International Journal in Physical and Applied Sciences
Volume 5 Issue 05, May 2018 ISSN: 2394-5710 Impact Factor: 4.657
Journal Homepage: http://ijmr.net.in, Email: irjmss@gmail.com
Double-Blind Peer Reviewed Refereed Open Access International Journal

Effect of Cobalt doping on the structural and optical properties of TiO_2 thin films prepared by sol-gel technique.

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Abstract

In this study, Pure and Co doped titanium dioxide (TiO_2) thin films on glass substrate were prepared by using sol-gel dip coating process. The effects of Co doping on the structural and optical properties of TiO_2 thin films were investigated. The as-prepared films were annealed at temperature 500℃ for 1h and characterized by X-ray diffraction (XRD), atomic force microscopy (AFM) and UV-Visible spectroscopic studies. The XRD patterns and AFM images revealed a polycrystalline structure for all samples. Optical band gap, refractive index, optical conductivity and extinction coefficients of these films were determined using transmittance spectra. Band gap energy of the Co doped anatase TiO_2 films is found to decrease with increasing Co concentration. The refractive index was found to increase from 2.12 to 2.33 with increase in Co concentration from 0 to 1.0-mol %.

Keywords: *Co-doped TiO_2; Sol Gel; Thin Films; Optical band gap;*

1. Introduction

TiO_2 thin films is a highly researched topic as the rutile and anatase phases of these materials have many important properties like effective transmittance in the visible spectral range, high chemical and thermal durability in hostile environments. Thin films of titania are frequently used for optical coatings due to their high refractive index and high stability [1 D. Mergela, 2000], antireflection coatings and optical wave-guides. Several attempts have been made to modify the physical, chemical and optical properties of TiO_2 thin films by doping with transition metal. One way of controlling its properties is by doping with different atoms. Recent discovery of ferromagnetism in Co- doped TiO_2 above room temperature has been drawing increased attention [2-4 S. A. Chamber, S. Thevuthasan, R. F. C. Farrow, R. F. Marks, J. U. Thiele, L. Folks N. J. Seong, S. G. Yoon, C.R. Cho, Appl. Phys. Lett. **81**, (2002), 4209. N. H. Hong, J. Sakai, W. Prellier, A. Hassini, Appl. Phys. Lett. **83**, (2003), 3129. **].** Earlier reports on Co doped TiO_2 revealed that most of the studies focus on the spintronic properties and there is no systematic study on the optical and structural properties of Co doped TiO_2 films for different Co concentrations. Haro-Poniatowski et al. [5 E. Haro-Poniatowski, S. V. Munos, a. Murillo, Mater. Res. Bull., 31, (1994), 329.] have reported a red shift upon Co doping in TiO_2 powders. Simpson et al. [6 J. R. Simpson, H. D. Drew, S. R. Shinde, R. J. Choudhary, S. B. Ogale, T. Venkatesan, Phys. Rev. B69, (2004), 193205.] have reported a blue shift in Co doped TiO_2 films prepared by pulsed laser deposition. The formation of Co doped TiO_2 is very much dependent on the preparation methods. In the present work, a systematic study has been made on the structural and optical properties of Co doped TiO_2 films with different Co concentrations using sol-gel method as it has the advantage of easy control of metallic or inorganic chemical composition of thin films [7 P. Chrysicopoulou,1998].

2. Experimental

2.1. Preparation of TiO_2 precursor sol

A 0.5M TiO_2 solution was prepared by the partial hydrolysis and poly-condensation of titanium tetra-butoxide with water using isopropyl alcohol (IPA) as a solvent and HNO_3 as a catalyst reported earlier [8 S. D sharma , 2006]. All the chemicals used were of AnalaR grade and were used as procured i.e. without further purification. The solution was kept overnight before film deposition.

2.2. Preparation of pure TiO_2 and Co/TiO_2 thin films

For the film deposition, the substrates were ultra cleaned thoroughly and dried before deposition. Then the substrate was dipped in the precursor solution bath and pulled out with a constant speed of 24 cm/min to obtain the films of uniform thickness. A very thin film of TiO_2 that formed on the substrate was first dried in air at room temperature, followed by drying at 100°C for 30 min in an electric oven. The films formed were further heated at 500 °C for 1 h in an electric furnace. For the preparation of the cobalt doped titania films, the procedure was performed as described above; besides that, the appropriate amount of cobalt acetylacetonate [Co (acac) $_2$] from 0.1 to 1.5 mol % was dissolved in the TiO_2 precursor sol.

2.3. Characterization techniques

AFM and XRD studies were performed to get the structure and final phase formation. XRD spectra of the samples have been recorded in the 2θ ranges 20° to 80° for crystal phase identification with a SIEMENS D-500 diffractometer using monochromatized CuKα radiation (λ = 1.541Å). The nanoparticle size and surface morphology were studied using a Nanoscope IIIa Atomic Force Microscope (AFM). Transmission and absorption spectra were recorded from 300 nm – 800 nm with a SHIMADZU UV-3101 PC UV-VIS spectrophotometer at normal incidence

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3. Results and discussion

3.1. XRD

XRD patterns of pure, 0.5 and 1.5-mol% cobalt doped TiO_2 thin films calcined at 500°C are shown in the Fig. 1. Only anatase phase was identified for pure and doped TiO_2 films. The average grain size of the particles is calculated from peak broadening by Scherer equation.

$$L = \frac{0.94\lambda}{\beta \mathrm{Cos}\theta} \qquad [9 \quad \text{B.D. Cullity,1978}]$$

Where λ is the wavelength of CuK_α line (1.542 Å); θ the Bragg's angle and β the half width in radians of the diffraction peak. The size of the particles is in the range of 2 to 5 nm. The particle size decreases as we increase the Co content in TiO_2. No phase was obtained corresponding to cobalt oxide, which implies that Cobalt was finely dispersed in the interstial positions of TiO_2 matrices.

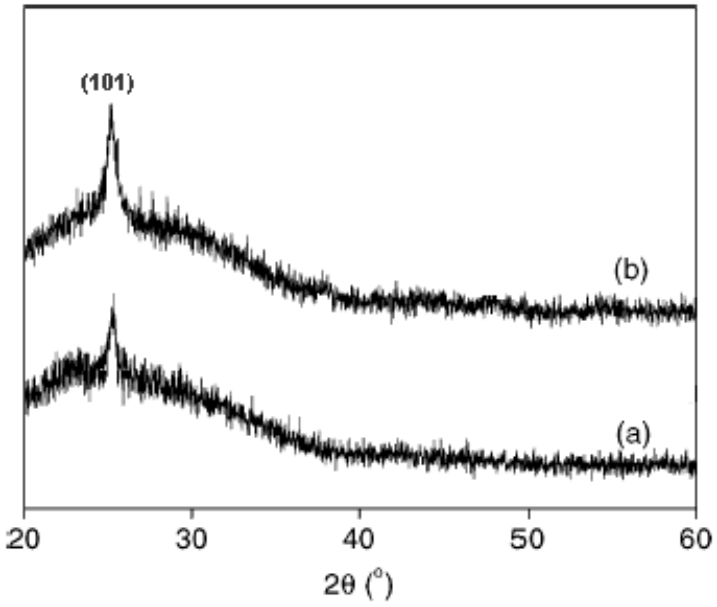
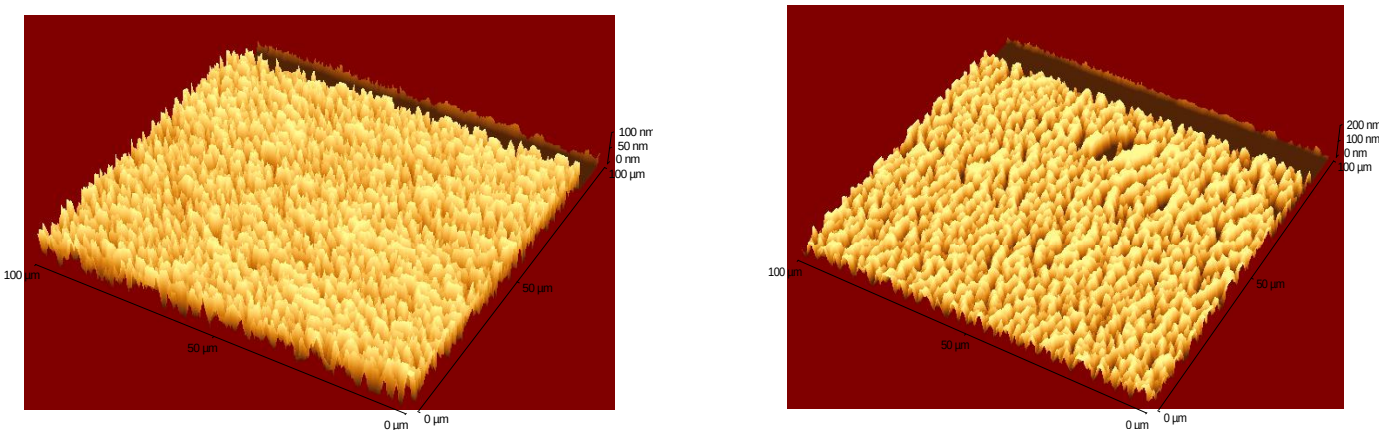


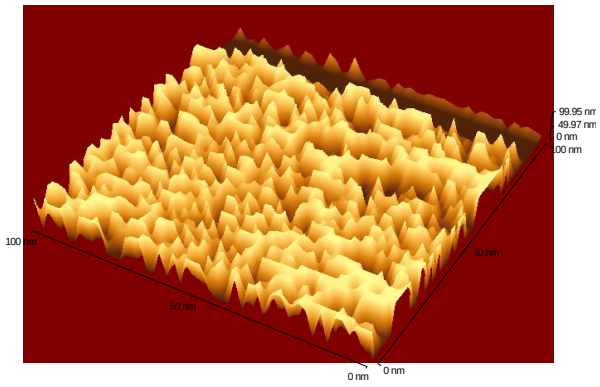
Fig. 1 XRD spectra of (a) undoped TiO_2 and (b) 1.5 mol% Co doped TiO_2 thin films

3.2. AFM Observation.

Fig 2. Shows the AFM three-dimensional images taken from pure, 0.5 and 1.5 mol% Co doped TiO_2 films. The studied surfaces are equal to 100×100 nm in area. The surface profiles reveal that samples are rough, but the shape and the spatial periods of the roughness are very different. The surface roughness of the samples is due to the well known columnar growth structure of TiO_2 [10 Y. Leprince Wang, 2001] AFM was also used to characterize the uniformity and particle size of pure and Co doped films. The pure film has a particle size of 5 nm whereas TiO_2 thin film doped with1.0 and 1.5 mol% Co ions have particle size as small as about 3 and 2 nm. The reduced in particle size by Cobalt doping titanium nano materials also reported by Radha Devi Chekuri et.al(11) [Radha Devi Chekuri, Shiva Rao Trikkovalluri, South African journal of chemical Engineering, 24(2017)183/195.



(a) (b)



(c)

Fig 2. AFM of (a) Pure TiO_2, (b) 0.5 Mol % Co/TiO_2 Co doped TiO_2 (c) 1.5 mol% Co/TiO_2

3.2 Photoluminescence of Co doped TiO_2 films.

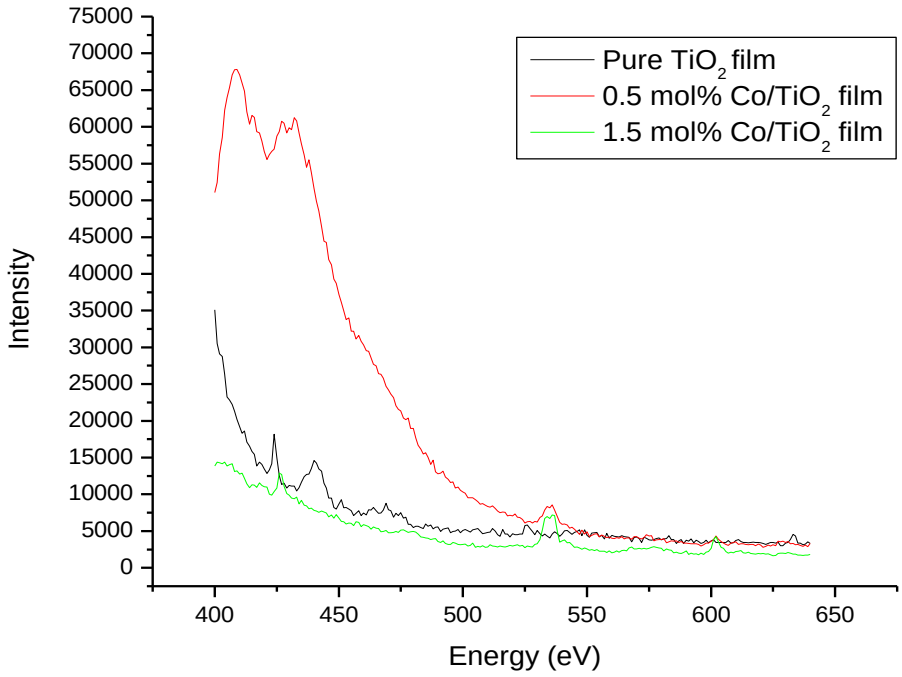


Fig. 3. Photoluminescence of pure, 0.5 and 1.5 mol% Co doped TiO_2

Fig 3. Shows the PL of Co doped TiO_2 films excited at 335 nm in the region from 400 nm to 650 nm. As it is clear from the figure that there is blue shift due to increase in Co concentration. The PL intensity decreases with increase in dopant concentration up to 1.0 mol%. There are four peaks corresponding to transitions from $^4D_{7/2} \rightarrow {}^4F_{3/2}$, $^4D_{7/2} \rightarrow {}^4F_{5/2}$, $^4D_{7/2} \rightarrow {}^4F_{7/2}$ and $^4D_{7/2} \rightarrow {}^4F_{9/2}$.

3.3. Transmittance

Fig.4. Shows the transmittance spectra of undoped and Co doped samples sintered at 500 ^oC. These films are found to be very hard and not possible to scratch them off from the substrate.The wave nature of transmittance between 350 and 700 nm is due to the interference between the TiO_2 film and the substrate.

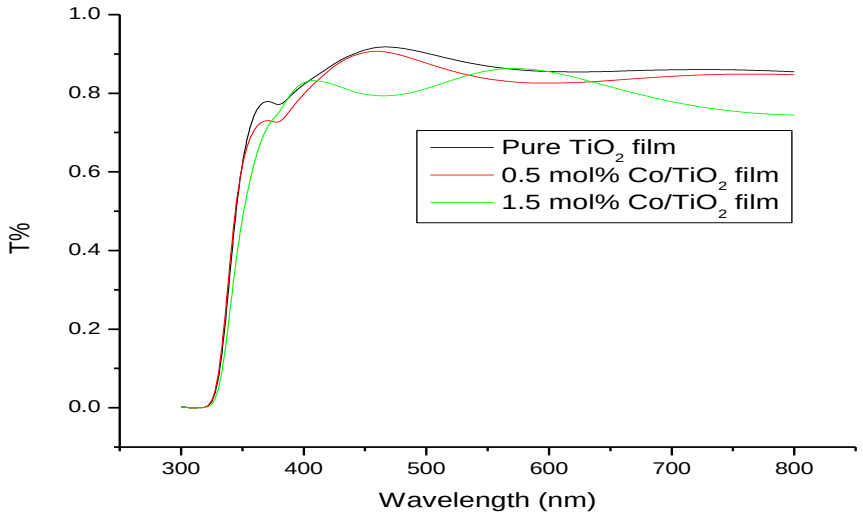


Fig. 4. Transmittance spectra of Pure and Co doped TiO_2 films.

The fast decrease in the transmittance below 400 nm is due to absorption of light caused by excitation of electrons from valence band to conduction band of TiO_2 [12 M. M. Rahman,1999]. Band edge absorption shifts towards the longer wavelength side, which shows the red shift and indicating the decrease in band gap.

3.4. Optical band gap

Determination of band gap energy (E_g) is often necessary to develop the electronic band structure of thin materials. In high absorption region (>10^4/cm) absorption coefficient α is related to the incident photons energy hν by this relation, which is known as Tauc's equation [13 X. K. Zhao].

$$\alpha = B\left[\frac{\left(E - E_g\right)^p}{h\nu}\right]$$

Where B is a constant and p is an index that characterizes the optical absorption process and is theoretically equal to1/2, 2, 3/2 or 3 for direct allowed, indirect allowed, direct forbidden and indirect forbidden transitions, respectively. Best fit in optical absorption data obtained from many oxide films as achieved when p=2, [14. I. B. Lucy, 1995]
The absorption coefficient (α) of undoped and Co doped samples was calculated from the transmittance by using the following formula

$$\alpha = \frac{1}{d} Log\left[\frac{1}{T}\right]$$ [15 D. Mardare, 2000].

Where d is the thickness of the film and T is the transmittance.

The optical band gaps have been calculated by using the well-known Tauc's equation by plotting $(\alpha h\nu)^{1/2}$ Vs hν and extrapolating the linear portion to $(\alpha h\nu)^{1/2} = 0$. The plots of $(\alpha h\nu)^{1/2}$ Vs hν for undoped and Co doped samples are shown in the following Fig.5. The band gap energies estimated from the intercept of the tangents to the plots are 3.07ev, 2.94ev, and 2.89 eV for 0.1,

0.5, and 1.5 Mol % Co doped TiO_2 samples respectively. The decrease in the band gaps of Co doped TiO_2 may be due to the introduction of electronic states by impurity Co 3d electrons.

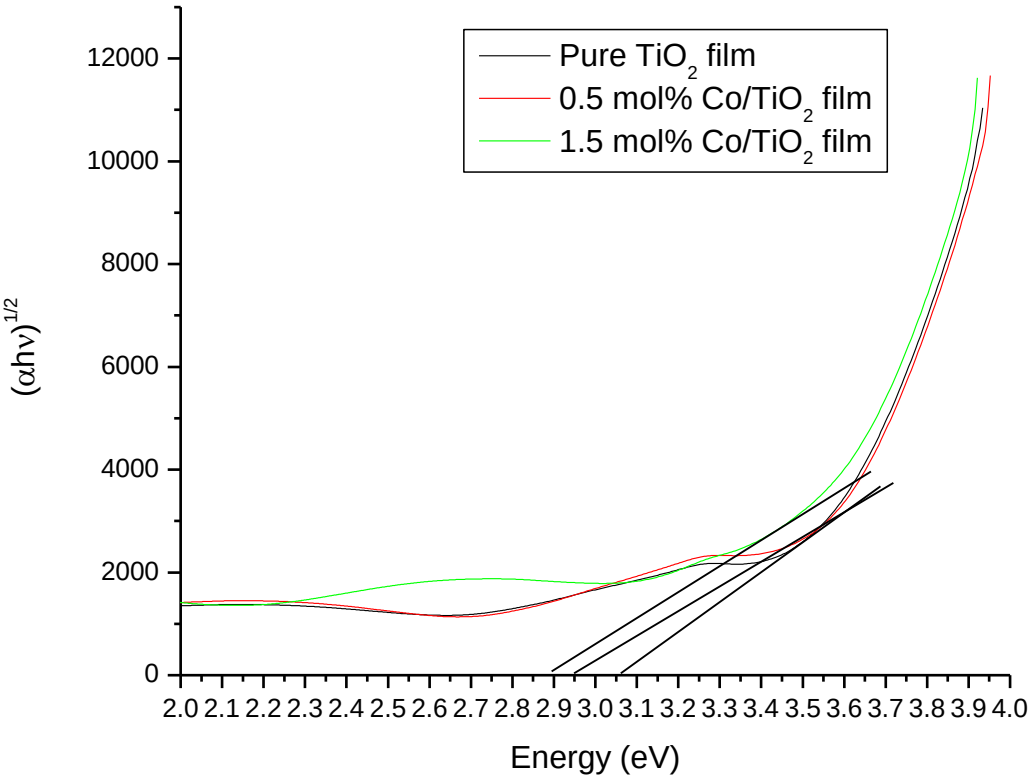


Fig. 5. Optical band gaps of Pure and Co doped TiO_2 films.

3.5. Refractive index

Refractive index, n (λ) of the pure TiO_2 and Co doped TiO_2 films corresponding to wavelength λ at first order transmittance minima position has been determined from absolute T_{min} value provided n_o and n_2 are known by using the following formula [16 Manoj Sreemany,2004]

$$n = \left[\sqrt{n_0 n_2} \left(\frac{1 + \sqrt{1 - T_{\min}}}{\sqrt{T_{\min}}} \right) \right]$$

n_o =1 (refractive index of air) and n_2=1.515 (refractive index of soda glass).

Refractive index of pure anatase TiO_2 film annealed at 500 ^oC for 1 hour is 2.12, which is nearly equal to the value reported by Hu et. al [17]. The value of refractive index in case of Co doped TiO_2 film increases with increase in the cobalt content. This is related to the densification of the film. The dependence of the refractive index on the film density should be easily explained by the well known Clausius-Mossotti relation [18, 19 C. Kittle, Solid State physics, John Willey& Sons, New York, 1971. W. Heitman, Thin Solid Films, 5, (1970), 61.]. The packing density was calculated as

$$P = \left(\frac{\rho_f}{\rho_b}\right) = \left[\left\{\frac{\left(n_f^2 - 1\right)}{\left(n_f^2 + 2\right)}\right\}\left\{\frac{\left(n_b^2 + 2\right)}{\left(n_b^2 - 1\right)}\right\}\right]$$ [20 C.R. Ottermann, 1996]

Where n_f and n_b are the refractive indices of the film and the bulk material of TiO_2. The

P_f and P_b are the density of the film and bulk material respectively.

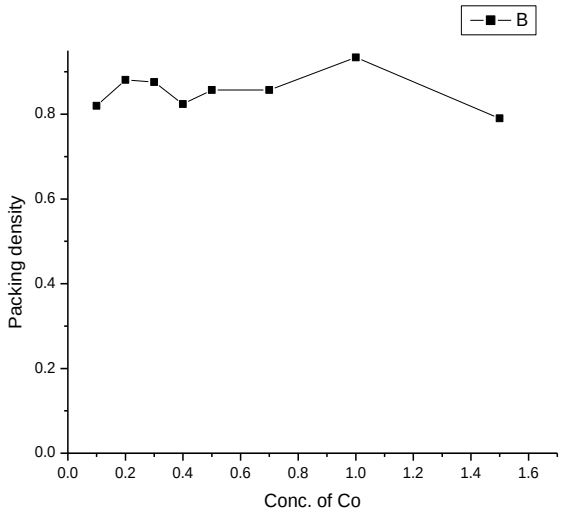


Fig. 6. Packing density of Co/TiO_2 films

The packing density of the films was calculated from refractive index values.

Porosity was calculated by using the following formula

$$Porosity = \left[1 - \frac{\left(n^2 - 1\right)}{\left(n_0^2 - 1\right)}\right]$$ [21 B. E. Yoldas, 1985]

Where n_0 is the refractive index of the pore free antase (n_0=2.52) [22 W. D. Kingery, 1976] and n is the refractive index of the porous thin film. Porosity of these films lies in the range from to 34.68 %. to 17.22 for n=2.12 and n=2.33. The decrease in porosity by cobalt doping indicates the densification of TiO_2 thin films. The same is supported by AFM analysis.

3.6. Extinction Coefficient

Fig. 7. Shows the variation of extinction coefficient k (λ) with wavelength of undoped and Co doped TiO_2 thin films in the range of wavelength 300 to 800 nm. Extinction coefficient increases with increase amount of Cobalt in pure TiO_2. It is calculated by using the formula

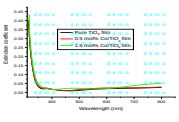
$$k(\lambda) = \left(\frac{\alpha\lambda}{4\pi}\right)$$ 

Fig.7. Extinction coefficient Vs Wavelength.

The AFM results show that the surface of sample 1.5 mol% Co doped TiO_2 is rougher than the other Co doped samples. So if the light scattering is due to the surface roughness, then 1.5 mol % Co doped TiO_2 film should have higher extinction coefficient. Similar effect of surface roughness on the extinction coefficient is reported [23 Li-Jian Meng, 2006].

3.7. Optical conductivity

From the absorption coefficient α we have calculated the optical conductivity σ_{opt} as

$$\sigma_{opt} = \left(\frac{\alpha n c}{4\pi} \right)$$ [24. J. I. Pankove, 1975]

Where α is the absorption coefficient, n is refractive index and c is the velocity of light. Fig. 8. shows the variation of optical conductivity as function of photon energy hν. For positive or negative inhomogeneous films the maximum transmittance will increase or decrease a little, which will sssssssssssscause errors in the refractive index and optical conductivity. Optical conductivity of pure and cobalt doped TiO_2 thin films is in the range of 10^{14} to 10^{15} sec^{-1}.

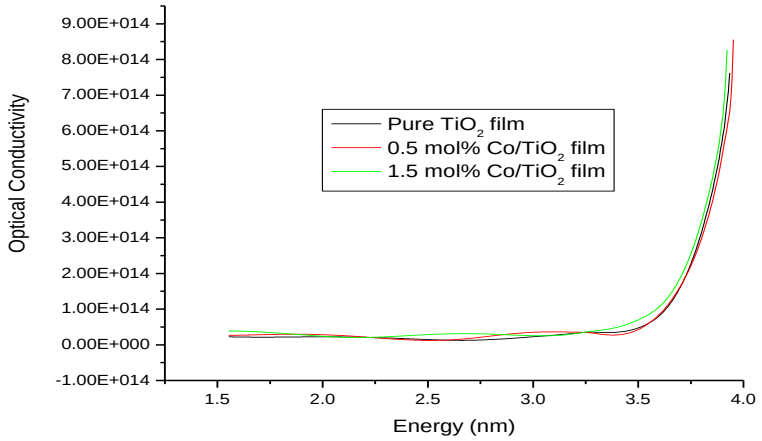


Fig. 8. Variation of Optical Conductivity Vs Photon Energy.

The increase in optical conductivity at high photon energies is due to high absorbance of the TiO_2 thin films and may also be due to electron excited by photon energy. [25 F. Yakuphanoglu, 2005]

4. Conclusions

The pure and Co doped films have an anatase phase and particle size decreases as the Co content increased. In cobalt doped films the band edge absorption shifted towards the longer wavelength side due to which energy gap decreased. Co doped films show red shift due to which energy gap decreased. The deposition conditions have been optimized to obtain nanocrystalline films of pure and doped titanium dioxide. Optical transmittance studies confirmed that the films are maximum transparent in the visible region and the absorption edge shifts towards the longer wavelength side upon increasing concentration upto 1.5 mol %. The observed decrease in band gap upon increasing Co concentration is attributed to the formation of Co impurity band into the TiO_2 energy bands. The reduction band gap is favorable for enhanced photocatalytic activity of TiO_2.

5.Acknowledgements

Authors are highly thankful to director National Physical Laboratory New Delhi for providing laboratory facilities We are also thankful to Dr. Nefa Singh, Dr. K.K. saini for their help in this work.

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