

SYNTHESIS AND CHARACTERIZATION OF CuWS_2 SPRAY PYROLYSIS IN THIN FILMS

S. MUTHUKRISHNAN¹, P. SUMATHI²

¹Department of Electronics, Cherraan's Arts Science College, Kangayam-638701.

²Department of Physics, SRMV CAS, Coimbatore-641020, India.

ABSTRACT

Copper doped Tungsten disulphide (CuWS_2) thin films have been synthesized on to glass substrates at 400°C temperatures by spray pyrolysis technique from aqueous solution using cupric acetate $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ as a precursor. The structure of the deposited CuWS_2 thin films characterized by X-ray diffraction, the surface morphology was observed by a scanning electron microscope, the optical transmission and absorption spectra was recorded by ultraviolet visible spectroscopy was studied. All the CuWS_2 thin films, irrespective of growth temperature, showed a monoclinic structure with the main CuO (111) orientation, and the crystallite size was about 8.9954 Å for the thin film synthesized at 300°C. The optical transmission of the as deposited film is found to decrease with the increase of substrate temperature, the optical band gap of the thin films varies from 1.60 to 2.43 eV and the electrical resistivity varies from 5 to 8 Ohm-cm for the films grown at the substrate temperatures.

Keywords: CuWS_2 Thin film spray pyrolysis, XRD, SEM,

1. Introduction

Copper oxide (CuWS_2) thin film has been reported to exhibit p-type conduction and shows a band gap of 2.44eV is a monoclinic crystal structure with lattice parameters $a = 5.4837 \text{ \AA}$ and $\beta = 89.45^\circ$ [1-3]. CuWS_2 , an important transition metal oxide semiconductor has been extensively studied for a number of applications like gas sensors [4-6], solar cells [7-8], lithium ion electrode [9], etc. Thermal preparation methods result in resistivities in the range 10^2 - 10^4 \Omega-cm and electrodeposition produces films with resistivities in the range 10^4 - 10^6 \Omega-cm . [10-11]. There are various established ways of fabricating CuWS_2 thin films like spray pyrolysis technique (SPT) [9], radio frequency magnetron sputtering [12], spin coating [13], dip coating [14], SILAR [15], thermal evaporation [16], etc. SPT is simple, fast, inexpensive, vacuum less process and is suitable for mass production among all of these. So, the aim is to grow CuWS_2 thin film by SPT and to study the effect of the substrate temperature (T_s) on the physical and chemical properties of CuWS_2 thin films.

2. Experimental Details

CuO thin films have been synthesized by spray pyrolysis technique (SPT) using 0.1 mole of cupric acetate ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$) which was dissolved in deionized 20 ml distilled water. The distance between substrate to spray nozzle was 19 cm and air pressure was 1 bar. The solution was sprayed onto the ultrasonically cleaned glass substrates heated at 300°C temperatures. The substrate temperature was recorded with the indium tin oxide glass substrate. The flow rate of the solution during spraying was adjusted at about 1 ml/min and was kept constant throughout the experiment and the spray time was 12 min.

The possible chemical reaction that takes place on the heated substrate to produce CuWS_2 thin film when the droplets of the solution reached the heated substrate, is the chemical reaction of the copper acetate with water solution under stipulated temperature which provides the formation of CuWS_2 thin films.

The surface morphology of the films was examined using a HITACHI S-3400N model scanning electron microscope (SEM), the elemental analysis was performed by an electron dispersive spectrometer attached to the SEM and X-ray diffraction (XRD) patterns were recorded using an identical uncoated glass substrate as reference. The electrical studies were carried out using Hall measurement system (D.O.No.SR/S2/CMP-35/2004).

3. Results and Discussion

3.1. X-ray Diffraction Analysis

XRD patterns for CuWS₂ thin films synthesized at substrate temperature of 300°C are shown in Fig. 1. The diffraction peaks observed at 2θ values of 35.23° and 38.53° correspond to the diffraction lines produced by (111) and (200) planes of the face-centered cubic structured CuO (JCPDS card No. 03-1005). Crystallite size of the prepared CuWS₂ thin film was determined from the strongest peak of (111) for every XRD pattern using Scherrer formula. The (111) surface of CuWS₂ thin film is energetically the most stable and the predominant crystal face found in polycrystalline samples. It is observed from Fig.1 that the diffraction peak positions are identical for all the CuO thin films, obtained at the substrate temperature of 300°C, indicating the formation of cubic phase CuO in all the cases. Although (111) and (200) reflections are present, for CuO. The lattice constants of the CuWS₂ thin films are found to be: a = 1.5405 Å and b = 2.4506 Å and are

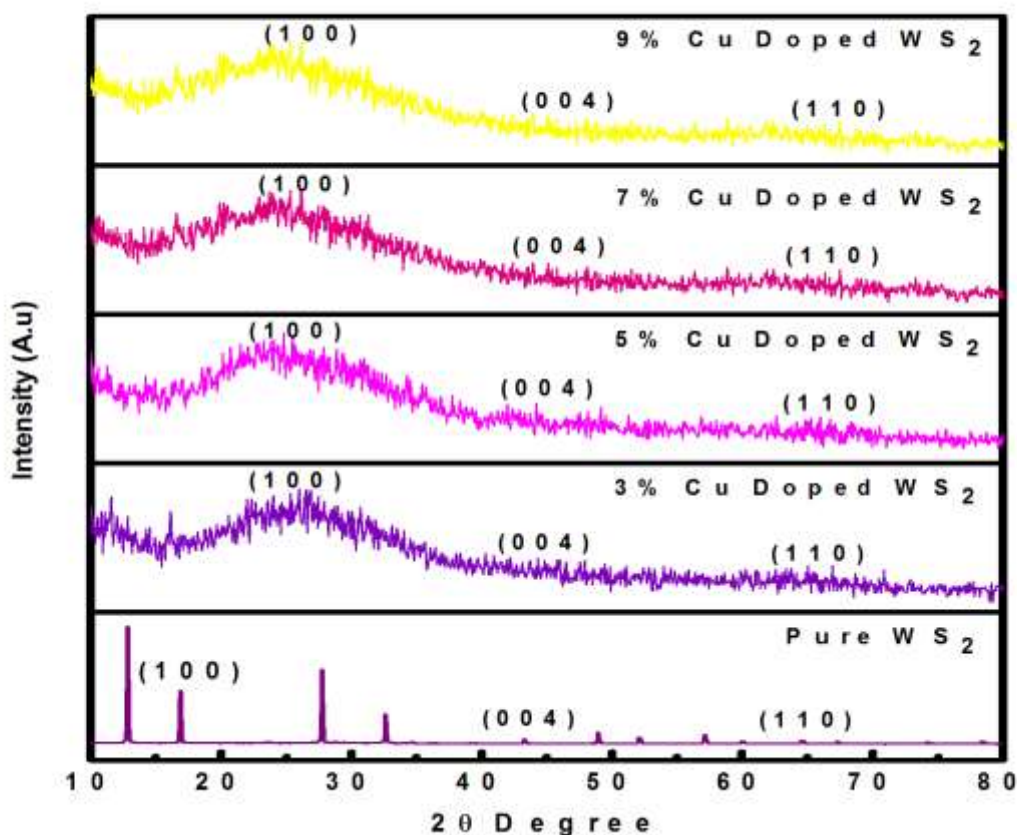


Fig. 1. XRD patterns of CuWS₂ thin film synthesized at 400°C substrate temperature

in good agreement with the standard JCPDS data for cubic structured CuWS₂. It is observed in the XRD patterns that the intensity of the peaks increases. For peak (111) the calculated values of the crystallite size for the CuWS₂ thin films are presented in Table 1.

Table 1. Crystallite size for the CuO thin films at 300°C substrate temperature

Substrate Temperature (T _s)	Crystallite size in Å	Thickness	D (nm)	FWHM (Radian)
400°C	03-1005	284	3.48	1.63002

It is seen in the Table 1 the crystallite size increases with the substrate temperature is exactly 300°C and then to decrease. For CuWS₂ there are many dangling bonds related to the copper and/or oxygen defects at the grain boundaries. As the result, these defects are favourable to the merging process to form larger CuWS₂ grains while increasing substrate temperature. It implies that the crystallinity of the CuWS₂ thin films is improved at

higher substrate temperatures. This may be due to gaining enough energy by the crystallites to orient in proper equilibrium sites at higher substrate temperatures, resulting in the improvement of crystallinity and degree of orientation of the CuWS₂ thin films[16-18].

3.2. Morphological Analysis

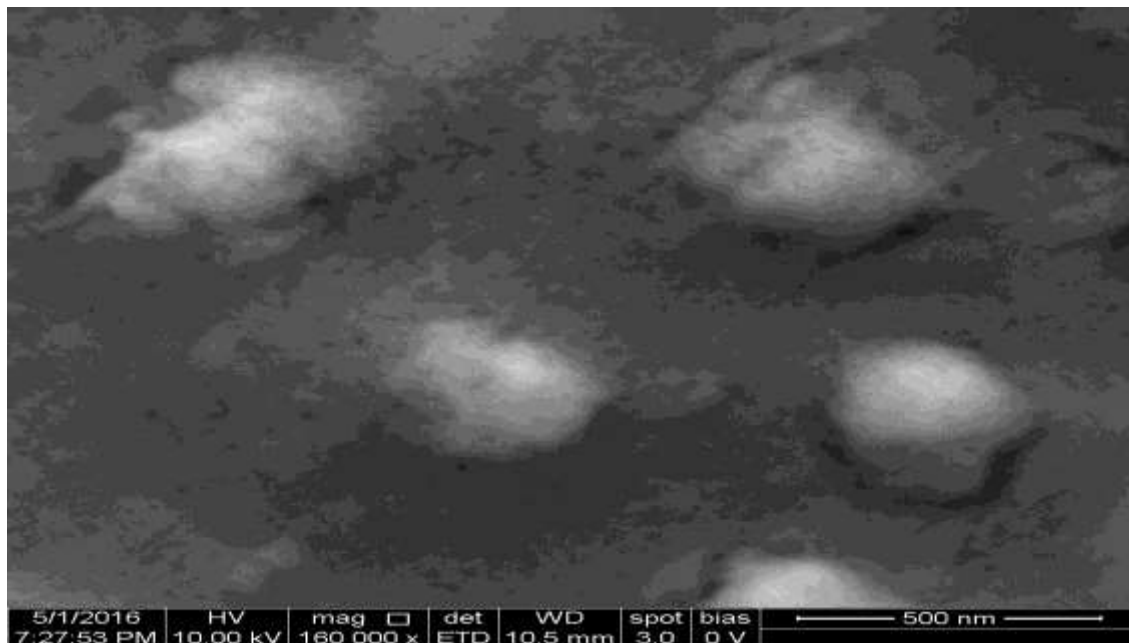


Fig.2. SEM image of CuWS₂ thin films at substrate temperature 400°C

SEM images were recorded to examine the surface morphology of the as deposited CuO thin films and the images obtained are shown in Fig. 2. The deposited films have islands of different sizes and shapes, and their distribution on the surface is quite homogeneous. These could be the result of the chemical reaction during the deposition. SEM micrographs reveal the formation of particles with different shapes and sizes, it seems appropriate to consider that the particles which appear in scanning electron microscopy(SEM) images are the grains of agglomerates.

3.3. Optical Properties

3.3.1. Transmittance and Optical Band Gap

The optical property of CuWS₂ thin films deposited at the substrate temperature of 400°C were investigated by means of the transmission spectra recorded and shown in Fig. 4 . It is seen that the transmittance is high in the visible and near infrared regions and minimum at wavelength ~ 200 nm. An average of 70% to 90% transmittance is observed in the wavelength range of 800-900 nm and below 800 nm transmittance decreases gradually. The transmittance increases from 300°C with the substrate temperature, and shows the highest transmittance of about 90% for the thin films grown at substrate temperature, $T_s = 400^\circ\text{C}$. The increase in transmittance may be due to the transition of the CuWS₂ films from monoclinic to polycrystalline structure.

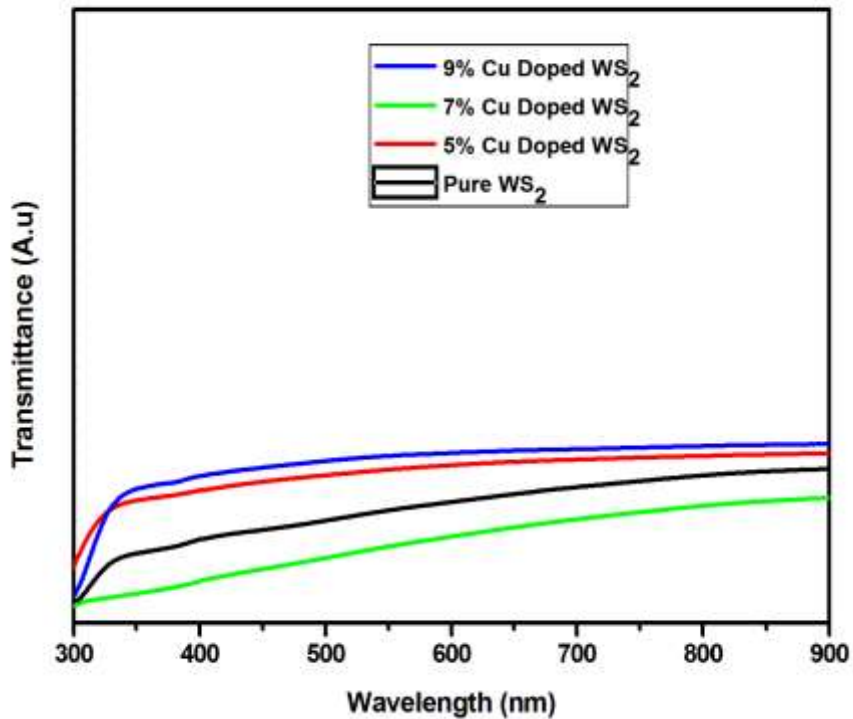


Fig.3. Transmittance vs wavelength at substrate temperature 400°C

A relatively high transmittance in the value for the thin film deposited at 300°C may be attributed to less scattering due to the decrease in the degree of irregularity in the grain size distribution [19]. The transmittance values are decreased for these substrate temperature. This suggests that the decrease in the transmittance of CuWS₂ thin films is with increase in the substrate temperature. This may lead to increase in the degenerate (metallic) nature of the films, which results in light absorption. The optical band gap for the direct band gap semiconductors is determined using the substrate temperature [20]. $(\alpha h\nu)^2 = A(h\nu - E_g)$, where A is a proportionality constant, $h\nu$ is the incident photon energy, α is the absorption coefficient, and E_g is the optical band gap. Fig. 4 shows the absorption coefficient squared $(\alpha h\nu)^{1/2}$ as a function of, $h\nu$ for the CuWS₂ thin films deposited at substrate temperature.

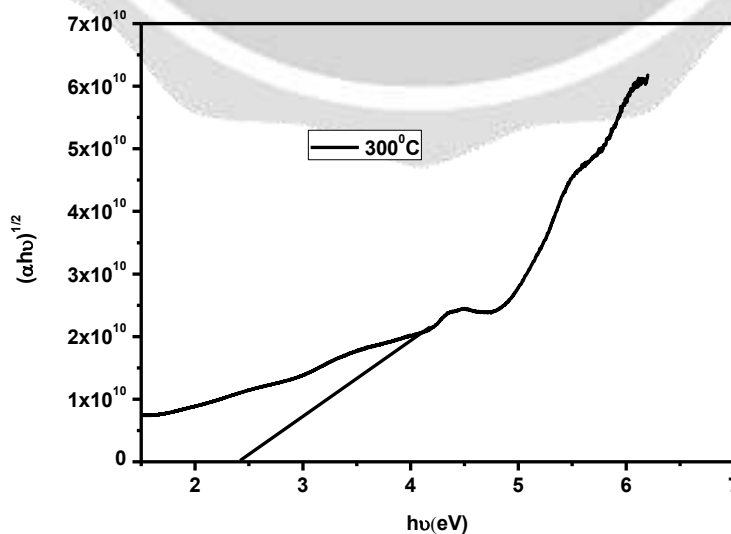


Fig.4. Optical transmittance vs. wavelength of CuO thin films at substrate temperature 400°C

The α was found in the order of 10^{10} m^{-1} which may be suitable for a transparent conducting film. The E_g of the CuO thin films deposited at $T_s = 400^\circ\text{C}$ the optical band gap is found to be 2.43 eV is found for sample obtained at 300°C . It can be seen that a band gap tuning of 0.30 eV occurs when the substrate temperature is 400°C . The value of the α and E_g decrease as the substrate temperature value of to 400°C where it starts to increase with further increasing of substrate temperature. It may be due to the removal of defects and disorderness in the as-deposited film by increasing substrate temperature.

Conclusion

Thin films of CuWS_2 have been spray pyrolysed successfully onto glass substrates using spray pyrolysis technique at the 0.1 molar concentration respectively. X-ray diffraction analysis revealed that the prepared films were polycrystalline in nature with monoclinic structure with preferential orientation along (111) plane. Also the crystallite size were estimated. Surface morphology showed that films are with spherical shaped grains and porous nature. Optical absorption measurements indicate that the deposited film has an indirect bandgap value of 2.43eV respectively.

References

- [1] Jundale D.M., Joshi P.B., Sen S., Patil V. B., Nanocrystalline CuO thin films; synthesis, microstructural and optoelectronic properties, Journal of Materials Science: Materials in Electronics, 23 (2012) 1492-1499.
- [2] Marabelli F., Parraviciny G.B., Salghetti-Drioli F., Optical gap of CuO, Physical Review B.3 (1995) 1433-1436.
- [3] Ghijsen J., Tjeng L.H., Elp J. V., Eskes H., Westerink J., Sawatzky G.A., Czyzyk M. T., Electronic structure of Cu_2O and CuO, physical Review B. 38 (1988) 11322-11330.
- [4] Mariammal R. N., Ramachandran K., Kalaiselvan G., Arumugam S., Renganathan B., Sastikumar D., Effect of magnetism on the ethanol sensitivity of undoped and Mn-doped CuO nanoflakes, Applied Surface Science.270 (2013) 545-552.
- [5] Hubner M., Simion C. E., Tomescu-Stanoiu A., Pokhrel S., Barsan N., Weimar U., Influence of humidity on CO sensing with p-type CuO thick film gas sensors, sensors and actuators B. 153 (2011) 347-353.
- [6] Verma M., Gupta V., A highly sensitive SnO_2 -CuO multi-layered sensor structure for detection of H_2S gas, Sensors and Actuators. 109 (2013) 220-226.
- [7] Chandrasekaran S., A novel single step synthesis, high efficiency and cost effective photovoltaic applications of oxidized copper nano particles, Solar Energy Materials and Solar Cells. 109 (2013) 220-226.
- [8] Amri A., Duan X. F., Yin C. Y., Jiang Z. T., Mahbubur R. M., Pryor T., Solar absorptance of copper-cobalt oxide thin film coatings with nano-size, grain-like morphology: Optimization and synchrotron radiation XPS studies, Applied surface Science.275 (2013) 127-135.
- [9] Morales j., Sanchez M., Use of low-temperature nanostructured CuO thin films deposited by spray-pyrolysis in lithium cells, Thin solid films. 474 (2005) 133-140.
- [10] Padyath R., Seth J., Babu S. V., Deposition of copper oxide films by reactive laser ablation of copper formate in an r.f.oxygen plasma ambient, Thin Solid Films.239 (1994) 8-15.
- [11] Drobny V.F., Pulfrey D.L., Properties of reactively sputtered copper oxide thin films, Thin Solid Films. 61 (1979)89-98.
- [12] M. Hari Prasad Reddy, P Narayana Reddy & Uthanna, Structural, electrical and optical behaviour of RF magnetron sputtered cuprus oxide films, Indian journal of pure and applied physics. 48 (2010) 420-424.
- [13] NalbantA., Ertek O., Okur I., Producing CuO and ZnO composite thin films using the spin coating method on microscope glasses, Materials Science and Engineering. 178 (2013) 368-374.
- [14] Zhang, H.L., Zhao G. Y., Xua L. Z., Preparation of the photosensitive copper complex and CuO film pattern, Applied Surface Science. 274 (2013) 397-400.
- [15] Mageshwari K., Sathyamoorthy R., Physical properties of nanocrystalline CuO thin films prepared by the SILAR method, Materials science in semiconductor. 16 (2013)337-343.

- [16] Akkari F. C., Kanzaria M., Rezig B., Preparation and characterization of obliquely deposited copper oxide thin films, *European Physical Journal-Applied Physics*. 40 (2007) 49-54.
- [17] Ghosh P. K., Maity R., Chattopadhyay K.K., Electrical and optical properties of highly conducting CdO:F thin film deposited by sol-gel dip coating technique, *Solar Energy Materials and Solar Cells*. 81 (2004) 279-289.
- [18] Gurumurugan K., Mangalraj D., Narayanadass S.K., Nakanishi Y., DC Reactive Magnetron Sputtered CdO Thin Films, *Materials Letters*. 6 (1996) 307-312.
- [19] Ghosh M., Rao C. N., Solvothermal synthesis of CdO and CuO nanocrystals, *Chemical Physics Letters*. 393 (2004) 493-497.

