Growth and Characterization of TiO$_2$ Thin Films by PLD Technique

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**ABSTRACT:** In this work, the structural, optical and electronic properties of TiO$_2$ thin films grown on glass substrate by Pulse Laser Deposition (PLD) technique are presented. The stoichiometry and the oxidation degree of films were analyzed by considering the Ti 2p and O 1s core energy levels with high resolution X-Ray Photoelectron spectroscopy (XPS). The structural characteristics of the thin films have been investigated by X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM) technique. The optical absorption region of growth TiO$_2$ films were analyzed by Photoluminescence spectroscopy (PL) technique. Spin-orbit coupling splitting of Ti 2p states was measured as 5.7 eV. The characterizations promote the existence of the metal and oxygen vacancies at the surface of film. These point defects enhance the hysteretic transport properties of the TiO$_2$ metal oxide.

**Keywords:** TiO$_2$, PLD, XPS, thin film

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INTRODUCTION

Titanium dioxide (TiO$_2$) have been studied intensively due to its strong oxidizing ability in the fields of biology, gas sensor, dental and orthopedic applications (Sittig, 1998; Bally, 1999). Transparent single crystals or thin films TiO$_2$ have been used for optical applications due to the high refractive index (Pulker et al., 1976; DeVore, 1951). Nowadays, the transport properties of TiO$_2$ thin films depend on the stoichiometry of oxygen and titanium play crucial role in electronic chip technology (Gale, 2014).

Different forms of TiO$_2$ in different research fields have been used such as bulk crystal, thin film, powder and composite materials. Generally the crystal structure of TiO$_2$ has two much-used forms: rutile and anatase phases. Anatase phase is thermodynamically unstable and it transforms into rutile phase at high temperatures (Jamieson et al., 1969; Pistorius, 1976; Murray et al., 1987; Gamboa et al., 1992; Ding et al., 1996; Ghosh et al., 2003; Smith et al., 2009). As in most transition metal oxides, the oxygen vacancies are the most encountered defects in TiO$_2$ due to the its nonstoichiometric properties at atmospheric oxygen pressure (Pan et al., 2013). The oxygen vacancies in the material introduces an excess of electrons resulting an increment for electrical conductivity (Wu et al., 2012). Therefore nonstoichiometric TiO$_{2-x}$ is an n-type semiconductor due to the oxygen vacancies which act as electron donors.

Information storage technologies are approaching to upper limit due to the physical smallest bit size. Therefore, intensive studies on new storage technologies have been initiated. Nowadays, a metal-insulator-metal structure called as memristive device theoretically offers almost unlimited information storage capacity on the same geometric bit size. Since the electrical resistance of these elements depend on the applied external electric field, and each resistance value of elements can represent different information. The first discovered memristor by Williams and his team was produced as a Pt/TiO$_2$/Pt thin film-based sandwich structure (Stukov et al., 2008).

MATERIALS AND METHODS

In this study, TiO$_2$ thin films have been fabricated by using pulsed laser deposition (PLD) method. A chemical cleaning process was applied on the substrates as each substrate was separately cleaned with acetone in an ultrasonic bath for 15 minutes. Then the samples removed from acetone were put into isopropanol and they were cleaned for 15 minutes in an ultrasonic bath. A KrF excimer laser (248 nm) source was used. After 6000 and 13500 laser pulses the thickness of deposited films of about 160, 260 and 300 nm were measured by small angle X-Ray reflectometry (XRR) technique as seen in Figure 1. During the deposition process the substrate temperature and the background oxygen pressure were maintained at 300 K and 1x10$^{-5}$ Torr. The stoichiometry and the oxidation degree of films were analyzed by considered the Ti$_{2p}$ and O$_{1s}$ core energy levels with high resolution X-Ray Photoelectron spectroscopy (XPS). The structural characteristics of the films have been investigated by XRD and SEM. The optical activities of growth TiO$_2$ thin films were analyzed by Photoluminescence spectroscopy.

RESULTS AND DISCUSSION

The metal oxide TiO$_2$ semiconductor thin films were deposited on a glass substrate by using pulsed laser deposition (PLD) technique using a high purity TiO$_2$ target. The physical density, roughness and the thickness of all growth thin film have been calculated from the simulation of XRR data.

Density of the growth films is calculated as 4.26 g/cm$^3$. The results of the XRR measurements are presented in Figure 1. The Kiessing fingers in XRR measurements were not observed as seen in Figure 1 due to the roughness on the surface of the films. Therefore the thickness and roughness of the films were checked with the cross-sectional SEM measurement as seen in Figure 2. The results were nearly
same with the XRR measurements. The roughness on the surface of the films is rather large so it explains the XRR results in Figure 1.

![Figure 1. Small angle X-Ray reflectivity results of growth TiO$_2$ films.](image1)

![Figure 2. Cross-section Scanning Electron Microscopy (SEM) image of TiO$_2$/Glass.](image2)

![Figure 3. XPS survey scan of the clean TiO$_2$ film on glass substrate.](image3)
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X-Ray photoelectron spectroscopy (XPS) is a very sensitive and non-destructive technique to provide remarkable information about the chemical composition and electronic structure of the surface. Moreover, formation of chemical bonds between components of metal oxide is investigated with XPS method. In this study the stoichiometry and the oxidation degree of films were analyzed by considering the Ti$2p$ and O$1s$ core energy levels with high resolution X-Ray Photoelectron spectroscopy (XPS) (Phoibos 100, SPECS GmbH, Berlin, Germany). Figure 3 shows a survey scan of the clean surface of the TiO$_2$ thin film grown on glass substrate. Figure 4a and 4b shows the simulation of high resolution XPS spectrum of Ti $2p$ and O $1s$. In this spectrum, the doublet Ti $2p_{3/2}$ (458.9 eV) and Ti $2p_{1/2}$ (464.6 eV) arises from spin orbit-splitting measured as 5.7 eV. These peaks are consistent with Ti$^{4+}$ in TiO$_2$ lattice (Sanjinés et al., 1994). Also, there are a shoulder in Ti $2p_{1/2}$ and Ti $2p_{3/2}$ corresponding to different valances of Ti ion such as Ti$^{3+}$ in Ti$_2$O$_3$ (Bertóti et al. 1995). Experimental results and fitting of data shows that both compositions of TiO$_2$ and Ti$_2$O$_3$ film are formed on the substrate. Narrow XPS scan of O $1s$ spectrum of TiO$_2$ thin film is shown in Fig 4b. The peak is at the binding energy of 530.7 eV and it is attributed to the TiO$_2$ lattice oxygen. Small amount of asymmetry in the peak is due to the non-
lattice oxygen ion or surface defects. Optical properties of growth film were measured with PL spectroscopy and the result is presented in Figure 5. A broad optical activities between 200 and 350 nm was observed in both absorbance and transmittance measurement. Generally the optical absorption activities at lower UV region of TiO$_2$ is attributed to electronic transition between the band gaps (band to band transition). In addition, in XPS result we observed Ti$^{3+}$ at the surface of the film and we attributed this result to the formation of Ti$_2$O$_3$ films. The absorbance curve of the film is nearly same with the absorbance curve of Ti$_2$O$_3$ (Ghamchia et al., 2007). Due to the surface effects such as oxygen defects and the broken bonds always it possible to grow a thin layer of Ti$_2$O$_3$. The transmittance spectra shows remarkable increase between 200 and 300 nm then decrease sharply means that transparent properties of the film was reduced and reflectance properties of the film was increased. Both absorbance and reflectance spectrum shows vibrionic behavior between the optical activity region.

**CONCLUSION**

In conclusion, the structural, electronic and the optical properties of the TiO$_2$ thin films grown on glass substrate by using the PLD technique have been investigated. Film thickness, physical density and roughness were determined by using small angle X-ray diffraction technique. Composition of the film and the spin-orbit coupling of Ti$^{4+}$ ion have been measured. Different compositions of titanium oxides were observed in X-Ray Photoelectron and Photoluminescence spectroscopy (PL). TiO$_2$ thin films were successfully synthesized in the form of thin film with surface Ti$^{3+}$ and oxygen point defects which play crucial role in resistive switching mechanism of TiO$_2$ metal-oxide. The existence of the surface point defects were promoted by PL measurements.

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