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TiO_2 and Cu/TiO_2 Thin Films Prepared by SPT

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Abstract: Titanium oxide (TiO_2) and copper (Cu) doped titanium oxide (Cu/TiO_2) thin films have been prepared by spray pyrolysis technique. Titanium chloride ($TiCl_4$) and copper acetate ($Cu(CH_3COO)_2.H_2O$) were used as source of Ti and Cu. The doping concentration of Cu was varied from 1-10 wt. %. The X-ray diffraction studies show that TiO_2 thin films are tetragonal structure and Cu/TiO_2 thin films implies CuO has present with monoclinic structure. The optical properties of the TiO_2 thin films have been investigated as a function of Cu-doping level. The optical transmission of the thin films was found to increase from 88 % to 94 % with the addition of Cu up to 8 % and then decreases for higher percentage of Cu doping. The optical band gap (E_g) for pure TiO_2 thin film is found to be 3.40 eV. Due to Cu doping, the band gap is shifted to lower energies and then increases further with increasing the concentration of Cu. The refractive index of the TiO_2 thin films is found to be 2.58 and the variation of refractive index is observed due to Cu doped. The room temperature resistivity of the films decreases with increasing Cu doping and is found to be 27.50 - 23.76 Ω·cm. It is evident from the present study that the Cu doping promoted the thin film morphology and thereby it is aspect for various applications. *Copyright © 2015 IFSA Publishing, S. L.*

Keywords: TiO_2, Cu doped, Structure, Band gap, Resistivity.

1. Introduction

Homogeneous and semiconducting oxide thin films, p or n type, such as aluminum oxide (Al_2O_3), copper oxide (CuO, Cu_2O), indium oxide (InO_x), titanium oxide (TiO_2) etc. play an important role in the fabrication of semiconductor devices in wide range of applications such as transparent conductors, smart windows, solar cells, optoelectronic devices, gas sensors, field emitters, optical switches, catalysts, high temperature superconductors and soil lignin study [1–6]. Both of TiO_2 and CuO/Cu_2O are stable in mechanical and chemical inertness and using various devices [7-8].

TiO_2 thin films have been deposited on microscopic glass substrate by spray pyrolysis technique (SPT) by variation of substrate temperature, molarity of solution and solution spray rate [9]. X-ray diffraction (XRD) patterns indicated that films have amorphous and polycrystalline structure and the size of the crystallites have been changed from 9 to 48 nm. The optical band gap of the TiO_2 films was determined to be about 3.40 to 3.65 eV due to the change of deposition conditions. The electrical conductivity of the TiO_2 film prepared by spin coating method on indium tin oxide glass substrate was found to be very high ($3.4 \times 10^5\ \Omega^{-1}\cdot cm^{-1}$) and comparable to that of the bare ITO glass [10]. The hemin-doped TiO_2 thin films have been prepared by liquid phase deposition

technique on to soda lime glass [11]. UV-vis spectrum shows the optical band gap of TiO_2 thin films to be 3 · 2 eV and XRD pattern of thin films shows a single anatase phase at annealing temperature of 500 °C with some orientation effect in [101] peak. However, the hemin-doped TiO_2 thin films degraded the dye at a surprisingly high rate under visible light. The rate of degradation increases with increasing concentration of hemin. CuO thin films prepared by SPDT using different molar concentrations of 0.10 M, 0.15 M and 0.20 M at 350 °C from copper (II) chlorite precursor solution on the glass substrate [12]. The XRD attained all the films exhibit polycrystalline nature with monoclinic crystal structure comprised uniformly distributed grains. The average crystallite size, optical band gap (E_g), and electrical resistivity (ρ) was found to vary from 22 to 14 nm, 1.42 to 1.47 eV, and 0.18×10^4 to 1.7×10^4 Ω·cm respectively with increasing in concentration.

There are different techniques to prepare oxide thin films, at different deposition parameters: substrate temperature, time and flow rate of deposition, amount of base material, distance between the substrate and spray gun tip, etc., such as spray pyrolysis technique (SPT) [9], solgel [13], vapour deposition technique [14], RF magnetron sputtering [15], etc. The present research work aimed at the production of uniform, transparent, and conductive pure and Cu/TiO_2 thin films by an inexpensive and homemade SPT system [16] using precursor solution of $TiCl_4$ and $Cu(CH_3COO)_2.H_2O$ + $TiCl_4$ respectively. The structural property, surface morphology, optical and electrical properties of the prepared thin films was studied.

2. Experimental

TiO_2 and Cu/TiO_2 thin films were deposited on to ultrasonically cleaned glass substrate by SPT. 0.1 M of $TiCl_4$ was added with 50 ml water and 50 ml ethanol for precursor solution of TiO_2 thin films. Again, (1-10) wt % of $Cu(CH_3COO)_2.H_2$ was added with $TiCl_4$ solution for Cu/TiO_2 thin films. Solution was stirred by a magnetic stirrer for enhance the solubility of prepared solution. The distance between substrate to nozzle was 25 cm, air pressures was 1 bar, spayed time was 5 min, substrate temperature was 400 °C and spray rate was kept constant. For each concentration the reproducibility of the films verified by repeating the experiments several times.

The thickness of the thin films was measured by the setup of Fizeau fringes method [17]. The surface morphology of the films was examined by a HITACHI S-3400N model scanning electron microscope (SEM), the elemental analysis was performed by a electron dispersive spectrometer attached to the SEM. The structural property were characterized using X-ray diffraction, The transmission and absorption spectra for the as-deposited thin films were recorded using a UV-VIS-NIR spectrophotometer as a function of wavelength ranging from 300 to 1100 nm. The electrical resistivity of the films was measured by Van der Pauw method.

3. Results and Discussion

The colour of the TiO_2 thin film is white (deep) which turns gray white on Cu/TiO_2. The thickness of the films was about 200 nm.

Table 1. Elemental analysis of Cu (0-10 %) TiO_2 thin films.

Element (Atom %)	% of Cu					
	0	**1**	**2**	**4**	**8**	**10**
Ti	67.34	65.23	64.53	63.46	60.67	60.02
Cu	0	0	1.45	3.24	7.32	8.64
O	32.22	34.49	33.43	33.12	31.28	30.75

3.1. Structural and Compositional Properties

SEM images were recorded to examine the surface morphology of as deposited TiO_2 and Cu/TiO_2 thin films and the images are shown in Fig. 1. The as-deposited films have islands of different sizes and shapes, and their distribution on the surface is not uniform. These could be the result of variant chemical reaction during the deposition. However, a comparative study shows that a rough surface was observed for pure, and a smooth surface for TiO_2 and Cu/TiO_2 thin films. This indicates that the morphology of particles depend on the precursor solution as well as Cu incorporation in TiO_2 matrix. The films consist of near-spherical particles with an average diameter. The surface morphology of Cu doped (more than 2 %) TiO_2 thin films are similar to that of the Cu doped deposited films, i.e. no significant differences can be discerned. The presence of Ti and O in TiO_2 and Ti, O and Cu in Cu/TiO_2 thin films were observed by energy dispersive analysis of X-rays (EDX).

Fig. 2 shows XRD patterns of the synthesized films. The prominent diffraction peaks can be identified as a TiO_2 phase with tetragonal crystal structure with characteristic peak at 2θ of 25.25, 38.05, and 48.50° corresponding to (hkl) values of (101), (004), and (200) respectively. It was observed that Δ2θ° value is different for Cu doped TiO_2 films than pure TiO_2 thin films and the peaks in the doped films shift from their standard positions in the presence of the dopant. From the broad backgrounds in the patterns, it is evident that the films are somewhat amorphous but with a mainly polycrystalline nature in all cases. From these peaks, using the Debye-Scherrer's formula given by the equation $D= K\lambda/(\beta\cos\theta)$, where D is the crystal size; λ is the wavelength of the X-ray radiation (λ =0.15406 nm) for CuK_α; K is usually taken as

0.89; and β is the line width at half-maximum height, crystallite size was calculated [18]. Lattice constant a, and c of TiO_2 were calculated from the formula of crystal system as follows by the equation $1/d^2 = (h^2 + k^2)/a^2 + l^2/c^2$ where, d is the inter planar spacing, is related to the diffraction angle by θ and these values are recorded in Table 2.

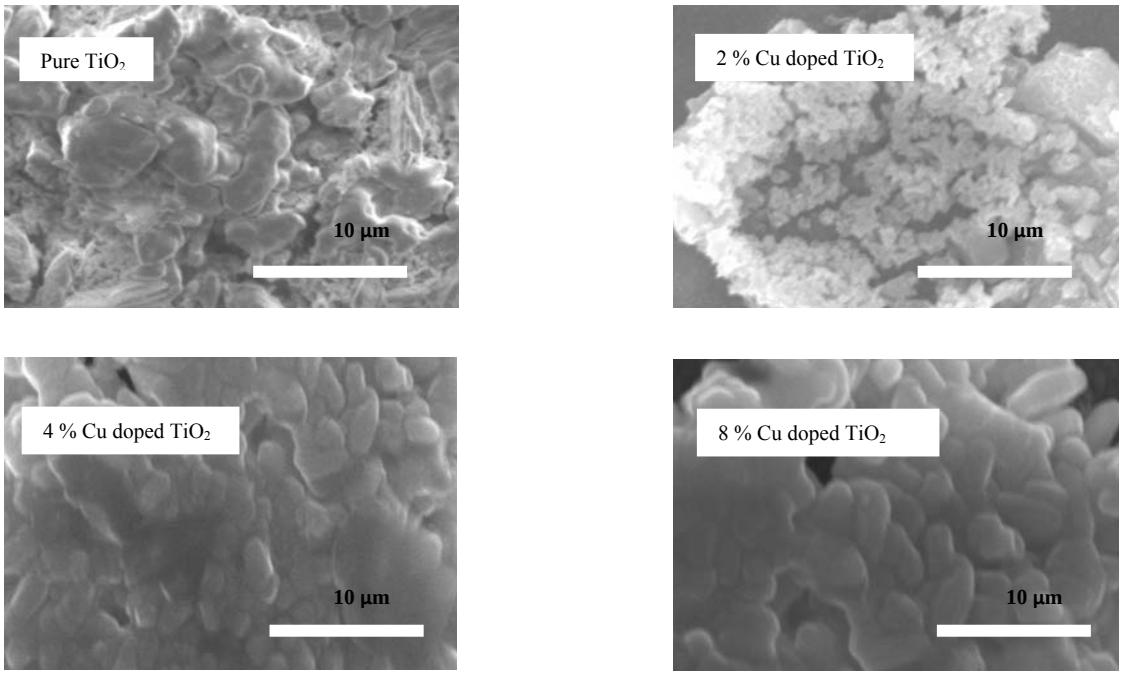

Fig. 1. SEM images of Cu (0-10 %) doped TiO_2 thin films.

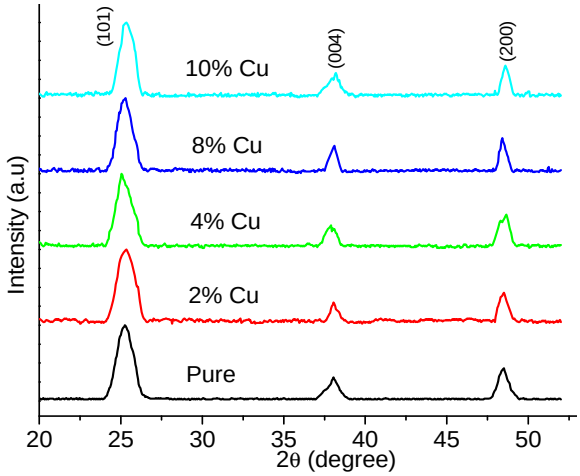

Fig. 2. XRD pattern Cu (0-10 %) doped of TiO_2 thin films.

Table 2. XRD data for the Cu (0-10 %) doped TiO_2 thin films for various MC.

% of Cu	0	8	10
D (nm)	13.5138	14.76	14.56
a, c (Å)	3.8067, 9.1021	3.8567, 9.2132	3.8567, 9.2132

For concentrations at or under % 8Cu, the Cu substitutes into the Ti sites of the lattice, while higher concentrations led to formation of a CuO-like phase. It is evident that the lattice parameters remain almost constant as the doping changes, with slight increase for increasing Cu up to 8 % and then a decrease in the lattice constant is observed as the doping concentration increased to 10 %. Also evident in the higher doped samples is a peak at 2θ = 38.75°, indicative of a segregated CuO-like phase being formed. The appearance of a secondary phase at this doping is reasonable, as earlier studies have suggested that maintaining a single phase beyond this level is difficult. A minimum crystallite size at Cu = 8 %, similar to a study on Cu(0-10 %) TiO_2 thin films prepared via a solid-state reaction technique.

3.2. Optical Characterization

Fig. 3 shows the variation of transmittance with wavelength for TiO_2 and Cu/TiO_2 thin films in the wavelength range of 300 to 1100 nm. It is seen from Fig. 3 that the transmittance is high in the visible and IR region. It is minimum at wavelength ~ 300 nm. Films prepared at 400 ºC exhibit a transmission of > 60 % in the visible and near IR (NIR) region; again it is found > 70 % in the visible and NIR region for Cu doped film, which is found to be greater than that of undoped film. It is found that transmittance decreases with increasing concentration of the dopant, which is due to the increase in the amorphous

nature of the doped films. The transmittance of the films is also influenced by a number of effects, which include surface roughness and optical inhomogeneity in the direction normal to the film surface. The absorption coefficient is of the order of 10^6 m^{-1} which may also be suitable for a transparent conducting film. From both the figures it is observed that the absorption coefficient first increases slowly in the low energy region i.e. in the high wavelength region and then increases sharply near the absorption edge. So the value of the absorption coefficient depends on Cu doping. It is decreases as the concentration of Cu increases but it is increases as Cu doping as more.

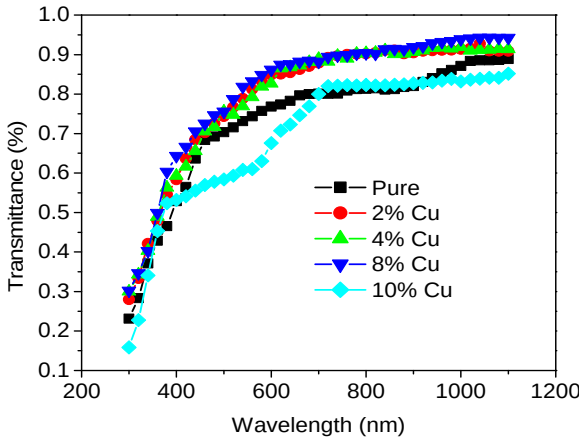

Fig. 3. Variation of transmittance as a function of wavelength for Cu (0-10 %) doped TiO_2 thin films.

The absorbance spectrum for TiO_2 and Cu/TiO_2 thin film is shown in Fig. 4, absorbance spectrum shows low absorbance in the entire wavelength region but it high at wavelength <350 nm.

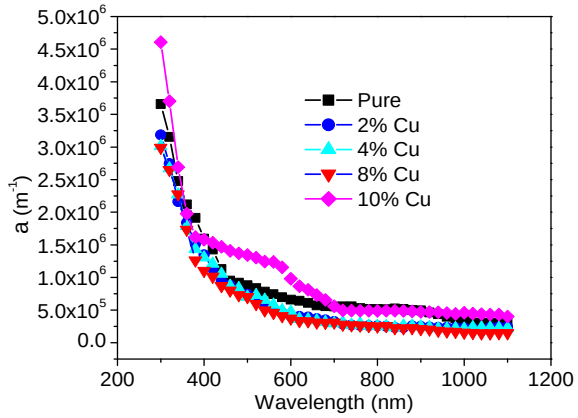

Fig. 4. Variation of absorption coefficient with respect to wavelength for Cu (0-10 %) doped TiO_2 thin films.

This reduction of absorbance in Cu doped samples can be explained as due to the removal of defects and disorder in the as-deposited film by Cu doping. The important optical characteristic of TiO_2 film is that they are transparent in the wavelength ranging from 400 to 1100 nm. At wavelengths shorter than 400 nm, absorption occurs due to the fundamental band gap, and thus light cannot be transmitted due to quantum phenomenon. At longer wavelengths, reflection occurs because of the plasma edge, and light cannot be transmitted due to a classical phenomenon. The corresponding wavelengths for those transmissions are determined by a number of fundamental characteristics as well as by the concentration of free electrons.

The direct transition optical band gap (E_g) is determined from the plots of $(\alpha h\nu)^2$ vs. photon energy ($h\nu$) for E_g of TiO_2 and Cu/TiO_2 thin films as shown in Fig. 5. E_g of the films has been obtained from intercept on the energy axis after extrapolation of the straight line section of $(\alpha h\nu)^2$ vs. $h\nu$ curve. The variation of E_g for concentration of Cu is shown in Fig. 6. The E_g of TiO_2 thin films is obtained 3.40 eV which is in excellent agreement with the reported value of band gap determined by other workers. For 8 % Cu doping the direct band gap of the film becomes 3.20 eV. So it is clear that for Cu doping change E_g of the pure TiO_2 thin films. These values are small compare to the reported values. The variation of refractive index (n) for TiO_2 and Cu/TiO_2 thin films statesman are graphically shown in Fig. 7.

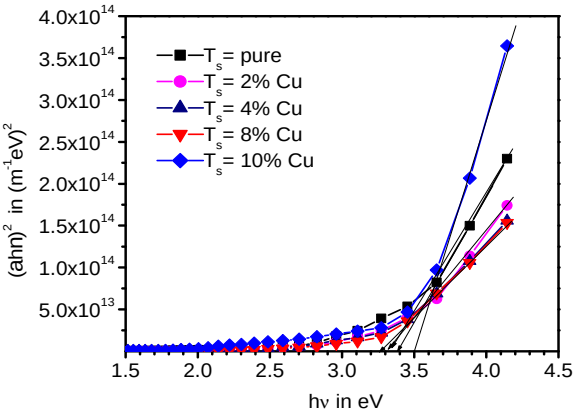

Fig. 5. Variation of $(\alpha h\nu)^2$ with photon energy (h ν).

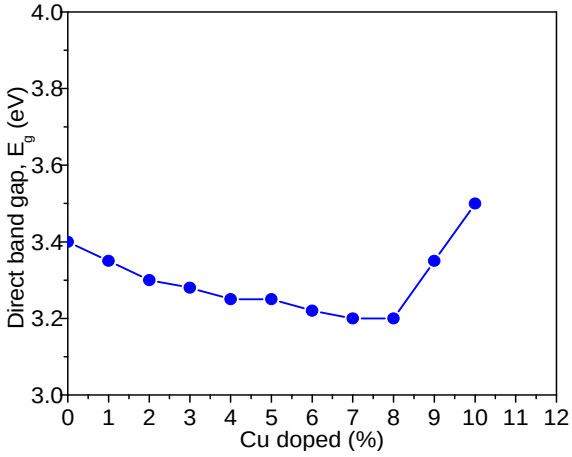

Fig. 6. Variation of band gap with Cu doped.

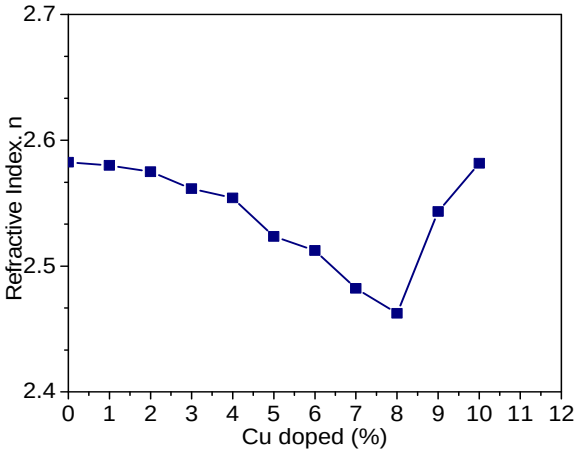

Fig. 7. Variation of refractive index with Cu doped.

The n of TiO_2 thin film is obtained 2.58 which is very close to the reported values 2.6 to 2.55 and lowest n to be becomes 2.45 for 8 % Cu doping. The observed value is low compared to the reported values for similar films [19]. As suggested by Arai [20] this low value of refractive index may probably due to the smaller density of the films. It is observed that n increases further than Cu doped. At the films shows high index because the impurity in the film increases optical properties. The reason is that, at high temperature the mechanism of impurities thermal activation becomes the dominant one. It is seen from the graph that the transmittance decreases with Cu doping up to 8 % once more transmittance increases. The decrease of transmittance means increase of band gap with Cu doping may due to the increase of carrier mobility or due to increase of carrier concentration. So it is clear that beyond 8 % Cu doping for more carrier concentration exists such that scattering occurs and then band gap increases. The excess of Cu atoms do not occupy the popper lattice positions to contribute to the free carrier concentration while, at the same time, enhance the disorder of the structure leading to an increase in band gap [21]. This is expected as the periodicity of Ti matrix distributed in the film in presence of Cu atoms might enhance the scattering of the conduction electrons. On increasing the concentration of Cu the band gap of the Cu doped thin film decreases, further increase in the band gap of the Cu doped thin film due to the decrease in the atomic density in these planes. This process leads to the movement of Ti^{+4} ions in the interstitial sites and also an increase in the amorphous phase and disorder.

3.3. Electrical Properties

The resistivity of the pure TiO_2 and Cu doped TiO_2 thin films were measured by the Van der Pauw method. Resistivity measurements were made on as-deposited films from room temperature to 470 K in air. During each measurement, the temperature was increased slowly to ensure that the whole film had a uniform temperature. The variation of resistivity with temperature is shown in Fig. 8. One can see that the resistivity gradually decreases with increasing temperature, indicative of the semiconducting nature of the materials. Fig. 9 also shows that the resistivity decreases with increasing concentration of Cu, as has been noted in previous Zn1−xNixO studies [22]. The room temperature resistivity of the films decreases with increasing of Cu doped and is found to be 27.50 - 23.19 Ω·cm.

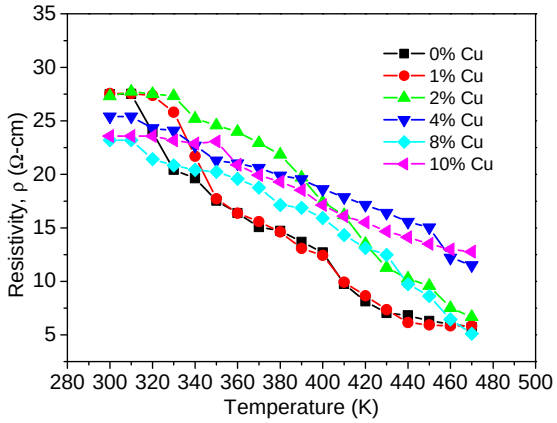

Fig. 8. Electrical resistivity vs. room temperature of Cu (0-10 %) TiO_2 thin films.

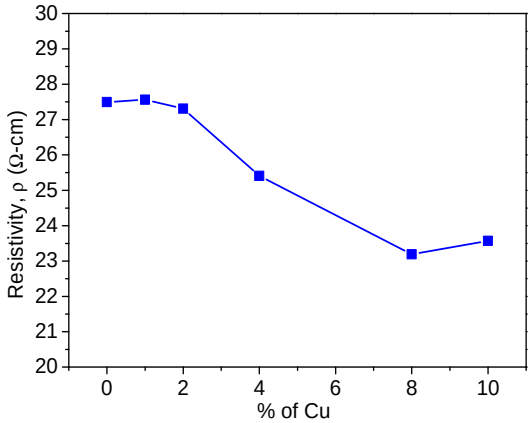

Fig. 9. Electrical resistivity vs. Cu (0-10 %) TiO_2 thin films at room temperature.

The conductivity of the prepared thin films is increased with Cu doping and increase of temperature as shown in Fig. 10 because of concentration of carrier increases. The variation of activation energy (E_a) with Cu doped is shown in Fig. 11.

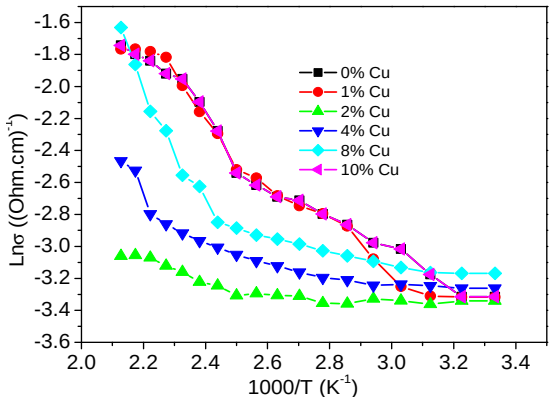

Fig. 10. Electrical conductivity (lnσ) vs. inverse of absolute temperature of Cu (0-10 %) TiO_2 thin films.

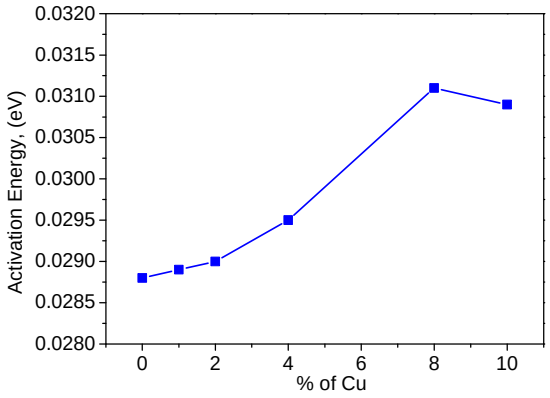

Fig. 11. Variation of activation energy vs. Cu (0-10 %) TiO_2 thin films.

It is observed that for Cu doping the E_a is increases. Variation of Figure of merit vs. Cu (0 - 10 %) TiO_2 thin films as shown in Fig. 12 it is also shown that because of Cu doping the Figure of merit is increased. This observed reduction in resistivity upon doping is understandable, as some Ti atoms with full 3d shells (providing only semicore valence band states) are replaced with Cu, where the 3d shell is not full (3d8) and has states near the bottom of the conduction band. This addition of conduction band states will accommodate more conduction electrons and therefore lower the resistivity. The increase of resistivity can be explained by more carrier concentration and disordering of crystal structures of thin films. It is finale that the optical and electrical characterization of TiO_2 thin films has been changed with Cu doping in thin films.

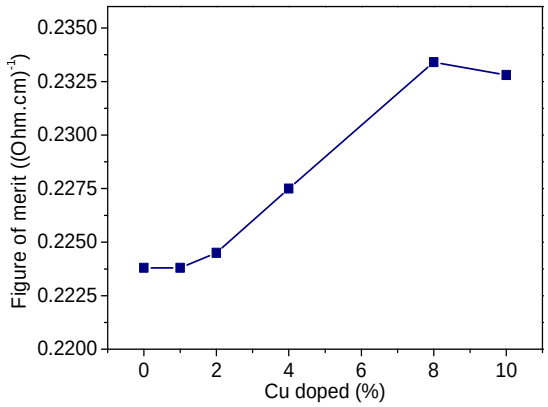

Fig. 12. Variation of Figure of merit vs. Cu (0-10 %) TiO_2 thin films.

4. Conclusions

Spray pyrolysis is a suitable and novel technique for the production of quality TiO_2 and Cu/TiO thin films. The average thickness of the film is found to be 200 nm. SEM image of TiO_2 thin film shows unique and homogeneous surface. EDX data reveals that Ti, Cu, and O are present in Cu/TiO thin films. TiO_2 thin film made up of tetragonal structure with anatase phase. After Cu doping no change in structure consequently, but at higher doping of Cu XRD shows that CuO also present at Cu/TiO thin films i.e. for Cu doped of 8 % of TiO_2 thin films implies that CuO has present. TiO_2 films have good optical transmission and it is about 88 %. Maximum transmission about 94 % is found for 8 % Cu doped TiO_2 films but beyond 8 % Cu doped, transmission decreases. The direct band gap of pure TiO_2 thin film is reduced after Cu doping. The UV-vis spectrum shows the optical band gap of TiO_2 thin films to be 3· 40 eV and after Cu doping it is reduced which is in good agreement with theoretical values. The refractive index of the pure films is bring into being 2.58 and for 8 % Cu doped TiO_2 thin film is 2.45. The thin films with good optical transparency are to be prepared with 8 wt% Cu doping. TiO_2 thin film shows resistivity 27.50 Ω·cm, after Cu doping it is decreased and reduces to 23.19 Ω·cm for 8 % of Cu doped in thin films, again resistivity of the Cu/TiO thin films increases whenever Cu doping is increased. These results demonstrate the ability of Cu doping for tuning the TiO_2 thin films band gap.

References

[1]. K. L. Chopra, Major S., D. K. Pandya, Transparent conductors — a status review, *Thin Solid Films*, Vol. 102, No. 1, 1983, pp. 1-46.

[2]. H. Luo, M. Jain, T. M. McCleskey, E. Bauer, A. K. Burrell, Q. Jia, Optical and Structural Properties of Single Phase Epitaxial p-Type Transparent Oxide Thin Films, *Advanced Materials*, Vol. 19, No. 21, 2007, pp. 3604-3607.

[3]. L. C. Olsen, F. W. Addis, W. Miller, Experimental and theoretical studies of Cu_2O solar cells, *Solar Cells*, Vol. 7, No. 3, 1982, pp. 247-279.

[4]. J. Hennemann, C.-D. Kohl, B. M. Smarsly, T. Sauerwald, J.-M. Teissier, S. Russ, T. Wagner, CuO thin films for the detection of H_2S doses: Investigation and application, *Physica Status Solidi (A)*, Vol. 212, Issue 6,2015, pp. 1281-1288.

[5]. G. Kiriakidis, N. Katsarakis, M. Bender, E. Gagaoudakis, V. Cimalla, InO_X Thin Films, Candidates for Novel Chemical and Optoelectronics

Applications, *Mater. Phys. Mech.*, Vol. 1, No. 2, 2000, pp. 83-97.
[6]. K. Zakrzewska, M. Redecka, M. Rekas, Effect of Nb, Cr, Sn additions on gas sensing properties of TiO_2 thin films, *Thin Solid Films*, Vol. 310, No. 1, 1997, pp. 161-166.
[7]. R. Manyala, Solar Collectors and Panels, *Theory and Applications*, 2010.
[8]. K. Matsuzaki, K. Nomura, H. Yanagi, T. Kamiya, M. Hirano, H. Hosono, Epitaxial growth of high mobility Cu_2O thin films and application to p-channel thin film transistor, *Applied Physics Letters*, Vol. 93, Issue 20, 2008, pp. 202107-202110.
[9]. A. G. Manohari, S. Dhanapandian, K. Santhosh Kumar, T. Mahalingam, Optimization of Deposition Parameters on the Physical Properties of TiO_2 Thin Films by Spray Pyrolysis Technique, *Int. J. Thin Fil. Sci. Tec.*, Vol. 3, No. 1, 2014, pp. 1-6.
[10]. A. A. Daniyan, L. E. Umoru, A. Y. Fasasi, J. O. Borode, K. M. Oluwasegun, S. O. O. Olusunle, Electrical Properties of Nano-TiO_2 Thin Film Using Spin Coating Method, *Journal of Minerals & Materials Characterization & Engineering,* Vol. 2, 2014, pp. 15-20.
[11]. N. S. Begum, H. M. F. Ahmed, Synthesis of nanocrystalline TiO_2 thin films by liquid phase deposition technique and its application for photocatalytic degradation studies, *Bull. Mater. Sci*., Vol. 31, No. 1, 2008, pp. 43-48.
[12]. V. Saravanakannan, T. Radhakrishnan, Structural, Electrical and Optical Characterization of CuO Thin Films Prepared by Spray Pyrolysis Technique, *International Journal of ChemTech Research,* Vol. 6, No. 1, 2014, pp. 306-310.
[13]. M. Keshmiri, M. Mohseni, T. Troczynski, Development of novel TiO_2 sol-gel-derived composite and its photocatalytic activities for trichloroethylene oxidation, *Applied Catalysis B: Environmental*, Vol. 53, No. 4, 2004, pp. 209-219.
[14]. J. Joseph, V. Mathew, J. Mathew, K. E. Abraham, Studies on physical properties and carrier conversion of SnO_2:Nd thin films, *Turk J. Phys*, Vol. 32, 2008, pp. 1-10.
[15]. Hao-Long Chena, Yang-Ming Lub, Weng-Sing Hwanga, Characterization of sputtered NiO thin films, *Surface & Coatings Technology*, Vol. 198, 2005, pp.138-142.
[16]. S. S. Roy, A. H Bhuiyan, J. Podder, Optical and Electrical Properties of Copper Oxide Thin Films Synthesized by Spray Pyrolysis Technique, *Sensors & Transducers*, Vol. 191, Issue 8, 2015, pp. 21-27.
[17]. J. Kongsakul, N. Witit-anun, S. Chaiyakun, P. Kaewtrakulpong, Measurement of Aluminum Thin Film Thickness by Fizeau Interferometer Technique, *Dept. of Physics*, Burapa University, 2005.
[18]. P. Debye, Zur Theorie der spezifischen Waerme, Annalen der Physik,German, Leipzig, Vol. 39, No. 4, 1912, pp. 789-839.
[19]. M. I. B. Bernerdi, E. J. H. Lee, P. N. Lisboa-Filho, E. R. Leite, E. Longo, J. A. Varela, TiO_2 Thin Film Growth Using the MOCVD Method, *Materials Research*, Vol. 4, No. 3, 2001, pp. 223-227.
[20]. T. Arai, *J. Phys. Soc. Jpn.*, Vol. 15, No. 916, 1960.
[21]. J. Mohapatra, D. K. Mishra, S. K. Kamilla, V. R. R. Medicherla, D. M. Phase, V. Berma, S. K. Singh, Ni-Doped ZnO: Studies on Structural and Magnetic Properties, *Phys. Status Solidi B*, Vol. 248, Issue 6, 2011, pp. 1352-1359.
[22]. S. Singh, N. Rama, M. S. R. Rao, Influence of d−d Transition Bands on Electrical Resistivity in Ni Doped Polycrystalline ZnO, *Applied Physics Letters*, Vol. 88, 2006, 222111-1 – 222111-3.