

Study of Some Optical Properties of Mixed SnO₂-CuO Thin Films

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We report the transparent conducting mixed SnO₂-CuO oxides films fabricated by chemical spray pyrolysis technique (CSPT). The effects of the film thickness on the optical absorptance of the TCO films are assessed. Optical absorption measurements were studied by UV-VIS technique in the wavelength ranges 400-1100 nm. Characteristics and optical constants of the mixed oxides thin film such as refractive index, extinction coefficient, real and imaginary parts of dielectric constant have been studied. The optical conductivity and the skin depth are increased with increasing the film thickness.

Keywords: Transparent conducting oxides, Optical constants, Spray pyrolysis, SnO₂-CuO.

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1. INTRODUCTION

Transparent conductive oxide films are currently of great importance as optoelectronic devices such as solar cells, optical filters, high stability resistors, covering layers for fiber optical systems, photovoltaic devices, optical gas sensors and electrochromic devices [1-6]. Among them, tin oxide (SnO₂) is the most widely used due to its broad range of applications. SnO₂ presents outstanding optical and electrical properties accompanied with an excellent chemical and mechanical stability and heat resistant [7]. It has been projected due to its large direct band gap (3.6 eV) and its high exciton binding energy (130 meV) at room temperature [8-11]. In addition, tin oxide exhibits low electrical resistivity and high optical transmittance.

Either doped or undoped tin oxide thin films can be fabricated by a number of techniques such as chemical vapor deposition [12, 13], canon-ray evaporation [14], sol-gel coating [15], laser pulse evaporation [16, 17], magnetron sputtering [18-22], electron beam evaporation [23, 24] and spray pyrolysis [25-27]. The simplest way to form SnO₂ films is the spray pyrolysis technique, it is well suited for the preparation of doped tin oxide thin films because of its simple and inexpensive experimental arrangement, ease of adding various doping materials, reproducibility, high growth rate and mass production capability for uniform large area coatings [28].

Previous investigations published in the literature [29-31] were aimed to obtain tin oxide films with low electrical resistance ($10^{-2} \Omega\cdot\text{cm}$) and high optical transmittance (75 %). These studies show a strong correlation between the electrical response of the SnO₂ films and the incorporation of metallic aggregates. By dispersing a low concentration of small metallic particles (Pd, Pt, Cu, etc.) on the surface of the SnO₂ grains, the sensitivity and selectivity of SnO₂ based sensors can be improved [32-33]. Therefore, the doping method is preferable in which a suitable dopant is added to SnO₂ and thereby free electrons are generated. For optoelectronic applications, a good estimation and tun-

ing of the optical properties of the SnO₂ films is an important and primordial step.

In this work, we have paid a specific attention to the influence of thickness on the optical parameters of the mixed SnO₂-CuO films. In fact, the increasing of thickness may have an influence on the film microstructure and its optical and electrical properties. The metal doping-induced optical change of SnO₂ has been correlated to the morphological and structural characteristics of the films.

2. EXPERIMENTAL DETAILS

Thin films of mixed tin and copper oxides have been prepared by chemical pyrolysis technique. The starting solution was achieved by aqueous solutions of 0.1 M SnCl₄·5H₂O from Fluka Germany and 0.1 M CuCl₂ from Merc Germany used as a doping agent to form (SnO₂)_{0.5}(CuO)_{0.5}. These materials were dissolved in deionized water and ethanol, formed the final spray solution and a total volume of 50 ml was used in each deposition, a few drops of HCl were added to make the solution clear. The spraying process was done by using a laboratory designed glass atomizer, which has an output nozzle about 1 mm. The films were deposited on preheated glass substrates at a temperature of 500 °C, with the optimized conditions that concern the following parameters, spray time was 10 sec and the spray interval 3 min was kept constant, the carrier gas (filtered compressed air) was maintained at a pressure of 10^5 Nm^{-2} , distance between the nozzle and substrate was about $29 \pm 1 \text{ cm}$, solution flow rate 5 ml/min. Optical transmittance and absorbance were recorded in the wavelength range (400-1100 nm) using UV-VIS spectrophotometer (Shimadzu Company Japan). In order to explore the influence of films thickness on the parameters under investigation, the films prepared with different thickness in the range of 400, 450 and 500 nm. film thickness was determined by Fizeau fringes. The estimated error for our experimental set-up did not exceed 2%.

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3. RESULTS ANF DISCCUSION

It is important in the device design to optimize the TCO thickness to achieve the sufficient optical conductivity and at the same time to keep the optical absorption losses low. Fig. 1 shows how the optical absorptance of three TCO films prepared under the same conditions increases with the thickness starting from 400 nm to 500 nm. The surface roughness increases with the film thickness giving the thickest sample a milky appearance (haze) when observed in air. The optical absorptance increases with TCO thickness in all spectral range.

According to the Drude model [34] the IR optical absorption is related to free carriers(When the absorbance increase ,the transmittance of the film is decreased due to thickness effect. These changes of transmittances are associated to the increase of carrier concentration [35]), which are expected to increase in highly thickness samples. The band-to-band absorption (the fundamental optical absorption edge) of TCO films is revealed in the absorptance spectra below 500 nm. However, we see that even at 400 nm the optical absorptance in the films does not saturate, and the films are partly UV transparent.

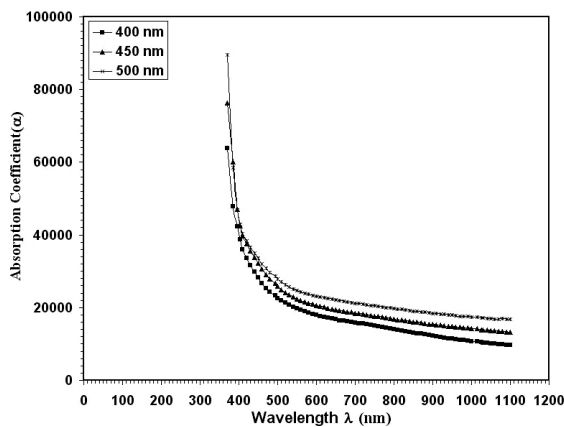


Fig. 1 – Absorption versus wavelength of SnO₂-CuO thin films

The optical properties of mixed SnO₂-CuO thin films by means of optical absorption in the UV to Vis region of (400-1100) nm have been investigated. The absorption coefficient (α) could be calculated using the following relation [36]:

$$\alpha = 2.303A/t \tag{1}$$

Where A is the absorption and t is the film thickness. Fig. 2 shows the dependence of the absorption coefficient α on the wavelength. The absorption coefficient increases with the increasing of the film thickness. It can be seen from the figure that the position of the absorption edge is slightly changes, this could be due to the presence of Cu atoms that limit the growth of SnO₂ grains (decrease of grain size with metal concentration). In fact, this could induce a significant deformation of the crystalline state, which suggests modifications in the electronic structure [37]. As a result the decrease in the optical band gap with increasing film thickness can be attributed to the presence of unstruc-

tured defects that increase the density of localized states in the band gap and consequently decrease the energy gap [38].

The extinction coefficient k can be determined by using the relation [39]:

$$k = \alpha\lambda/4\pi \tag{2}$$

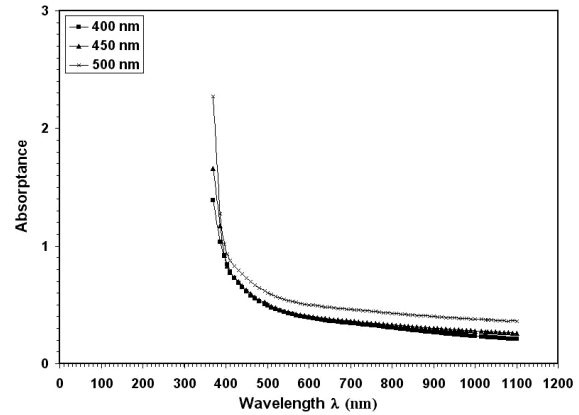


Fig. 2 – Absorption coefficient versus Wavelength of SnO₂-CuO thin films

Where, α is the absorption coefficient and λ is the wavelength of the incident photon.

The behavior of extinction coefficient k is nearly similar to the corresponding absorption coefficient at different thicknesses. It can be notice from Fig. 3 that the extinction coefficient increases with the increasing of the film thickness. This is attributed to the same reason mentioned previously in absorption coefficient.

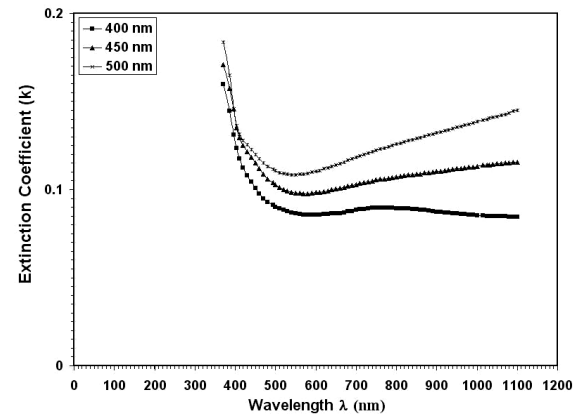


Fig. 3 – Extinction coefficient versus wavelength of SnO₂-CuO thin films

The refractive index is a suitable state parameter directly correlated to the material density. Fig. 4 shows the variation of the refractive index with the films thickness. It is clear from this figure that the films are influenced by the film thicknesses. The refractive index of these films is slightly increases with the increase in the films thickness. The refractive-index measurements can have a correlation with the electrical properties of the prepared films. The refractive index n can be determined from the reflectance R using the relation [40]:

$$n = \left(\frac{1+R}{1-R} \right) + \sqrt{\frac{4R}{(1-R)^2} - K^2} \quad (3)$$

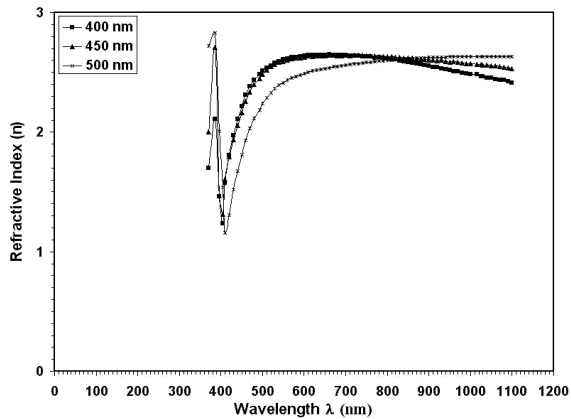


Fig. 4 – Refractive index versus wavelength of SnO₂-CuO thin films

The real ϵ_1 and imaginary ϵ_2 parts of the dielectric constant were obtained using the formula as [41]:

$$\epsilon_1 = n^2 - k^2 \quad (4)$$

$$\epsilon_2 = 2nk \quad (5)$$

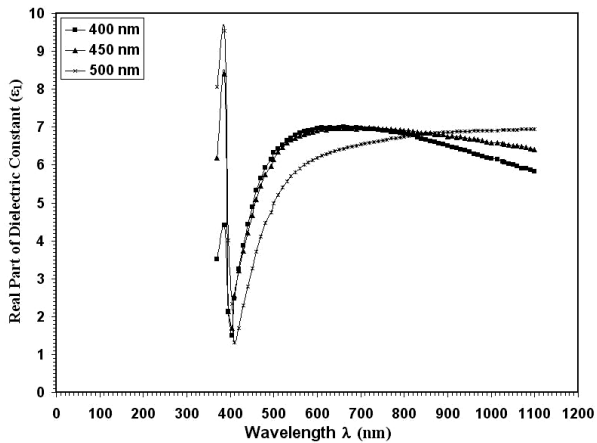


Fig. 5 – Real part of dielectric constant versus wavelength

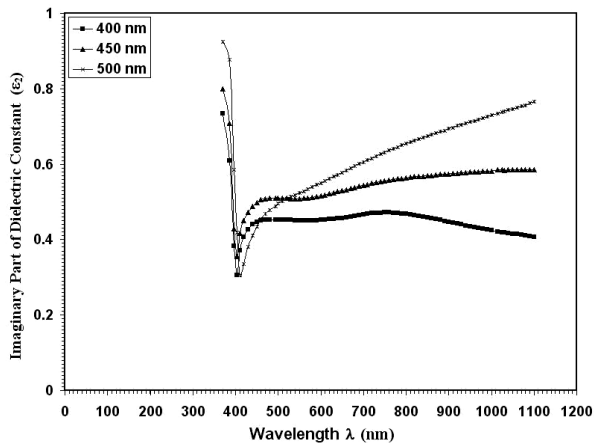


Fig. 6 – Imaginary part of dielectric constant versus wavelength

The variation in the real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric constant for different SnO₂-CuO film thickness are shown in Fig. 5 and 6. The values of the real part are higher than those of the imaginary part.

The optical conductivity was calculated using the relation [42]:

$$\sigma = \frac{\alpha nc}{4\pi} \quad (6)$$

where c is the velocity of light.

Fig. 7 shows the variation of the optical conductivity with the wavelength. It can be observed that the optical conductivity increases as the film thickness increase to 500 nm. The increased optical conductivity at high photon energies is due to the high absorbance of the films in that region.

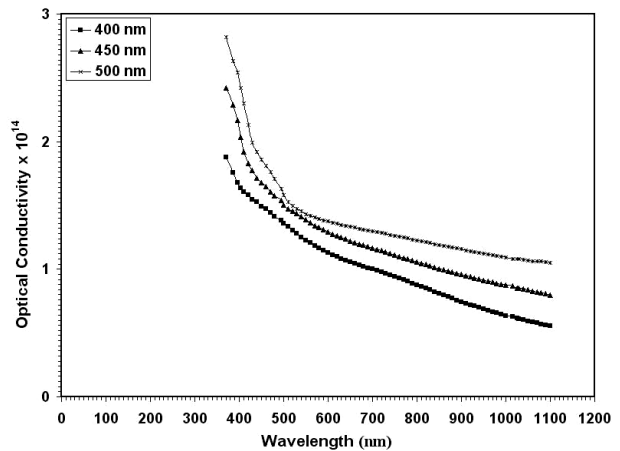


Fig. 7 – Optical conductivity versus wavelength of SnO₂-CuO thin films

The skin depth could be calculated using the following relation [43]:

$$x = \frac{\lambda}{2\pi k} \quad (7)$$

Where λ is the wavelength of the incident photon, k is the extinction coefficient. Fig. 8 shows the variation of skin depth as a function of wavelength for different thickness thin films.

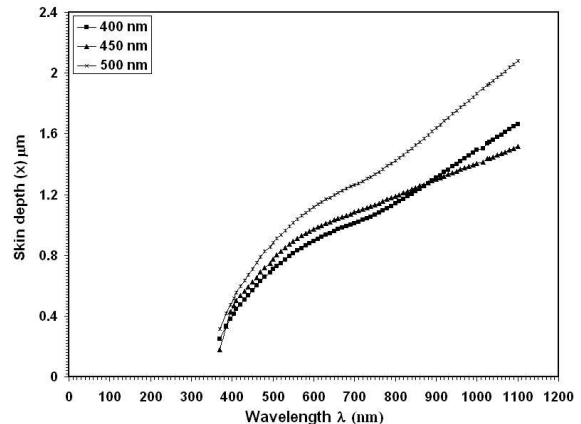


Fig. 8 – Skin depth versus wavelength of SnO₂-CuO thin films

It is clear from the figure that the skin depth increase as the wavelength increase, this behavior could be seen for all samples, but the skin depth increases as the film thickness increases, so the skin depth is transmittance related.

4. CONCLUSIONS

Transparent conducting SnO₂-CuO thin films were prepared by an ultrasonic spray pyrolysis technique.

REFERENCES

1. B.G. Lewis, D.C. Paine, *Mater. Res. Bull.* **25**, 22 (2000).
2. M. Chen, Z.L. Pei, C. Sun, L.S. Wen, X. Wang, *J. Cryst. Growth* **220**, 254 (2000).
3. M.V. Bestaev, D.Ts. Dimitrov, A.Yu. Ilin, V.A. Moshnikov, F. Trager, F. Steitz, *Semiconductors* **32**, 587 (1998).
4. J.C. Manificier, *Thin Solid Films* **90**, 297 (1982).
5. P.M. Gorley, V.V. Khomyak, S.V. Bilichuk, I.G. Orletsky, P.P. Horley, V.O. Grechko, *Mat. Sci. Eng. B* **118**, 160 (2005).
6. K.D. Schierbaum, U. Weimar, W. Gopel, *Sensor. Actuat. B-Chem.* **2**, 71 (1990).
7. M. Gaidi, A. Hajjaji, M.A. El Khakani, B. Chenevier, M. Labeau, B. Bessaïs, *Jpn. J. Appl. Phys.* **48**, 072501 (2009).
8. S.S. Pan, C. Ye, X.M. Teng, H.T. Fan, G.H. Li, *Appl. Phys.* **A 85**, 21 (2006).
9. S.S. Pan, C. Ye, X.M. Teng, L. Li, G.H. Li, *Appl. Phys. Lett.* **89**, 251911 (2006).
10. R. Dolbec, M.A. El Khakani, A.M. Serventi, R.G. Saint-Jacques, *Sensor. Actuat. B-Chem.* **93**, 566 (2003).
11. R. Dolbec, M.A. El Khakani, A.M. Serventia, M. Trudeau, R.G. Saint-Jacques, *Thin Solid Films* **419**, 230 (2002).
12. J.R. Brown, P.W. Haycock, L.M. Smith, A.C. Jones, E.W. Williams, *Sensor. Actuat. B-Chem.* **63**, 109 (2000).
13. K.H. Kim, J.S. Chun, *Thin Solid Films* **141**, 287 (1986).
14. C.A. Pan, T.P. Ma, *Appl. Phys. Lett.* **37**, 163 (1980).
15. S.C. Lee, J.H. Lee, T.S. Oh, Y.H. Kim, *Sol. Energ. Mat. Sol. C.* **75**, 481 (2003).
16. C.K. Kima, S.M. Choia, I.H. Noha, J.H. Leea, C. Hongb, H.B. Chaeb, G.E. Jangc, H.D. Parkd, *Sensor. Actuat. B-Chem.* **77**, 463 (2001).
17. R.D. Vispute, V.P. Godbole, S.M. Chaudhari, S.M. Kanetkar, S.B. Ogale, *J. Mater. Res.* **3**, 1180 (1988).
18. S. Muranaka, Y. Bando, T. Takada, *Thin Solid Films* **86**, 11 (1981).
19. K. Suzuki, M. Mizuhashi, *Thin Solid Films* **97**, 119 (1982).
20. T. Minami, H. Nanto, S. Takata, *Jpn. J. Appl. Phys.* **27**, L287 (1988).
21. S.I. Rembeza, T.V. Svistova, E.S. Rembeza, O.I. Borsyakova, *Semiconductors* **35**, 762 (2001).
22. T. Minami, T. Miyata, T. Yamamoto, *Surf. Coat. Tech.* **108-109**, 583 (1998).
23. K.S. Shamala, L.C.S. Murthy, K. Narashima Rao, *Bull. Mater. Sci.* **27**, 295 (2004).
24. D. Debajyoti, R. Banerjee, *Thin Solid Films* **147**, 321 (1987).
25. T. Fukano, T. Motohiro, *Sol. Energ. Mat. Sol. C.* **82**, 567 (2004).
26. B. Thangaraju, *Thin Solid Films* **402**, 71 (2002).
27. E. Elangovan, K. Ramesh, K. Ramamurthi, *Solid State Commun.* **130**, 523 (2004).
28. A.V. Moholkar, S.M. Pawar, K.Y. Rajpure, C.H. Bhosale, *J. Alloy. Compd.* **455**, 440 (2008).
29. S. Semancik, J.B. Fryberger, *Sensor. Actuat. B-Chem.* **1**, 97 (1990).
30. J.K. Kwak, K.H. Park, D.Y. Yun, D. Lee, T.W. Kim, *J. Korean Phys. Soc.* **57**, 1803 (2010).
31. B. Stjerna, C.G. Granqvist, *Thin Solid Films* **193-194**, 704 (1990).
32. M. Gaidi, B. Chenevier, M. Labeau, *Sensor. Actuat. B-Chem.* **62**, 43 (2000).
33. R. Dolbec, M.A. El Khakani, *Appl. Phys. Lett.* **90**, 173114 (2007).
34. M. Fox (Ed.), *In Optical properties of Solids* (Oxford: ISBN: 978-0-19-850612-6: 2001).
35. X. Zi-Qiang, D. Hong, L. Yan, C. Hang, *Mat. Sci. Semicon. Proc.* **9**, 132 (2006).
36. X. Han, R. Liu, W. Chen, Z. Xu, *Thin Solid Films* **516**, 4025 (2008).
37. C. Korber, S.P. Harvey, T.O. Mason, A. Klein, *Surf. Sci.* **602**, 3246 (2008).
38. S. Shanthi, C. Subramanian, P. Ramasamy, *Cryst. Res. Technol.* **34**, 1037 (1999).
39. S.W. Xue, X.T. Zu, W.L. Zhou, H.X. Deng, X. Xiang, H. Deng, *J. Alloy. Compd.* **448**, 21 (2008).
40. A. Ashour, M.A. Kaid, N.Z. El-Sayed, A.A. Ibrahim, *Appl. Surf. Sci.* **252**, 7844 (2006).
41. F. Buet, J. Olivier-Fourcade, Y. Bensimon, P. Belougne, *Solid State Commun.* **77**, 29 (1991).
42. J.I. Pankove, *Optical processes in semiconductors* (New York: Dover Publications Inc.:1975).
43. J.F. Eloy, *Power Lasers National School of Physics* (Grenoble, France: John Wiley and Sons: 1984).