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Effect of oxygen partial pressure on the structural and optical properties of ion beam sputtered TiO_2 thin films

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Abstract. We report the effect of oxygen partial pressure on the structural, electronic and nonlinear optical properties of ion beam sputtered TiO_2 thin films deposited on glass substrate at 40% of oxygen (S1) and 20% of oxygen (S2) partial pressure. XRD data shows the crystalline nature of S1 film while the film S2 was amorphous in nature. The energy band gap of the thin films calculated from their UV-Vis spectra was found to be 3.63 eV (S1) and 3.56 eV (S2). The decrease in the band gap with decrease in oxygen partial pressure may be attributed to the amorphous nature of the film. The nonlinear refractive indices for both the films were obtained from the closed aperture Z-scan experiment performed using a cw He-Ne laser source operating at 632.8 nm and were found to be 17.6×10^{-9} m^2/W and -5.64×10^{-9} m^2/W for S1and S2 films, respectively. The reversal in the sign of the nonlinear refractive index may also be ascribed to the crystallinity of the grown films.

1. Introduction

TiO_2 thin films are well known transparent conducting oxides and the knowledge of their nonlinear refractive index makes them potential candidate material for optoelectronic device applications. As a semiconductor material with long-term stability, non-toxic environmental acceptability and broadly low cost availability, TiO_2 has also been taken into account for photovoltaic applications. However, due to optical gaps slightly above 3 eV, and high refractive index, natural TiO_2 is only photoactive in the UV region of the electromagnetic spectrum and an efficient active solar cell material [1-3]. The structural and optical properties of these films are highly sensitive to the environment in which they are grown and are dependent on many parameters such as thickness, film structure, oxygen partial pressure and substrate temperature.

In view of the above, the present manuscript focuses on the study of the effect of oxygen partial pressure on the structural and optical properties of TiO_2 thin films.

2. Experimental details

TiO_2 thin films designated as S1 and S2 were deposited on corning glass substrate by ion beam sputtering technique. Before deposition, substrates were ultrasonically cleaned in acetone. The base pressure was 6×10^{-7} Torr and the films were deposited at a working pressure of 1.4×10^{-5} Torr. The

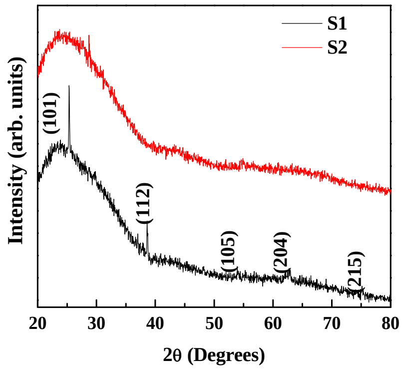

Figure 1. X-ray diffraction patterns of S1and S2 TiO_2 thin films.

deposition time for both the films was 90 minutes. Pure Oxygen and Argon were used as reactive and sputtering gas, respectively. Sample S1 is deposited at 3 sccm Ar gas and 2 sccm Oxygen gas while the film S2 is deposited at 4 sccm Ar gas and1 sccm Oxygen gas. The thickness of both the films was measured by stylus profilometer and was found to be 200 nm. The grown films were characterized by X-ray diffraction (XRD) technique for the structural analysis. The energy band gaps were determined from ultraviolet visible spectroscopy (UV-Vis). The nonlinear optical properties were investigated by performing the Z-scan technique using a 20 mW cw He-Ne laser operating at wavelength of 632.8 nm. The closed aperture Z-scan experiment was done to determine the nonlinear refractive index of the deposited films. The laser beam waist was precisely determined by performing knife edge experiment and was found to be $w_o \approx 26.77$ µm, and the corresponding Rayleigh range ($z_R = \pi w_0^2/\lambda$) is 3.55 mm. Thickness of the films is much smaller than z_R and ensures that the film experiences uniform intensity throughout its thickness. The film area was large (1×1 cm^2) as compared to the spot size and thereby allowing us to neglect the probable diffraction errors in the experiment. Initially, the Z-scan experiment was performed on bare quartz substrate and negligible contribution for nonlinear refraction was found at the input intensity used.

3. Results and discussions

Figure 1 shows the XRD patterns of the grown films. No sharp peak was observed in S2 film (amorphous nature) as compared to S1 (crystalline nature) film which suggests that decrease in the oxygen partial pressure reduces the crystallinity of the TiO_2 thin films [4]. Since S1 film is crystalline in nature, we have determined the particle size using Scherrer formula and found it to be 51.8 nm.

In figure 2, we have represented the $(\alpha h\nu)^2$ vs photon energy ($h\nu$) for both the films. The energy band gap was determined by Tauc plot and was found to be 3.63 eV and 3.56 eV for S1 and S2 films, respectively. The decrease in the band gap of S2 film compared to S1 film by decreasing oxygen partial pressure may be attributed to the amorphous nature of the S2 film and thus it is assumed as indirect band gap. This result is consistent with the earlier reported work of Hassan et.al. [5].

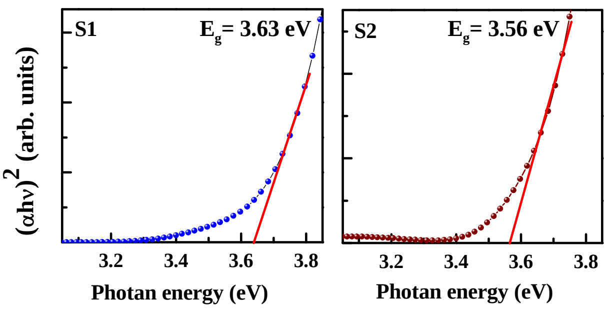

Figure 2. $(\alpha h\nu)^2$ versus photon energy ($h\nu$) plot of S1 and S2 TiO_2 thin films

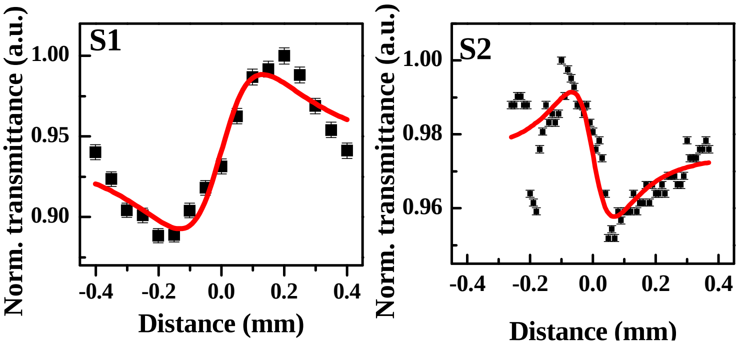

Figure 3. Closed aperture z-scan measurements (at 632 nm) of the grown films. Symbols represent the experimental curve and the solid lines shows theoretical fit using eq. (1)

Figure 3 exhibits the normalized transmittance as a function of distance near the focal region of the lens. Symbols in the figure indicate the experimental data while the solid lines show the theoretical fit to the experimental data. The appearance of transmittance peak followed by valley or vice versa in closed aperture (CA) experimental curve decides the nature of the sample lens and signatures the sign of nonlinear refractive index (NLRI). A peak (valley) followed by a valley (peak) in the CA curve is indicative of negative (positive) lens behaviour of the sample and consequently negative (positive) NLRI. The experimental curves obtained by us exhibit a prefocal transmittance minima (maxima) (valley/peak) followed by postfocal transmittance maxima (minima) (peak/valley) for S1 (S2) films and confirm the positive (negative) NLRI of the films.
Under CA z-scan condition, the normalized transmittance as a function of distance is given by [6, 7]

$$T[x, \Delta\phi_o]=1+\frac{4\,\Delta\phi_o x}{[x^2+1][x^2+9]} \quad (1)$$

Here, x is the dimensionless sample position, $\Delta\phi_o$ is the induced phase shift ($\Delta\phi_o=n_2I_okL_{eff}$) treated as the fitting parameter, k is the propagation vector, L_{eff} is the effective length of the samples, I_o is the intensity at the focal plane and n_2 is the nonlinear refractive index.

Using the value of $\Delta\phi_o$, we have determined the values of nonlinear refractive index using equation (1) for both the films and was found to be 17.6 x 10^{-9} m^2/W and -5.64 x 10^{-9} m^2/W for S1 sample the S2 sample, respectively.

The origin of NLRI is mainly due to electronic and thermal effects. The electronic effect occurs due to band-to-band transition and can be measured only by ultrashort pulse excitation. Laser irradiation also gives rise to thermal lensing effect leading to thermal nonlinearity. In the present experimental situation, we have employed the cw He-Ne laser and have attributed the cause of nonlinear refractive index in the thermal lensing effect [8, 9]. However, we have also observed change in the sign of NLRI from positive (S1) to negative (S2) with the decrease in the oxygen partial pressure. Such a reversal of sign of NLRI may be attributed to crystallinity of the grown films.

4. Conclusion

In conclusion, we have grown the TiO_2 thin films at different oxygen partial pressure using ion beam sputtering technique. The film grown at higher oxygen partial pressure shows the crystalline nature whereas the crystallinity destroys as oxygen partial pressure is decreased during the deposition process. Energy band gap of the films decreases with decrease in oxygen partial pressure. The nonlinear refractive index was determined using closed aperture Z-scan technique. The positive and negative nonlinear refractive indices were observed for S1 and S2 films, respectively. The origin of nonlinear refractive index is ascribed to the thermal lensing effect and the change in the sign is attributed to the crystalline nature of the films. The observed nonlinearity suggest the utility of the grown TiO_2 films for optoelectronic device applications.

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