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RESEARCH ARTICLE OPEN ACCESS

Structural and Optical Properties of Co-, Ni- Doped TiO_2 Nanostructured Thin Films Grown by rf-Sputtering Technique

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ABSTRACT
Present work reports the structural, morphological and optical properties of Co-, Ni-doped TiO_2 thin films grown on ITO substrates by rf- sputtering technique through precise control of basic parameters. The X-ray diffraction curves confirm the anatase single-phase crystalline structure with a plane (101) and no traces of secondary phases in all these films. The crystallite size varies from 24 nm to 16 nm due to doping. The optical study is performed from the optical transmittances of the doped and undoped films obtained from UV-Visible spectrometer measured in the range 300 nm to 800nm. The thickness of films are 305 nm, 265 nm and 269 nm for undoped , Co- and Ni- doped TiO_2 respectively. The optical energy gap obtained from Tauc plots decreases with doping. The decrease in the energy gap makes these films more suitable for photocatalytic applications. The morphology of the created films is examined from Field Emission Scanning Electron Microscopy (FESEM) and noticed that films revealed the uniform distribution of grains of spherical size. Other important parameters like refractive index and microstrain are determined for the synthesized films.
KEYWORDS: THIN FILMS, ENERGY GAP, NANOSTRUCTURES>

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I. INTRODUCTION

TiO_2 thin films find intriguing place in many technological applications like photocatalysis, photoelectrodes, dye sensitized solar cells etc. [1]. Different techniques including sol–gel, RF and DC sputtering, spray pyrolysis, chemical vapor deposition (CVD) and pulsed laser deposition (PLD) were used in past to prepare doped and undoped TiO_2 thin films [1]. TiO_2 is a large band-gap semiconductor (i.e. 3.2 eV), [2] therefore to improve the photoactivity of this semiconductor, the band structure is to be tuned via suitable doping. In this direction, the doping with transition metals is an effective way to improve the same via shifting the absorption band in visible region. Since last decade, various researchers had shown more interests in transition metal doped TiO_2 to increase the potential of TiO_2 for photocatalytic and spintronic applications. Among the preparation techniques of new materials, PLD has great importance and useful to maintain the same roughness of the target during the fabrication process [3].

Vyas et al [4] grown TiO_2 films for the gas sensing application and concluded that the properties of nanomaterials rely mainly upon interface and surface properties which are to a great extent represented by the deposition procedure and its ambiance, post-deposition annealing, annealing ambiance and nature of the substrate utilized. A stable, thinner, uniform film with smaller particle size can be synthesized via solvothermal method as compare to sol-gel method [5]. Viana et al [6] reported the pure, crystalline, adherent, transparent, homogeneous, and free of microcracks thin film of TiO_2 through sol-gel method and concluded that the crystallinity increases and the porosity decreases with the increasing in the thermal treatment temperature. Rutile phase Co doped TiO_2 via sol-gel route shows the increase in refractive index and transmittance with increase in Co concentration [7]. De et al [8] demonstrated that Ni-TiO_2 thin film grown using RF magnetron sputtering technique is generally effective for catalytic application because of its reasonable energy band positions in the electronic structure. From various reports it is concluded that there is still contradiction that which dopant is suitable to enhance the optical properties of TiO_2 thin films synthesized through rF sputtering.

The main motivation of present investigation is to deposit Co-, Ni- doped and

undoped TiO_2 films by rf- sputtering technique on ITO substrates and further to analyze the relative effect of Co and Ni dopant on structural and optical properties of TiO_2.

Experimental Details

The target to deposit thin film by rf-sputtering technique, we favored the sol-gel route as it is a basic and interesting preparation method for nanomaterials. The extra advantage of utilizing this technique is that sol concentration, temperature and sintering conditions can be changed in accordance with the composition, particle size and porosity required for undoped/doped TiO_2. For the current examination, the nanocrystalline samples of Co-, Ni-doped and undoped TiO_2 with total 5% doping concentration were prepared by this technique with Titanium Tetrabutoxide ($Ti(OC_4H_9)_4$**)**, Cobalt Acetate Tetrahydrate ($Co(C_2H_3O_2)_2.4H_2O$) and Nickel Acetate Tetrahydrate ($Ni(CH_3COO)_2{\cdot}4\ H_2O$) as the source of Ti, Co and Ni, respectively. To obtain 5% doping of Co or Ni, appropriate proportion of Titanium Tetrabutoxide, Cobalt Acetate Tetrahydrate or Nickel Acetate Tetrahydrate were stirred glacial acetic acid for 5 hour on magnetic stirrer at room temperature to get homogeneous solution. Further, during stirring deionized water was added to mixture for hydrolysis and polycondensation response. The resultant consistent solution was retained at 80 °*C* in hot air oven for gelation procedure until it got dried. The dried material of fine powder nanocrystals were pelletized to two-inch diameter and 3 mm thick using a hydraulic press with a pressure of ~ 8 Tons and sintered at 1000 °*C* for 12 hours. This target was used for thin film deposition using rf- sputtering technique on ITO substrate. Thoroughly cleaned substrates, via acetone and distilled water, were mounted on the substrate holder and the deposition chamber was evacuated to a base pressure of 2×10^{-5} Torr. The Argon (Ar) and oxygen (O_2) gasses were allowed to flow in the deposition chamber in ratio 4:1, respectively. The pressure during deposition was 20 mTorr and rf power supplied to the target was 200 W. The substrate temperature was maintained at 500°C during the film growth. Grazing angle X-ray diffraction (GXRD) studies have been performed to identify the phase. Optical transmittance and spectroscopic ellipsometry studies were performed in the UV–visible region to study Optical properties of doped and undoped TiO_2 films.

II.RESULT AND DISCUSSION

The Grazing angle X-ray diffraction (GXRD) studies were performed first to understand the structure and for this, the grazing angle of 0.5° was chosen. The XRD pattern (Fig. 1) confirms the crystalline anatase structure without any secondary phase for all thin film samples. Similar pattern of XRD TiO_2 films on ITO was reported by Sima et al [3]. Here, in fig. 1 XRD pattern is mentioned only for differentiate the ITO peaks. Slight shifting in position of peak indexed (101) is observed. The crystallite size (D) was calculated using Debye Scherrer's formula [4]i.e.

$$D = \frac{k\lambda}{\beta Cos\ \theta}. \qquad (1)$$

where λ represents wavelength of incident beam (i.e 1.54059 Å), β is the Full Width Half Maxima (FWHM) of the diffraction peak, k is the shape factor (i.e. 0.9) and θ represents scattering angle of reflection. The calculated values of crystallite size for all thin films are mentioned in Table-I, indicates decrease in crystallite size with doping. It is believed that with doping, the substituted Ni-, Co- ions provide a retarding force on the grain boundaries. On the off chance, that the retarding force produced is more than the main driving force for grain development because of Ti, the development of the grain limit is obstructed [9,10]. This in turn decreases the crystallite size with doping. The crystallite sizes with doping Ni- is smaller as compared with Co- doping, which is might be due to deference in ionic radii resulting in structural defects and suppression of grain growth.

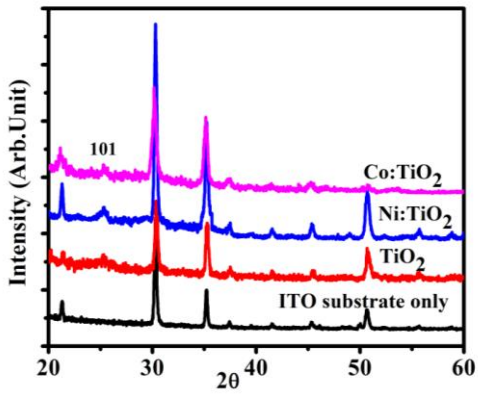

FIGURE 1. XRD patterns for bare ITO substrate, Co-, Ni- doped and undoped TiO_2

The microstrain (ε) developed in doped and undoped TiO_2 thin films were calculated from the equation- 2 and depicted in Table-1.

$$\varepsilon = \left(\frac{1}{Sin\ \theta}\right)\left[\left(\frac{\lambda}{D}\right) - \left(\beta Cos\ \theta\right)\right]. \qquad (2)$$

TABLE 1. Crystallite size and Microstrain (ε) for Co-Ni- doped and undoped TiO_2 thin films

Sample	2θ	FWHM	Crystallite size (nm)	Microstrain (ε)
TiO_2	25.28	0.33824	24	0.00292
Co:TiO_2	25.32	0.47013	17	0.00406
Ni:TiO_2	25.36	0.49525	16	0.00427

size decreases with doping. That shows the good agreement with the XRD results. The incorporation of Ni-, Co- in TiO_2 lattice affect the surface morphology. Similar trend also reported for undoped and Co-doped SnO_2 [11].

In order to understand optical properties of Ni- and Co- doped and undoped TiO_2 films, the optical transmittance obtained from the UV–Visible spectrometer. The refractive index (μ_f) and thickness of the films was calculated using envelope method [12,13].

$$\mu_f = \sqrt{N + \sqrt{N^2 - n^2}}. \quad (3)$$

where

$$N = 2n\frac{T_M - T_m}{T_M \times T_m} + \frac{n^2 + 1}{2} \quad (4)$$

T_M and T_m are the maxima and minima of the envelope in the transmittance spectra and n is the refractive index of the ITO coated glass which can be calculated from the transmittance T of the ITO coated glass using equation [12,13] i.e.

$$n = \frac{1}{T} + \left(\frac{1}{T^2} - 1\right)^{\frac{1}{2}} \quad (5)$$

The thickness of the film was calculated [12, 13] using the relation i.e.

$$d = \frac{\lambda_1\lambda_2}{2(\mu_1\lambda_2 - \mu_2\lambda_1)} \quad (6)$$

where μ_1 and μ_2 are the refractive index at the two adjacent maxima at λ_1 and λ_2. The measured thickness for TiO_2, Ni:TiO_2 and Co:TiO_2 was found 305 nm, 269 nm and 263 nm, respectively. The absorption coefficient (α) of films was determined using the equation [12,13] from transmittance data.

$$\alpha = \frac{\ln\left(\frac{1}{T}\right)}{d} \quad (7)$$

The band gap (E_g) was calculated using Tauc equation for all thin films.

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (8)$$

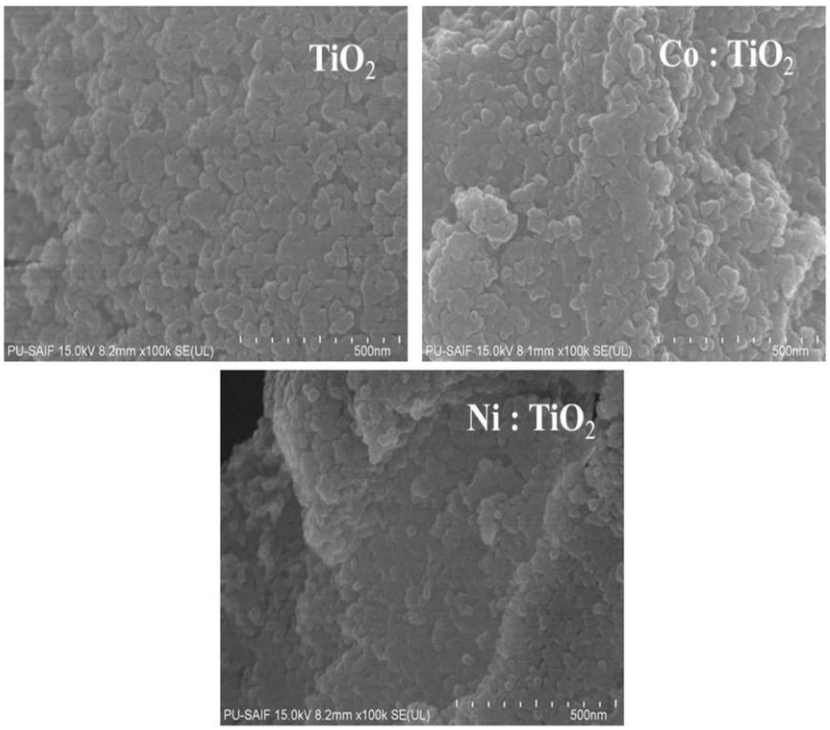

FIGURE 2. FESEM image for Doped and undoped TiO_2 thin films

The Tauc plots; $(\alpha h\nu)^2$ vs. $(h\nu)$ corresponding to all samples were presented in Fig. 2. The bandgaps were obtained by linear fitting of the rising part of the plots to the energy-axis. The estimated bandgap for Ni-, Co-doped and undoped TiO_2 samples were found to be 3.77, 3.87 and 3.95, respectively. The undoped TiO_2 shows absorbance in the shorter wavelength region while the doped nanomaterials result shows a red shift in the absorption spectra. The doping of Co/Ni in TiO_2 shows shifting in optical absorption edge from UV to visible light range. Vyas et al [4] also reported the band gap 3.75 eV for TiO_2 thin film Rf sputtering on ITO substrate. The greater band gap may be because of an axial strain impact from lattice distortion created by a mismatch among film and substrate lattice constant as that brought up for films [14]. Asashi et al. [15] referenced that the substitutional doping of N is viable in the light of the fact that its p states add to the band-hole narrowing by covering with O 2p states, and this has been demonstrated to be essential for band-hole narrowing and improved photocatalytic action. With decrease in the grain size, the disorder increase in the sample. Further, it is very apparent that more defects ought to be presented in the sample with doping if the ionic radii of dopant is greater than that of Ti. Thus with increase in defects the energy gap decreases.

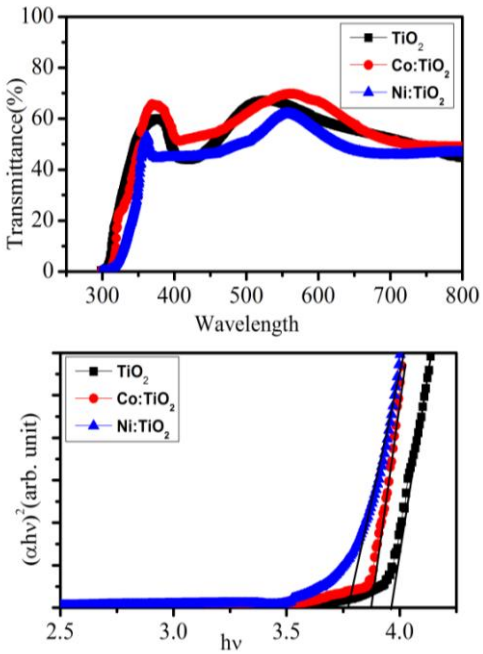

FIGURE 3. Transmittance spectra and Tauc plot for Doped and undoped TiO_2 thin films

The impact of disorder due to doping is progressively articulated in the lower energy of the energy gap, where interaction between valence band holes and /or conduction band electrons and dopant Ni-, Co- particles prompts bending of bands. This band bending, known as Urbach tail, influences energy gap structure and henceforth optical change [9]. Both conduction and valence groups can have tail states inside the forbidden region depending on the nature of the disorder itself .

III. CONCLUSION

In the present work, we concentrated the structural and optical properties of Ni-, Co- doped and undoped TiO_2. The single phase anatse structure of TiO_2 has been confirmed via XRD analysis for all thin films grown on ITO substrate. FESEM images confirm that films revealed the uniform distribution of grains of spherical in shape As ITO has good electrical conductivity and optical transparency, hence it increases its applicability of resultant films in solar cell applications. As energy gap changes with transitional metal doping and hence it is conceivable to tune the band gap of TiO_2 films for any ideal applications, which makes this material to be progressively appealing for photocatalytic applications.

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REFERENCES

[1]. Karabay, I., Yüksel, S. A., Ongül, F., Öztürk, S., & Ash, M. (2012). Structural and Optical Characterization of TiO_2 Thin Films Prepared by Sol-Gel Process. *Acta Physica Polonica-Series A General Physics*, *121*(1), 265.

[2]. Saif, M., El-Molla, S. A., Aboul-Fotouh, S. M. K., Hafez, H., Ibrahim, M. M., Abdel-Mottaleb, M. S. A., & Ismail, L. F. M. (2013). Synthesis of highly active thin film based on TiO_2 nanomaterial for self-cleaning application. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *112*, 46-51.

[3]. Sima, C., & Grigoriu, C. (2009). Study on TiO_2 thin films grown by advanced pulsed laser deposition on ITO. *Thin Solid Films*, *518*(4), 1314-1317.

[4]. Vyas, S., Tiwary, R., Shubham, K., & Chakrabarti, P. (2015). Study the target effect on the structural, surface and optical properties of TiO_2 thin film fabricated by RF sputtering method. *Superlattices and Microstructures*, *80*, 215-221.

[5]. Lee, S. H., Kang, M., Cho, S. M., Han, G. Y., Kim, B. W., Yoon, K. J., & Chung, C. H. (2001). Synthesis of TiO_2 photocatalyst thin film by solvothermal method with a small amount of water and its photocatalytic

performance. *Journal of Photochemistry and Photobiology A: Chemistry*, *146*(1-2), 121-128.

[6]. Viana, M. M., Mohallem, T. D., Nascimento, G. L., & Mohallem, N. D. (2006). Nanocrystalline titanium oxide thin films prepared by sol-gel process. *Brazilian Journal of Physics*, *36*(3B), 1081-1083.

[7]. Tian, J., Deng, H., Sun, L., Kong, H., Yang, P., & Chu, J. (2012). Effects of Co doping on structure and optical properties of TiO_2 thin films prepared by sol–gel method. *Thin Solid Films*, *520*(16), 5179-5183.

[8]. De, R., Haque, S. M., Tripathi, S., Rao, K. D., Singh, R., Som, T., & Sahoo, N. K. (2017). Temperature dependent optical characterization of Ni-TiO_2 thin films as potential photocatalytic material. *AIP Advances*, *7*(9), 095115.

[9]. Karmakar, R., Neogi, S. K., Banerjee, A., & Bandyopadhyay, S. (2012). Structural; morphological; optical and magnetic properties of Mn doped ferromagnetic ZnO thin film. *Applied surface science*, *263*, 671-677.

[10]. Neogi, S. K., Chattopadhyay, S., Banerjee, A., Bandyopadhyay, S., Sarkar, A., & Kumar, R. (2011). Effect of 50 MeV Li3+ irradiation on structural and electrical properties of Mn-doped ZnO. *Journal of Physics: Condensed Matter*, *23*(20), 205801.

[11]. Mazloom, J., & Ghodsi, F. E. (2013). Spectroscopic, microscopic, and electrical characterization of nanostructured SnO2: Co thin films prepared by sol–gel spin coating technique. *Materials Research Bulletin*, *48*(4), 1468-1476.

[12]. Hemissi, M., Amardjia-Adnani, H., & Plenet, J. C. (2009). Titanium oxide thin layers deposed by dip-coating method: Their optical and structural properties. *Current Applied Physics*, *9*(4), 717-721.

[13]. Hanini, F., Bouabellou, A., Bouachiba, Y., Kermiche, F., Taabouche, A., Hemissi, M., & Lakhdari, D. (2013). Structural, optical and electrical properties of TiO_2 thin films synthesized by sol–gel technique. *IOSR Journal of Engineering (IOSRJEN)*, *3*(11), 21-28.

[14]. Ong, H. C., Zhu, A. X. E., & Du, G. T. (2002). Dependence of the excitonic transition energies and mosaicity on residual strain in ZnO thin films. *Applied Physics Letters*, *80*(6), 941-943.

[15]. Asahi R.; Morikawa T.; Ohwaki T.; Aoki K.; Taga Y., "Visible-Light Photocatalysis in Nitrogen-Doped Titanium Oxides", Science, 293 (5528), pp. 269–271, 2001

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