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# Effect of Concentration of CuSe Thin Film as Photo Anode on its Morphology and Photovoltaic Response

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**Abstract:** ***The development of thin film solar cell is an active area of research at this time. Nanocrystalline thin films of copper selenide have been grown on glass and indium tin oxide (ITO) substrates using chemical method. At different temperature, different deposition time and different concentration of solution golden films have been synthesized and annealed at 200ºC for 2H and were examined by means of X-ray diffraction (XRD) and (AFM) micrographs for their structural and morphological properties. Average spherical grains of the order of 25.49 nm for half concentration 29.3nm for normal concentration and 34.06nm for double concentration in size aggregated over about 120 ± 10 nm for normal concentration islands were seen by AFM images. Conductivity in copper selenide thin films make it a suitable candidate for solar cells. Their photoelectrochemical performance was investigated in standard two electrode configuration with redox electrolyte. The investigation may be useful in obtaining efficient, stable and low cost solar cell to compete with the existing technology.***

**Keywords:** Copper selenide thin films; Photoelectrochemical cells; XRD; Surface morphology

## 1. Introduction

Solar energy source is only long term natural source of energy. The photo electrochemical cells are considered as potential energy source for future. The photo electrochemical cell (PEC) is an attractive means of converting solar energy into electricity. It is considered a major candidate for obtaining energy from the sun, since it can convert sunlight directly into electricity. It can provide nearly permanent power and is virtually free of pollution.

Solar photovoltaic energy conversion is a one-step conversion process which generates electrical energy from light energy. The explanation relies on ideas from quantum theory. Light is made up of packets of energy, called photons, whose energy depends only upon the frequency, or colour, of the light. The energy of visible photons is suficient to excite electrons, bound into solids, up to higher energy levels where they are more free to move. An extreme example of this is the photoelectric effect, the celebrated experiment which was explained by Einstein in 1905, where blue or ultraviolet light provides enough energy for electrons to escape completely from the surface of a metal. Normally, when light is absorbed by matter, photons are given up to excite electrons to higher energy states within the material, but the excited electrons quickly relax back to their ground state.[1]

Photovoltaic effect is a process in which two dissimilar materials in close contact produce an electrical voltage when struck by light. The research work describes the photovoltaic effect and characteristics of CuSe thin film solar cells. The photo electrochemical effect is exhibited by the semiconductor (SC) and electrolytic junction in a cell consisting of photo-responsive electrode, an electrolyte and a suitable counter electrode. When SC-electrolyte junction is illuminated by the high energy photon of hv> Eg, photons are absorbed by SC electrode producing electron-hole pairs. This separation of electron hole pairs results in photo-voltage. The working of solar cell is related to photo voltaic effect. Copper selenide has many phases and structural forms: stoichiometric $Cu_2Se$, $Cu_3Se_2$, CuSe and $CuSe_2$, as well as non-stoichiometric, $Cu_{2-x}Se$.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 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. The inorganic thin films of copper selenide is focused in this work by direct chemical deposition method and annealed at 200°C for 2 h for crystallinity improvement. These nanocrystalline film are used as photo electrode in PEC cell to study photovoltaic effect. Solar cells are the type of devices which efficiently and directly converts the sunlight into electricity by the use of photovoltaic technology. These devices are specifically designed for the energy storage significantly in the situations where the source of light is not specific. Solar panels are developed in the cells that are responsible for storage and the solar power is generated by these solar panels.

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## 2. Experimental Details

In the present work nanocrystalline thin film of copper-selenide were grown on glass and indium tin oxide (ITO) substrates (were purchased from Neuchem international JBP.) using chemical method. Preparation of photo- anodes are done with different consentrations, deposition time 120min, at controled the accurate temperature $45^0$c. and golden film are synthesized. The sample of CuSe thin films were annealed at 200ºC for 2H in Oven.

### 2.1. Reaction mechanism of nanocrystalline CuSe thin film deposition:

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

$$Na_2SeSO_3 + OH^- \rightarrow Na_2SO_4 + HSe^- \quad \text{.......(1)}$$

$$2HSe^- + 2OH^- \rightarrow 2H_2O + Se^{2-} \quad \text{............. (2)}$$

In presence of $Cu^{2+}$ ions in the bath, copper selenide will be formed, if the ionic product of $Cu^{2+}$, $Se^{2-}$ exceeds the solubility product of copper selenide. The formation of particular phase such as $Cu_2Se$, $Cu_2Se_3$, $Cu_{2-x}Se$ will be governed by copper ion concentration, deposition temperature, rate of release of $Cu^{2+}$ from the tartaric acid complex as facilitating the desired ion transport.

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.

**Composition of solutions for:**

**(A) Half concentration**

The reaction vessel was filled with the composition of solution: 0.05 M (50 ml) $CuSO_4$, 0.5 M (2 ml ) tartaric acid and 0.05 M (6 ml) $Na_2SeSO_3$ solution.

**(B) Normal concentration**

The reaction vessel was filled with the composition of solution: 0.1 M (50 ml) $CuSO_4$, 1 M (2 ml) tartaric acid and 0.1M (6 ml) $Na_2SeSO_3$ solution.

**(C) Double concentration**

The reaction vessel was filled with the composition of solution: 0.2 M (50 ml) $CuSO_4$ 2M (2ml) tartaric acid and 0.2M (6 ml) $Na_2SeSO_3$ solution.

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. These glass and ITO substrates are used as substrates for deposition,

ITO side facing towards the solution and allowed to rotate with a speed of 25 rpm. The thermostat was set to a temperature of 45°C and the reaction was carried out for 1H with constant stirring of the solution throughout the experiment. Good golden adherent films were deposited onto both glass and ITO substrates.

### 2.2 Characterization of samples

The samples of CuSe thin film deposited onto glass substrates for different deposition time were examined by means of X-ray diffraction (XRD) and (AFM) micrographs for their structural and morphological properties.

### 2.3 Photoeletrochemical cell studies

The configuration of PEC cell is a single glass vessel surrounded by dark black paint, using CuSe nanocrystalline film on ITO substrate as photoanode, graphite as counter electrode and polysulphide solution as electrolyte. Photo-electrochemical (PEC) performance of copper selenide formed onto ITO was investigated. The distance between working electrode and counter electrode was fixed. Photocurrent–voltage (I–V) characteristics of copper selenide photoelectrodes were measured with change in resistance using potentiometer in circuit, with 80mW/$cm^2$ light illumination intensity.

## 3. Results and Discussion

### 3.1 Characterization of nanocrystalline CuSe thin Film-

### (a)Characterization of nanoparticles using Atomic Force Microscopy

CuSe thin film prepared for normal consentration on glass substrate are used for characterization by AFM in the dynamic mode. The goal is to determine the shape, size and size distribution of nanoparticles.

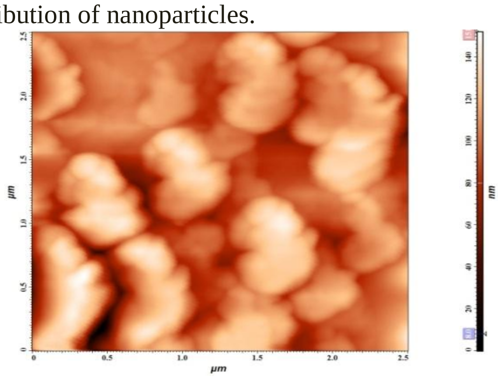

**Figure 1(a):** 2D atomic force microscopy image (2.5x2.5nm) for normal consentration.

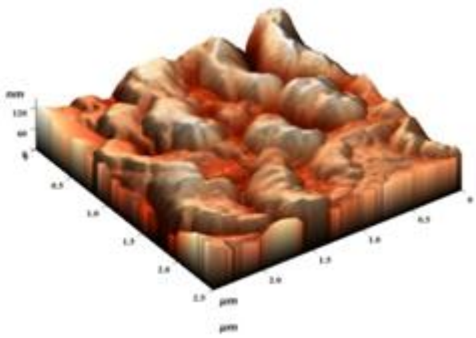

**Figure 1(b):** 3D atomic force microscopy image (2.5x2.5nm) for normal consentration

Fig.1a shows 2D atomic force microscopic image (2.5x2.5nm) of CuSe thin film for deposition time 2 hour. From the image it is clear that the film is uniform and the substrate surface is well covered by fine spherical or elliptical nature of the grains.

There was agglomeration of particles in most of the cases as evident from the 3D image (Fig.1b) The average cluster size on the surface is determined to be **120±10** nm and the surface roughness is **14.62** nm. The surface roughness of the film is unavoidable because particles are spherical in shape. This observation reveals that the films are crystalline in nature

**(b) X-ray diffraction studies (XRD)**
From the XRD profiles (fig.2) a narrowed peak (horizontal width) in CuSe thin film confirms grain size growth. The inter planar spacing for (h k l) plane is calculated using the Bragg's relation. The Bragg's angle is **θ** and the wavelength is **1.54** nm .Fig2 shows X-ray diffraction patterns of CuSe thin film deposited for half, normal and double consentration .

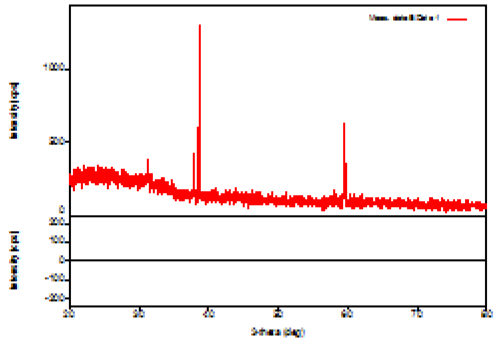

**Figure 2 (a):** X-Ray diffraction pattern deposited CuSe thin film (for half consentration)

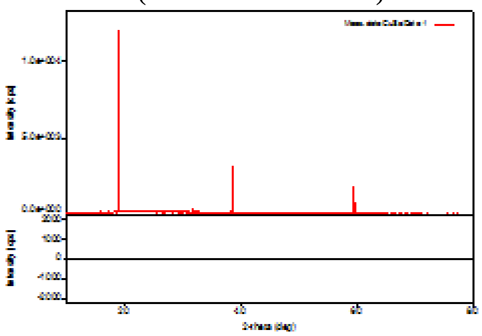

**Figure 2 (b):** X-Ray diffraction pattern deposited CuSe thin film (for normal consentration)

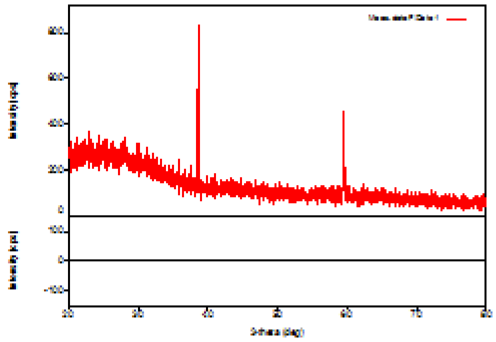

**Figure 2 (C):** X-Ray diffraction pattern deposited CuSe thin film (for double consentration)

From PDF card no. 9000063, the crystal structure is found to be **hexagonal**. The diffractogram of the copper selenide thin films seems to exhibit nanocrystalline and amorphous nature. The calculated average grain size using observed peaks of copper selenide thin film for half consentration is about **25.49** nm., for normal consentration is about **29.3** nm. and for double consentration is about **34.06** nm.

### 3.2 Photoeletrochemical cell studies

Copper selenide is studied with great interest during the past decades because of its potential application in the fabrication of photovoltaic devices. Fig. 3 shows the I–V characteristics of solar cell that uses photo anode with copper selenide deposited on it. The characteristics is ploted for three different anode. The concentration of CuSe for each anode is kept different, viz. half, normal and double consentration.

The light illumination used is 80mW/cm$^2$ intensity and polysulphide solution serves as a redox to maintain the stability of the copper selenide photoelectrodes. Observing I-V curve it can be concluded that with change in resistence, increase in current the terminal potential of solar cell decreases. The different behavior of I-V curve is obtain because the roughness of anode surfaces changes with deposition time and the smoothness of surface increase with increases in deposition time. It is observed that the solar cell is more efficient which uses anode with double concentration.

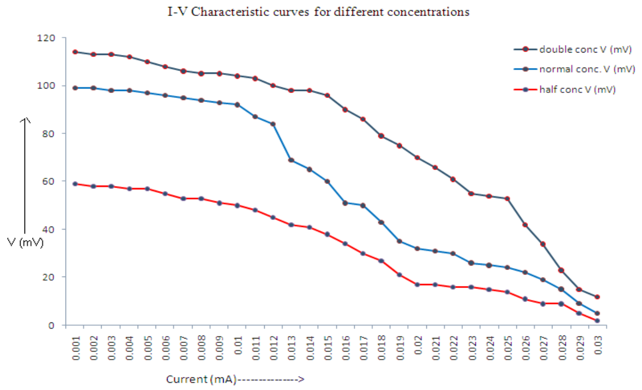


**Figure 3:** (I-V characteristics of PEC solar cells for photo electrodes prepared at different consentration)

Observation shows copper selenide electrode in solar cell is suitable P -type candidate. It was observed that the solar cell parameters short circuit current (Isc), open circuit voltage (Voc). Fill factor (FF) and efficiency (η%) are influenced by deposition time used for preparation of photo electrodes.

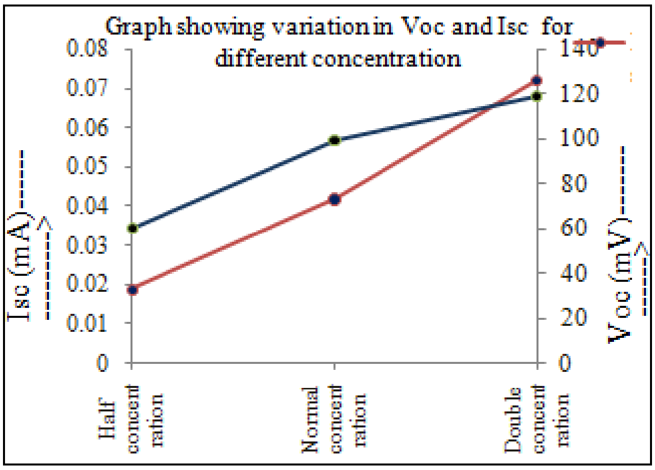


**Figure 4:** Graph showing Voc and Iso with different deposition time of photo electrodes

Fig.4 shows Variation of solar cells parameters Voc and Isc with different deposition time of photo electrodes. From the results it may be observed that performance of solar cell is best for double concentration.

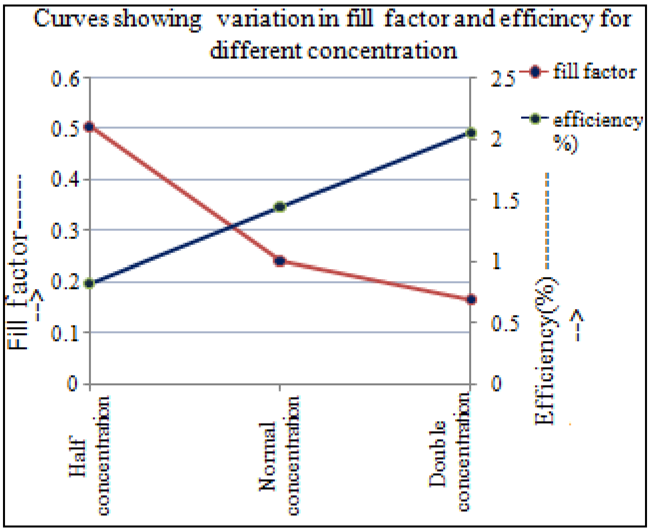


**Figure 5:** (Graph showing Fill factor and efficiency with deposition time of photo electrodes)

Fig.5 shows variation of solar cell parameters fill factor and efficiency with different deposition time of CuSe photo electrodes. The value of fill factor and efficiency increases with increases in concentration because the amount of deposited CuSe increases. We see that solar cell efficiency as well as fill factor is maximum when electrodes are prepared with double concentration.

## 4. Conclusions

The chemically synthesized copper selenide photo electrode have been introduced which exhibits p-type photoconductivity. The above experiment indicate that the best results are obtained with deposition of CuSe for 120 min at 45$^{o}$ctemperature.

XRD and AFM shows that the average spherical grains of 14.78nm in size aggregated over about120±10nm. A photoelectrochemical study confirms p-type conductivity and thus copper selenide can be considered as a potential candidate for solar cells. In preparation of photo electrodes, deposition time and temperature plays an important role. The investigation may be useful in obtaining efficient, stable and low cost solar cell to compete with the existing technology. This may help to overcome the energy crisis due to exhausting fossil fuels.

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