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Selected morphological, Structural and Optical properties of Cu_2O thin films at elevated annealing temperatures

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Abstract - *Cuprous oxide (Cu_2O) thin films were prepared on to FTO glass substrate by electrodepositionmethod at optimized bath temperature 60°C and then annealed at varying temperatures of 200°C and 300°C for 1hr each. The structural, morphological,optical and vibrational properties of Cu_2O thin films were studied using X-ray diffraction (XRD), Scanning electron microscopy (SEM),UV-Visible and Micro Raman spectrometry.X-ray diffraction patterns revealed that the deposited films were cubic structure with predominant orientation of (111) crystallographical lattice plane and the crystallinityof the film has improved at an annealed temperature 300°C. Since that, the crystallite size (D), dislocation density (δ) and stacking fault probability (α) for preferential orientations are calculated and discussed in detail.SEM micrographs revealed high densed nanoparticle facets of truncated cubes which are more essential for fabricating thin film solar cells.Optical properties of Cu_2O films were analyzed by transmittance spectra using UV-Vis-NIR wavelength region. Raman spectra showed that the vibrational peak centered at 637cm^{-1} attributes the formation of Cu_2O in as-prepared and annealed thin films.*

Keywords: *Electrodeposition, Cu_2O thin films, XRD, SEM, Micro Raman*

I. INTRODUCTION

Cuprous oxide (Cu_2O) is a P-type semiconducting material with cubic lattice that has a been studied for long time [1,2]. It has a direct band gap of 1.9eV -2.2eV, since which is used for solar cells , photoelectrochemical cells [3,4] , photocatalysts [5,6], field effect transistors [7,8] and sensor application [9].Many techniques have been explored to prepare the Cu_2O thin films are pulsed laser deposition [10],magnetron sputtering[11],radical oxidation [12] and electrodeposition[13].Among these methods, electrodeposition offers a facile route to control the morphologies of interfacial structure of the films by including additives in the plating media [14]. After the deposition,Cu_2O film was annealed at temperatures as-prepared, 200˚C and 300˚C. In this article, we investigated and analyzed the micro structural, morphological and optical characteristics were investigated by X-ray diffraction, Scanning electron microscopy, Photoluminescence, UV-Vs-NIR spectroscopy and Micro Raman spectroscopy at different annealed temperatures.

II. EXPERIMENTAL DETAILS

Potentiostatically deposition of Cu_2O thin films grown on fluorine doped tin oxide glass substrates (7Ω/square).Prior to the deposition; FTO substrates were ultrasonically cleaned in acetone, isopropanol and deionized water sequentially. A standard three electrodes cell system was used for electrodeposition of Cu_2O films. FTO substrates as working electrode, platinum rod as counter electrode and a Ag/ AgCl as reference electrode .The electrodeposition was carried out using a solution mixture containing $CuSO_4$(0.15M) and Lactic acid (1.25M).The deposition has been carried out in the temperature range 60˚C and pH of the electrolytic was maintained at10 using the NaOH. The potential was maintained the range is -0.4V for 30 min with a scanning potentiostat (Model 362, EC& G Princeton Applied Research,USA).After deposition, Cu_2O films were annealed at various temperatures such as as-prepared, 200˚C and 300˚C.

An X-ray diffract meter system (X'PERTPRO PAN analytical,Netherlands) with CuKα radiation(λ=0.1540) nm was used to study the crystal structure of the films. Surface morphological study was carried out using a Scanning electron microscopy (ZEISS -Instrument).Photoluminescence spectroscopy (RF-6000, SHIMADZU Instrument) was employed for analyzing photoluminescence properties of Cu_2O thin films. Optical properties of the films were studied using UV-Vis-NIR spectroscopy (UV-1800,SHIMADZU Instrument).The vibrational modes of the Cu_2O films were analyzed using Micro Raman spectroscopy.

III. RESULTS AND DISCUSSION

A. Structural analysis

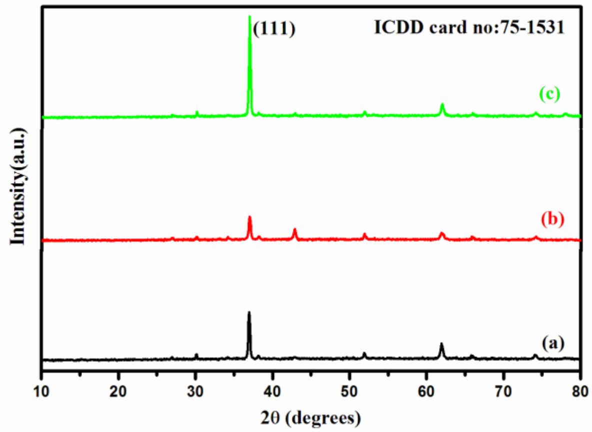

Figure .1 XRD patterns of Cu_2O thin films deposited atdifferent annealed temperatures (a) as-prepared, (b) 200˚C and (c) 300˚C.

P-type Cu_2O films were annealed at various temperatures in air 30 min on FTO glass substrate.Fig.1 shows the XRD patterns of Cu_2O films annealed in the various temperatures as-prepared, 200˚C and 300˚C.The unassigned diffraction peaks are related to FTO glass substrates. The remaining diffraction peaks are well indexed to cubic structure of Cu_2O and good in accord with ICDD card no: 75-1531. The diffraction peaks appeared at 2θ values of 36.52˚ correspond to (111) planes. The decreased in crystallinity of Cu_2O films with increased annealed temperature up to 200˚C, and there after the crystallinity of the film has improved at annealed temperature 300˚C. This indicates a conversion of cuprous oxide in to cupric oxide which is evidenced by color change from brick red Cu_2O to black CuO [15].

CuO may be obtained by oxidation of cuprous oxide at high temperature as represented by following reaction (1),

$$Cu_2O + \frac{1}{2} O_2 \rightarrow 2CuO \qquad \text{— (1)}$$

Further, the films annealed above 300˚C, the films peeling out from the FTO substrates.In this XRD patterns, it can be observed that annealed temperature 300˚C, the increase of peak height of XRD spectrum. The crystalline size of the prepared thin films is calculated using Scherer's formula [16]

$$D = \frac{0.9\lambda}{\beta \cos(\theta)} \qquad \text{— (2)}$$

where D is the crystalline size, λ is the wavelength of the X-ray, β is the full width half maximum of the diffractions peak in radians and θ is the diffraction angle. The crystalline size of the films deposited at various annealed temperatures as-prepared, 200˚C and 300˚C found to be 40.58 nm, 34.12 nm, and 42.66 nm. The dislocation density (δ) is defined as the length of the dislocation per unit volume (lines/m^2) and was estimated using the following equation.

$$\delta = \frac{1}{D^2} \qquad \text{— (3)}$$

In the way, the micro strain (Ɛ) developed in Cu_2O films is calculated using the formula given below

$$\varepsilon = \frac{\beta}{4\tan(\theta)} \qquad \text{— (4)}$$

The calculated values of the crystallite size, dislocation density, and micro strain are summarized. The crystallite size of the Cu_2O thin films increased from 34.12nm to 42.66nm when the annealing temperature increased from 200˚C to 300˚C.It is observed that the increase of nucleation site leads to an improvement of the crystallinity [17].Further, close scrutiny from the calculation, the dislocation density (δ) and the micro strain(Ɛ) of the Cu_2O films values are decreased from $8.589x10^{-4}$ to $5.494x10^{-4}$ lines/m^2 and $0.315x10^{-2}$ to $0.253x10^{-2}$,with increasing annealing temperature from 200˚C to 300˚C respectively. This is attributed to the decrease the defect level and grain boundaries due to increased crystallite size. It indicates the presence Cu_2O film has formation of higher quality films.

B. Surface morphology analysis

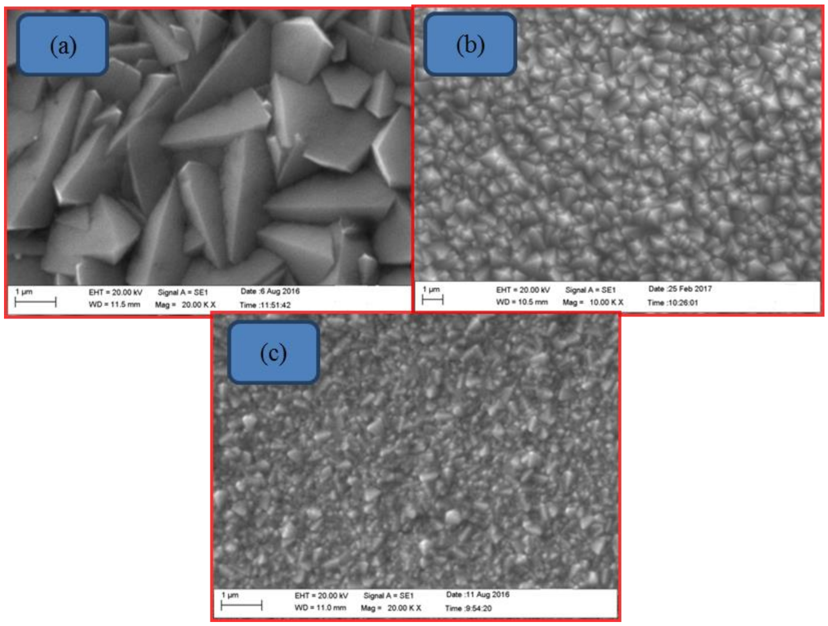

Figure.2.SEM images of Cu_2O thin films deposited at different annealing temperatures (a) as prepared,(b) 200°C and (c) 300°C

SEM images of the Cu_2O films that were electrodeposited from the solution containing at different annealing temperatures as-prepared, 200˚C, and 300˚C are shown in fig.2. Fig.2(a) show that the faceted crystalline grains on the surface of as-prepared Cu_2O films were observed as the corners of the cube (three-side-pyramids).It can be assigned to preferred crystal orientation plane at (111) and the surface of the film as no homogeneity. The average grain size of the particle is 2.98 µm. Fig.2(b) shows the Cu_2O film was annealed at 200˚C, the film appear at 4-sided pyramids with a 4 fold symmetry, the faces of which should be ascribed to preferred crystal orientation plane at (111) and the grains a relatively uniform size distribution. The average grain size of the particle is 0.65µm.It is observed from fig.2(b) and the homogeneity of the film is improved. In fig.2(c), the film was annealed at 300˚C, it is observed as the corners of the cubes, truncated cubes, and triangular prisms. The facets of truncated cubes can be assigned to (111) crystal lattice (or) high index planes and the particle size is reduced to nanoparticle range with high dense of particle is essential for the application solar cells[18]. The average grain size is 87nm at annealed temperature 300°C. It is also reveals various types of distribution of particles on the film surface depending on the annealing temperature.

C. Micro Raman analysis

MicroRaman spectra of Cu_2O films grown at different annealed temperatures on FTO glass substrates. Fig.3 shows that intense peak at 263cm^{-1} is due to second order overtone. The strongest peak 160cm^{-1} is attributed to Raman scattering from phonons of symmetry$\Gamma 15^{-1}$.The intense peak at 263cm^{-1} is second- order overtone mode $2\Gamma 15cm^{-1}$ and the Raman allowed mode of the Cu_2O films [19, 20].The weak line at 416 is assigned to four phonon mode $3\Gamma 12 + \Gamma 25^{+}$.The final intense line at 637cm^{-1} is attributed to the infrared-allowed mode.Raman results shows for surface vibrations of Cu_2O and CuO phase is formed, no other impurities like CuO andCu peaks are observed. Finally, Micro Raman spectroscopic revealed that Cu_2O thin films were more concentrated at 300°C.

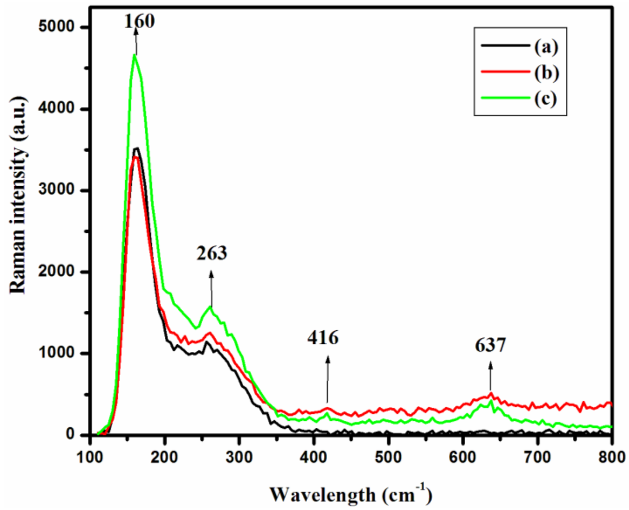

Figure 3.Micro Raman spectra of Cu_2O thin films deposited at different annealing temperatures (a) as prepared, (b) 200°C and (c) 300°C

D. Optical studies

Photoluminescence analysis

Photoluminescence (PL) spectrum is a powerful tool which gives the information about band structure and crystalline quality [21]. Fig.4 shows photoluminescence spectra of Cu_2O films grown on FTO substrates at different annealing temperatures as-prepared, 200˚C and 300˚C.It is illustrated that the emission peak around at 650 nm is attributed to near band edge emission, and the film prepared at 300˚C exhibits too higher intensity than that of all other Cu_2O films [22].It is also observed that the PL intensity is greatly improved with increase of annealing temperature and photoluminescence stability is also increased after annealing temperature 300˚C.

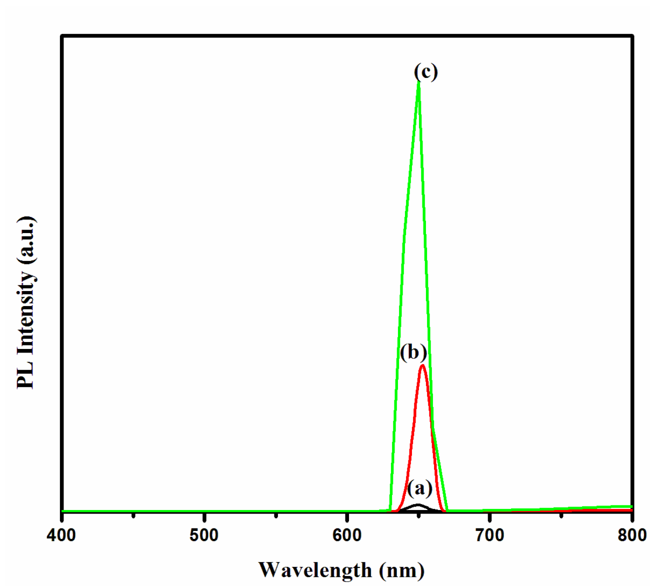

Figure 4.Photoluminescence spectra of Cu_2O thin films deposited at of various annealed temperatures (a) as-prepared, (b) 200˚C and (c) 300˚C.

UV-Visible spectra studies

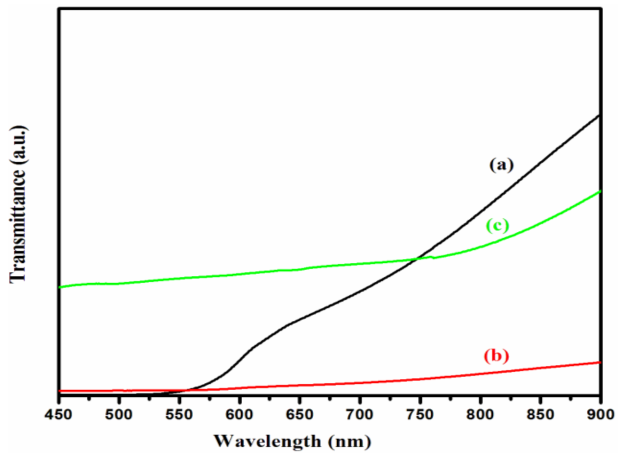

Figure 5.Transmittance spectra of Cu_2O thin films deposited at various annealed temperatures (a) as-prepared, (b) 200˚C and (c) 300˚C.

Optical transmittance spectra were recorded in order to determine the absorption coefficient and electron transition in the deposited Cu_2O semiconducting thin films and is shown in fig.5.The transmittance is decreased as the annealing temperature is increased upto 200˚C.Further increasing the annealing temperature at 300˚C, the transmittance is increased which might be peeled off Cu_2O [23]. The band gap is important parameter to determine the optical properties. The cuprous oxide is a typical direct band semiconductor. Therefore the band gap of Cu_2O thin films is calculated using Tauc's formula [24]

$$\alpha = \frac{1}{t}\ln\left(\frac{A}{T}\right) \qquad \text{— (5)}$$

Where, α is the absorption coefficient, A is the optical absorbance, T is the transmittance and t is the thickness of the thin films .The absorption coefficient satisfies the equationfor a direct band gap material [25].

$$(\alpha h\nu)^2 = A(h\nu - E_g) \qquad \text{— (6)}$$

whereα is the absorption coefficient, A is the constant, hν is the discrete photon energy. The band gap E_g is obtained by extrapolation of the plot of $(\alpha h\nu)^2$*vs.*hν.

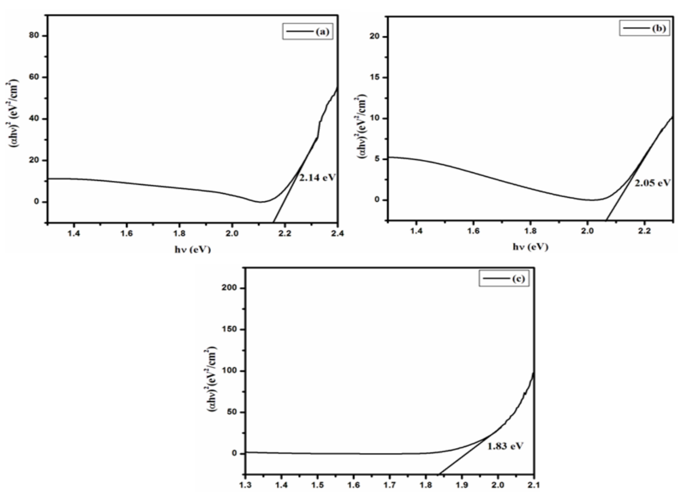

Figure 6.Tauc's plot of Cu_2O thin films deposited at various annealed temperatures (a) as-prepared, (b) 200˚C and (c) 300˚C.

The band gaps of the Cu2O films were prepared in FTO substrates at different annealed temperatures.From fig.6.,shows that the band gap of Cu_2O thin films was decreased from 2.2eV to 1.8 eV with increase of annealed temperatures, it is due to decrease of thickness from 2.72µm to 1.46 µm of the Cu_2O thin films at different annealed temperatures.

IV. CONCLUSION

Semiconducting Cu_2O thin films with three side pyramid crystal structure were deposited potentiostatically on FTO glass substrate at bath temperature 60˚C. XRD, SEM and Micro Raman confirm the crystal structure of Cu_2O thin films. XRD results revealed that the crystallinity is decreased with increasing the annealing temperature upto 200˚C, and thereafter the crystallinity of the film has improved at the annealing temperature at 300˚C.Optical band gap values of the films, measured by employing a UV-vis spectrophotometer, were 2.14eV and 2.05eV for cuprous oxide, and for cupric oxide 1.83eV. Finally, SEM micrographs revealed compact nanoparticle facets of truncated cubes which are more essential for fabricating thin film perovskite solar cells and dye sensitized solar cells.

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