Preparation and Characterization of Copper Oxide Thin film by SILAR Method

1Chetan R. Yewale, 2Mangesh B. Deore, 3Upendra D. Lad
1Assistant Professor, 2Assistant Professor, 3Associate Professor
1M.S.G. College, Malegaon Camp, Nasik, Maharastra,
2M.S.G. College, Malegaon Camp, Nasik, Maharastra,
3L.V.H.College, Panchavati, Nashik-03, Maharastra

Abstract **- Nanocrystalline copper oxide thin film was fabricated by successive ionic layer adsorption and response (silar) approach. The copper oxide thin film was deposited on corning glass substrate at room temperature. The present work is aimed at studying the behaviour of copper oxide thin film which was annealed at 450 0C temperature for 2 hours in air atmosphere then its electrical characteristics was measured and its effect is discussed in this paper. The DC resistance of the film was measured by half bridge method in air condition at different temperature (Between 40 0C to 350 0C). Film shows increase in temperature with decrease in resistance of film indicating semiconductor behaviour. The TCR, activation energy, specific resistance of film was evaluated at 450 0C. Thickness of the film was measured by gravimetric method.**

keywords **- Silar, CuO, Thickness, Activation energy, UV, IR.**

I. Introduction:

The synthesis and characterization of copper oxide (CuO2) thin films through unique methods have attracted tremendous interest due to their possible utility possibilities in solar cells [1]. Copper Oxide is P- type semiconductor having bandgap 2 ev [1-2] with cubic shape. Cupric oxide (CuO) is also a p-type type material with 1.21–1.51 eV band gap energy and monoclinic crystal shape. The specific physical and chemical deposition strategies used to develop CuO2 thin film on glass [2] consist of reactive sputtering, chemical vapor deposition, spraying, thermal oxidation, electro deposition etc. Ristov et al. [3] and after that Nair et al [1] suggested deposition of CuO_2 via SILAR. In SILAR, thin films are bought through immersing the substrate one by one into positioned cationic and anionic precursors. Between each and every immersion it is rinsed in condense water or ion interchanged water. For CuO deposition, the approch consists of fluctuate immersion of a glass substrate in a composite of copper ion and hot NaOH solution[4]. So far, copper oxide thin films have been produced by variety of deposition methods. Between this methods, SILAR has a variety of convenience, does not require vacuum at any step, can be carried out at room temperature, have no limitations on substrate materials, deposition tools is easy and cheap [5]. And now the electrical characterization of CuO thin film is reported in this presented paper.

II. Preparation:

Prior to the deposition of CuO thin film on microscope glass slide substrates, the substrates were cleaned thoroughly to avoid any surface contamination. The glass substrates were kept overnight in a mixture of chromic and sulphuric acid, it was then washed with detergent (soap solution), This was followed by cleaning the substrate in equal volume mixture of acetone and ethanol and finally rinsed with distilled water. It was then hung in air for it to dry.

For the preparation of CuO thin film, the cationic precursor was 0.1M copper chloride this was obtained by dissolving distilled water while the anionic precursor was obtained by dissolving 0.1M sodium hydroxide in above solution. Copper Chloride solution complex was prepared by adding 25% Ammonia (NH3) to prepared solution upto it going to deep blue.

To deposit nanocrystalline CuO thin film, one SILAR cycle involves the following four steps: a well cleaned glass substrate was first immersed into cationic precursor (0.1M copper complex solution at pH ~8 kept at room temperature) , so the Cu2+ ions were adsorbed onto the substrate surface; (ii) then the substrate was rinsed with distilled water to remove loosely bonded Cu2+ ions from the substrate; (iii) further, the substrate was immersed into anionic precursor (1 M hot NaOH solution) maintained at 70oC, this temperature was achieved by making use of a constant temperature bath, so OH2– ions were adsorbed and reacted with Cu2+ ions (iv) again the substrate was rinsed with distilled water to remove unadsorbed and unreacted OH2– ions from the substrate. Therefore, we obtained a Copper Oxide thin film by successive 40 cycles. The rinsing time of anionic solution was 10s and cationic solution was 20s. After deposition, the ready film was dip in double distilled water, and then dried under IR lamp. This procedure was also done for both anionic and cationic precursors kept at room temperature. Finally the deposited film is annealed at 500^0C.

III. Results

Thickness: The prepared CuO thin film thickness is measured by weight difference method by considering bulk density of CuO material. Film thickness is observed by 170 nm for 40 repeated cycles of CuO thin film.

Electrical properties:

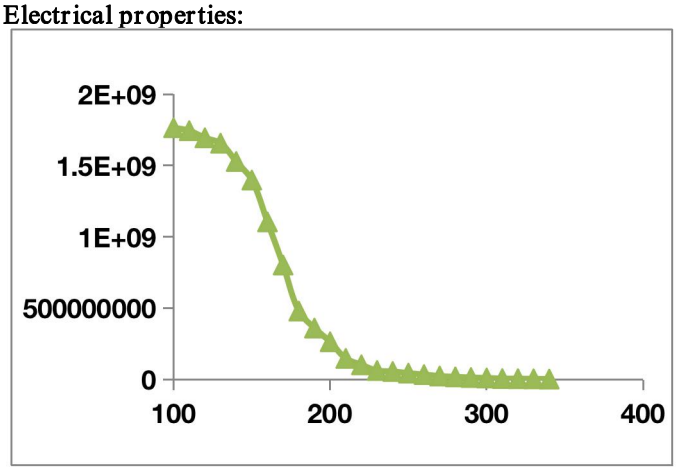


Fig 1) Resistance Vs Temperature

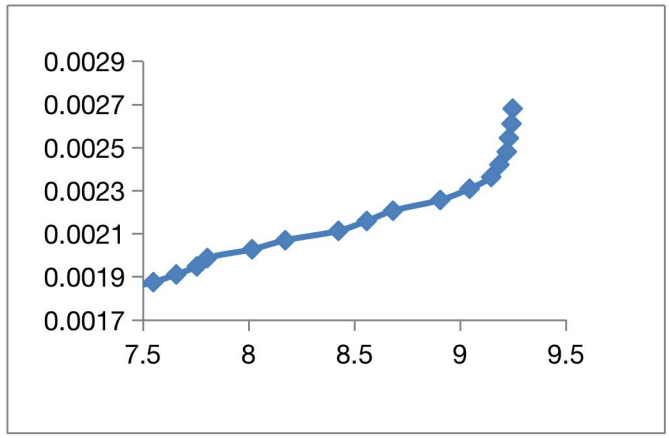


Fig 2) Log R Vs 1000

The electrical characterization of prepared thin film was carried out by potential divider arrangement circuit. The series of readings were performed on the CuO sample shown in fig 1 and fig 2. The decrease of resistance with increasing temperature indicates that 450^{0}C CuO thin film is N type. Log R vs 1000/T graph shows that the resistance of CuO thin film is higher for high temperature region and low for low temperature region that means film are temperature dependant.

Annealing Temperature at ^{0}C	Resistance at Room temperature in G ohm	Film Thickness in Nm	TCR / ^{0}C	Activation Energy	
				HTR	LTR
500	1.8	170	2910.33	0.043016	0.38961

Table 1) Parameters of electrical parameters

X-Ray diffraction:

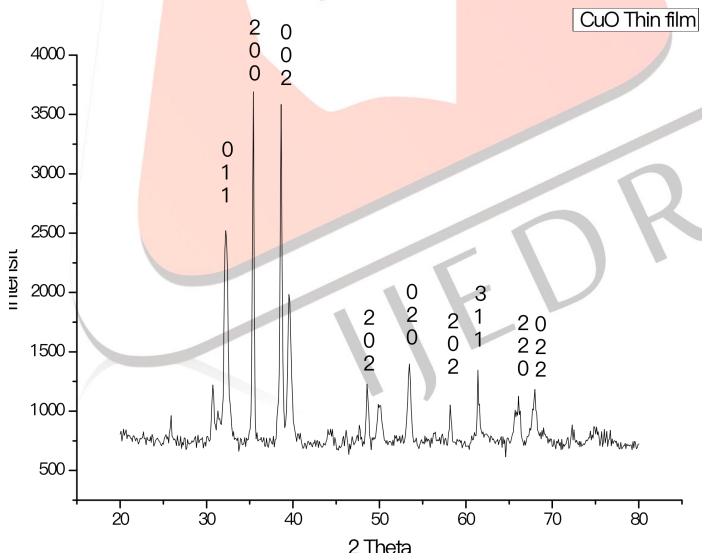


Fig.3) XRD pattern of CuO thin film

Figure 3 shows X-Ray diffraction pattern of the thin film prepared by Silar method. XRD pattern of prepared thin film is compared with standard JCPDS data card no. (892-531) and it confirms Copper oxide film. XRD pattern of prepared nanoparticles shows polycrystalline nature with h, k, l indices (0,1,1), (2,0,0), (0,0,2), (2,0,2), (0,2,0), (2,0,2), (3,1,1), (2,2,0) and (0,0,2) with corresponds to peak angle 32.16, 35.37, 38.66, 48.59, 53.54, 58.25, 61.3, 66.18,and 68.01 as shown in table 1. Crystal structure of copper oxide thin film determines from X-ray diffraction peaks it varies between 21.79 nm to 144 nm.

Thin Film	2 Theta	h k l	β Cosθ	Intensity In A.U	Crystalline Size in Nm
Copper Oxide	32.16	011	0.237	2521	58.48
	35.37	200	0.244	3691	56
	38.66	002	0.242	3585	57.27
	48.59	202	0.191	1228	72.56
	53.54	020	0.106	1399	130

	58.25	202	0.147	1053	94.28
	61.30	311	0.624	1346	21.79
	66.18	220	0.096	1126	144
	68.01	002	0.112	1184	123.75

Table 2) X-Ray diffraction parameters

UV Spectroscopy:

Figure 4 shows a plot of $(\alpha hv)^2$ versus photon energy (hv) to find the type of the optical transition for copper oxide thin film, which describes the allowed direct transition. The optical energy gap values were calculated from Tauc equation by selecting the optimum linear part, which determines by the extrapolation of the portion at (α=0). The energy band gap of prepared copper oxide thin film is 2.15 eV.

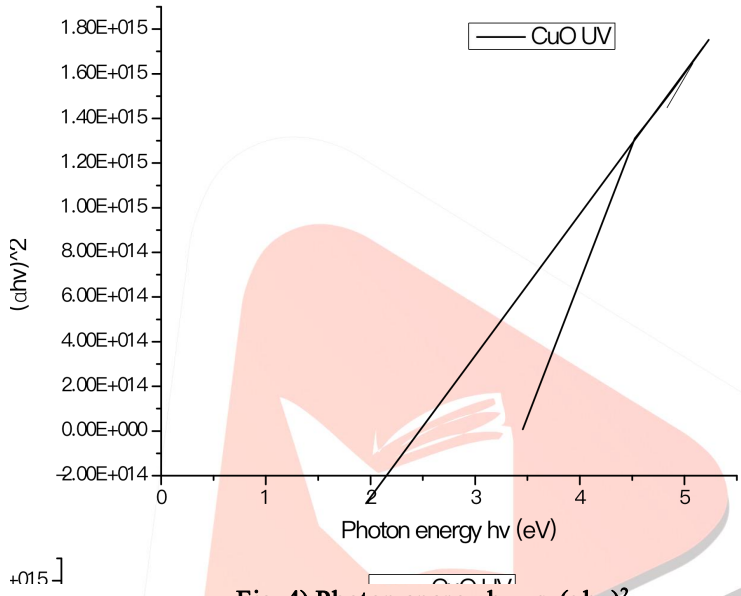


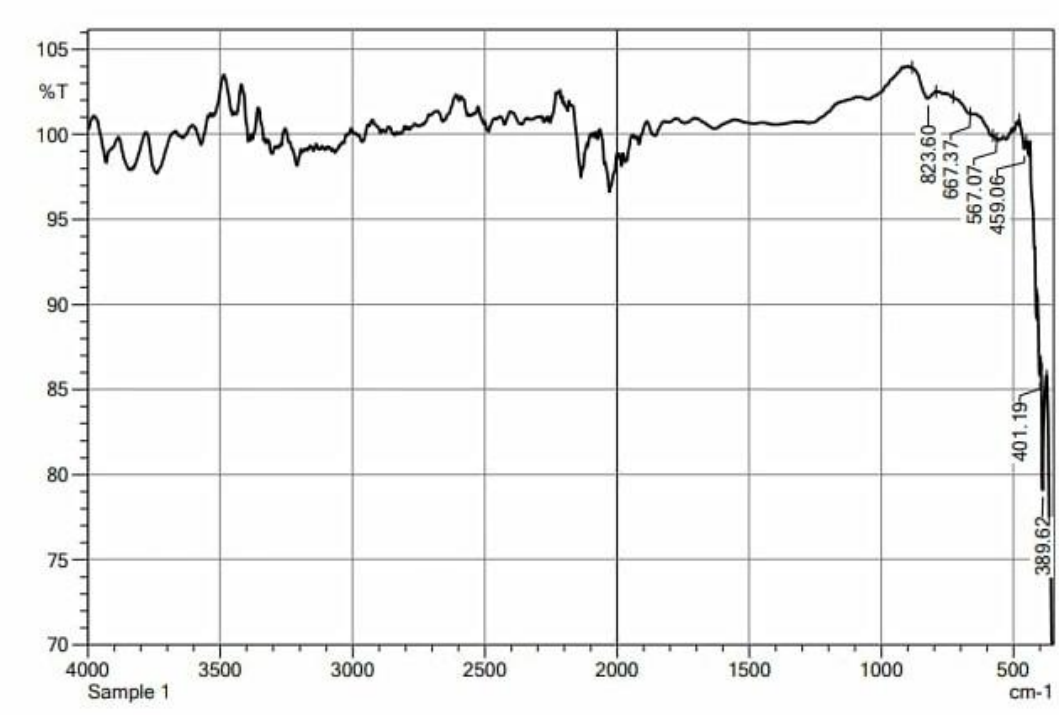
Fig. 4) Photon energy hv vs $(\alpha hv)^2$

IR Spectroscopy:

Figure shows a typical infrared spectrum, that of copper oxide, the spectrum exhibits two absorption peaks at 2050 cm^{-1} and 2200 cm^{-1} for the Cu-O and O-Cu-O stretching frequency respectively. The Strong absorption at 2050 cm^{-1} that corresponds to O-Cu-O is quite intense. In addition to the characteristics positron of absorption, the shape and intensity of this peak are unique to the Cu-O. For instance to some extend Cu-O and O-Cu-O bond absorb in the same region of IR.

Cu-O = 2050-2000 cm^{-1}

O-Cu-O = 2200-2150 cm^{-1}



IV. Conclusion

The temperature dependant characteristics of 500 ^{0}C annealed CuO thin film shows N type nature. The increase of resistance with reciprocal temperature shows film is temperature dependant. Film resistance is nearly same from 250 ^{0}C to 350 ^{0}C. XRD graph confirms that the prepared film is copper oxides film and its crystalline size is varies in between 21 nm to 144 nm. Energy band gap of prepared film is 2.15 eV

V. Acknolgement

The authors are thankful also to Management authority of M.G.Vidyamnadir and Principal of M.S.G. College Malegaon Camp, Nasik, Maharashtra, India. Authors are also thankful to Dr. Latesh Nikam (Head of department Chemistry) Baburaoji gholap college, new sangavi pune for XRD facility.

References:

[1] M. T. S. Nair, L. Guerrero, O. L. Arenas and P. K. Nair, Chemically deposited copper oxide thin films: structural, optical and electrical characteristics, Applied Surface Science, 150 (1999) 143-151.

[2] G Papadimitropoulos, N Vourdas, V Em Vamvakas and D Davazoglou, Deposition and characterization of copper oxide thin films, Journal of Physics: Conference Series 10 (2005) 182–185.

[3] M. Ristov, G. I. Sinadinovski and I. Grozdanov, Chemical deposition of Cu2O thin films, Thin solid films, 123 (1985) 63-67.

[4] Mageshwari, K., Sathyamoorthy, R. 2013. Physical properties of nanocrystalline CuO thin films prepared Avrupa Bilim ve Teknoloji Dergisi www.ejosat.com ISSN:2148-2683 128 by the SILAR method. Materials Science in Semiconductor Processing 16 (2) 337-343.

[5] Pathan, H.M., Lokhande, C.D. 2004. Deposition of metal chalcogenide thin films by successive ionic layer adsorption and reaction (SILAR) method. Bulletin of Materials Science 27, 85-11