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Studies on physical properties of nanocrystalline Cu_2S thin films prepared by modified chemical bath deposition method (M-CBD)

M. S. Shinde[1], P.B.Ahirrao[2], I. J.Patil[1], S.K. Disawal[3], R. S. Patil[1*]

[1]*Department of Physics, P. S. G. V. P. M'S Arts, Science & Commerce College Shahada, Dist.-Nandurbar - 425 409, India*
[2]*Department of Physics, S.V.S.'s Arts and Science College Dondaicha, Dist.-Dhule, India*
[3]*Department of Physics, S.V.S.'s Arts and Science College Dondaicha, Dist.-Dhule, India*

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Abstract

Nanocrystalline Copper sulphide (Cu_2S) thin films have been grown on glass surface by Modified chemical bath deposition method (M-CBD). The optimized preparative parameters including temperature, pH of solution, immersion time, immersion cycles, have been optimized for fine nanocrystalline film growth. As deposited nanocrystalline Copper sulphide (Cu_2S) thin films have been made characterized for the structural, surface morphological, optical and electrical properties using X-ray diffraction (XRD), Scanning electron microscopy (SEM), UV-VIS Spectra and d.c. two point probe method.

Keywords: Thin films, Nanocrystalline, SEM, optical properties, Electrical properties.
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1. Introduction

Nanocrystalline Copper sulphide thin films evoked much attention due to their vast potential in various fields. The Cu_2S thin films have wide range of well perspective applications such as photovoltaic cells, tubular solar collectors ,automobile glazing, solar control coatings, dye-sensitized solar cells, gas sensors, Photodetectors, electroconductive electrode, microwave shielding coatings, super conductors, potential nanometer-scale switch. There are several techniques such as Spray pyrolysis[1], Reactive magnetron sputtering[2], Atomic layer deposition (ALD)[3], Activated reactive evaporation [4], Electrochemical methods [5], Chemical vapor deposition (CVD) [6], Chemical bath deposition(CBD)[7,8], Modified chemical bath deposition[9], Successive ionic layer adsorption and reaction (SILAR) [10], Microwave assisted chemical bath deposition (MA-CBD)[11] have been used for the deposition of Copper sulphide thin films, among them M-CBD is simple, economic and convenient, for large area deposition.

In this paper we report the preparation of Copper sulphide thin films from alkaline bath and studies the structural, surface morphological, optical and electrical properties of the as deposited thin films.

[*]) For correspondence, Tel: +91-9421530100, E-mail: rspatil_shahada@yahoo.co.in, mahen3569@rediffmail.com

2. Experiment Details

For the deposition of Cu_2S thin films in aqueous medium A.R. grade Copper Chloride, ammonia, hydrazine hydrate & thiourea were used. The cationic precursor for Cu_2S was 0.1 M dm^{-3} $CuCl_2$ solution which was complex with mixture of hydrazine hydrate & ammonia. The substrate was immersed in the cationic precursor for 25 sec where absorption of Cu^+ ions takes place on the surface of substrate and the unabsorbed ions were removed by rinsing the substrate in double deionised water for 15 sec. Then substrate was immersed in an anionic precursor for 25 sec., so S^- ions are reacted with Cu^+ ions. The loosely bound ions were removed by rinsing the substrate in the deionised water for 15 sec. thus one layer of Cu_2S is formed, this completes one M-CBD cycle. Such M-CBD cycles were repeated until the required film thickness was reached .The complete deposition process was carried out at room temperature the optimized preparative parameters are listed in Table 1.

Table 1

Deposition Condition	Precursors Solution	
	0.1Mdm^{-3} $CuCl_2$+hydrazine hydrate + ammonia	0.1Mdm^{-3} thiourea
pH	8.5	6
Immersion time (S)	25	25
Rinsing time (S)	15	15
Immersion cycles	25	25

The variation of film thickness with concentration of Copper Chloride is as shown in Figure 1.

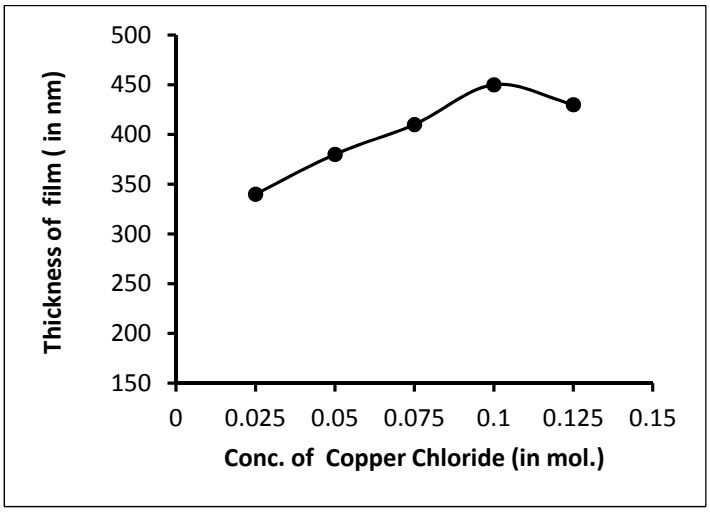

Figure 1: The Variation of Cu_2S film thickness as function of concentration of Copper Chloride for fixed concentration of Thiourea.

Keeping concentration of thiourea 0.1M, the Cu_2S film formation was started at concentration of 0.025M of Copper Chloride but it optimize for maximum thickness at 0.1M concentration. After this Cu_2S film thickness was decreased due to formation of outer porous layer and peeling off from glass substrate [12].The thickness of Cu_2S thin film was measured by profilometer. Figure 2 shows the variation of film thickness with number of immersion cycles.

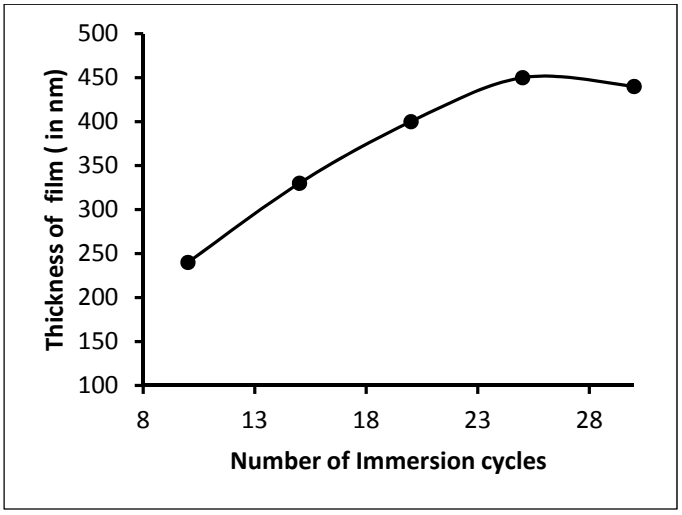

Figure 2: Graph of as deposited Cu_2S film thickness as a function of Number of Immersion cycles.

Initially film thickness increases with number of immersion cycles. This Cu_2S film had maximum terminal thickness of 450 nm for 25 immersion cycles. After this film thickness starts to decrease due to peeling off the material from the substrate [13].

3. Characterization Techniques

The thickness of the thin films was measured by a surfcom 480^{o}A profilometer. The structural characterization of the films was carried out using Philips (PW-3710) X-ray diffractometer with CuKα radiation (α= 1.5404^{o}A) in 2θ range from 20^{0}-$80^{0.}$ The surface morphological study of Cu_2S films was carried out by scanning electron microscopy using a Model JOEL, JSM 6360 A. The electrical resistivity of the films was measured by two probe technique. The optical absorption spectra of the figure were recorded on Systronic spectrophotometer in the wavelength range of 350-850 nm.

4. Results and Discussion

4.1 Structural Studies

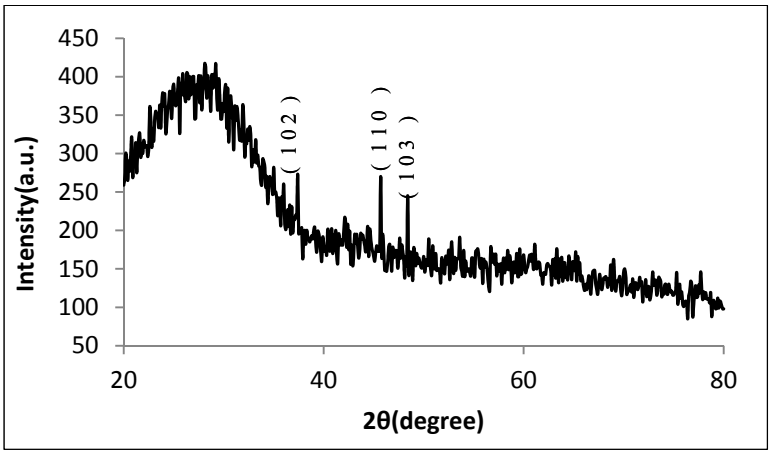

Figure 3: The X-ray diffraction pattern of as-deposited Cu_2S on glass substrate at room temperature.

Figure 3 shows the X-ray diffraction pattern of as-deposited Cu_2S thin film on to the amorphous glass substrate. The short intense peaks at 2θ = 37.423 (d = 2.4010Å), 2θ = 45.774 (d=1.9805 Å) and 2θ = 48.484 (d = 1.8759 Å) corresponding to the (1 0 2), (1 1 0) and (1 0 3) planes of Cu_2S with Hexagonal crystal phase . The crystallite size was estimated by using the well-known Scherrer's formula as,

$$D = 0.9\lambda/\beta\cos\theta \quad (1)$$

where λ = 1.5406 Å for CuKα, β is the full width at half maximum (FWHM) of the peak corrected for the instrumental broadening in radians and θ is the Bragg's angle. The sample of as-deposited Cu_2S thin film resulted in an average crystallite size of 20-30 nm.

4.2 Surface Morphological Studies

Scanning electron microscopy (SEM) is a versatile technique for studying microstructure of thin films. The Cu_2S thin film with 450nm thickness was used to study the surface morphology using a scanning electron microscopy.

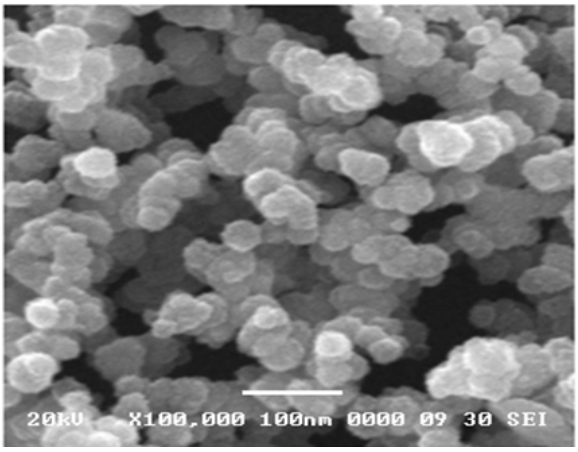

Figure 4: The surface morphology of as-deposited Cu_2S on glass substrate at room temperature by scanning electron microscopy studies.

Figure 4 shows a scanning electron microscope of Cu_2S thin film at X 100,000 magnification, the scale bar length is 100nm. The microstructure of the Cu_2S thin film on glass substrate shows uniform surface morphology with confined particle size 20-30 nm. From Figure 4, it can be inferred that the particles with well-defined shape could not be detected. Instead, these films showed surfaces with a spongy looking texture due to extra deposition of Cu_2S material. Agglomeration of small size particles gathers to form spherical structure.

4.3 Optical Properties

The optical properties of Cu_2S thin films are determined from absorbance measurement in the range 350-800nm. Figure 5 shows the absorbance spectra of Cu_2S thin film.

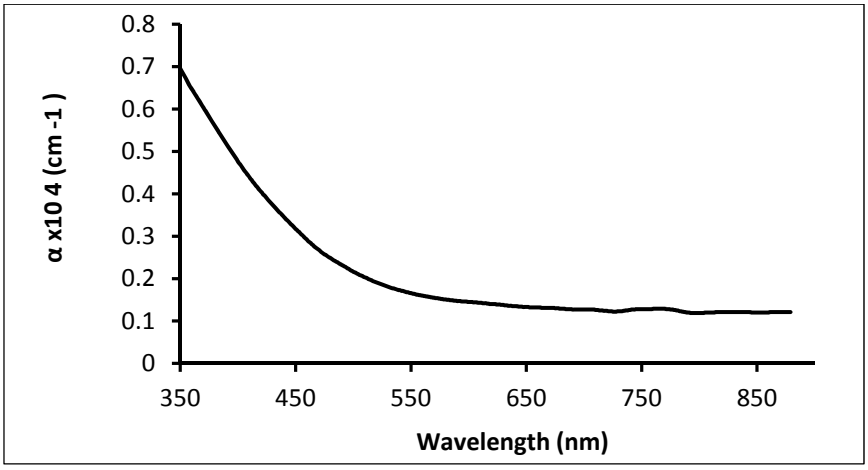

Figure 5: The absorbance spectra of as-deposited Cu_2S on glass substrate.

Absorbance coefficient α associated the strong absorption region of the films was calculated from absorbance (A) and the film thickness (t) using relation [14].

$$\alpha = 2.3026\ A/t \tag{2}$$

The absorption coefficient α was analyzed using the following expression for near-edge optical absorption of semiconductors [15].

$$(\alpha h\upsilon) = K\ (h\upsilon - E_g)^{n/2} \tag{3}$$

Where k is Boltzmann's constant, E_g is separation between valance and conduction bands and n is constant that is equal to 1 for direct band gap semiconductor. The band gap were determined from the intersect of straight line portion of $(\alpha h\upsilon)^2$ versus hυ graph shown in Figure 6 The observed band gap values of the film was 2.36 eV. This is good agreement with reported values [7-9].

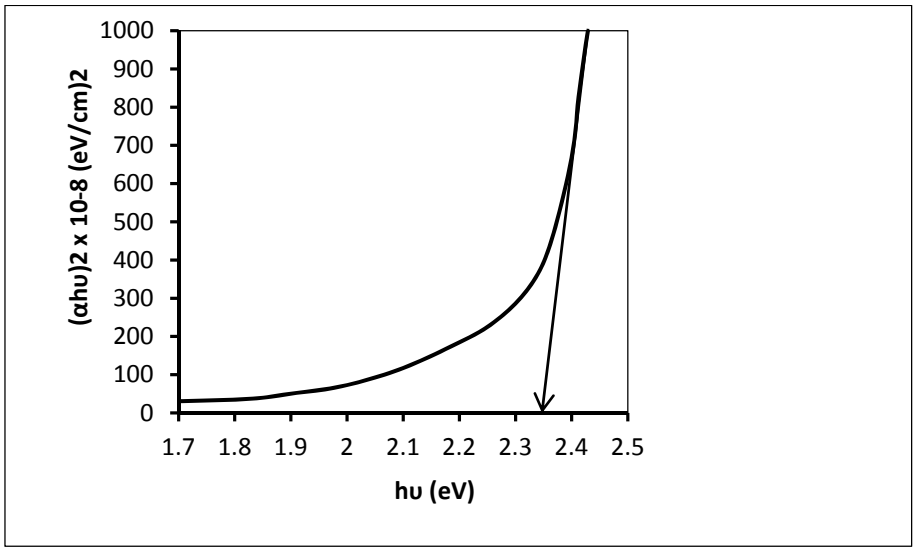

Figure 6: The variation of $(\alpha h\upsilon)^2$ verses hυ of as-deposited Cu_2S thin film on glass substrate at room temperature.

4.4 Electrical Resistivity

The electrical resistivity of Cu_2S thin films was measured using D.C. two point probe method.

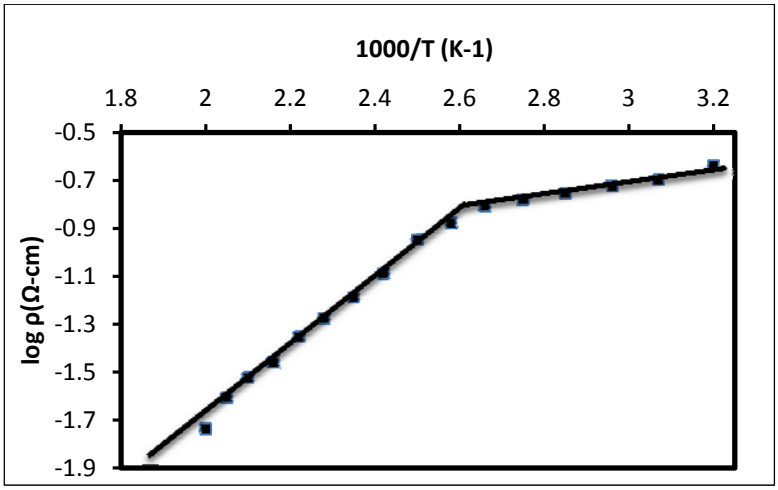

Figure 7: The variation of (log ρ) with (1000/T) for as-deposited Cu_2S thin film on glass substrate.

Figure 7 shows the variation of log of resistivity (log ρ) with reciprocal of 1/T X 10^3K for all films. The resistivity follows the relation

$$\rho = \rho_0 \exp (Ea/kT \quad (4)$$

Where ρ is resistivity at temp T, ρ_0 is a constant, k is Boltzmann constant, E_a is activation energy for conduction. From Figure 7 resistivity of Cu_2S sample decreases with temperature indicating semiconducting nature of thin film. The electrical resistivity at room temperature of the Cu_2S thin film onto the glass substrate was found to be of the order of 10^{-1} to 10^{-2} Ω-cm. This agrees with the reported value. The thermal activation energy was calculated using relation **(4) [**13] for Cu_2S thin film. The activation energy is 0.1048 eV in the low temperature regime 300–375 K and 0.6547 eV in high the temperature regime of 375–500 K.

5. Conclusion

Modified chemical bath deposition method was used for preparation of Cu_2S thin films on glass substrate. The XRD study showed the Hexagonal structure of Cu_2S thin films. The SEM micrograph reveals that substrate is well covered and average grain size is 20-30nm. The Optical band gap was found to be 2.36 eV. The electrical resistivity is in order 10^{-1} to 10^{-2} Ω-cm with activation energy 0.1048 eV and 0.6547 eV for high and low temperature region.

References

[1] E. Pop, V. Popescu, M. Danila and M. N. Batin, Chalcogenide Letters, **8**(6) (2011) 363

[2] Cristina Nagcu, Ileana Pop , Violeta Ionescu , E. Indrea and I. Bratu, Materials Letters, **32** (1997) 73

[3] H. M. Pathan, J. D. Desai, C. D. Lokhande, Applied Surface Science, **202** (2002) 47
[4] H. S. Randhawa, R. E. Bunshah, D. G. Brock, B. M. Basol and J. B. Philips, *Sol. Energy Mater*, **6** (1982) 445
[5] J. Johansson, J. Kostamo, M. Karppinen and L. Niinist, J. Mater. Chem. **12** (2002) 1022
[6] J. A. Thronton, D. G. Cornog, W. W. Anderson, R. B. Hall and J. E. Philips, in: *Proc. 16th IEEE Photovoltaic Specialists Conf.*, San Diego (1982) 737
[7] K. M. Gadave and C. D. Lokhande, Thin Solid Films, **229** (1993) 1
[8] M. Kemmler, M. Lazell, P. O. Brien, D. J. Otway, J.-H. Park and J. R. Walsh, J. Mater. Sci. Electron, **13** (2002) 531
[9] Mudi Xin, Kun Wei Li and Hao Wang, Applied Surface Science, **256** (2009) 1436
[10] R. S. Longhurst, *Geometrical & Physical Optics*, Longmans Green, Londan (1957)
[11] R. S. Patil, C. D. Lokhande, R. S. Mane, H. M. Pathan, Oh-Shim Joo and Sung-Hwan Han, Materials Science and Engineering, **B129** (2006) 59
[12] R. S. Patil, T. P. Gujar, C. D. Lokhande, R. S.Mane and Sung-Hwan Han, Journal of non-crystalline Solids, **353** (2007)
[13] S. D. Sartale and C. D. Lokhande, Materials Chemistry and Physics, **65** (2000) 63
[14] T. Kuzuya, K. Itoh, M. Ichidate, T. Wakamatsu, Y. Fukunaka and K. Sumiyama, Electrochem. Acta, **53** (2007) 213
[15] Vipin Kumar, K. L. A. Khan, G. Singh and T. P. Sharma, Appl .Surf. Sci., **253**(7) (2007) 2543