, B, C and D: the conducting area), Sr 3d and Zr 3d (red solid line) have highly shifted around 2 eV while those (blue solid line) in area 2 (the middle area of pad C, D, E and F: the insulating area) are well settled at low binding energies. Interestingly, the O 1s spectra in both areas were almost unchanged. Taking core-level spectra of Sr 3d and Zr 3d in the vicinity of Pt pads (A, B, C, D, E and F) as seen in figure 8 show similar tendencies, high-binding energy (A and B: solid lines of yellow and green) for the conducting area and low-binding energy (C, D, E and F: solid lines of other colors) for the insulating area while the O 1s spectra in both areas were almost unchanged.
It implies that surface chemistry of the conducting area can be different from that of the insulating area. We could not explain this result with the creation oxygen vacancies because the binding energy of O 1s spectra is almost unchanged. In chapter 6, the high binding energy shift of Sr 3d, Zr 3d and O 1s by 0.2 eV indicate the creation of oxygen vacancies. Therefore, we deduced that local structure of SrZrO$_3$ has been modified by an electric-field. Especially Zr and Sr ions are strongly influenced by an electric-field. However, we could not find any evidences for the change of chemical state of Cr ions on the surface region.
4. Discussion

Previously we observed a new peak on the surface region of Cr:SrZrO$_3$ which exhibited the reversible RS behavior. The film after applying an electric-field has a new emerged peak around 529.2 ~530.5 eV compared with the spectra of the film before applying an electric-field. This new peak doesn’t originate from the inter-mixing states between Cr:SrZrO$_3$ and electrodes. In the vicinity of Pt electrode, the total intensity of O K-edge spectra was degraded and two peaks corresponding to Zr 4d$_{t2g}$ (532eV) and 4d$_{eg}$ (536.7eV) almost disappeared after applying an electric-field. We can explain that the structure of SrZrO$_3$ was deformed on the surface region and new structure may arise on the surface region. This new structure can be the origin of new peak in O K-edge spectra. One explanation for surface modification is that some of Cr$^{3+}$ ions are changed to other valence state, Cr$^{4+}$, Cr$^{5+}$ or Cr$^{6+}$. This valency mixture of Cr ions can enhanced new peak below the conduction band minimum of SrZrO$_3$. However, we could not find any evidences of valence change of Cr ions because of small intensity of Cr L-edge spectra. However, in chapter 6, we verified that Cr doped SrZrO$_3$ has a lot of Cr ions on the surface, 6%, more than nominal doping concentration of target, 0.2 mol%. We confirmed that as-deposit Cr:SrZrO$_3$ films have Cr$^{3+}$-rich surface. Therefore after applying an electric-field, the surface chemistry underneath Pt electrode can be influenced by accumulated Cr$^{3+}$ ions indirectly.

4. Summary

We observed the surface modification of Cr:SrZrO$_3$ films after applying an electric-field. This chemical reaction may be related with Zr and Sr ions. SPEM and position-dependent photoemission spectroscopy on patterned Cr:SrZrO$_3$ films show that the electrical measurement was obviously connected with the chemical reaction on the surface region.
Bibliography


Conclusion

In this thesis, transition metal doped refractory oxides (Cr doped TiO$_2$, V doped TiO$_2$, Cr doped SrTiO$_3$ and Cr doped SrZrO$_3$) and oxygen-deficient TiO$_2$ were investigated. Polycrystalline samples are prepared because they can easily be fabricated in large scale. For studies where the surface properties are important, single crystals or thin films are prepared. Their structural, physical and electronic properties were measured by bulk-sensitive techniques (X-Ray Diffraction, SQUID magnetometry and EPR) or surface-sensitive techniques (Photoemission spectroscopy and x-ray absorption spectroscopy in total electron yield).

Polycrystalline Cr:TiO$_2$ and V:TiO$_2$ were studied by X-ray diffraction, SQUID and EPR (chapter 3). The SQUID measurements show that Cr:TiO$_2$ and V:TiO$_2$ have strong paramagnetic behaviors. They also exhibit a weak ferromagnetic contribution which is found even at room temperature. However, their magnetic moments per doping ion are extremely small. The SQUID measurements show not only their magnetic properties but also the valence state of dopant. We guess that there are Cr$^{3+}$ ions and a small number of higher valence states of Cr ions in Cr:TiO$_2$. In the case of V:TiO$_2$, V$^{4+}$ and some V$^{5+}$ may substitute Ti$^{4+}$ ions in V:TiO$_2$. EPR spectra suggest the presence of some ions with a higher valence than 3+ in the case of Cr:TiO$_2$. It seems that Cr$^{3+}$ ions mainly substitute Ti$^{4+}$ ions and higher valence state of Cr ions can exist in the grain boundaries or metallic clusters in Cr:TiO$_2$.

In the case of polycrystalline samples, we could not extract the effect of grain boundaries in which a lot of defects exist. Therefore, we undertook to grow single crystals of Cr:TiO$_2$ by the floating zone method (chapter 4). We have studied Cr:TiO$_2$ system by growing single crystals under different atmospheres, O$_2$ flow and Ar flow during the synthesis of single crystals. The type of gas flow is important to decide the magnetic properties of Cr:TiO$_2$ single crystals. This Cr:TiO$_2$ system grown under Ar flow shows strong paramagnetic behavior with valence state of Cr$^{3+}$. However Cr:TiO$_2$ system grown under O$_2$
flow contains a mixture of Cr valence states which can exist in the form of clusters within the single crystal. The formation of cluster can explain the ferromagnetic signals. The ferromagnetic signal of Cr:TiO$_2$(O$_2$) is stronger than that of polycrystalline samples. But in all cases, Cr:TiO$_2$ single crystals exhibit only a weak ferromagnetic contribution.

For technological applications, this kind of system is often prepared in the form of thin films which may exhibit properties different from those of the bulk material. As film preparation by pulse laser deposition (PLD) required the use of a polycrystalline target, polycrystalline Cr:SrTiO$_3$ samples were synthesized by a standard solid state reaction in air. polycrystalline 10.0 mol% Cr:SrTiO$_3$ has unintentional compositions with various valences of Cr ions, for example, SrCrO$_4$. Cr:SrTiO$_3$ films were grown by pulsed laser deposition method and subsequently post-annealed under O$_2$ poor (~10$^{-6}$ Torr) and O$_2$ rich (2.0 × 10$^2$ Torr) atmosphere. Unintentionally formed second phases with various valence states of Cr were removed when Cr:SrTiO$_3$ films were post-annealed under O$_2$ poor environment. Therefore we were able to obtain the single valence state, Cr$^{3+}$, doped SrTiO$_3$ films when they are post-annealed under O$_2$ poor environment.

The properties of film samples are strongly influenced by the conditions of film synthesis. Therefore we studied the behavior of Cr dopant in Cr:SrZrO$_3$ films by changing the growth temperature and oxygen pressure during the film synthesis. Cr doped SrZrO$_3$ films were deposited by PLD and analyzed by \textit{in-situ} XPS. During the deposition and the post-annealing process, behavior of Cr dopants in SrZrO$_3$ film was quite different. When growth temperature is increased up to 700 $^\circ$C, Cr ions migrate to the surface area of Cr:SrZrO$_3$ film. These migrated Cr ions have different valence states depending on the oxygen pressure during the post-annealing process. The Cr ions exist as Cr$^{3+}$ or Cr$^{6+}$ in the film surface. The exposure to oxygen gas can produce Cr related oxides such as CrO$_3$ or SrCrO$_4$ in the film surface.

This formation of Cr related oxides can be harmful for the performance of memory devices. Therefore, we study the correlation between the surface chemistry of deposited films and I-V characteristics by changing the deposition conditions (chapter 7). It has been shown that the resistive-switching (RS) behavior of Cr:SrZrO$_3$ depends strongly on the surface chemistry and the valence state of Cr ions. We determined the factors controlling RS behavior in Cr:SrZrO$_3$ films by measuring the electrical properties of samples grown from targets with various Cr concentrations (0, 0.1, 0.2 and 0.3 mol% in the target), at different substrate temperatures (T = 400 $^\circ$C, 550 $^\circ$C, and 700 $^\circ$C), and post-annealed under various
oxygen partial pressures ($P_{O2} = 5.0 \times 10^{-6}$ Torr, $2.0 \times 10^{-1}$ Torr, and $3.3 \times 10^{2}$ Torr). We found that the electrical properties of these films were different. The optimum RS behavior was observed in the films that were grown at high substrate temperature (~700 °C) which induces Cr migration to the surface region and post-annealed at low oxygen partial pressures ($P_{O2} < 10^{-5}$ Torr) which maintains the valence of Cr ions as $3^+$. The abundance of the stable Cr$^{3+}$ appears to be prerequisite for appreciable RS behavior in Cr-doped SrZrO$_3$.

The surface chemistry of Cr:SrZrO$_3$ films has been investigated before and after applying an electric-field (chapter 8). Photoemission spectroscopy (PES) and X-ray absorption spectroscopy (XAS) show that there are some surface modifications of Cr:SrZrO$_3$ films after applying an electric-field. This chemical reaction may be related with Zr and Sr ions. By investigation with SPEM and I-V characteristics on patterned Cr:SrZrO$_3$ films we found that the electrical measurement was obviously connected with the chemical reaction on the surface region.

As it appears as a determinant parameter, we verify the valence state of Cr ions in polycrystals, single crystals, and thin films. In film studies, we find the key parameters of the sample synthesis which control the valence state of Cr ions in Cr:SrTiO$_3$ and Cr:SrZrO$_3$ films. The increase of the ratio of Cr$^{6+}$/Cr$^{3+}$ might indicate the emergence of segregated phases such as CrO$_3$ or SrCrO$_4$. These secondary phases were easily found in Cr:SrTiO$_3$ and Cr:SrZrO$_3$ polycrystals and thin films. We found that these phases were formed when the sample was synthesized under O$_2$ rich environment. Cr ions tend to be oxidized easily under O$_2$ rich environment.

This thesis provides an important insight into transition metal doped refractory oxides. We showed that the chemical state of dopant can be easily controlled by conditions of sample synthesis. We also describe in detail how different chemical states of Cr dopant can induce the changes in the physical properties of samples, for examples, resistive-switching phenomena. Therefore to control the behavior of dopant ions appears as a mandatory task for the applications in many industrial areas.
Résumé
(Summary in french)


Parmi ces applications, l'utilisation comme catalyseurs est l'application la plus importante dans de nombreuses technologies de pointe car la réaction photocatalytique est un moyen potentiel de résoudre les problèmes énergétiques et environnementaux. TiO2 et SrTiO3 ont été largement et longuement étudiés dans le domaine de la photocatalyse [6-8]. Comme ils sont semi-conducteurs à large gap (3,5 eV pour le TiO2 et 3,2 eV pour SrTiO3), la lumière UV est nécessaire pour générer des paires électrons/trous par photoexcitation. Pour les applications industrielles, l'absorption de la lumière visible est souhaitable. Par conséquent, pour le développement des photocatalyseurs en lumière visible, le dopage de TiO2 et SrTiO3 par des ions de métaux de transition a été proposé. Il a été rapporté que le dopage avec des ions de métaux de transition est un moyen efficace pour améliorer l'activité photocatalytique dans la région visible à cause du décalage vers le rouge de la limite d'absorption [5]. L'ordre d'efficacité dans le décalage vers le rouge a été estimé comme suit: V> Cr> Mn> Fe> Ni [9].
FIGURE 1. Absorbance UV-Vis des échantillons TiO₂ dopés aux V, Cr, Fe, et N. En comparaison avec TiO₂, la limite d’absorption de TiO₂ dopé V, Cr, Fe, et N est apparue dans la région de la lumière visible à environ 500-600 nm [10].

Par ailleurs, une forme inattendue de ferromagnétisme à température ambiante a été signalée dans des oxydes réfractaires dopés par des cations de métaux de transition, qui sont alors qualifiés de «semiconducteurs magnétiques dilués (DMS)». Il existe de nombreux systèmes qui ont été proposés en tant que matériaux DMS. Par exemple, TiO₂, ZnO, SnO₂, BaTiO₃, SrTiO₃, et KTaO₃ dopés au Co, Fe, Mn, Cr, V, La, ou Mn présentent du ferromagnétisme à température ambiante d’après certains auteurs [11-14]. Matsumoto et al
ont été les premiers à rapporter cette propriété pour TiO₂ dopé au Co. Après cette première découverte, de nombreux chercheurs ont rapporté des moments magnétiques effectifs inhabituels et même des températures de Curie supérieures à la température ambiante dans TiO₂ dopé par différents ions de métaux de transition. Une des explications pour l’existence de ces DMS est que des polaron magnétiques délimités peuvent servir de médiateurs de l’interaction entre dopants [15]. D’un autre côté, Kim et al ont rapporté que des clusters de cobalt peuvent induire le comportement ferromagnétique dans les couches de TiO₂ dopé au Co [16]. D’autres rapports suggèrent que le dopant n’est pas important pour le ferromagnétisme de ce type de couche [17].

En outre, les oxydes comportant des défauts ont de nombreux avantages pour des applications industrielles en raison de la facilité de contrôle des porteurs de charge. TiO₂, SrTiO₃, et SrZrO₃ totalement oxydés, sont des isolants possédant une haute résistivité d’environ 10¹³ ohm·cm à température ambiante. Une fois qu’ils sont réduits dans certaines conditions [18], de nombreux ions oxygène sont éliminés des échantillons. Par conséquent, la résistivité diminue de manière spectaculaire jusqu’à quelques ohm·cm. Le nombre d’électrons de conduction créés peut atteindre le double du nombre de lacunes d’oxygène.
[19]. Par conséquent, une transition isolant-métal peut être obtenue par la création de ces lacunes comme le montre la figure 4.

![Figure 4. Transition isolant-métal dans des monocristaux de SrTiO$_3$. Mesures de la résistance en fonction de la température: (1) cristal stœchiométrique initial présentant un comportement isolant, (2) cristal après traitement thermique à des températures élevées dans des conditions réductrices présentant un comportement métallique, (3) cristal après ré-oxydation dans des conditions ambiantes et (4) après électroréduction à la température ambiante dans des conditions de vide poussé à tension constante avec restauration de la conductance métallique. [20]]

Les TiO$_2$, SrTiO$_3$, et SrZrO$_3$ déficients en oxygène sont également connus comme matériaux pour mémoires RAM à commutation de résistivité (RRAM : «Resistive-switching Random Access Memory ») [20]. Des pérovskites dopées par des ions de métal de transition présentent également des phénomènes de commutation de résistivité. Cr: SrTiO$_3$ et Cr: SrZrO$_3$ sont largement étudiés en tant que matériaux RRAM. Le rôle du dopant et des lacunes d'oxygène n’est pas clairement identifié. Meijer et al. ont suggéré que la commutation de résistivité provient d'un processus de piégeage/dépiégeage d'électrons grâce à des
changements de valence des ions Cr dans un monocristal Cr: SrTiO₃[21]. Janousch et al, cependant, ont par la suite déclaré que le phénomène avait plutôt pour origine un déplacement de lacunes d’oxygène[22]. En outre, certains autres groupes ont indiqué que la commutation de résistivité provenait d’états de valence mixte de cations tels que Cr, Ce, et Mn [23-24].

Lors de ce travail, des systèmes à base de TiO₂, SrTiO₃ déficients en oxygène et des systèmes de TiO₂, SrTiO₃ et SrZrO₃ dopés par des ions de métaux de transition (Cr ou V) ont été étudiés. Nous avons préparé et caractérisé des échantillons sous formes de monocristaux, de céramiques polycristallines et de couches minces avec des objectifs différents.


Après l’étude des matériaux massifs, les propriétés de films minces dopés au Cr sont discutées dans le chapitre 6. Parmi les oxydes réfractaires dopés au Cr, nous avons sélectionné Cr: SrZrO₃ pour cette étude parce que les propriétés de films Cr: SrZrO₃ dopés à 0.2mol% ont été intensivement étudiées dans le domaine des RRAM. Les propriétés des films ont été mesurées par diffraction des rayons X, spectroscopie de photoémission et spectroscopie d'absorption des rayons X. La spectroscopie de photoémission est très sensible à la chimie de surface. Par conséquent, nous avons préparé des films sous vide et les avons mesurés par spectroscopie de photoémission sans casser le vide pour éviter la présence d'espèces chargées adsorbées. Nous avons essayé de trouver les conditions de synthèse qui
contrôlent le comportement des ions Cr. Ensuite, les propriétés RRAM des films Cr:SrZrO$_3$ sont examinées au chapitre 7. Différents comportements de commutation de résistivité des films 0.2mol% Cr:SrZrO$_3$ sont présentés en fonction de leur chimie de surface. Nous avons trouvé des conditions de synthèse permettant d’obtenir un effet de commutation de résistivité appréciable. Dans le dernier chapitre, nous présentons les modifications de la chimie de surface par un procédé d’électro-formage. Nous avons constaté l’existence d’une certaine corrélation entre les caractéristiques I-V et la chimie de surface, ce qui signifie que les propriétés d’interface jouent un rôle crucial sur le mécanisme de commutation de résistivité.

Comme nous l’avons indiqué, dans le chapitre 3, les propriétés de Cr:TiO$_2$ et V:TiO$_2$ massifs sont étudiées. Nous avons préparé des échantillons polycristallins de Cr:TiO$_2$ et V:TiO$_2$ par la méthode de réaction à l'état solide. Il est connu que les ions Cr et V ont une grande solubilité dans les films de TiO$_2$ rutile jusqu'à 50% pour V:TiO$_2$ et 20% pour le Cr:TiO$_2$. A l’inverse dans les matériaux massifs dopés au chrome, nous avons observé la présence d’une phase secondaire identifiée comme Ti$_{0.78}$Cr$_{0.12}$O$_{1.74}$ pour des concentrations en dopant supérieures à 5,0 mol% (fig.5). La différence observée par rapport aux films minces peut provenir des conditions plus réductrices dans lesquelles ceux-ci sont préparés. Dans le cas de V:TiO$_2$, les échantillons ne présentent pas d'autres phases.

Les mesures au SQUID montrent une forte composante paramagnétique dans Cr:TiO$_2$ et V:TiO$_2$ (tableau 1). Le moment magnétique effectif moyen dans Cr:TiO$_2$ est proche de celui des ions Cr$^{3+}$ alors que le moment magnétique effectif moyen dans V:TiO$_2$ est inférieur à celui de V$^{4+}$. Une certaine quantité d'ions V$^{5+}$ pourrait exister dans V:TiO$_2$. 
FIGURE 5. Diffractogrammes de rayons X (a) x mol% Cr:TiO\textsubscript{2}; (b) 5 mol% et (c) 10 mol% Cr:TiO\textsubscript{2} après plusieurs traitements thermiques à 1100°C (pour faciliter la comparaison les pics de TiO\textsubscript{2} autour de 27,4 ° ont été recalés). Les triangles indiquent les pics provenant de la phase Ti\textsubscript{0.78}Cr\textsubscript{0.12}O\textsubscript{1.74} (ICDD/JCPDS 30-0413).

<table>
<thead>
<tr>
<th>x mol% Cr:TiO\textsubscript{2}</th>
<th>(μ\textsubscript{B}/Cr)</th>
<th>x mol% V:TiO\textsubscript{2}</th>
<th>(μ\textsubscript{B}/V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0,5</td>
<td>3,84</td>
<td>0,5</td>
<td>1,36</td>
</tr>
<tr>
<td>1,0</td>
<td>3,60</td>
<td>1,0</td>
<td>1,47</td>
</tr>
<tr>
<td>2,0</td>
<td>3,80</td>
<td>5,0</td>
<td>1,38</td>
</tr>
<tr>
<td>5,0</td>
<td>3,92</td>
<td>10,0</td>
<td>1,40</td>
</tr>
</tbody>
</table>

TABLEAU 1. Moment magnétique effectif dans Cr:TiO\textsubscript{2} et V:TiO\textsubscript{2} polycrystallins. Le moment magnétique effectif calculé de Cr\textsuperscript{3+} est de 3,87 μ\textsubscript{B} et celui de V\textsuperscript{4+} de 1,73 μ\textsubscript{B}.

Nous avons enregistrés les spectres RPE des échantillons de Cr:TiO\textsubscript{2} (fig.6). Nous pouvons voir 5 résonances, B, C, D, E, et F qui sont attribués à des ions Cr\textsuperscript{3+} occupant un site de substitution du titane dans TiO\textsubscript{2} [19]. La résonance A, dont la position est très proche de celle attendue pour un électron libre, est en général attribuée à la présence d’ions chrome de valence plus élevée pouvant appartenir à des trimères de valence mixte [26]. Par conséquent, Cr:TiO\textsubscript{2} contient un mélange de valences du Cr qui peut exister sous les formes d’ions Cr interstitiels ou de clusters dans TiO\textsubscript{2}.
Les échantillons polycristallins de Cr:TiO₂ et V:TiO₂ ne montrent que de très faibles traces d’une composante ferromagnétique, ce qui les distingue des films Cr:TiO₂ et V:TiO₂ qui d’après certains auteurs présentent un fort comportement ferromagnétique.

Dans le cas de Cr:TiO₂ polycristallin, nous avons observé un mélange de valences des ions Cr éventuellement répartis en surface ou aux joints de grains. En général, les propriétés physiques sensibles aux états de surface peuvent varier avec la morphologie, la composition et la structure de la région de surface qui dépendent de la procédure de préparation. Dans le cas d’échantillons polycristallins, il n’est pas possible de séparer simplement l’effet des joints de grains. Par conséquent, pour les études où les propriétés de surface sont importantes, des monocristaux ou des couches minces sont nécessaires. Il est alors possible d’étudier des échantillons avec des surfaces bien ordonnées cristallographiquement.

Dans le chapitre 4, nous présentons l’étude de monocristaux de Cr:TiO₂ dont nous avons effectué la croissance parla méthode de la zone flottante. Deux types de gaz, oxygène et argon, ont été utilisés afin de faire varier la pression partielle d’oxygène lors de la croissance des cristaux. Un monocristal de TiO₂ obtenu sous flux d’oxygène (désigné par
Cr0,00% (O2) par la suite) présente les caractéristiques d’un monocristal totalement oxydé. En revanche, un monocristal de TiO2 obtenu sous flux d’argon (Cr0,00%(Ar) à partir de maintenant) apparaît comme partiellement réduit. La nature du gaz sous lequel est effectuée la croissance a une influence sur les propriétés physiques du cristal.

Comme on le voit sur la figure 7, des monocristaux Cr:TiO2 de même dopage (0,30% molaire) montrent des aimantations différentes selon le type de gaz utilisé lors de la synthèse des cristaux. Le paramagnétisme de Cr0,30%(Ar) est beaucoup plus grand que celui de Cr0,30%(O2). Ces échantillons présentent de faibles composantes ferromagnétiques dont la valeur à saturation à 300K est d'environ 0,07 emu/mole pour Cr0,3%(O2), 0,09 emu/mole pour Cr0,65%(O2), 0,008 emu/mole pour Cr1,0%(O2), 0,009 emu/mole pour Cr0,3%(Ar), 0,03 emu/mole pour Cr0,65 (Ar) et de 0,01 emu / mole pour Cr1,0%(Ar). Cr0,65%(O2) et Cr0,65%(Ar) ont les valeurs les plus élevées tandis que Cr1,0%(O2) et Cr1,0%(Ar) ont les plus petites valeurs de leur groupe.

![FIGURE 7. Susceptibilité magnétique en fonction de la température pour les monocristaux 0,3 mol%Cr:TiO2 préparés sous argon et sous oxygène.](image)

Nous avons estimé l’état de valence des ions Cr dans les différents monocristaux à partir de mesures SQUID (tableau 2). Les cristaux Cr:TiO2(Ar) ont des moments magnétiques effectifs un peu inférieurs à 3,87 μB (moment magnétique effectif de Cr3+) tandis que les cristaux Cr:TiO2(O2) ont des moments magnétiques effectifs nettement plus...
faibles. Par conséquent, la valence des ions Cr semblent plus élevées que 3+ dans Cr:TiO$_2$(O$_2$).

<table>
<thead>
<tr>
<th>échantillons</th>
<th>$\mu_{\text{eff}}$ ($\mu_B$/Cr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr 0,30%(Ar)</td>
<td>3,377</td>
</tr>
<tr>
<td>Cr0,65%(Ar)</td>
<td>3,397</td>
</tr>
<tr>
<td>Cr1,00%(Ar)</td>
<td>3,141</td>
</tr>
<tr>
<td>Cr0,30%(O$_2$)</td>
<td>2,076</td>
</tr>
<tr>
<td>Cr0,65%(O$_2$)</td>
<td>1,976</td>
</tr>
<tr>
<td>Cr1,00%(O$_2$)</td>
<td>2,665</td>
</tr>
</tbody>
</table>

TABLEAU 2. Moments magnétiques effectifs dans les monocristaux Cr:TiO$_2$. Les moments magnétiques effectifs calculés valent 3,87$\mu_B$, 2,83$\mu_B$, 1,73 $\mu_B$, et 0 $\mu_B$ pour Cr$^{3+}$, Cr$^{4+}$, Cr$^{5+}$, et Cr$^{6+}$, respectivement.

Nous avons enregistré les spectres RPE des monocristaux Cr:TiO$_2$. Ceux-ci sont dominés par les cinq résonances B, C, D, E et F (figure 8). La différence entre les deux types de monocristaux provient de la résonance A attribuée comme pour les polycristaux à la présence d’ions Cr de valence plus élevées que 3+. Il semble donc qu’il y a un mélange de valences des ions Cr dans les monocristaux Cr:TiO$_2$(O$_2$). L’analyse des données peut être compliquée par la présence d’ions Ti$^{3+}$ qui peuvent également être à l’origine de la résonance A. Il est enfin important de noter que des ions Cr$^{6+}$ isolés ne donnent aucun signal en RPE.
FIGURE 8. Spectres RPE des cristaux Cr:TiO₂ broyés enregistrés à 100K.

En tenant compte des résultats de RPE, nous avons analysé les moments magnétiques effectifs des cristaux du tableau 2 en supposant qu’ils correspondaient à des mélanges de Cr³⁺ et Cr⁶⁺. La fraction de Cr⁶⁺ a été calculée avec l’équation :

\[ f(\text{Cr}^{6+}) = 1 - \frac{\mu_{\text{eff}}}{3.87} (3.87 \mu_B: \text{Cr}^{3+}). \]

Les résultats sont présentés dans le tableau 3. Les fractions de Cr⁶⁺ dans Cr:TiO₂(O₂) sont beaucoup plus grandes que celles de Cr:TiO₂(Ar). Près de la moitié des ions Cr peut exister sous la forme de Cr⁶⁺ dans Cr0,3%(O₂) et Cr0,65%(O₂). On ne doit cependant pas oublier que d’autres états de valence peuvent être présents dans le cas des cristaux Cr:TiO₂(O₂). Les calculs ont par ailleurs été effectués avec les teneurs nominales en chrome des cristaux, les concentrations réelles peuvent être différentes.
En résumé, nous avons étudié les propriétés de monocristaux Cr:TiO₂ préparés sous deux atmosphères différentes. Il apparaît clairement que celles-ci ont une influence sur les propriétés physiques des cristaux. Une atmosphère d’argon favorise l’existence des ions Cr sous la forme d’ions Cr³⁺. Ce système de TiO₂ dopé au Cr³⁺ montre un fort comportement paramagnétique. Les faibles composantes ferromagnétiques détectées dans tous les cristaux sont plus fortes dans les cristaux préparés sous oxygène que dans ceux préparés sous argon.

Dans le chapitre 5, nous présentons l’étude d’échantillons Cr:SrTiO₃ polycristallins préparés sous air. Les diagrammes de diffraction des rayons X montrent la présence d’une phase pérovskite unique sauf pour le polycristal 10,0 mol%Cr:SrTiO₃ pour lequel de petits pics supplémentaires révèlent la présence d’une seconde phase identifiée comme SrCrO₄ qui contient des ions Cr⁶⁺ (figure 9).
Nous avons déduit les moments magnétiques effectifs des mesures au SQUID (tableau 4). Les polycristaux Cr:SrTiO₃ ont des moments effectifs nettement inférieurs à 3,87 \(\mu_B\), valeur attendue pour Cr\(^{3+}\). Cela donne à penser qu'une partie des ions Cr se trouvent dans des états de valence plus élevée.

<table>
<thead>
<tr>
<th>Doping rate (mol%)</th>
<th>(\mu_{\text{eff}}) ((\mu_B/\text{Cr}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0,5</td>
<td>3,390</td>
</tr>
<tr>
<td>1,0</td>
<td>2,630</td>
</tr>
<tr>
<td>2,0</td>
<td>2,316</td>
</tr>
<tr>
<td>5,0</td>
<td>1,589</td>
</tr>
<tr>
<td>10,0</td>
<td>1,158</td>
</tr>
</tbody>
</table>


Nous avons calculé les fractions minimum et maximum d’ions Cr\(^{6+}\) dans les échantillons en supposant que les ions Cr ne se trouvent que sous formes de Cr\(^{4+}\) (ou Cr\(^{3+}\)) et Cr\(^{6+}\). Dans le tableau 5, la fraction de Cr\(^{6+}\) augmente rapidement avec le dopage. La moitié des ions Cr peut exister sous une forme de Cr\(^{6+}\) pour les polycristaux Cr:SrTiO₃ substitués à
5,0 mol% et 10,0 mol%. Par conséquent, il est clair que les ions Cr peuvent exister en tant que mélange d'états de valence du Cr. Cela indique qu'il est difficile d'obtenir une solution solide de SrTiO₃ dopée uniquement par des ions Cr³⁺ quand le dopage augmente.

<table>
<thead>
<tr>
<th>Doping of Cr (mol%)</th>
<th>fraction minimum (%)</th>
<th>fraction maximum (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,0</td>
<td>7,1</td>
<td>32,0</td>
</tr>
<tr>
<td>2,0</td>
<td>18,2</td>
<td>40,2</td>
</tr>
<tr>
<td>5,0</td>
<td>43,9</td>
<td>58,9</td>
</tr>
<tr>
<td>10,0</td>
<td>59,1</td>
<td>70,1</td>
</tr>
</tbody>
</table>

**TABLEAU 5. Fraction estimée de Cr 6⁺ dans Cr:SrTiO₃.**

Le mélange de valences des ions Cr a été confirmé par spectroscopie d’absorption des rayons X (XAS). Les spectres d’absorption sont présentés sur la figure 10 qui révèlent la présence simultanées des valences 3⁺, 4⁺ et 6⁺.

**FIGURE 10.** Seuils d’absorption L du chrome (transition 2p-3d) des polycristaux Cr:SrTiO₃, substitués : (a) 10,0 mol%, et (b) 5,0mol%; Seuils L de références : (c) K₂CrO₄ with contenat Cr⁶⁺ [27], (d) CrO₂ film avec Cr⁺⁺, et (e) Cr₂O₃ film avec Cr³⁺. En comparant avec les références, nous pouvons attribuer les pics (1, 2, 3, 7, et 8) à Cr³⁺, les pics (1,2,3,5,7 et 8) à Cr⁴⁺ et les pics (4, 6, 8, et 9) à Cr⁶⁺.
Après l’étude des polycristaux, des films Cr: SrTiO₃ ont été synthétisés par dépôt dans une chambre à vide. Nous avons prévu que la phase secondaire qui contient des ions Cr⁶⁺ disparaîtrait sous faible pression d’oxygène (10⁻⁶~10⁻⁷ Torr). Nous avons déposé des films Cr: SrTiO₃ substitué 10,0 mol% à partir d’un polycristal qui contenait diverses valences du Cr. Les films ont été préparés à 700 °C sous P₀₂ = 2,0 × 10⁻¹ Torr. Puis l’un des échantillons de film a été recuit à 400 °C sous P₀₂ = 5 × 10⁻⁶ Torr et un autre échantillon a été recuit à 400 °C sous P₀₂ = 2 × 10² Torr. Les mesures XPS et XAS montrent que le film recuit sous P₀₂ = 5 × 10⁻⁶ Torr ne contient que des ions Cr³⁺ tandis que celui recuit sous P₀₂ = 2 × 10² Torr a deux valences, Cr³⁺ et Cr⁶⁺ comme on le voit sur la figure 11. Par conséquent, nous pouvons conclure qu’en l’absence d’oxygène lors de la synthèse, il est facile de supprimer la deuxième phase et d’obtenir le système SrTiO₃ dopé au Cr³⁺.

A partir du chapitre 6 nous décrivons les résultats obtenus sur des films Cr: SrZrO₃ qui ont été testés pour des applications industrielles pour les dispositifs, RRAM. Les propriétés du film ont été étudiés par des techniques de surface, comme la spectroscopie de photoémission et également par spectroscopie d’absorption des rayons X. Les films ont été préparés par dépôt laser pulsé (PLD) et caractérisés par spectroscopie de photoémission sans rompre le vide pour éviter la présence d’espèces chargées adsorbées.

![Figure 11. Spectres XPS et XAS des films 10,0 mol% Cr: SrTiO₃ recuits](image)

(a) sous P₀₂ = 5 × 10⁻⁶ et (b) sous P₀₂ = 2 × 10² Torr.
Comme les oxydes étudiés dans les chapitres précédents, les films Cr:SrZrO₃ montrent des comportements différents du dopant Cr, en fonction des conditions de croissance. En particulier, les ions Cr migrent vers la surface des films Cr:SrZrO₃ lorsque la température de croissance atteint 700 °C (figure 12). Nous avons estimé les rapports des concentrations [Cr]/[Sr] à la surface des films à environ 4%, 6%, et 9% pour des films obtenus à partir de cibles à 0,1mol%, 0,2mol% 0,3mol% Cr:SrZrO₃. D’autre part, les ions Cr ayant migré ont des états de valence différents selon la pression partielle d’oxygène imposée lors des recuits ultérieurs. Les ions Cr existent en tant que Cr³⁺ ou Cr⁶⁺ au voisinage de la surface lorsque les recuits ont été effectués dans un environnement riche en oxygène (figure 12). L’exposition de l’oxygène peut induire la formation d’oxydes de chrome tels que CrO₃ ou SrCrO₄ à la surface du film.

FIGURE 12. (A gauche) Spectres XPS de Cr 2p des films 0.2mol%Cr:SrZrO₃/SrRuO₃/SrTiO₃(100) déposés à différentes températures du substrat : (a) 400 °C, (b) 550 °C, et (c) 700 °C. (A droite) spectres des films 0.2mol% Cr:SrZrO₃/SrRuO₃/SrTiO₃(100) recuits sous différentes pressions d’oxygène: (a) avant recuit, (b) sous 5,0 × 10⁻⁶ torr, ( c) sous 2 × 10⁻¹ torr, et (d) sous 3,3 × 10² torr. (Toutes les intensités des pics ont été normalisées par rapport à la surface des pics 3d des spectres Zr)
Dans le chapitre 7, nous présentons l’étude de la corrélation entre les propriétés électriques et la chimie de surface, principalement les caractéristiques I-V. Celle existant entre la commutation de résistivité et la chimie de surface des films 0.2mol% Cr: SrZrO₃ films est montrée. La migration des ions Cr à la surface semble jouer un rôle clé dans les phénomènes de commutation de résistivité. La migration des ions Cr³⁺ substituant Ti⁴⁺ à la surface peut fournir une interface claire, sans oxydes non stœchiométriques. Une terminaison nette de l’interface entre les films et les électrodes résultent dans de bonnes performances de la commutation de résistivité.

Comme on le voit dans le tableau 6 (conditions de croissance) et la figure 13 (caractéristiques I-V), l’échantillon 1 a une tension « SET » (tension de transition de l’état de haute résistance (HRS) vers l’état de faible résistance (LRS) d’environ 3,5 V alors que celle de l’échantillon 2 est d'environ -3,5 V. La tension de réinitialisation (RESET: tension de retour à l’état HRS) est de -4 V pour l’échantillon 1 et de +4 V pour l’échantillon 2. En dépit des polarités différentes des tensions de SET et RESET, la quantité de courant de fuite est presque la même.

| Tableau 6. Conditions de préparation de quatre films 0.2mol% Cr: SrZrO₃ films.
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Echantillon</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Depôt P(O₂) (Torr)</td>
<td>2.5×10⁻¹</td>
<td>2.5×10⁻¹</td>
<td>2.5×10⁻¹</td>
<td>2.6×10⁻¹</td>
</tr>
<tr>
<td>Température</td>
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<td>700°C</td>
<td>700°C</td>
<td>700°C</td>
</tr>
<tr>
<td>Durée</td>
<td>7 min</td>
<td>20 min</td>
<td>20 min</td>
<td>20 min</td>
</tr>
<tr>
<td>Réfrigérissement P(O₂) (Torr)</td>
<td>3.2×10⁻¹</td>
<td>3.2×10⁻¹</td>
<td>5.0×10⁻¹</td>
<td>3.2×10⁻⁷</td>
</tr>
<tr>
<td>Température</td>
<td>Until 300°C</td>
<td>Until 300°C</td>
<td>Until 400°C</td>
<td>Until RT</td>
</tr>
<tr>
<td>Durée</td>
<td>30 min</td>
<td>30 min</td>
<td>30 min</td>
<td>30 min</td>
</tr>
<tr>
<td>Refroidissement P(O₂) (Torr)</td>
<td>vacuum</td>
<td>vacuum</td>
<td>5.0×10⁻²</td>
<td>vacuum</td>
</tr>
<tr>
<td>Température</td>
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<td>400°C</td>
<td>400°C</td>
<td>400°C</td>
</tr>
<tr>
<td>Durée</td>
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<td>30 min</td>
<td>30 min</td>
<td>30 min</td>
</tr>
<tr>
<td>Valence du Cr</td>
<td>Cr³⁺</td>
<td>Cr³⁺</td>
<td>Cr³⁺, Cr⁶⁺</td>
<td>Cr³⁺</td>
</tr>
</tbody>
</table>

Pour l’échantillon 3, un recuit a été fait sous une pression d'oxygène de 5 × 10² Torr. Les spectres XPS de l’échantillon 3 montrent la coexistence de Cr³⁺ et Cr⁶⁺ ions à la surface du film. Les caractéristiques I-V montrent un faible ratio entre les résistivité des états HRS et LRS et des tensions de SET et de RESET élevées. La tension SET n'est pas bien définie, mais
la tension RESET est nette à -4 ou -6 V. La courbe d'hystérésis I-V pourrait être influencée par la phase secondaire à la surface du film.

Dans le cas de l'échantillon 4, des ions Ru de l'électrode inférieure SrRuO$_3$ se substituent à des ions Zr du film Cr:SrZrO$_3$. Par conséquent, la zone d'interface entre le mélange et SrZrO$_3$ SrRuO$_3$ s’élargit avec la formation de Sr(Ru,Zr)O$_3$. Il montre un effet de trainée de la commutation de résistivité en raison d’une zone d'interface mal formée. Des tensions de +20 V et -20 V sont nécessaires pour la commutation de résistivité.

Nous avons également étudié l'influence de l'état de valence des ions Cr sur les caractéristiques I-V. Lorsque le film a été recuit sous P$_{O_2} = 5,0 \times 10^{-6}$ Torr, le spectre XPS (Fig 14(a)) montre un doublet à proximité des énergies de liaison (BE : Binding Energy) de 576,8 et 586,6 eV correspondant à une valence des ions Cr de +3. Lorsque la P$_{O_2}$ du processus de recuit a été augmentée, deux pics à proximité de 579,8 eV et 589,3 eV se
développent fortement, ce qui indique la formation de Cr\textsuperscript{6+}. La courbe I-V de l'échantillon recuit sous P\textsubscript{O2} = 3,3 × 10\textsuperscript{2} Torr est représentée sur la Fig. 14 (b). Les courbes I-V de l'échantillon préparé à basse P\textsubscript{O2} présentent des transitions résistives bien définies alors que celles de l'échantillon préparé sous P\textsubscript{O2} élevée sont mal formées. Par conséquent, nous supposons que c'est la présence d'ions Cr\textsuperscript{3+} et non celle d'ions Cr\textsuperscript{6+} à la surface qui permet d'améliorer les comportements de commutation résistive des films Cr: SrZrO\textsubscript{3}.

**FIGURE 14.** Spectres XPS de films Cr: SrZrO\textsubscript{3} (Cr: 0,2 mol%). Les caractéristiques I-V des échantillons dans le cas du P\textsubscript{O2} = 3,3 × 10\textsuperscript{2} Torr et P\textsubscript{O2} = 5,0 × 10\textsuperscript{-6} Torr sont indexés (b) et (c), respectivement.

L'augmentation du rapport Cr\textsuperscript{6+}/Cr\textsuperscript{3+} indique l'apparition de phases ségréguées comme CrO\textsubscript{3} ou SrCrO\textsubscript{4}. Ces phases très oxydées sont facilement éliminées par des traitements thermiques sous vide. Quand ces phases sont présentes, elles sont à l’origine de chemins de fuite électrique qui ne permettent pas de maintenir l’état de haute résistance, ce qui entraîne une dégradation de la commutation de résistivité.
Nous avons ainsi établi les conditions de croissance de Cr: SrZrO₃ pour l’obtention d’un effet appréciable de commutation de résistivité. Le comportement optimal a été observée dans des films qui ont été préparés à haute température du substrat (~700 °C) pour induire la migration du chrome Cr au voisinage de la surface et qui ont été recuits sous une pression partielle d’oxygène faible (Pₒ₂<10⁻⁵ Torr) qui maintient la valence des ions Cr³⁺. Cet état de valence semble indispensable à un l’établissement d’un effet notable de commutation de résistivité.

Dans le dernier chapitre, nous avons étudié la chimie de surface de films Cr: SrZrO₃ modifié par un procédé d’électro-formage. Nous observons une nouvelle structure sur la région de surface de Cr: SrZrO₃ après le processus d’électro-formage. Comme on le voit sur la figure 15, les états Zr 4d₂g sont séparés des états Zr 4d₄g par le champ cristallin (pics à 532 et 537 eV respectivement). Les pics associés aux états Sr 4d sont situés autour de 536 eV. Il est intéressant d’observer l’émergence d’un nouveau pic vers 531 eV au voisinage de l’électrode de platine après l’application d’une tension. Les intensités des pics Zr 4d diminuent quand on se rapproche de l’électrode de platine. Dans le voisinage de l’électrode Pt, les pics Sr 4d apparaissent plus clairement en raison de la dégradation des pics Zr 4d. On observe également l’élargissement des pics dans la région entre 538 eV et 545 eV dans cette même région. Par conséquent, la structure originale de SrZrO₃ sur la région de surface peut être modifiée après le processus d’électro-formage. Une explication possible de la nouvelle structure au voisinage de la surface est que le film électro-formé contient un mélange de Cr³⁺ et Cr⁶⁺ ions dans cette région. L’épaulement sous la bande de conduction peut provenir d’orbitales d vides des ions Cr⁶⁺ ions. L’état de valence des ions Cr peut changer de Cr³⁺ en Cr⁶⁺ sous l’électrode de platine en appliquant une tension. Cependant, nous n’avons pu trouver aucune preuve de changement de valence des ions Cr.
La figure 16 montre l'image SPEM (« scanning photoelectron microscopy ») d'une cellule de mémoire Pt/0.2mol%Cr:SrZrO$_3$/SrRuO$_3$/SrTiO$_3$ avec l'énergie du photon fixée à 531eV, énergie du nouveau pic apparaissant sur les spectres d’absorption O-1s. Avant de prendre les spectres d'absorption des rayons X nous avons effectué un balayage en tension sauf sur l’électrode supérieure de platine (6ème plot) utilisée comme référence. L’image montre la distribution spatiale du nouveau pic en fonction de son intensité. Tous les pics ont été normalisés à l’intensité maximale du pic Zr 4d t$_{2g}$. La région de A avec la couleur jaune a un pic de préseuil d’intensité plus élevée que dans la région C où celui-ci a son intensité minimum.

FIGURE 15. Spectres d’absorption au seuil K de l’oxygène des cellules de mémoire Pt/0.3mol% Cr: SrTiO$_3$ avant électroformage (ligne pointillée) et après application d'une tension de 5V (trait plein) en déplaçant le faisceau en direction de l’électrode de Pt.
La répartition spatiale du pic de préseuil des films Cr: SrZrO₃ décorés de plots sont en accord avec les propriétés de transport électronique. Nous avons mesuré la caractéristique I-V à chaque plot. On peut séparer une zone conductrice (A, B, D et F: zone 1) et une zone isolante (C et E: Zone 2), comme le montre la figure 16. La photoémission à résolution spatiale de rayons X montre que les spectres de spectroscopie des niveaux de cœur de Sr 3d et Zr 3d dans la zone 1 ont fortement évolué d'environ 2 eV, tandis que ceux dans la zone 2 conservent de faibles énergies de liaison. Fait intéressant, les spectres O 1s dans les deux domaines sont demeurés pratiquement inchangés.

FIGURE 16. Numérisation de la photo de microscopie électronique du film 0.2mol% Cr: SrZrO₃ électro-formé et enregistrements des niveaux de cœur O 1s, Zr 3d et Sr 3d dans différents domaines.
Cela implique que la chimie de surface de la zone conductrice peut être différente de celle de la zone isolante. Nous n'avons pas pu expliquer ce résultat par la création de lacunes d'oxygène, car l'énergie de liaison de O spectres 1s est presque inchangée. Par conséquent, nous avons déduit que la structure locale de SrZrO₃ a été modifiée par le champ électrique. Surtout Zr et les ions Sr sont fortement influencés par un champ électrique. Cependant, nous n'avons pas pu trouver aucune preuve d’un changement d'état chimique des ions Cr dans la région de la surface.

En conclusion, nous avons observé une nouvelle structure au voisinage de la surface de films Cr:SrZrO₃ présentant un effet réversible de commutation de résistivité. Les spectres d’absorption du film, après l'opération d’électroformage, comporte un nouveau pic qui apparaît dans la bande interdite. Nous suggérons que la structure de SrZrO₃ a été déformée au voisinage de la surface. Cette modification peut être due à l’apparition d’un mélange de Cr³⁺ et Cr⁶⁺ ions à la surface du film électroformé. Cependant, nous n'avons pu trouver aucune preuve de changement de valence des ions Cr. Toutefois, dans le chapitre 6, nous avons montré que le Cr:SrZrO₃ a beaucoup d'ions Cr près de la surface, soit environ 6%, pour une concentration de dopage nominale de la cible, de 0,2mol%. Nous avons vérifié par XPS que cette surface riche en Cr contenait principalement des ions Cr³⁺ avant le processus d’électroformage. Ainsi, après le processus d’électroformage, la structure locale de SrZrO₃ a été modifiée par le champ électrique. Ce sont surtout les ions Zr et Sr qui sont fortement influencés par un champ électrique. Ce genre de la modification de la chimie de surface peut être influencée par l'accumulation des ions Cr³⁺ indirectement.

Pour résumer l’ensemble de notre travail, les systèmes de TiO₂, SrTiO₃ déficients en oxygène, et les systèmes TiO₂, SrTiO₃ et SrZrO₃ dopés aux ions de métaux de transition (Cr ou V) ont été étudiés. Dans ces derniers l’augmentation du rapport Cr⁶⁺/Cr³⁺ peut indiquer l'émergence de phases ségrégées comme CrO₃ ou SrCrO₄. Ces phases non désirées peuvent être éliminées dans un environnement pauvre en oxygène.

Nous avons constaté que l'accumulation d'ions Cr³⁺ près de la surface du film conduit à une interface nette, sans oxydes non stœchiométriques, et que celle-ci favorise de bonnes performances de commutation de résistivité. A l’inverse, la formation d'oxydes tels CrO₃ ou SrCrO₄, cependant, peut dégrader ces performances. Celle-ci sont optimales pour
des films qui ont été préparés sur un substrat à haute température (~ 700 °C) ce qui induit la migration du chrome dans la région de surface puis recuits sous de faibles pressions partielles d'oxygène (P_{O2}<10^{-5} \text{ Torr}) pour assurer que les ions chrome soient sous forme Cr^{3+}.

Pour étudier le processus d'électroformage, nous avons préparé un film 0.2mol% Cr: SrZrO₃ décoré d'électrodes. L'étude de ces films par microscopie à balayage de photoélectrons a montré que les résultats des mesures électriques étaient clairement liés à l'état chimique dans la zone de surface. Nous suggérons que la structure des films Cr: SrZrO₃ a été déformée dans cette région par le processus d'électro-formage. Cette modification peut être influencée indirectement par l'accumulation des ions Cr^{3+}.
Bibliography


