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Effect of substrate temperature on microstructure and properties of nanocrystalline titania thin films prepared by pulsed laser deposition

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Titanium oxide (TiO_2) films were deposited on silicon (100) and quartz substrates at various substrate temperatures (300 – 873 K) at an optimized oxygen partial pressure of 3.0×10^{-2} mbar by pulsed laser deposition. The effect of substrate temperature on structure, surface morphology and optical properties of the films were investigated using X-ray diffraction (XRD), atomic force microscopy (AFM) and photoluminescence spectroscopy (PL) respectively. The XRD results showed that the films are polycrystalline in nature and have tetragonal structure. The film prepared at higher substrate temperature showed strong rutile phase. The results indicated that all the films possess both phases (anatase and rutile) of titania. The AFM shows the crystalline nature, dense, uniform distribution of the nanocrystallites with a surface roughness of 2 – 8 nm. The photoluminescence studies showed the asymmetric peak $\sim$ 370 nm indicating the bandgap for the TiO_2 films.

Keywords: Titania, thin films, pulsed laser deposition, X-ray diffraction (XRD), atomic force microscopy (AFM), photoluminescence spectroscopy (PL).

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1. Introduction

Titania (TiO_2) exists in rutile, anatase and brookite phases. TiO_2 thin films are widely studied due to their interesting chemical, electrical and optical properties. TiO_2 thin films exhibit unique properties such as high dielectric constant, wide optical bandgap, high refractive index, photo catalytic, low absorption and high transparency with high chemical and thermal stabilities. Because of its excellent properties, it finds applications in heterogeneous catalysis, photocatalysts, self cleaning windows, solar cells, gas sensors, corrosion resistant coatings, optical coatings, metal oxide field effect transistors, varistors, Li-based batteries and electro chromic devices [1–3]. The occurrence of anatase and rutile phase of TiO_2 thin films mainly depends on the deposition method, process parameters and substrate temperature. Many techniques are used to deposit TiO_2 films, including sol-gel processes [4], reactive evaporation [5], chemical vapor deposition [6], sputtering [7, 8] and pulsed laser deposition (PLD) [9]. Among these techniques, pulsed laser deposition (PLD) is a simple technique to prepare high quality films from metal, semiconductors and ceramics. The rapid rate of ablation from target surface promotes the constituents of the target to evaporate congruently and to retain the stoichiometry in the film. There are many deposition parameters to be optimized to achieve the optimum properties. The oxygen partial pressure and the substrate temperature play an important role to produce high quality films by PLD. The preparation method and process parameters of TiO_2 films are of fundamental importance for obtaining the optimum properties for various applications. In the present work, nanocrystalline TiO_2 films were deposited on silicon and quartz substrates as a function of substrate temperature by PLD and their microstructure and optical properties were investigated.

2. Experimental details

TiO_2 powder was compacted into a pellet of 30 mm diameter and 5 mm thickness using a uni-axial press. The pellet was sintered $\sim$ 1473 K for 8 hours and used as a target for the PLD. TiO_2 films were deposited on Si (100) and quartz substrates at various substrate temperatures from 300 K to 873 K. The films were deposited using KrF excimer laser ($\lambda = 248$ nm) with a repetition rate of 10 Hz. X-ray diffraction (XRD) studies were carried out using X'pert PW 3040 D-8 (PANalytical) diffractometer with $CuK_{\alpha1}$ radiation. The surface topographies and roughnesses of the films were analyzed using atomic force microscope (XE-100 Park systems) in non-contact mode. The photoluminescent spectra of these films were recorded using a (Shimadzu, RF-5301PC) spectrofluorophotometer.

3. Results and Discussion

3.1. Microstructural studies

XRD pattern of the TiO_2 thin films is shown in Fig. 1. The XRD pattern shows the peaks at angles 25.8 ° and 37.9 °, corresponding to the anatase phase ((JCPDF # 21-1272), while the peaks at angles 27.5 °, 44.2 °, 56.5 °, 64.3 ° indicate the rutile phase (JCPDS # 21-1276) of titania. In the XRD pattern, A and R denotes the anatase and rutile phase of titania respectively [9]. The XRD results showed that the films were polycrystalline in nature and had tetragonal structure. The films deposited in the lower substrate temperatures (300 – 673 K), showed the small intense peaks corresponding to both anatase and rutile phases, while the films deposited at higher substrate temperatures (773 K and 873 K) indicated the strong peaks corresponding to the rutile phase. This indicated the higher rutile phase content and smaller anatase phase content in the films with increasing substrate temperature. The formation of rutile phase with temperature was due to the high energy of particles impinging on the substrate kept at higher temperature. The thickness of the films increased with increasing temperature. The anatase to rutile phase transformation takes place over a wide range of temperatures (from 823 to 1073 K). Ben Amor et al. [10] investigated the properties of TiO_2 films and observed the amorphous nature in the as-deposited condition, while the annealed films at 873 K showed anatase phase.

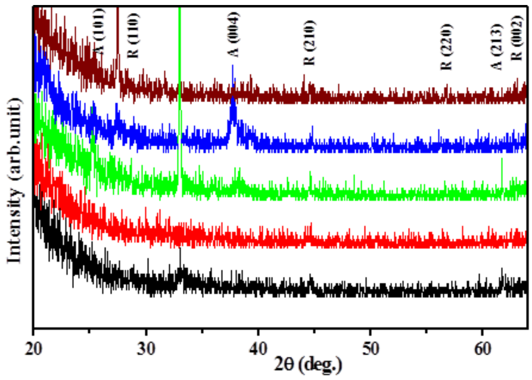

FIG. 1. XRD pattern of the TiO_2 thin films deposited on Si (100) at different substrate temperatures

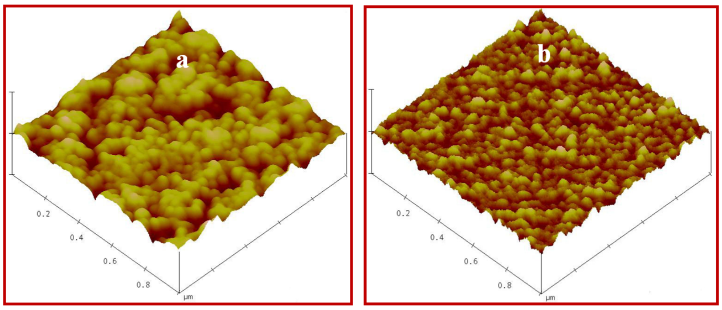

FIG. 2. AFM images of the TiO_2 films prepared at (a) 300 K and (b) 873 K

Figure 2 shows the AFM images of the typical films prepared at room temperature (300 K) and 873 K. The images showed the dense crystallites, uniform formation of the crystallites and smooth morphology. The mobility of the ad-atoms is higher at higher substrate temperatures and the film prepared at 873 K showed the coalescence of the crystallites. The surface roughness of the films were measured and found to be in the range 3 – 8 nm.

3.2. Photoluminescence studies

Figure 3 shows the photoluminescence (PL) spectra of the TiO_2 films deposited on silicon (100) substrates at various substrate temperatures. The PL spectra of the films were analyzed using 325 nm laser excitation wavelength. PL spectra showed broad and asymmetric peaks, indicating the presence of both anatase and rutile phases. At 873 K, two PL peaks were observed, indicating the clear anatase and rutile peaks. The small intense peak $\sim$ 470 nm (2.7 eV) is probably due to the structural defects, which are related to deep-level emissions like oxygen vacancy [9, 11, 12]. The PL peak intensity of TiO_2 films with respect to substrate temperature is associated with its crystallinity and defects. The glancing incidence X-ray diffraction (GIXRD) results of the films showed more rutile phase (Fig. 1) at higher substrate temperatures. The PL peak intensity decreases systematically with the increased substrate temperature [9]. The variation of PL peak intensity is related to the formation of rutile and anatase phases at different substrate temperatures. The PL results are consistent with our XRD results [13]. All these results showed that the optical properties of TiO_2 films are dependent on their microstructure influenced by substrate temperature. Table 1 gives the details for the crystallite size, surface roughness and bandgap of the titania films with respect to the substrate temperature.

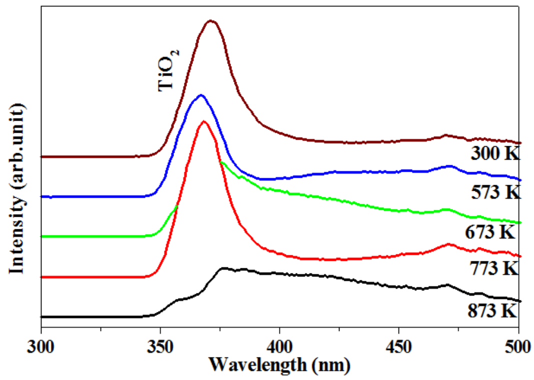

FIG. 3. Photoluminescence spectra of the TiO_2 films prepared at different temperatures

TABLE 1. Substrate temperature *vs* crystallite size, surface roughness and bandgap

Substrate Temp. (K)	Crystallite size Rutile (110) (nm)	Surface roughness AFM (nm)	Bandgap (eV) PL
300	—	3.0	3.35
573	—	5.2	3.37
673	—	6.5	3.37
773	30	7.2	3.37
873	48	8.0	3.30

4. Conclusions

The TiO_2 thin films were deposited on Si (100) and quartz substrates at various substrate temperatures by pulsed laser deposition. The XRD studies indicated small intense peaks corresponding to both anatase and rutile phases at low substrate temperatures, while the strong peaks indicated higher rutile phase content at higher substrate temperatures. The rutile phase content increased with increased substrate temperature. The AFM studies illustrated the dense, uniform distribution of the crystallites with smooth morphology. PL studies demonstrated the broad and asymmetric peaks $\sim$ 370 nm, indicating a bandgap of $\sim$ 3.30 – 3.37 eV.

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