Effect of Substrate on Structural and Optical Properties of TiO_2 Thin Films Prepared by Pulsed Laser Deposition

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Abstract: **In this paper, the effect of substrate on the structural and optical properties of TiO_2 thin film prepared by pulsed laser deposition technique employing a KrF laser source (λ=248 nm) has been studied. Structural properties have been studied using XRD and AFM and optical properties have been studied using photoluminescence and transmission spectra. TiO_2 thin film deposited on different substrates shows pure anatase phase structure with (004) and (101) plane. In PL spectra, emission peaks superimposed on the broad emission band has been observed. It has been concluded that ITO glass substrate is the best choice for ITO thin film among the substrates studied here.**

Key Words: **Pulsed laser deposition, TiO_2, Substrate effect.**

1. INTRODUCTION

TiO_2 thin film has been widely studied due to refractive index is high [1], photocatalytic behavior is good [2], and visible light transparency is high [3]. In addition, its high dielectric constant and good thermal stability make it potential materials for high-density dynamic-memory devices, capacitors in microelectronics, insulator gate in MIS structures [4-7]. Moreover, it has been reported that the good crystallinity of dielectric film results in high dielectric constant [8] and smooth film surface leads to the decrease in leakage current [9]. In this chapter, we report the success of preparing high epitaxial anatase TiO_2 thin film using ZnO buffer layer on Si substrate and glass substrate. TiO_2 thin films have been deposited by many research workers using different techniques like, molecular beam epitaxy, chemical vapor deposition [10], aerosol pyrolysis [11], electro-deposition [12] and sol–gel method [13-14].

2 EXPERIMENTAL DETAILS

(i) Film preparation: TiO_2 thin films has been deposited on different substrate using pulsed laser deposition (PLD) technique employing a KrF laser source (λ=248 nm). The thickness of the grown film is typically ~200 nm which is confirmed using surface profilometer.

(ii) Film characterization: The phase and orientation of as-grown thin films were characterized by X-ray diffractometeter (XRD, Bruker AXS D-8 Advance Diffarctometer) using CuK_α (λ=1.5407 Å) radiation. The surface topography and microstructure were examined by atomic force microscope (NTMDT: NTEGRA model). Transmission spectra have been taken using UV-VIS-NIR spectrophotometer (Varian Cary 5000) in the wavelength range 200 to 800 nm and photoluminescence study was done using Perkin Almer LS-55.

3 RESULTS AND DISCUSSION

Fig 1 shows the X-ray diffraction patterns for the TiO_2 thin films deposited on Si (100), glass and ITO coated glass substrate. TiO_2 thin film grown on different substrates shows pure anatase phase structure. The intensity of [004] plane is higher in thin film deposited on Si (100) substrate and the intensity of (101) plane is higher in ITO coated glass substrate compared to film deposited other substrate because the crystalline nature of Si substrate in (100) direction and ITO substrate in (440) direction.

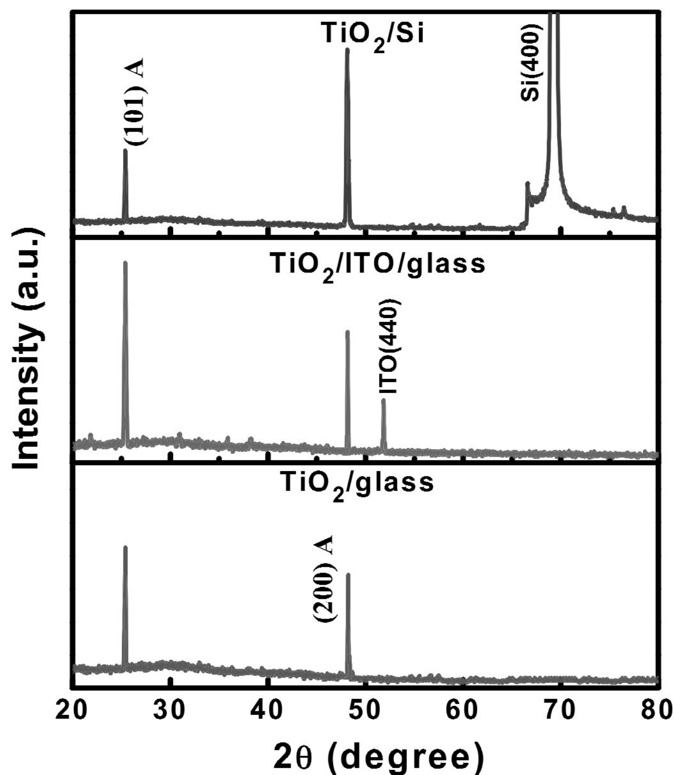

Fig 1: XRD pattern of the TiO_2 thin films deposited at glass, ITO coated glass and Si (100) substrate

The crystallite size of these samples were calculated along the (101) orientation using the Scherrer's formula and are shown in Table 1. During the growth process of thin films, mismatching of lattice parameters between film and substrates can results in unreliable degrees of stress. The values of stress can be calculated by the following formula:

$$\sigma = \frac{2c_{13}^2 - c_{33}(c_{11}+c_{12})}{2c_{13}} \times \frac{c-c_0}{c_0} \quad (1)$$

$$\sigma = -282.76 \times 10^9 \ \frac{c-c_0}{c_0} \quad (2)$$

where c_{ij} is elastic constant, c_0 is the lattice constant of bulk and c is the lattice constant of thin films. The value of compressive stress is larger in TiO_2 thin film deposited at glass substrate due to amorphous nature of glass. Meanwhile the compressive stress has been released to a certain extent for Si (100) substrate and attained minimum for ITO coated glass substrate. The lattice parameter is calculated using the following formulas:

$$\text{Tetragonal: } \frac{1}{d^2} = \left(\frac{h^2+k^2}{a^2}\right) + \frac{l^2}{c^2} \quad (3)$$

where h, k, l are miller indices of crystal planes and d is the spacing between adjacent planes.

Table 1: Various parameters of TiO_2 thin films deposited on to different substrate

Substrate	Lattice Constants		FWHM (degrees)	Crystallite Size (nm)	Grain size AFM (nm)	Strain (× 10-2)	Stress (× 10^9 N/m^2)
	a (Å)	*c* (Å)					
Glass	3.771	9.361	0.3679	23.41	61	1.487	4.205
ITO/glass	3.775	9.445	0.2651	30.71	103	0.603	1.705
Si(100)	3.778	9.427	0.3184	25.57	82	0.792	2.241

Fig. 2 shows the AFM images of TiO_2 films deposited onto different substrates. The grain size is given in Table 1. We found that the film grown over ITO coated glass substrate shows larger grain size in as compared to thin film grown on Si and glass substrate. This is in good agreement with XRD data. However over all particle size shown by AFM was much higher as compared with that calculated from the XRD results **(Table 1)** due to the fact that AFM showed agglomeration of the particles.

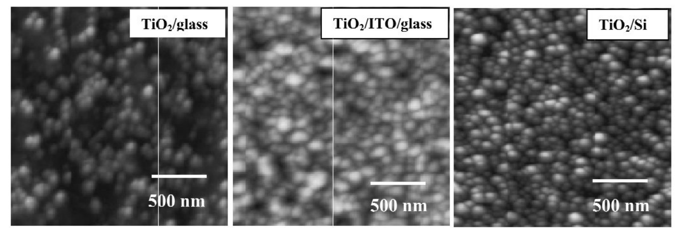

Fig .2: AFM image (2μm ×2μm) of TiO_2 thin film deposited on various substrates

Fig.3 shows room temperature photoluminescence of TiO_2 thin film deposited on to different substrates. Broad emission band is observed from 360 to 435 nm for all the samples and many emission peaks superimposed on the broad emission band. The peak before 350 nm (3.5 eV), is attributed to direct electron-hole recombination which should be equal/slightly bigger than the TiO_2 band gap. The emission band from 390 to 450 nm (corresponding to 3.2–2.75 eV) arises from indirect band gap and surface recombination processes. Further observation indicates that there are two small peaks at the wavelength range from 460 to 500 nm. These PL signals are attributed to excitonic PL, which mainly result from surface oxygen vacancies and defects of the films. The PL peaks at near about 465 nm is attributed to band edge free excitons, and other peak at near about 490 nm is attributed to bound excitons [15-17].

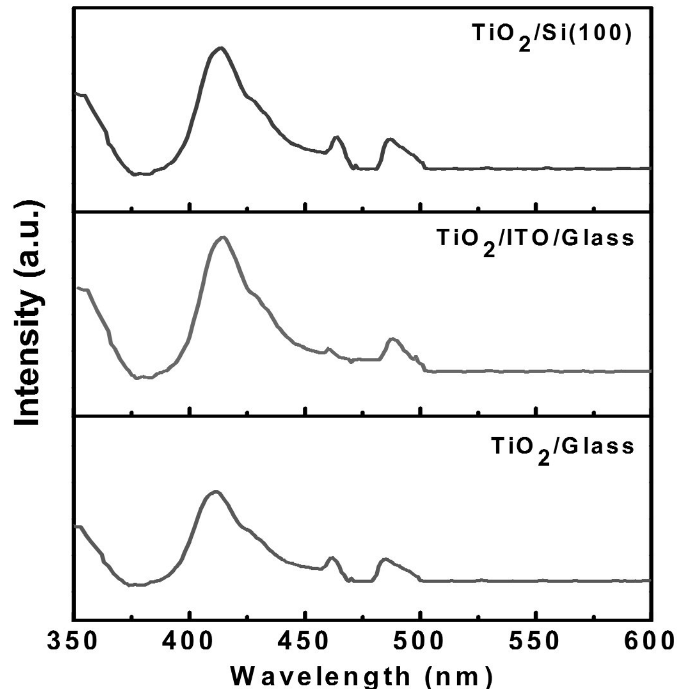

Fig.3: Room temperature photoluminescence of TiO_2 thin film deposited on different substrates

Fig. 4 shows the transmittance spectra of TiO_2 thin film grown on glass and ITO/glass substrate. The transmittance spectra demonstrate that TiO_2 thin films exhibit high transmittance in the 400-1000 nm range. The overall transmission is more for TiO_2 thin film grown on ITO coated glass substrate than glass substrate.

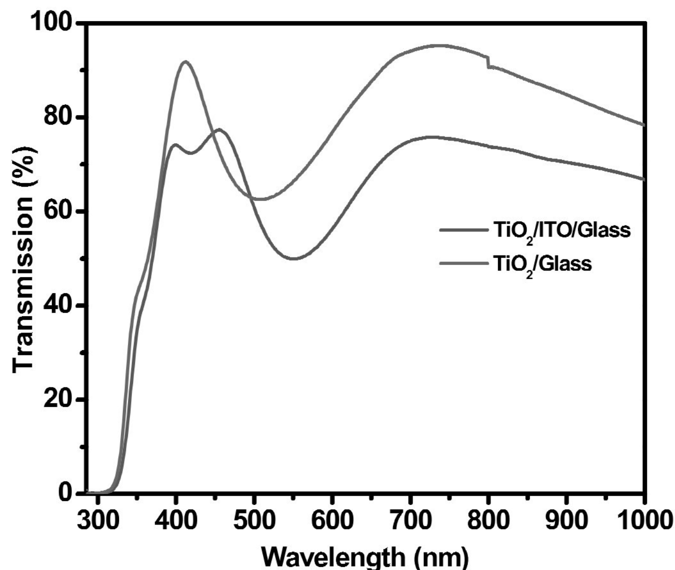

Fig. 4: Transmission spectra of TiO_2 thin film deposited on different substrates

CONCLUSION

TiO_2 thin films have been deposited on glass, ITO coated glass and Si (100) substrate using pulsed laser deposition (PLD) technique employing a KrF laser source (λ=248 nm). The XRD pattern showed that TiO_2 thin film grown on different substrates exhibit pure anatase phase structure. All the results suggest that ITO coated glass substrate is the best choice for TiO_2 thin film deposition among the substrates studied here.

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