

Luminescent Properties of Cu²⁺ Doped SnO₂ Thin Films by Spray Pyrolysis

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Abstract: Transparent conducting oxide films have been widely used in the fields of flat panel displays, solar cells, touch panels and other optoelectronic devices owing to their high electrical conductivity and optical transmittance in visible region. Tin oxide with a wide band gap is one of the excellent semiconductors which can be applied to solid state gas sensors, sensing arrays photovoltaic cells, organic light emitting diodes. Cu²⁺ doped tin oxide thin films were prepared by chemical spray pyrolysis synthesis and characterized by different spectroscopic techniques. The morphology of prepared sample was analyzed by using SEM and TEM studies. Functional groups of the prepared sample were observed in the FT-IR spectrum. PL studies of Cu²⁺ doped SnO₂ thin films exhibit ultraviolet and blue emission bands. CIE chromaticity coordinates were also calculated from emission spectrum of Cu²⁺ doped SnO₂ thin films.

Keywords: SnO₂, Thin films, Spray pyrolysis, SEM, TEM, FT-IR and Photoluminescence.

Introduction:

Lithium-ion batteries (LIBs) have great application in electric vehicles, laptop computers, and other portable electrical devices because of their high energy storage capacities and long cyclic life. Although graphite anodes are widely used in commercial LIBs due to high cyclability, their capacity can hardly meet the increasing demand for batteries with higher capacity. Thus, there is urgent need to exploit novel anode materials for LIBs, and a large number of transition metal oxide nanomaterials, such as SnO₂, Fe₃O₄, MnO₂, WO₃, NiO, MoO₃, and Co₃O₄, have been widely investigated as LIB anodes [1-3]. Nowadays, many research efforts have been made to overcome their two serious disadvantages: (i) poor cyclability arising from the significant volume change during Li insertion/extraction; (ii) high irreversible capacity caused by the formation of Li₂O [4-8]. Semiconducting tin oxide (SnO₂) thin films with suitable catalysts in the form of nanoparticles, over layers, clusters etc. are known to exhibit enhanced sensitivity, better selectivity and fast response speeds to various reducing gases. SnO₂ has been intensively investigated because of its rich physical properties and large applications in commercial devices. SnO₂ with a wide band gap ($E_g = 3.6 - 4.0$ eV) is one of the excellent semiconductors which can be applied to solid state gas sensors, sensing arrays, solar cells, photovoltaic cells, organic light emitting diodes, touch sensitive screens and thin film transistors [9-11].

SnO₂ is a special oxide material because it has a low electrical resistance with high optical transparency in the visible range. Due to these properties, apart from gas sensors, SnO₂ is being used in many other applications, such as electrode materials in solar cells, light-emitting diodes, flat-panel displays and other optoelectronic devices where an electric contact needs to be made without obstructing photons from either entering or escaping the optical active area and in transparent electronics, such as transparent field effect

transistors [12, 13]. SnO₂ owing to a wide band gap is an insulator in its stoichiometric form. However, due to the high intrinsic defects, that are oxygen deficiencies, tin oxide possesses a high conductivity. It has been shown that the formation energy of oxygen vacancies and tin interstitials in SnO₂ is very low. Therefore, these defects form readily, which explains the high conductivity of pure, but nonstoichiometric, tin oxide [14, 15].

SnO₂ thin films can be fabricated by a number of techniques such as chemical vapour deposition, metal-organic deposition, RF sputtering, sol-gel dip coating and spray pyrolysis [16-20]. It was clearly established that structural, electronic transport and optical properties of SnO₂ thin films are very sensitive to preparation method, deposition conditions, dopant atoms and amount of dopant atoms. The spray pyrolysis, among the various deposition techniques, is the well suited for the preparation of doped tin dioxide thin films because of its simple and economic experimental arrangement, ease of adding various doping material, reproducibility, high growth rate and mass production capability for uniform large area coatings, which are desirable for industrial and solar cell applications. In the present work, Cu²⁺ doped (0.01 mol %) SnO₂ thin films were prepared by using chemical spray pyrolysis method. The prepared thin films were characterized by SEM with EDS, TEM, FT-IR and PL studies to collect the information about the luminescent properties of the prepared sample.

Experimental:

All the chemicals used in the work were of analytical grade. Cu²⁺ doped SnO₂ thin films were prepared by chemical spray pyrolysis. Spray solution was prepared by mixing 0.1 M aqueous solutions of SnO₂ and CuO (0.01 mol %) using magnetic stirrer. The automated spray solution was then transferred to the hot substrate kept at the normalized deposition temperature of 673 K using filtered air as carrier gas at a flow rate normalized to approximately (1.8) ml/min. To prevent the substrate from excessively cooling, the prepared solution was sprayed on the substrate for 10 s with 15 s intervals. The films deposited onto micro-glass slides were first cleaned with detergent water and then dipped in acetone [21-23]. Scanning electron microscope (SEM) and energy dispersive spectrum (EDS) images are taken on ZEISS EVO 18. Transmission electron microscope (TEM) images are recorded on HITACHI H-7600 and CCD CAMERA system AMTV-600 by dispersing samples in ethanol. Bruker FT-IR spectrophotometer is used for recording FT-IR spectrum of the prepared samples in the region 400-4000 cm⁻¹. Photoluminescence (PL) spectrum is taken at room temperature on Horiba Jobin-Yvon Fluorolog-3 spectrofluorimeter with Xe continuous (450 W) and pulsed (35 W) lamps as excitation sources.

Results and Discussion:

Cu²⁺ doped (0.01 mol %) SnO₂ thin films were prepared by using chemical spray pyrolysis method. The prepared thin films were characterized by SEM with EDS, TEM, FT-IR and PL studies to collect the information about the luminescent properties of the prepared sample. The analysis of X-ray diffraction pattern revealed that the prepared tin oxides films are pure crystalline in nature.

Morphological Studies: The morphology and chemical composition of as synthesized thin film was investigated by SEM and EDS analysis. Fig. 1 shows the SEM micrographs of Cu²⁺ doped SnO₂ thin films taken with different magnifications. It can be clearly observed from low resolution SEM images that, the prepared sample show many agglomerates with an irregular morphology. The agglomeration could be induced by densification resulting from the narrow space between particles [24, 25]. SEM images reveal that the sample consists of irregular shaped sphere like structures. The incorporation of copper into the host material was confirmed by EDS measurements. The observed EDS pattern was shown in Fig. 2. The pattern showed the elemental compositions of Sn, O and copper. From this it was confirmed that the prepared samples contains doped copper species.

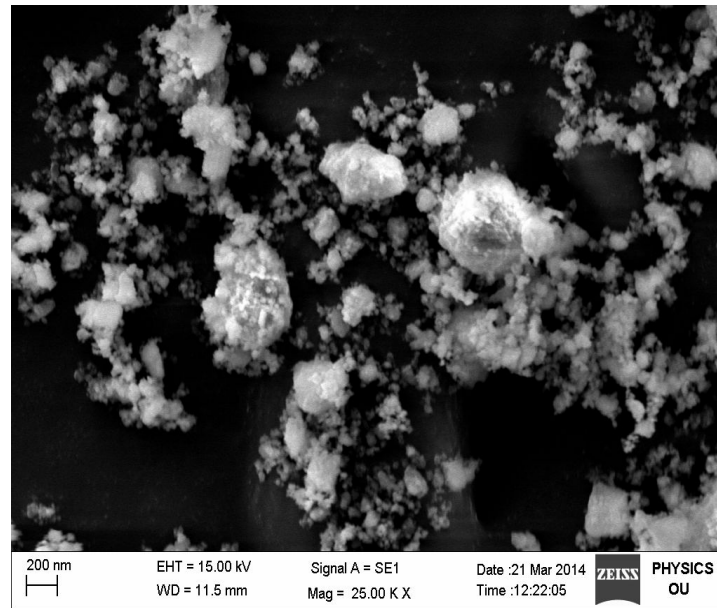


Fig. 1 SEM image of Cu^{2+} doped SnO_2 thin films

TEM measurements were performed to confirm the nanocrystalline nature of the samples and to study the morphology of the particles. The TEM images of Cu^{2+} doped SnO_2 thin films are depicted in Fig. 3. The particles are more or less uniform in size and of irregular shape [26, 27].

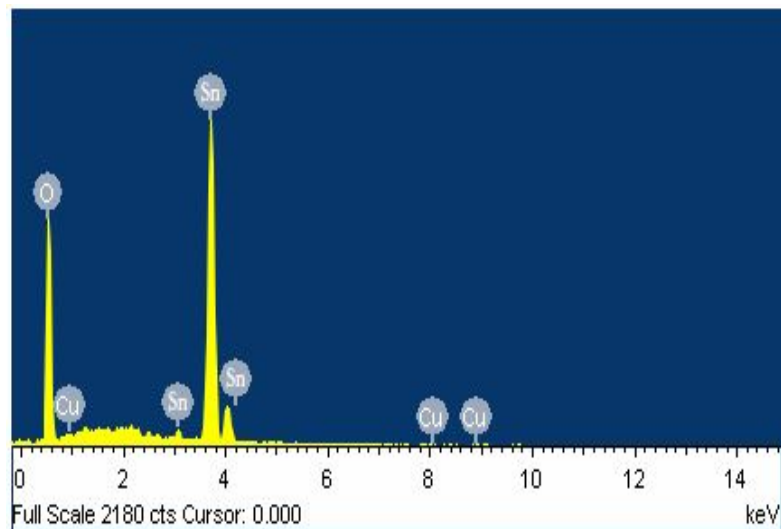


Fig. 2 EDS spectrum of Cu^{2+} doped SnO_2 thin films

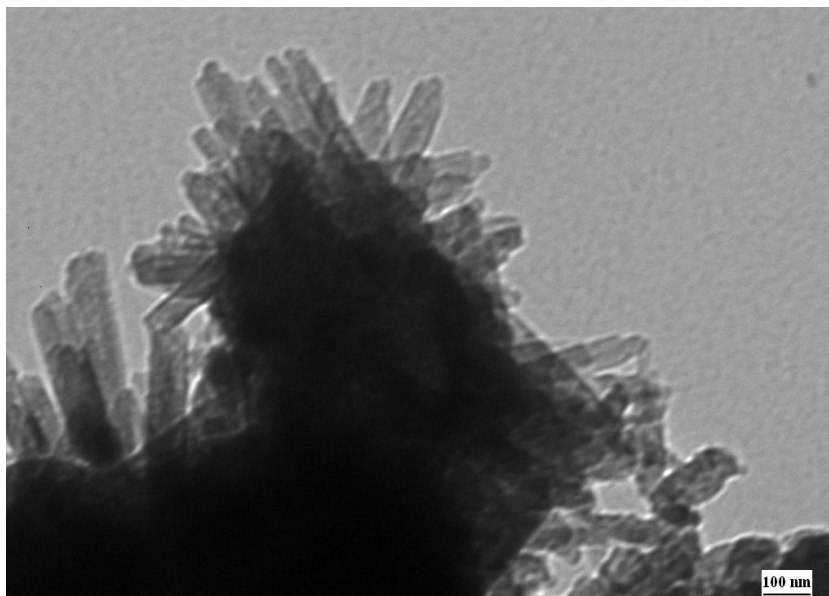


Fig. 3 TEM image of Cu^{2+} doped SnO_2 thin films

FT-IR Studies: FT-IR spectrometry was used for the determination of existing surface species. The FT-IR spectrum of Cu^{2+} doped SnO_2 thin films was illustrated in Fig. 4. The bands at low wavenumbers ($500\text{-}1000\text{ cm}^{-1}$) could be attributed to SnO_2 . The peaks at 677 , 786 and 965 cm^{-1} were assigned to O–Sn–O, Sn–O–Sn stretching vibrations and lattice vibrations, while the peaks at 569 and 864 cm^{-1} were due to Sn–OH bonds of the SnO_2 crystalline phase [28]. The bands observed in the region $2500\text{-}1640\text{ cm}^{-1}$ are due to symmetric and asymmetric vibrations of hydroxyl ions situated at different sites in the lattice.

Photoluminescence Studies: Photoluminescence (PL) phenomenon is directly related to electronic structure and transitions. Differences in the electronic behavior between bulk and low-dimensional semiconductors arise due to difference in the electronic density of states. PL emission spectrum of Cu^{2+} doped SnO_2 thin films under the photon excitation of 355 nm is shown in Fig. 5. An intense blue emission at 425 nm is a deep level emission usually appears due to surface effects.

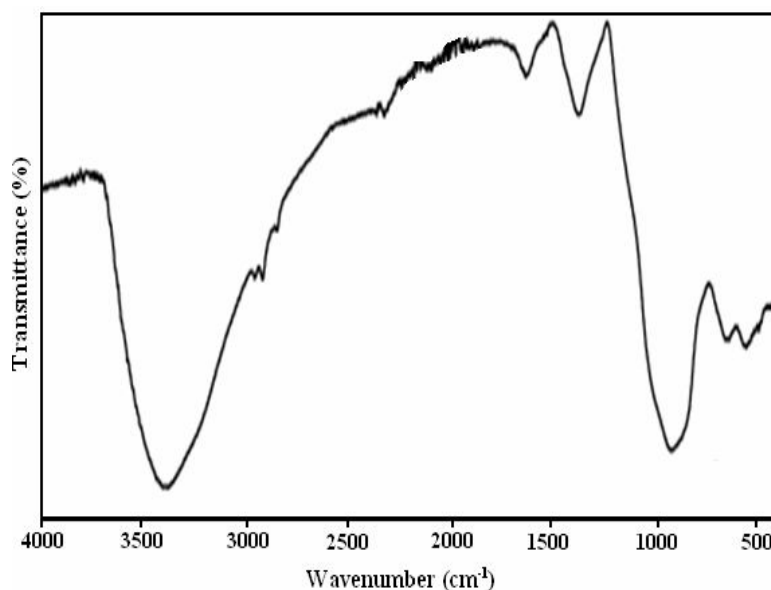


Fig. 4 FT-IR spectrum of Cu^{2+} doped SnO_2 thin films

The emission mechanism arises due to a donor-acceptor pair recombination involving the Cu^{2+} ions acceptor and a shallow donor impurity. An intense blue emission peak at around 425 nm is due to transition from

conduction band of host to the “ t_2 ” state of Cu^{2+} ions and the green emission band at around 533 nm is from the shallow donor to the “ t_2 ” state [29]. The prepared samples with blue emission are promising for applications in light emitting nanodevices [30].

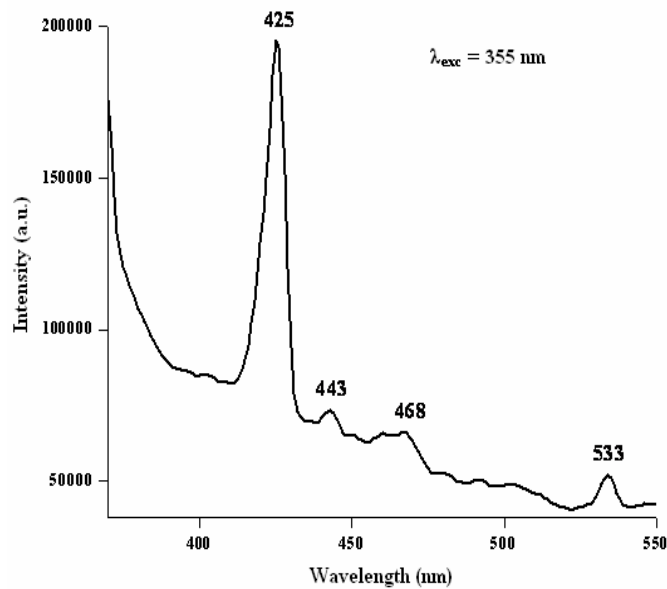


Fig. 5 PL spectrum of Cu^{2+} doped SnO_2 thin films

Chromaticity Properties: Most lighting specifications refer to colour in terms of the Commission Internationale de l'Eclairage (CIE) 1931 chromatic colour coordinates which recognize that the human visual system uses three primary colours: red, green and blue [31]. In general, the colour of any light source can be represented on the (x, y) coordinate in colour space. Colour purity was compared to the 1931 CIE Standard Source C (illuminant Cs). The chromatic coordinates (x, y) was calculated using the CIE coordinate calculator. The CIE chromaticity coordinates of Cu^{2+} doped SnO_2 thin films were calculated from the emission spectrum. The location of the colour coordinates for Cu^{2+} doped SnO_2 thin films in the CIE chromaticity diagram is shown in Fig. 6 by a solid circle sign (\bullet). From this figure, one can see that the colour of Cu^{2+} doped SnO_2 thin films located in the blue region and the CIE coordinates are $(x = 0.148, y = 0.174)$. These characteristic features may represent the possible applications in the fields of UV back lights, UV LEDs and display devices [32-34].

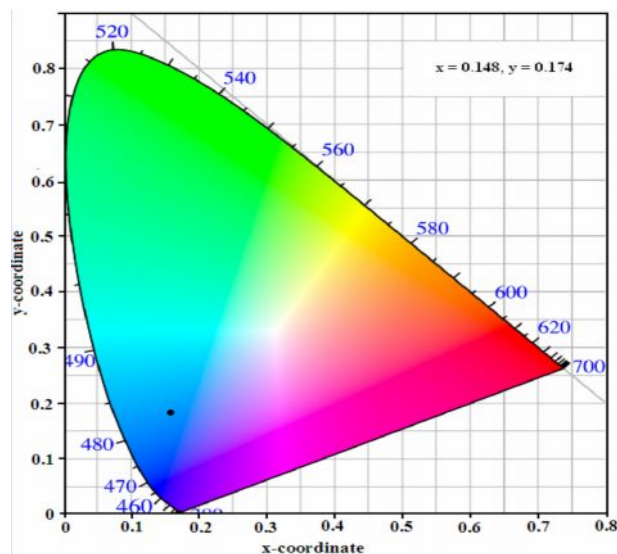


Fig. 6 CIE diagram of Cu^{2+} doped SnO_2 thin films

Conclusions:

Cu²⁺ doped SnO₂ thin films were prepared successfully by chemical spray pyrolysis method. SEM images taken at different magnifications clearly showed prepared sample contains irregular shaped nanoclusters with agglomeration. The presence of constituent elements of prepared material is confirmed from EDS analysis. TEM images clearly show the formation of nano rods. FT-IR spectrum showed the characteristic vibrational modes of host lattice. PL spectrum of Cu²⁺ doped SnO₂ thin films shows strong UV emission with suppressed blue emission. From CIE diagram, Cu²⁺ doped SnO₂ thin films emits blue colour light and the corresponding coordinates are (x = 0.148, y = 0.174).

References:

1. Rao M.C., Res. J. Rec. Sci. 2013, 2(4), 67-71.
2. Rao M.C., J. Non-Oxide Glasses, 2013, 5, 1-8.
3. Rao M.C., Hussain O.M., Res. J. Chem. Sci., 2011, 1, 92-95.
4. Rao M.C., *J. Crys. Growth*, 2010, 312, 2799–2803.
5. Rao M.C., *Optoelect. & Adv. Mater., (Rapid Commu.)*, 2011, 5, 85-88.
6. Rao M.C., Hussain O.M., *J. Alloys and Comp.* 2010, 491(1), 503-506.
7. Rao M.C., Hussain O.M., *IOP Conf. Series: Mater. Sci. Eng.*, 2009, 2, 012037 (p.1-4).
8. Rao M.C., *J. Optoelect. & Adv. Mater.*, 2011, 13, 428-431.
9. Bagheri Mohagheghi M.M., Shahtahmasebi N., Alinejad M.R., Youssefi A. and Shokooh Saremi M., *Physica B*, 2008, 403, 2431 - 2437.
10. Khan A.F., Mehmood M., Aslam M. and Ashraf M., *Appl. Sur. Sci.*, 2010, 256, 2252 - 2258.
11. Rani S., Roy S.C. and Bhatnagar M.C., *Sensors and Actuators B*, 2007, 122, 204 - 210.
12. Maekava T., Suzuki K., Takada T., Kobayashi T. and Egashira M., *Sensors and Actuators B*, 2001, 80, 51 - 58.
13. Agashe C., Hupkes J., Schope G. and Berginski M., *Solar Energy Mater. Solar Cells*, 2009, 93, 1256 - 1262.
14. Kikuchi N., Kusano E., Kishio E. and Kinbara A., *Vacuum*, 2002, 66, 365 – 371.
15. Kim W.J., Koo W.H., Jo S.J., Kim C.S., Baik H.K., Lee J. and Im S., *Appl. Sur. Sci.*, 2005, 252, 1332 - 1338.
16. Fang T.H. and Chang W.J., *Appl. Sur. Sci.*, 2003, 220, 175 – 180.
17. Dippel A.C., Schneller T., Gerber P. and Waser R., *Thin Solid Films*, 2007, 515, 3797 – 3801.
18. Ma J., Hao X., Huang S., Huang J., Yang Y. and Ma H., *Appl. Sur. Sci.*, 2003, 214, 208 – 213.
19. Elangovan E., Ramesh K. and Ramamurthi K., *Solid State Commun.*, 2004, 130, 523 – 527.
20. Serin T., Serin N., Karadeniz S., Sari H., Tugluoglu N. and O. Pakma, *J. Non-Cryst. Solids*, 2006, 352, 209 - 215.
21. Rao M.C., Ravindranadh K., *Int. J. Chem. Con.*, 2015, 1, 114-119.
22. Rao M.C., Ravindranadh K., *Int. J. Chem. Con.*, 2015, 1, 120-124.
23. Rao M.C., Ravindranadh K., *Int. J. Chem. Con.*, 2016, 2, 24-27.
24. Ravindranadh K., Rao M.C., Ravikumar R.V.S.S.N., *J. Mater. Sci: Mater. Electron.*, 2015, 26, 6667–6675.
25. Rao M.C., Ravindranadh K., *Der Pharma Chemica*, 2016, 8, 243-250.
26. Ravindranadh K., Rao M.C., Ravikumar R.V.S.S.N., *Appl. Mag. Reson.*, 2015, 46, 1-15.
27. Ravindranadh K., Rao M.C., Ravikumar R.V.S.S.N., *J. Luminesce.*, 2015, 159, 119-127.
28. Muthukumar S. and Gopalakrishnan R., *Opt. Mater.*, 2012, 34, 1946 – 1953.
29. Yang P., Lu M., Xu D., Yuan D. and Zhou G., *Chem. Phys. Lett.*, 2001, 336, 76 – 80.
30. Umesh B., Eraiah B., Nagabhushana H., Sharma S.C., Nagabhushana B.M., Shivakumara C., Rao J.L. and Chakradhar R.P.S., *Spectrochim. Acta A*, 2012, 94, 365 – 371.
31. Shionoya S. and Yen W.M., *Phosphor Handbook*, Phosphor Research Society, CRC Press, 1998, pp. 459-487.
32. Begum S.M., Rao M.C., Ravikumar R.V.S.S.N., *J. Inorg. Organomet. Poly. Mater.* 2013, 23, 350-356.
33. Begum S.M., Rao M.C., Ravikumar R.V.S.S.N., *J. Mol. Struct.* 2011, 1006, 344-347.
34. Begum S.M., Rao M.C., Ravikumar R.V.S.S.N., *Spectrochim. Acta Part A: Mol. & Biomol. Spec.* 2012, 98, 100-104.
