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Annealing Effect on the Physical Properties of Chemically Prepared $Cu_{2-x}Se$ Films

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In the present work, copper selenide ($Cu_{2-x}Se$) thin films were prepared on amorphous glass substrate by chemical bath deposition (CBD) method at room temperature. $Cu_{2-x}Se$ thin films were further annealed at 473 K, and the effect of annealing on the physical properties of $Cu_{2-x}Se$ thin films is reported. The structural properties of as-deposited and annealed films were studied by X-ray diffraction (XRD), and XRD analysis revealed that both films are polycrystalline in nature, possessing a cubic structure with (111) preferential orientation. Also, it was observed that the crystallinity of the films increased after annealing. Scanning electron microscopy (SEM) study confirmed that annealing plays a significant role in the nature of the surface morphology of $Cu_{2-x}Se$ thin film. A surface topographic study was carried out by atomic force microscopy (AFM), which indicates that the surface becomes smoother after annealing. A study of the optical properties from the absorbance spectra revealed that the absorbance in the visible region increases after annealing, resulting in a decrease in the band gap from 2.30 to 2.25 eV. The electrical resistivity of chemically prepared $Cu_{2-x}Se$ thin films is about 19.32×10^{-4} Ω.cm, which further decreases after annealing.

Keywords: Thin films, Annealing, X-ray diffraction, Atomic force microscopy, UV absorption spectra.

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1. INTRODUCTION

In the last few decades, a lot of attention and efforts were dedicated to the potential use of copper selenide in many technological applications due to its phase/ stoichiometric dependent structural, optical and electrical properties [1]. Copper selenide has a large number of applications in various electronic and optoelectronic devices such as super-ionic conductors, optical filters, thermoelectric converters, absorber layers in solar cells, field-effect transistors, gas sensing, as anode material for lithium batteries, photocatalysis etc. [2-4]. Generally, copper selenide crystallizes in many phases and structural forms: stoichiometric CuSe, α-Cu_2Se, Cu_3Se_2, $CuSe_2$ as well as non-stoichiometric form such as $Cu_{2-x}Se$ and also in various crystallographic forms: monoclinic, cubic, tetragonal, hexagonal, orthorhombic etc. [1, 4]. Among these phases, $Cu_{2-x}Se$ is the most stable form and might be used as an absorber layer or as a window layer in thin film solar cells and photoelectrodes in PEC solar cells [5-7]. It has p-type electrical conductivity and not only a direct band gap of 2.2 eV, but also an indirect band gap of 1.4 eV [7, 8].

$Cu_{2-x}Se$ thin films are produced using various low-cost chemical techniques including solvothermal method [1], two electrode electrochemical technique [3], chemical bath deposition (CBD) [2, 4, 8], and successive ionic layer adsorption and reaction (SILAR) [9, 10], etc. But of all, CBD is widely known as a solution growth technique that offers the most attractive way to deposit thin films of metals, metal oxide superconducting compounds, metal chalcogenides, etc. [11]. CBD offers an easy way to dope films with virtually any element in any proportion by simply dipping it into a solution to be deposited. A large number of film samples can be grown in one run. By controlling the growth parameters, one can easily control the film thickness and growth rate. It is a low-temperature method, which avoids the oxidation and corrosion of substrates [12]. Hence, CBD has been found simple and economically viable as compared to other sophisticated techniques for the large area deposition. Also, it is obvious that the physical properties of $Cu_{2-x}Se$ thin films can be influenced by heat treatment conditions.

In this work, $Cu_{2-x}Se$ thin films were prepared by the CBD method, and to obtain high-quality films and improve their properties, the deposited films were annealed at 473 K. The efect of annealing on the physical properties of $Cu_{2-x}Se$ thin films was demonstrated.

2. EXPERIMENTAL DETAILS

2.1 Chemical Deposition of $Cu_{2-x}Se$ Thin Films

All chemicals used in the present investigation were AR grade, and the solutions were prepared in fresh double distilled water. Cupric chloride dehydrate ($CuCl_2.2H_2O$), freshly prepared sodium selenosulfate (Na_2SeSO_4), triethanolamine ($C_6H_{15}NO_3$), and aqueous ammonia solution (NH_3OH) were used for the chemical synthesis of $Cu_{2-x}Se$ thin films. The deposition of $Cu_{2-x}Se$ thin films on cleaned glass substrates by CBD was done using a cupric chloride-triethanolamine-ammonia-sodium selenosulfate system that consists of complexation of copper cations by triethanolamine and thereby consecutive reaction with selenium ions. More specifically, for the deposition of $Cu_{2-x}Se$ thin films we used reaction bath which contains 18 ml 0.1 M $CuCl_2.2H_2O$, 10 ml of 0.1 M $C_6H_{15}NO_3$, 10 ml of freshly prepared solution of Na_2SeSO_3 in 100 ml beaker, and to maintain the pH of the solution, aqueous ammonia solution was added proportionally in the reaction bath. Double distilled water was then added to the reaction bath to make the volume to 50 ml. By controlling

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pH ~ 10, films of $Cu_{2-x}Se$ can be obtained on glass substrates. Well-cleaned glass substrates were then immersed vertically into the deposition bath against the wall of the beaker containing the reaction mixture. The deposition was allowed to proceed at room temperature for 6 h. After deposition, glass microslides were taken out from the bath, washed with de-ionized water and dried in air. The resulting films were homogenous, adherent well to the glass substrate, and a reddish-brown thin film was formed on the substrate. The as-deposited films of $Cu_{2-x}Se$ were further annealed at 473 K and studied for various properties.

2.2 Characterization of $Cu_{2-x}Se$ Thin Films

Thin films of $Cu_{2-x}Se$ were characterized for structural, compositional, surface morphological, optical and electrical properties. Film thickness measurement of $Cu_{2-x}Se$ material was carried out by weight difference method. The film thickness was ~ 300 nm for a deposition time of 6 h. Structural analysis of the films was made on an X-ray diffractometer (Bruker AXS, D8 Advance, Germany, CuKα radiation at $\lambda = 1.5406$ Å) in the 2θ range of 20-60°. The X-ray diffractometer operated at 40 kV, 100 mA. The surface morphology and composition were studied by scanning electron microscopy (SEM) and energy dispersive analysis by X-rays (EDAX) using JEOL-JSM 6360, respectively. The films were first coated with a gold-palladium (Au-Pd) layer of a thickness of 10 nm using polaron sputter unit, E-5200 assembly before taking SEM for good ohmic contacts. An atomic force microscopy (AFM) study was done using Nanoscope IIIa provided by Vecco digital instruments. To study the optical characteristics of the film, absorbance and transmittance spectra were recorded in the range 400-800 nm by means of an UV-VIS-NIR spectrophotometer (Perkin Elmer, Lambda 25). Room temperature resistivity measurement was performed with *I-V* characteristics unit (Lab equipment unit model no. 2004) interfaced with computer.

3. RESULTS AND DISCUSSION

3.1 Structural Analysis

The XRD study was carried out on as-grown and annealed (at 473 K) $Cu_{2-x}Se$ thin films prepared by the CBD, as shown in Fig. 1. XRD analysis revealed that both films are polycrystalline in nature possessing a cubic structure (JCPDS Card No. 06-0680) for $Cu_{2-x}Se$ phase. For the as-grown film, diffraction peaks are observed at a 2θ value of ~ 26.6, 44.4 and 52.6°. The peaks were identified as originated from the (111), (220) and (311) planes, respectively. No other peaks were observed besides these, which indicates a single-phase cubic structure of the films.

Also, it can be noticed that after annealing, no shift in the peak position was observed, however, the intensity of all peaks increased. These results indicate that heat treatment increases the crystallite size of $Cu_{2-x}Se$ (sharp peaks with less FWHM) and hence reduces the number of grain boundaries in the polycrystal. This is in good agreement with the previous results [13].

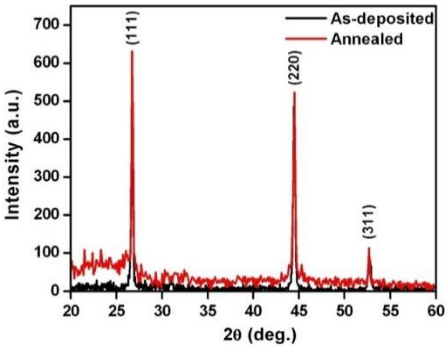

Fig. 1 – XRD pattern of the $Cu_{2-x}Se$ thin film as-grown and annealed at 473 K

3.2 Surface Morphological Analysis

SEM is an excellent tool to study the morphology of deposited films. Also, the morphology and performance of semiconductor films are closely related to the deposition conditions and post-deposition treatment. SEM images of as-grown and annealed (at 473 K) $Cu_{2-x}Se$ thin films are shown in Fig. 2. The surface of both films covers the entire glass substrate. It is observed that the morphology/structure of the grains changed from cubic ice to spherical after annealing. This spherical morphology is attractive for semiconductor electrodes used in photovoltaic device applications [14]. Also, the average grain size slightly increased from 250 to 270 nm after annealing. This result is consistent with the observations of XRD and optical absorption.

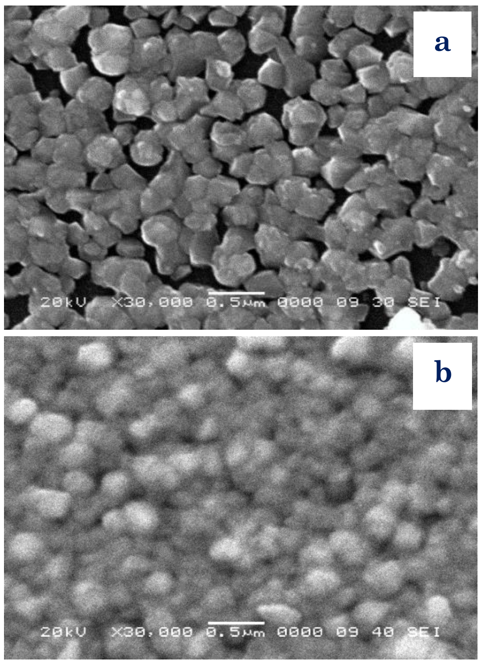

Fig. 2 – SEM images of the $Cu_{2-x}Se$ thin film before (a) and after (b) annealing (at 473 K)

Also, the surface morphology and roughness of films were assessed based on AFM measurements. Fig. 3 illustrates two-dimensional (2D) surface morphologies of as-deposited and annealed $Cu_{2-x}Se$ thin film. The deposit was found to exhibit a compact, void-free, granular morphology with a grain size of ~ 100 nm for as-grown $Cu_{2-x}Se$ thin film. While the average grain size and RMS roughness of the film calculated from the AFM image were ~ 200 nm and 10.2 nm, respectively, for annealed $Cu_{2-x}Se$ thin film suggesting that the surface becomes smoother after annealing due to a decrease in voids, grain boundaries, dislocations, stresses and inhomogeneities [15].

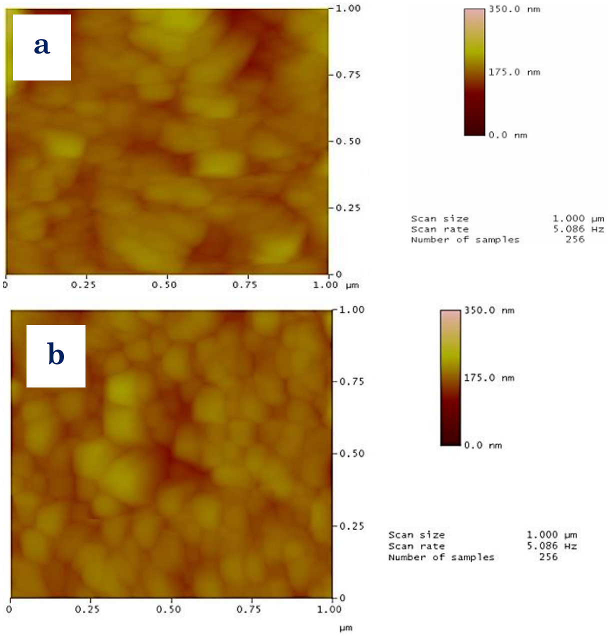

Fig. 3 – AFM images of the $Cu_{2-x}Se$ thin film before (a) and after (b) annealing (at 473 K)

3.3 Optical Studies

Optical studies were performed by measuring the absorbance of as-grown and annealed $Cu_{2-x}Se$ films on glass substrates in the wavelength range 400-800 nm. Fig. 4 shows the optical absorption for the as-grown and annealed $Cu_{2-x}Se$ films. The absorption edge of the films was observed to shift towards longer wavelengths after annealing. Optical energy gap values of the as-grown and annealed $Cu_{2-x}Se$ thin films were obtained by plotting $(\alpha h\nu)^2$ versus $h\nu$, shown in Fig. 5. The direct band gap value of the as-deposited film decreased from 2.30 to 2.25 eV after annealing at 473 K, which is in

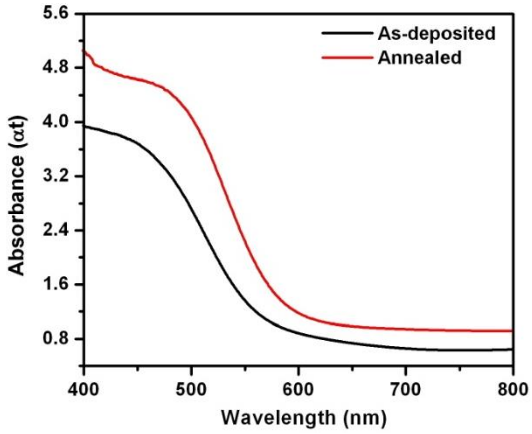

Fig. 4 – Variation of optical absorbance (αt) with wavelength (λ) for $Cu_{2-x}Se$ thin film

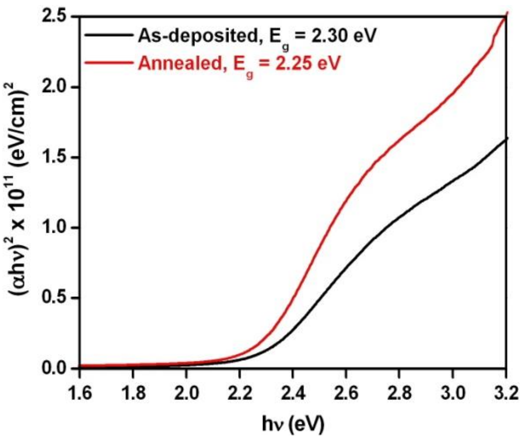

Fig. 5 – Typical plot of $(\alpha h\nu)^2$ against $h\nu$ of $Cu_{2-x}Se$ thin film before and after annealing (at 473 K)

good agreement with the results reported earlier by other authors [16]. The larger band gap values in the as-deposited samples compared with those of annealed samples are attributed to the smaller grain size in the former [17]. Improvement of the crystalline nature and decrease in the optical band gap are important physical properties that are useful for both photoelectrochemical cells and solar cell applications [18].

3.4 Electrical Studies

The dark electrical resistivity of as-deposited and annealed $Cu_{2-x}Se$ films was measured at room temperature. Fig. 6 shows the *I-V* plot for as-deposited and annealed $Cu_{2-x}Se$ thin film. It was found that the room temperature electrical resistivity of the film was 19.32×10^{-4} Ω·cm which then decreased to 13.79×10^{-4} Ω·cm after annealing at 473 K. Heat treatments reduces the number of grain boundaries (improvement in grain size) within the $Cu_{2-x}Se$ polycrystal which is responsible for decrease in electrical resistivity after annealing.

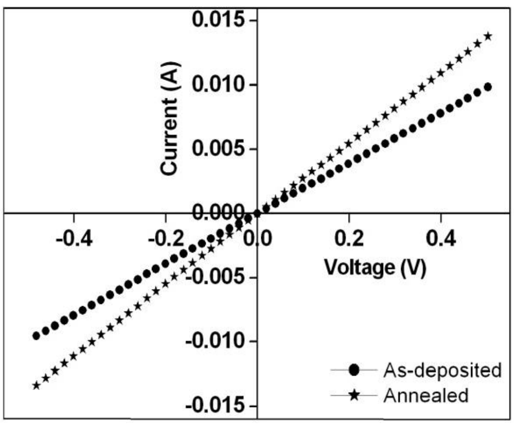

Fig. 6 – *I-V* plot for as-deposited and annealed $Cu_{2-x}Se$ thin film

4. CONCLUSIONS

In this study, the effect of annealing on the structural, morphological, optical, and electrical properties of $Cu_{2-x}Se$ films deposited by CBD method has been investigated. The structural investigation showed that as-grown and annealed $Cu_{2-x}Se$ thin films are polycrystalline in nature with a cubic structure and their crystallinity increases after annealing. SEM study showed that sample annealing improved the surface morphology. Surface analysis performed using AFM showed that much larger particles were formed in the annealed film compared to the as-grown sample. Optical study revealed that the direct band gap shifts to lower energies as a result of annealing of the films. The room temperature electrical resistivity of the films decreased from 19.32×10^{-4} to 13.79×10^{-4} Ω·cm after annealing due to the improvement of the film crystallinity.

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Вплив відпалу на фізичні властивості хімічно виготовлених плівок $Cu_{2-x}Se$

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У роботі тонкі плівки селеніду міді ($Cu_{2-x}Se$) були виготовлені на підкладці з аморфного скла методом хімічного осадження у ванні (CBD) при кімнатній температурі. Тонкі плівки $Cu_{2-x}Se$ були додатково відпалені при 473 K, і ми повідомляємо про вплив відпалу на фізичні властивості тонких плівок $Cu_{2-x}Se$. Структурні властивості осаджених і відпалених плівок досліджували за допомогою рентгенівської дифракції (XRD), і XRD-аналіз показав, що обидві плівки є полікристалічними за своєю природою, мають кубічну структуру з переважною орієнтацією (1 1 1). Крім того, було помічено, що кристалічність плівок зросла після відпалу. Дослідження скануючої електронної мікроскопії (SEM) підтвердило, що відпал відіграє значну роль у природі морфології поверхні тонкої плівки $Cu_{2-x}Se$. Топографічне дослідження поверхні було проведено за допомогою атомно-силової мікроскопії (AFM), яке вказує на те, що поверхня стає більш гладкою після відпалу. Дослідження оптичних властивостей за спектрами поглинання показало, що поглинання у видимій області збільшується після відпалу, що призводить до зменшення забороненої зони з 2,30 до 2,25 еВ. Питомий електричний опір хімічно виготовлених тонких плівок $Cu_{2-x}Se$ становить приблизно $19{,}32\times10^{-4}$ Ом·см, який ще більше зменшується після відпалу.

Ключові слова: Тонкі плівки, Відпал, Рентгенівська дифракція, Атомно-силова мікроскопія, УФ-спектри поглинання.