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Synthesis of Cu_2O by SILAR and the impact of Annealing on the Structural Properties

[1] Dr. K. Amudhavalli, [2] Dr. N. Neelakandapillai, [3]Dr. M. Nagarajan
[1][2][3] Associate Professor, Department of Physics
[1][3]V.O.Chidambaram College, Thoothukudi,TamilNadu, [2] Arignar Anna College, Aralvoimozhi, Tamil Nadu.

Abstract:- **The present study focuses on fabrication of Cuprous oxide thin film on an amorphous glass substrate using SILAR technique. Four samples were prepared in total and three samples were annealed at various temperatures, 200℃, 300℃, and 400℃. The annealed samples were compared with the as-deposited sample.**

The structural analysis of the prepared samples was examined by X-Ray Diffraction. The analyses revealed that annealing converts cuprous oxide into cupric oxide at higher temperatures. Also, the preferred orientation for Cu2O is along (111) plane and for CuO the predominant peak is along (002). The particle size, lattice parameters, dislocation density and micro-strain values of the samples were calculated.

Key Words: Cuprous oxide, Cupric oxide, SILAR, Particle size, Lattice constant, Dislocation density, Micro strain.

1. INTRODUCTION

The cost effective thin film preparation for the application of solar cell is one of the most important challenges in the recent research. Copper oxide has been considered a cheaper material and is selected for the present work. Also, it has a wide application particularly they can be used as an absorber layer for solar cells. The two well-known forms of copper oxide are Cuprous oxide (Cu_2O) or Cuprite and Cupric oxide (CuO) or Tenorite. Cu_2O belongs to cubic crystal structure and is naturally a p-type material due to the negatively charged Cu vacancies and has a direct band gap with values from 1.9 eV to 2.6 eV [1]. The colour of the Cu2O usually varies from yellow to brick red. Cupric oxide belongs to the monoclinic crystal system and has an indirect band-gap of 1.2 eV to 1.9 eV [1]. And, the colour of CuO is either of dark brown or of black.

So far, different deposition techniques were adopted for the preparation of thin film. For the present study Successive Ionic Layer Absorption and Reaction Method (SILAR) is used to develop thin films of Cuprous oxide on a plane glass plate. The main advantage of the SILAR deposition method is of low cost. It does not require any high quality materials. The deposition rate and the thickness of the film can easily be controlled by changing the deposition cycles [3]. Thin films can be grown on the glass plate in a large area and any substrate can be used for deposition and metallic films can also be prepared by the SILAR method.

This paper focuses on the preparation of cuprous oxide thin films on an amorphous glass plate by SILAR method. The prepared samples were annealed and the structural properties of the same were investigated using X-Ray diffraction pattern.

2. EXPERIMENTAL PROCEDURE

Copper Sulphate Pentahydrate ($CuSO_4.5H_2O$) of AR grade, Sodium Thiosulphate ($Na_2S_2O_3.5H_2O$) and Sodium hydroxide (NaOH) were used for the preparation of the films. Initially 0.5M of Copper Sulphate Pentahydrate and 0.5M of Sodium Thiosulphate ($Na_2S_2O_3$) were prepared [6]. A precursor was prepared by taking Copper Sulphate and Sodium Thiosulphate in the ratio 1:4 and was well stirred. This is the cationic precursor and is named as solution A. Then 0.5M of Sodium hydroxide (NaOH) was prepared and this anionic precursor is named as solution B. 80ml of solution A was taken in a beaker and was kept at room temperature. Then 100ml of NaOH solution B was taken in another beaker and heated at 700 C and the temperature is maintained in the water bath. Four plane glass plate of size 76mm X 26mm X 1mm were taken as a substrate and were thoroughly washed with soap water, acetone and deionized water. A glass plate was first dipped in the hot NaOH solution for 20 sec. Initially the OH^- ions from solution B adhered to the surface of the glass plate. After this, it was dipped in the 80 ml stock solution A for another 20 sec. Here Cu^+ adheres to the substrate and reacts with OH^- and forms Cu_2O. It was then rinsed with distilled water for few seconds, with which the process completes a cycle. The above procedure is repeated for 20 cycles. The same procedure was repeated for all the other samples. It was observed that after 10 cycles the film is tinged with red colour. After 20 cycles, the colour of the film was brick red. This indicates the presence of Cuprous oxide[1,2,4]. When

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copper sulphate and sodium thiosulphate are dissolved, thiosulphate ions and cupric ions are formed. In this redox reaction the cupric ion acts as an oxidizing agent and so the blue cupric ion becomes colourless cuprous ion. It is important to note that only when thiosulphate is in excess of cupric then the reduction of cupric to cuprous ions is fast. The reaction is as follows [2,3]:

$2Cu^{2+} + 4S_2O_2^{3-} \rightarrow 2[Cu(S_2O_3)]^{-} + [S_4O_6]^{2-}$ ----(1)

$[Cu(S_2O_3)]^{-} \rightarrow Cu^{+} + S_2O_3^{2-}$ -----(2)

$2Cu^{+} + 2OH^{-} \rightarrow Cu_2O + H_2O$ -----(3)

Then each of these three prepared samples was heated in a muffle furnace at temperatures 200℃, 300℃ and 400℃ respectively. The annealed samples appear black from dark red and it indicates the conversion of Cu_2O to CuO. CuO obtained by oxidation of cuprous oxide at higher temperature is represented by the equation:

$$Cu_2O + ½\ O_2 \rightarrow 2CuO$$

The as-deposited film is named as sample 1 and the plates heated at temperatures 200℃, 300℃ and 400℃ were named as sample 2, 3 and 4 respectively. The structural analyses and optical properties of the prepared samples were carried out by X-Ray Diffraction and UV Vis-Spectrophotometry.

3. RESULTS AND DISCUSSION

3.1 X-Ray Diffraction

For the present study XRD measurements were made to identify the crystal structure of the film using XPERT-PRO Diffractometer with CuKα (λ=1.5406) radiation at 40 kV and 30mA with a scanning rate of 10°/min and the scan range was fixed from 2θ=10° to 90°.

Assuming a homogeneous strain across crystallites, the average crystallites size can be estimated from the full width at half maximum (FWHM) values of the diffraction peaks. The average grain size of the thin films prepared for all the samples is estimated from Debye Scherrer's formula:

$$D = \frac{0.94\lambda}{\beta \cos\theta}\ m$$

where β is the full–width at half maximum (FWHM) of a Bragg peak, λ the X-ray wavelength (=1.5406 nm) and θ the Bragg angle. K is a shape factor and usually takes a value of 0.94. Using the values of crystallite size and from FWHM values, the dislocation density values are calculated. The dislocation density δ is defined as the length of dislocation lines per unit surface of the crystal and can be calculated through the following relation:

$$\delta = n/D^2$$

where δ is the dislocation density, n is a factor, when equal to unity gives minimum dislocation density and D is the crystallite size.

The lattice constant for all the deposited cubic Cu2O films are calculated from the formula

$$a^2 = \frac{\lambda^2 (h^2 + k^2 + l^2)}{4Sin^2\theta}$$

where a is the lattice constant, λ the wavelength of X-ray and θ the glancing angle.

Similarly, the lattice constant for all the deposited monoclinic CuO films are calculated from the formula

$$\frac{1}{d^2} = \frac{1}{Sin^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2}{b^2}Sin^2\beta + \frac{l^2}{c^2} - \frac{2hlCos\beta}{ac}\right)$$

Using the values of crystallite size and from FWHM values, micro strain values are calculated. The micro strain is a lattice misfit and it depends on deposition condition. The lattice strain values are calculated from the William Hall equation:

$$\beta\cos\theta = K\lambda/D + 4\varepsilon\sin\theta$$

where β is the FWHM, D the crystal size, λ the X-ray wavelength and θ the Braggs diffraction angle. βcosθ is plotted against Sinθ for all the samples. The value of strain can be calculated from the slope and the intercept will give the value of the particle size.

Fig. 1 shows the diffraction pattern of samples 1, 2, 3 and 4. In the XRD graph the peaks are indexed, and the peaks corresponding to CuO are indicated with a star (*). It is observed from the XRD graph that the films prepared at room temperature and heated at 200℃ correspond to Cuprous oxide. When the films are heated at 300 ℃ there is a mixture of Cu_2O and CuO as indicated in the graph. When heated at 400 ℃, Cu_2O is completely converted into CuO. Also, the preferred orientation for Cu2O is (111) plane which occurs at 2θ=36.32 and for CuO the predominant peak is at 2θ=35.45 and this corresponds to (002) plane. The strongest peak of CuO (002) indicates the perpendicular alignment of the c- axis of the grains [5]. Also it is observed that the intensity of the peak decreases when annealing temperature is increased from 300℃ to 400℃ and this

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indicates that the crystallinity decreases when there is a complete conversion of the film from 300℃ to 400℃ . Hence it is concluded that the cuprous oxide thin films prepared on an amorphous glass plates can be converted into cupric oxide when the film is heated upto 400℃.

The particle sizes of the fabricated samples are calculated by Debye Scherrer formula. The particle size, the dislocation density, the lattice constant and the micro strain values are listed in Table 1. It is observed from the result that the particle size invariably varies with the temperature and the dislocation density decreases as particle size increases. The lattice constant values agree well with the standard JCPDS value (Cu2O: Card No. 05 0667, CuO: Card No.05-0661). The percentage of micro strain values calculated for the samples shows that the strain values are very less for all the deposited films.

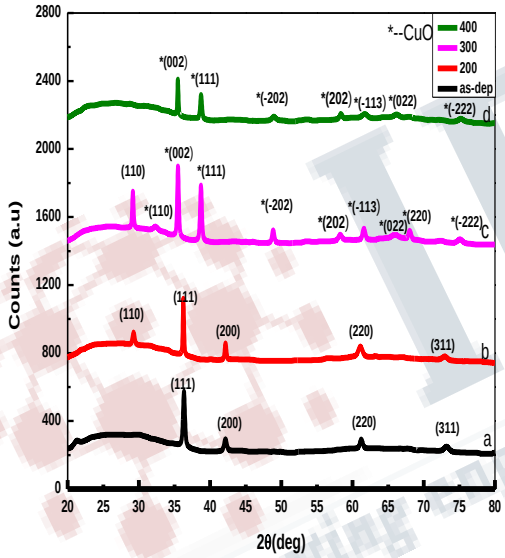

Fig.1 XRD pattern of samples prepared at a) as-deposited b) 200 ℃, c) 300 ℃ and d) 400 ℃

4. CONCLUSION:

Cuprous oxide thin films were successfully coated on the amorphous glass substrate by SILAR Technique. The samples were annealed at various temperatures, 200℃, 300℃, 400℃ and was compared with the as-deposited sample. The Structural analyses of the prepared samples were done using X-Ray Diffraction. From the XRD analysis it is concluded that sample1 and sample 2 prepared by SILAR comprises only Cuprous oxide. When the annealing temperature is increased to 300℃ we could observe a mixture of cuprous and cupric oxide. But at temperature 400℃ the sample is completely converted to cupric oxide. Thus the analyses revealed that the annealing converts cuprous oxide into cupric oxide at higher temperatures.
The particle size, the lattice parameters and the dislocation density values were calculated for both cuprous and cupric oxide. The particle size varies from 27-62nm. The lattice constant well matches with the standard JCPDS data.

Table 1: Results from XRD

Sample code	Particle size(nm)	Lattice constant a(A°)	Dislocation Density ($X10^{14}$)lines/ m^2	Micro strain %
1. As-deposited	27.7616	4.2811	12.97511	0.50
2. 200℃	49.9489	4.2957	4.008189	0.42
3. 300℃	40.8813	4.3055	5.983435	0.43
4. 400℃	62.3179	a= 4.1132 b= 3.8133 c= 5.1379	2.574983	0.46

Hence the samples, Cuprous and Cupric oxide, prepared by low cost SILAR method can well be used as an absorber in a solar cell.

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