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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 stochiometry 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; Murrray 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.

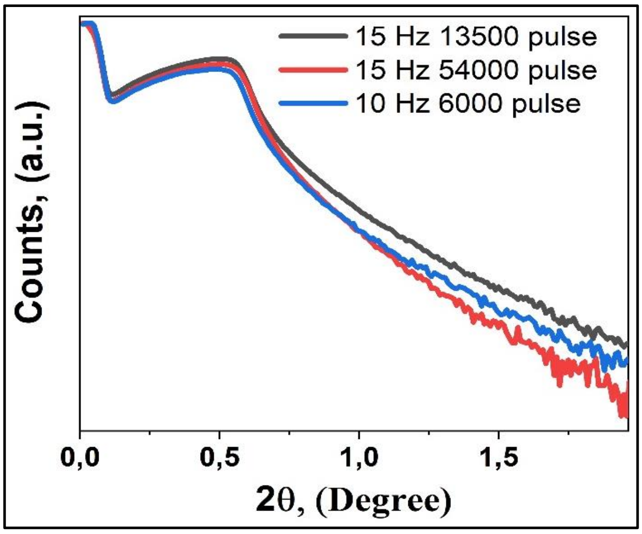

Figure 1. Small angle X-Ray reflectivity results of growth TiO_2 films.

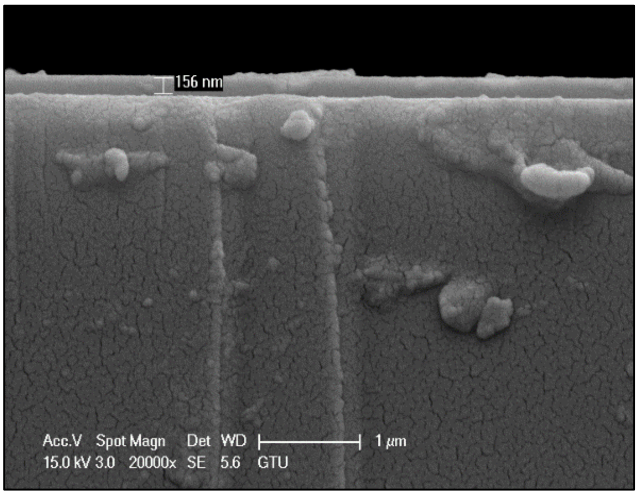

Figure 2. Cross-section Scanning Electron Microscopy (SEM) image of TiO_2/Glass.

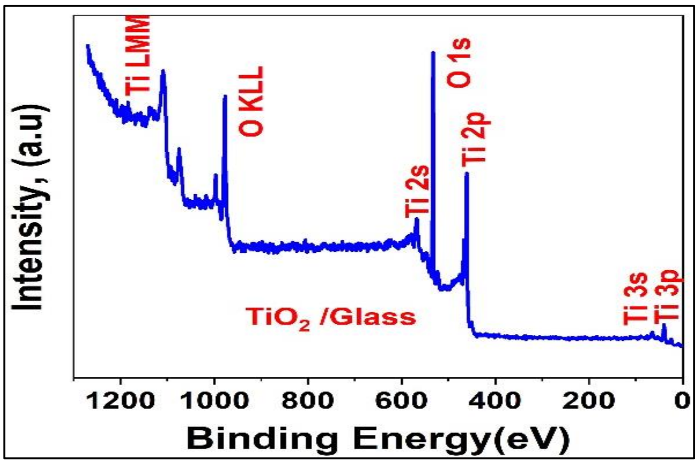

Figure 3. XPS survey scan of the clean TiO_2 film on glass substrate.

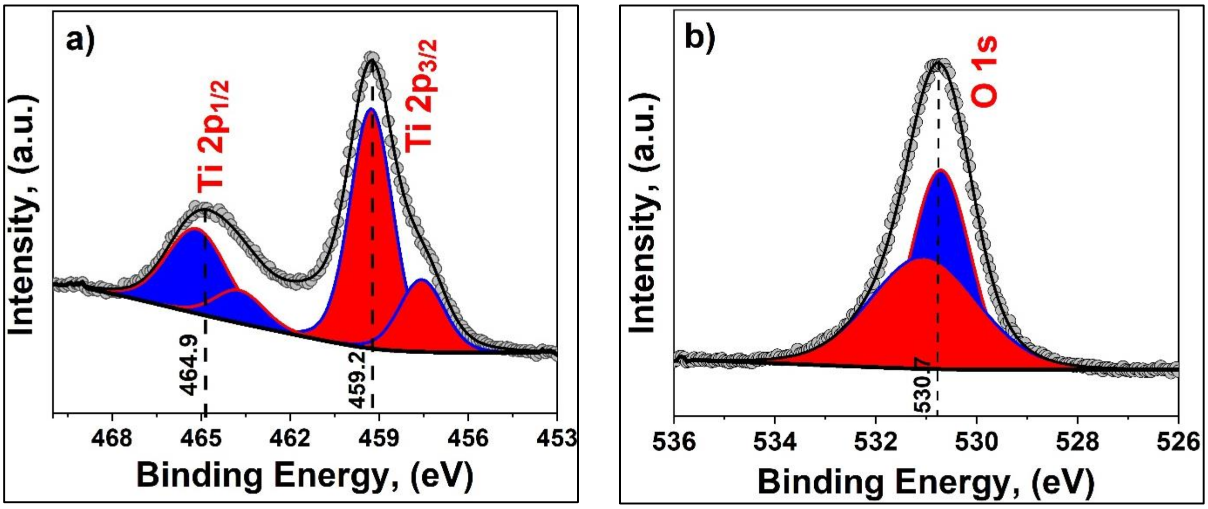

Figure 4. High resolution XPS scan of the (a) Ti 2p and (b) O 1s of TiO_2 film on glass substrate. Solid circle shows experimental results and solid line shows simulation of the experimental results.

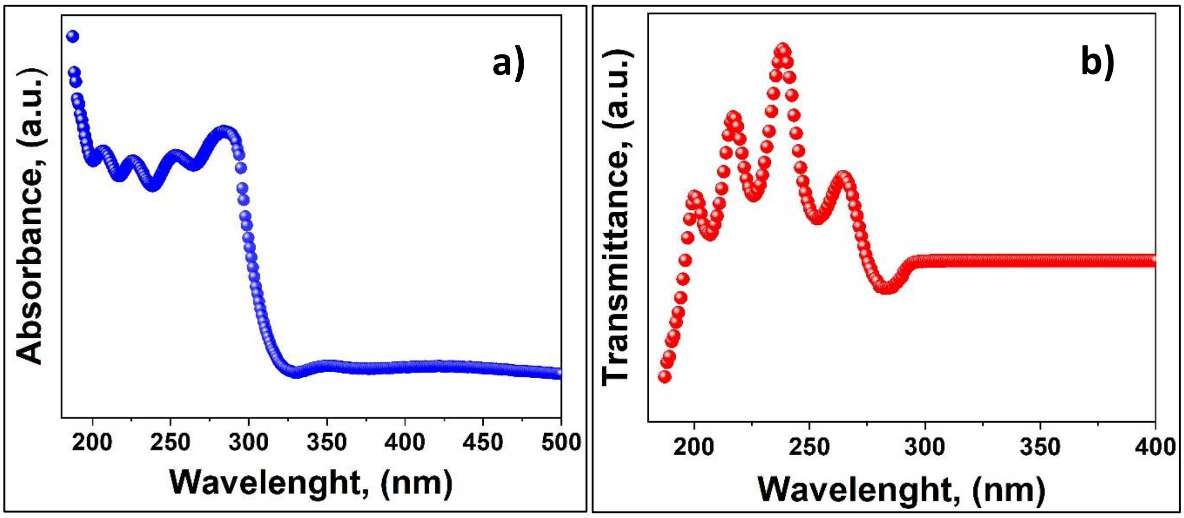

Figure 5. Photoluminescence measurements of TiO_2 thin film grown on glass substrate a) absorbance and b) transmittance

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 considered 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_2O_3 (Bertóti et al. 1995). Experimental results and fitting of data shows that both compositions of TiO_2 and Ti_2O_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 nonlattice 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_2O_3 films. The absorbance curve of the film is nearly same with the absorbance curve of Ti_2O_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_2O_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.

REFERENCES

Sittig CE, 1998. Charakterisierung der oxidschichten auf titan und titanlegierungen sowie deren reaktionen in kontact mit biologisch relevanten modellösungen. Dissertation ETH Nr. 12657, Zürich.

Bally A, 1999. Electronic properties of nano-crystalline titanium dioxide thin films. Dissertation ETH Nr. 2094, Zürich.

Pulker HK, Paesold G and Ritter E, 1976. Refractive indices of TiO_2 films produced by reactive evaporationof various titanium–oxygen phases. Applied Optics 15, 2986-2991.

DeVore JR, 1951. Refractive Indices of Rutile and Sphalerite. Journal of the Optical Society of America.41, 416-419.

Gale E, 2014. TiO_2-based memristors and ReRAM: materials, mechanisms and models (a review).Semiconductor Science and Technology. 29, 104004 (10pp).

Ding XZ, Liu XH and He YZ, 1996. Grain size dependence of anatase-to-rutile structural transformation in gel-derived nanocrystalline titania powders. Journal of Materials Science Letters. 15, 1789–1791.

Jamieson J, Olinger B, 1969. Pressure-temperature studies of anatase, brookite rutile, and TiO_2(II): A discussion. American Mineralogist. 54 (9-10): 1477–1481.

Gamboa JA, Pasquevich DM, 1992. Effect of chlorine atmosphere on the anatase-rutile transformation. Journal of the American Ceramic Society. 75, 2934.

Pistorius CWFT, 1976. Phase relations and structures of solids at high pressures. Progress in Solid State Chemistry 11, Part 1, 1-151.

Smith SJ, Stevens R, Liu S, Li G, Navrotsky A, Boerio-Goates J, Woodfield BF, 2009. Heat capacities and thermodynamic functions of TiO_2 anatase and rutile: Analysis of phase stability. American Mineralogist, 94, issue 2-3, pp. 236-243.

Ghosh TB, Dhabal S, Datta AK, 2003. On crystallite size dependence of phase stability of nanocrystalline TiO_2. Journal of Applied Physics 94, 4577.

Murrray JL, Wriedy HA, 1987. The O−Ti (oxygen-titanium) system. Journal of Phase Equilibria 8, 148–165.

Pan X, Yang MQ, Fu X, Zhang N and Xu YJ, 2013. Defective TiO_2 with oxygen vacancies: synthesis, properties and photocatalytic applications. Nanoscale 5, 3601.

Wu J**,** Cao J**,** Han W-Q, Janotti A, Kim H-C, 2012. Functional Metal Oxide Nanostructures, Electronic ISBN: 978-1-4419-9931-3.

Stukov DB, Snider GS, Stewart DR, Williams RS, 2008. The missing memristor found. Nature 80,453.

Sanjinés R, Tang H, Berger H, Gozzo F, Margaritondo G, and. Lévy F, 1994. Electronic structure of anatase TiO_2 oxide. Journal of Applied Physics. 75, 2945–2951.

Bertóti I, Mohai M, Sullivan JL, Saied SO, 1995. Surface characterization of plasma-nitrided titanium: an XPS study. Applied Surface Science 84, 357-371.

Ghamchia HS, Hassanzadehb A, Talebiana M, Chenari HM, 2007. Thickness influence on optical andelectrochemical properties of dititanium trioxide (Ti_2O_3) films deposited on glass substrates by electron beam gun evaporation. Physica B: Condensed Matter 389, 329–334.