

# Chemical synthesis of p-type nanocrystalline copper selenide thin films for heterojunction solar cells

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## Abstract

Nanocrystalline thin films of copper selenide have been grown on glass and tin doped-indium oxide substrates using chemical method. At ambient temperature, golden films have been synthesized and annealed at 200 °C for 1 h and were examined for their structural, surface morphological and optical properties by means of X-ray diffraction (XRD), scanning electron microscopy and UV–vis spectrophotometry techniques, respectively. Cu<sub>2–x</sub>Se phase was confirmed by XRD pattern and spherical grains of 30 ± 4 – 40 ± 4 nm in size aggregated over about 130 ± 10 nm islands were seen by SEM images. Effect of annealing on crystallinity improvement, band edge shift and photoelectrochemical performance (under 80 mW/cm<sup>2</sup> light intensity and in lithium iodide electrolyte) has been studied and reported. Observed p-type electrical conductivity in copper selenide thin films make it a suitable candidate for heterojunction solar cells.

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## 1. Introduction

Deserve investigations are needed in the field heterojunction of low-cost solar energy converters. CdS and CdTe are the most interesting materials for solar cell applications, photoconductors, laser materials and optical devices. Due to presence of toxic cadmium as a major element, these materials found practical and industrial limitations that eventually open the era of other alternates including CuInS<sub>2</sub>, CuInSe<sub>2</sub> and many more copper-indium chalcogenides. Copper selenide has been studied with great interest during the past decades because of its potential application in the fabrication of photovoltaic devices. It has many phases and structural forms: stoichiometric  $\alpha$ -Cu<sub>2</sub>Se, Cu<sub>3</sub>Se<sub>2</sub>, CuSe and CuSe<sub>2</sub>, as well as non-stoichiometric, Cu<sub>2–x</sub>Se [1]. The thermal stability of these compounds varies depending on their composition.

Among various techniques for preparation of nanometer size materials, chemical methods offer better orientation, which are least expensive, non-polluting and easy to incorporate suitable doping materials for altering the film properties [2]. These processes are the low-temperature processes which enables formation of thin films onto plastic as well as glass substrates in addition to the conducting films (substrates) which can potentially lead to a new generation of photovoltaic devices that are light in weight, foldable, flexible and moldable. A number of methods have been reported [3–5] for producing copper selenide wherein the experimental conditions determine the crystallographic phase. As the monoclinic/orthorhombic form might be used as a p-type window material for solar cells and the cubic form a superionic conductor [6], a great deal of attention has been focused on its crystallographic phase transformation recently. The phase transformation of the cubic phase into the orthorhombic phase has not been achieved so far although individual crystallographic phases have been produced by either chemical deposition or from the elements by a thermal process.

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The object-well-known inorganic thin films of copper selenide is focused in this work by direct chemical deposition method and annealed at 200 °C for 1 h for crystallinity improvement. The wide range of associated structural, surface morphological, optical properties, coupled with photoelectrochemical performance, makes this film potentially attractive for application as an active cadmium free p-type material for solar cell devices.

## 2. Experimental details

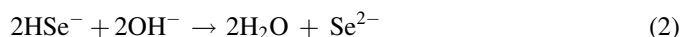
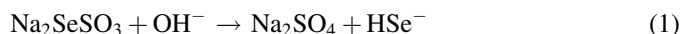
A reaction vessel containing glass and tin doped-indium oxide (ITO) substrates was used in the experiment connected to computerized auto-thermostat to maintain and control the accurate temperature of reaction solution. The reaction vessel was filled with the composition of solution: 0.1 M 50 mL  $\text{CuSO}_4$  + 1 M 1–2 mL tartaric acid and 0.1 M 6 mL  $\text{Na}_2\text{SeSO}_3$  solution. For preparing  $\text{Na}_2\text{SeSO}_3$  0.1 M stock solution, our earlier reported procedure was used [7–9]. The glass slides were cleaned with a suitable cleanser, scrubbed with soft cotton, washed thoroughly with de-ionized water followed by rinsing and drying in air. The substrates were kept in an airtight box in order to avoid contact of moisture. These glass and ITO (SAMSUNG make) substrates were used as substrates for deposition, which were carefully fixed to the circular holder; ITO side facing towards the solution and allowed to rotate with a speed of 20 rpm. The thermostat was set to a temperature of 45 °C and the reaction was carried out for 60 min with constant stirring of the solution throughout the experiment. Good golden adherent films were deposited onto both glass and ITO substrates. Intension to carry out deposition on two substrates here is to understand information about its phase and stoichiometry of copper and selenide, due to presence of other elements including indium, tin and dominant intense X-ray diffraction (XRD) peaks reveal serious limitations if only ITO substrate is used. Substrates after film formation were washed with double distilled water and allowed to dry in vacuum desiccators before characterization.

A  $354 \pm 10$  nm copper selenide film thickness was measured by the ellipsometry after standardization with silicon single crystal using 630 nm monochromatic light source. Considering above limitation, structural and phase confirmation of as-deposited and annealed copper selenide films were carried out using a XRD using  $\text{Cu K}\alpha$  radiation taken from 10° to 80°. The surface morphology and chemical composition analysis were studied using scanning electron microscopy (SEM) attached with energy dispersive analysis of X-rays (JSM 35 CF JEOL model). Optical absorbance spectra of the films were obtained using a double beam UV–vis spectrophotometer (VARIAN CARY SCAN-500). Photo-electrochemical (PEC) performance of copper selenide formed onto ITO were made using 0.5 M potassium iodide electrolyte, which is assumed to be an efficient hole scavenger. The distance between working electrode and counter electrode was fixed to 0.5 mm with plastic cello-tape spacer. Photocurrent–voltage ( $I$ – $V$ ) performances of as-deposited and annealed copper selenide photo-electrodes were measured under dark and 80  $\text{mW/cm}^2$  light illumination intensity.

## 3. Results and discussion

### 3.1. Reaction mechanism

It is well known that sodium selenosulphate hydrolyzes in alkaline medium to give  $\text{Se}^{2-}$  ions as



In presence of  $\text{Cu}^{2+}$  ions in the bath, copper selenide will be formed if the ionic product of  $\text{Cu}^{2+}$ ,  $\text{Se}^{2-}$  exceeds the solubility product of copper selenide. The formation of particular phase such as  $\text{Cu}_2\text{Se}$ ,  $\text{Cu}_2\text{Se}_3$ ,  $\text{Cu}_{2-x}\text{Se}$  will be governed by copper ion concentration, deposition bath temperature, rate of release of  $\text{Cu}^{2+}$  from the tartaric acid complex as facilitating the desired ion transport.

### 3.2. Structural characterization

Fig. 1 shows the X-ray diffraction pattern of a chemically deposited copper selenide thin film of typical thickness deposited on glass substrates at room temperature (a) and to that of annealed at 200 °C (b), respectively. The structure of the as-deposited and annealed films is of  $\text{Cu}_{2-x}\text{Se}$  kind with predominant orientation along the (2 2 2) and (0 1 2) planes. The diffractogram of the as-deposited and annealed copper selenide thin films seems to exhibit nanocrystalline and/or amorphous nature. JCPDF: 06-0680 is used for comparing the standard values with the experimental data. A narrowed peak (horizontal) width in annealed film confirms grain size growth. From the XRD profiles, the inter planar spacing,  $d_{hkl}$  is calculated using the Bragg's relation with some known parameters including  $\lambda$  as the wavelength of the X-ray used,  $n$  as the order of diffraction and  $\theta$  is the angle between the incident and the scattered X-ray. The grain size ( $D$ ) is calculated using the Scherrer's formula from the full-width at half maximum (FWHM),  $\beta$  corresponding peak of the XRD pattern. The calculated average grain size using two observed

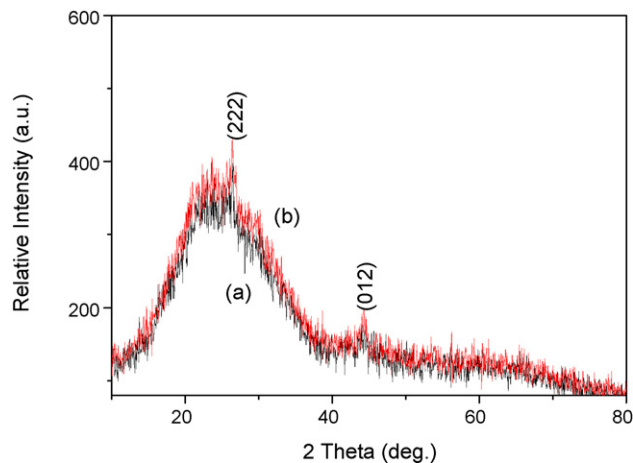


Fig. 1. XRD patterns of copper selenide thin films for as-deposited (a) and annealed (b) recorded at room temperature.

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