Chemical Analysis and Non-Linear Optical Properties of TiO_2 Thin Films

Firdous Ahmad Tantray[1,a)], M. Saleem[2], Mukul Gupta[3], Azher Majid Siddiqui[1], Aurangzeb Khurram Hafiz[4], and Pratima Sen[2]

[1]*Department of Physics, JamiaMilliaIslamia, New Dehli-110025*
[2]*School of Physics, VigyanBhawan, Devi Ahilya University, Khandwa Road Campus, Indore 452001,India*
[3]*UGC-DAE Constorium for Scientific Research, Khandwa Road Campus, Indore 452001, India.*
[4]*Centre for Nanoscience and Nanotechnology, JamiaMilliaIslamia, New Dehli-110025*
[a)]tantrayfirdoos@gmail.com

Abstract: In the present work, TiO_2 thin films were deposited on quartz substrate by ion beam sputtering method at varying oxygen partial pressure. The film deposition on the substrate was confirmed by x-ray photoelectron spectroscopy technique. From the results of closed aperture z-scan performed using He-Ne laser, the value of non-linear refractive indices were found decreasing with increase in partial pressure. Thermo-optic coefficient also decreased with increase in oxygen partial pressure, operated during the process of deposition.

Keywords: Ion beam sputtering technique, X-ray photoelectron spectroscopy, non-linear absorption coefficient.

INTRODUCTION

TiO_2 has been known as a material with a high refractive index, high transparency in the visible and near-infrared wavelength region, high dielectric constant, very good wear resistance and stability. Due to these special properties, TiO_2 has become the subject of many investigations for applications in optical coatings [1, 2], microelectronic devices [3] and protective layers [4]. In the last decade, TiO_2 has also attracted a great deal of interest due to its photocatalytic behavior [5, 6]. The decomposition of organic compounds on the surface of TiO_2 and the reduction of the contact angle between water and the surface of TiO_2 under UV irradiation results in self-cleaning and anti-fogging effects. However the application of said material in various device applicationdepends upon various aspects like process of deposition, thickness of film, substrate, surface morphology etc. The combination of TiO_2 with other lower refractive index materials makes it useful for optical wave guides and photonic crystal fabrication. It exhibits excellent photocatalytic oxidative.

EXPERIMENTAL DETAILS

TiO_2 thin films were deposited on quartz substrate by ion beam sputtering technique. Before deposition, substrates were cut into 1.5 cm x 1.5 cm square shaped pieces and were ultrasonically cleaned in acetone. Argon and Oxygen was used as sputtering and reactive gases respectively. During deposition the base pressure was kept at $6x10^{-7}$torr and the working pressure was kept at $1.4x10^{-5}$torr. All the films were deposited for 20 minutes. Three samples viz; S1, S2, and S3 were deposited at different oxygen and argon partial pressures. The oxygen pressure in S1, S2, and S3 was, 0.6 sccm, 0.7 sccm and 0.8 sccm, respectively and argon pressure was 4.4 sccm, 4.3 sccm and 4.2 sccm in S1, S2, and S3 samples respectively, i.e. percentage of oxygen partial pressure to that of argon pressure was 12%, 14% and 16% in S1, S2, and S3 samples respectively.

In order to find the structural properties of the deposited TiO_2 thin films, all the samples were investigated under X-ray diffraction probe. X-ray photoelectron spectroscopy and UV-Vis technique were used for the chemical analysis and linear optical properties of the deposited films. The nonlinear optical properties were determined by performing the Z-scan probe. For the determination of nonlinear refractive index, closed aperture z-scan was performed. While performing the z-scan a He-Ne laser operating at wavelength 632.8 nm was used. Before performing the z-scan, knife edge experiment was done for determining the properties of the laser. The laser beam waist was precisely measured and was found to be w_o= 26.77 μm and corresponding Rayleigh range ($Z_R=\pi\omega_o^2/\lambda$) is 3.55 mm.

RESULTS AND DISCUSSIONS

In order to determine the structure of the TiO_2 deposited films at varying oxygen partial pressure XRD measurement was performed reported in [7]. The results revealed the amorphous nature of the deposited TiO_2 thin films, however there was transition from amorphous to crystalline with increase in oxygen partial pressure during the process of deposition. To understand the mechanism, resulting in change in the band gap and nonlinear refractive index of the deposited TiO_2 thin films at different oxygen partial pressure, the films were investigated by XPS.

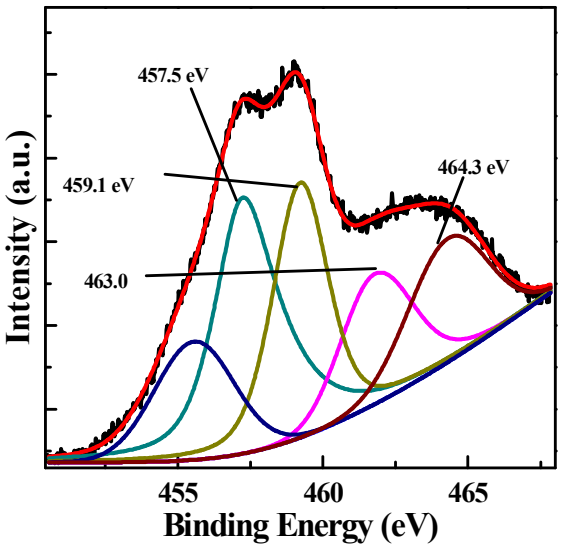

Figure 1(a): Titanium 2p core level spectra

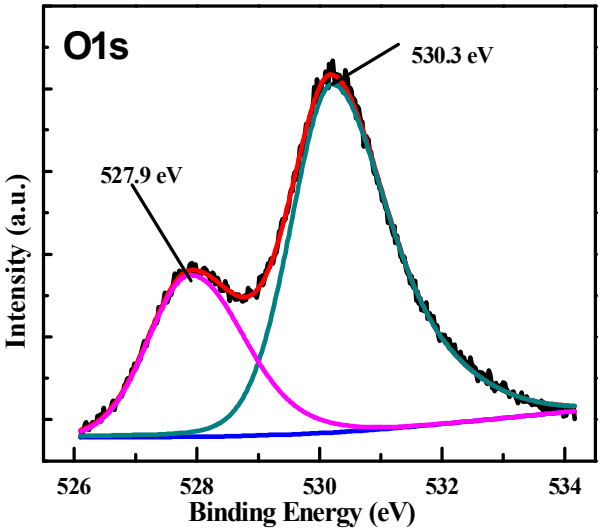

Figure 1(b) Oxygen 1s core level spectra

XPS being surface sensitive technique provides information about the change in chemical state of film constituting species. Here, the variation in the chemical state of elements 'O' and 'Ti' with change in oxygen partial pressure during the process of deposition was analyzed in detail to correlate it with the observed variations in the band gap and nonlinear refractive index of the films. Figure 1(A) shows the Ti 2p XPS core level spectra of TiO_2 film (S1 film) and Figure 1(B) represents the core level spectra of oxygen 1S. Wide survey and detailed scan spectra were recorded and after a Touguard background subtraction, raw spectra were fitted using Voigt (Gaussian–Lorentzian) peak shape. All the core level peak positions were carefully calibrated using the C 1s peak position appearing at 284.8 eV. The appearance of the peak at the binding energy position 457.5 eV and 463.0 eV corresponds to the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ and attributed to Ti^{3+} while the peak appearing at 459.1 eV and 464.3 eV are attributed to Ti^{+4}[8]. From the peak positions, it is clear that Ti ions coexist in two oxidation states. However, the larger area under the curve and the peak intensity of peak appearing at 459.1 eV and 464.3 eV suggests that the Ti^{3+} ions in sputtered TiO_2 films are more prominent in charge state of Ti^{4+}. A similar was obtained for the S2 and S3 sample.

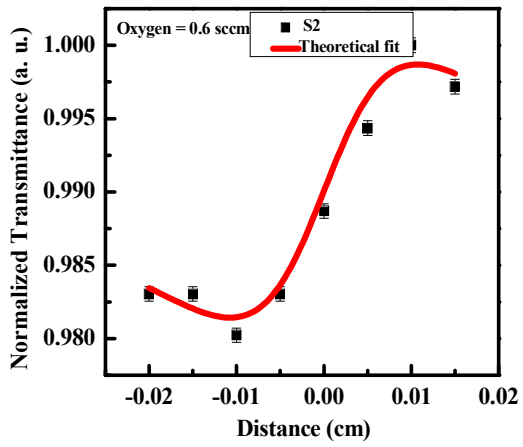

Figure 2(a) Closed aperture Z-scan of S1 sample

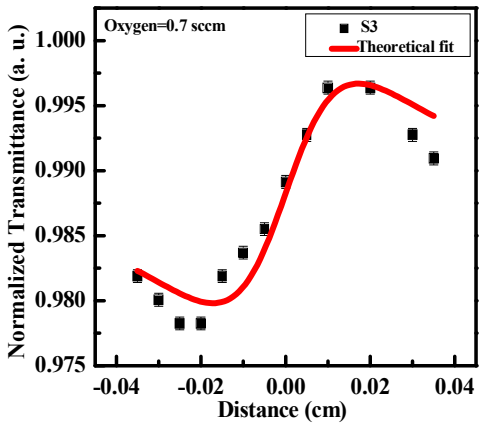

Figure 2(b) Closed aperture Z-scan of S2 sample

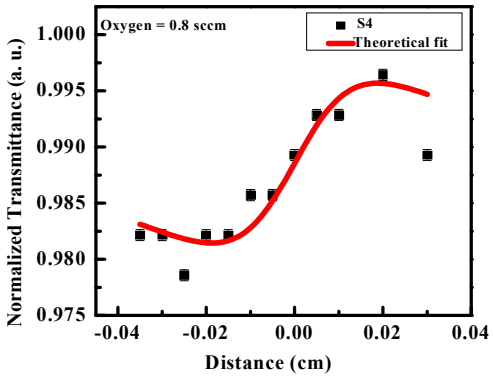

FIGURE 2(c) Closed aperture Z-scan of S3 sample

Figure 2(B) shows the detailed survey scan of O1s core level XPS spectrum. The peak at binding energy position 530.3 corresponds to O^{2-} that are attributed due to lattice oxygen in TiO_2[9]. The peak at lower binding energy (527.9 eV) corresponds to O^{3-}[10] and arises due to formation of Ti_2O_3 in the deposited thin films. The change in the nonlinear refractive index at different oxygen partial pressure arise due to the change in the oxygen vacancies so to understand the role of oxygen vacancies we also calculated the area of peak at binding energy at 530.3 with respect to peak at binding energy 527.9 by the relation, $\frac{\text{ar(peak at 530.3)}}{\text{ar (peak at 530.3) + ar (peak at 527.9)}} \times 100$

Using the result obtained from the above mentioned equation we calculated the ratio of O^{2-} ions to O^{3-} ions in the given samples. It was observed that the percentage of O^{2-} ions increases from 71.16% to 71.68% which suggests that the formation of TiO_2 increases with increase in oxygen partial pressure due to the excessive O^{2-} ions with respect to Ti_2O_3 which is due to presence of O^{3-} ions. To examine the nonlinear refractive index (NLRI) of the grown films, we have performed the closed aperture Z-scan experiment as shown in Figures 2(a), 2(b) and 2(c) for S1, S2 and S3 samples respectively.The appearance of valley followed by the peak suggests the positive sign of the nonlinear refractive index. The symbols are the experimental data points and the solid thick line is the theoretical fit using the equation [11];$T[x,\Delta\phi_o] = \left(1 + \frac{4\,\Delta\phi_o x}{[x^2+1][x^2+9]}\right)$, Here, x is the dimensionless sample position, $\Delta\phi_o$is the induced phase shift treated as the fitting parameter and is given by; $\Delta\phi_o = n_2 I_o k L_{eff}$, Where, $k=2\pi/\lambda$ is propagation wave vector and n_2 is the nonlinear refractive index. Using the value of '$\Delta\phi_o$' in above equation, we have determined the value of nonlinear refractive index for all the samples.It is found that values of nonlinear refractive index decreases with increase in oxygen partial pressure during the process of deposition due to the excessive O^{2-} ions.There are various

processes that might be responsible for the nonlinear refractive index (NLRI). When an intense beam of light is passed through a material, various phenomenon occur in the materials which are responsible for different properties. The NLRI is mainly due to electronic and thermal effects. During electronic effect electrons are excited from ground state to excited state that gives rise to the induced dipole moment. The NLRI in the material due to electronic effect is only possible when an ultra-short pulse (of the order picoseconds) laser source is used as this process occurs within a time duration of the order of picoseconds. Since the intense beam of light when passing through a material also gives rise thermal effect because a small amount of laser power is absorbed by the material that causes increase in the temperature of illuminated portion of sample which results in change in density of illuminated portion the sample, that leads to thermal nonlinear refractive index. In the present experimental situation,we are using He-Ne laser source and hence we attribute the origin of the nonlinear refractive index to the thermal lensing effect.

When NLRI is due to thermal effects, the sample behaves as a thermal lens and the refractive index is temperature dependent. The thermally induced time dependent nonlinear refraction is expressed as [12]; $\tilde{n}=n_0+\left(\frac{dn}{d\theta}\right)\theta$, where n_o is the linear refractive index, θ is the temperature within the illuminated portion and $\left(\frac{dn}{d\theta}\right)$ is the thermo-optic coefficient. In case of thermal lensing, the relation between nonlinear refractive index and thermo-optic coefficient given by [13].$n_2 = \frac{dn}{d\theta}\frac{\alpha R^2}{\kappa}$, where R is the beam waist radius (26.77 μm) and κ is the thermal conductivity of TiO_2 and is taken to be $5 Wm^{-1}K^{-1}$[14]. From the knowledge of nonlinear refractive index and using equation(1.3), we have also calculated the values of thermo-optic coefficient and were found to be 4.02 x 10^{-6} K^{-1}, 3.99 x 10^{-6} $K^{-1}$and 3.96 x 10^{-6} $K^{-1}$for S1, S2 and S3 TiO_2 thin film samples respectively.

In, conclusion,surface chemistry and surface states of TiO_2 thin films highly influence the properties of the thin films under investigation. Increase in oxygen partial pressure during the process of deposition results in increasing rate in the formation of TiO_2 on surface, which in turn results in decrease in non-linear refractive index due to presence of excessive O^{2-} ions in the prepared samples. The increased formation of TiO_2 with increase in oxygen partial pressure also results in decrease in the thermo-optic coefficient of the said deposited thin films.

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