Journal of Advanced Chemical Engineering

Patil et al., J Adv Chem Eng 2017, 7:1
DOI: 10.4172/2090-4568.1000171

Research Article | Open Access

Room Temperature Synthesis of Nanocubic $CuInSe_2$ Thin Films

Vidya Patil S, Neha Desai D, Suvarta Kharade D, Rahul Mane M and Poatrao Bhosale N*

Materials Research Laboratory, Department of Chemistry, Shivaji University, Kolhapur, Maharashtra, India

Abstract

The arrested precipitation technique (APT) is used to deposit $CuInSe_2$ thin films. The deposition of thin films is carried out at room temperature. The optical study reveals direct allowed type of transition for $CuInSe_2$ thin films. The XRD pattern confirms mixed phase of $CuInSe_2$ thin films. The SEM image reveals nanocubic thin film formation. The EDS analysis confirms presence of copper, indium and selenium elements in the synthesized thin film. The synthesized thin films are beneficial for the solar cell applications.

Keywords: APT; CuInSe2; Thin films

Introduction

Development of new materials is the major driving force of the technological evolution. During the last two decades immense progress has been achieved in the fabrication and manipulation of nanoscale crystallites and manipulation of the nanoscale crystallites and understanding of the size and shape dependent properties of the nanomaterial's [1,2].

Taking this fact into consideration, CIS based chalcopyrite thin films have found potential interest in the field of solar energy due to its absorbing property. The $CuInSe_2$ thin films possess characteristic properties such as high absorption coefficient, tunable band gap and high stability. Among the I-III-VI ternary chalcopyrite's $CuInSe_2$ thin films have a calculated exciton Bohr radius of approximately 10.6 nm and have a lowest band gap of 1.04 eV with largest absorption coefficient. It has less toxicity than other semiconductor nanomaterial's currently being used [3-6].

The electronic structure of these materials strongly relate with the [Cu]/[In] ratios there is a great need to precisely control their size, shape, surface and composition. Nowadays, great success has been achieved in the synthesis of ternary, quaternary nanomaterials via several routes. The methods for the synthesis are solvothermal approach, hot injection method, thermal decomposition, chemical bath deposition, electrode position etc. [7-11].

Considering all these facts we are reporting here a low cost arrested precipitation technique for the deposition of $CuInSe_2$ thin films. Further the optical, structural, morphological and compositional properties of $CuInSe_2$ thin films have been investigated.

Materials and Methods

All the chemicals were analytical reagent (AR) grade and used without further purification. The list of chemicals used to deposit $CuInSe_2$ thin films is given in Table 1. Herein the depositions of $CuInSe_2$ thin films were carried out onto glass substrates as well as FTO using APT at room temperature.

Chemicals	Chemical formula	Company
Copper sulphate (99.5%)	$CuSO_4{\cdot}5H_2O$	SD-fine Chem limited
Indium sulphate (99.9%)	$In_2(SO_4)_3$	Spectrochem
Triethanolammine (99.0%)	$N(CH_2\text{-}CH_2\text{-}OH)_3$	Merck
Liquor ammonia (28-30 %)	NH_3	Thomas Baker
Selenium metal powder (99.5%)	Se	Sigma Aldrich
Sodiumsulphite anhydrous (96.0%):	Na_2SO_3	SD-fine Chem limited

Table 1: Chemicals used to deposit $CuInSe_2$ thin films.

Deposition of $CuInSe_2$ thin films

The 0.05 M Cu-TEA and 0.05 M In-TEA complexes were used as a source of Cu^{2+} and In^{3+} ions respectively. They were prepared by dissolving the $[CuSO_4.5H_2O]$ and $In_2(SO_4)_3$ salts separately with TEA complexing agent. A 0.25 M Na_2SeSO_3 solution was prepared by dissolving 99% pure selenium metal powder in saturated solution of Na_2SO_3 by refluxing the whole solution for 8 h at 60°C and used as a source of Se^{2-} ions. In order to deposit $CuInSe_2$ thin films an 8 mL of 0.05 M Cu-TEA and 2 mL of 0.05 M In-TEA complex solutions were taken in reaction bath container. The pH of the reaction mixture was adjusted to 9.5±0.5 by drop wise addition of aqueous ammonia. Then 10 mL of 0.25 M Na_2SeSO_3 solution was added to the reaction mixture with constant stirring. The total volume of reaction bath was made to 40 ml by adding double distilled water. The reaction mixture was stirred for 10 minutes on a magnetic stirrer to get homogeneous solution. The precleaned glass substrates were immersed vertically in the reaction bath and then kept at room temperature without stirring for 3 hrs. When the terminal growth is over films withdrawn from reaction bath and designated as $CuInSe_2$. In detailed optimized parameters are given in Table 2.

Characterizations of $CuInSe_2$ thin films

The synthesized thin films were characterized for their thickness, optical, structural, morphological, compositional properties. Thickness of the films was measured by using Ambios XP-1 surface profiler. The absorption spectrum was recorded in the range of 400-1100 nm by using a UV-Vis-NIR spectrophotometer (Shimadzu UV-1800). XRD patterns were obtained using X-ray diffractometer (Bruker AXS Model D8 Advance) in the 2θ range 20-80° with Cu Kα as a target.

The surface morphology of films was studied using scanning electron microscopy (SEM-S-4700, Hitachi). Chemical compositions of synthesized thin films were studied by energy dispersive X-ray spectroscopy (EDS) technique attached to SEM equipment.

***Corresponding author:** Poatrao Bhosale N, Materials Research laboratory, Department of Chemistry, Shivaji University, Kolhapur, Maharashtra, India, Tel: +919420007500; E-mail: p_n_bhosale@rediffmail.com

Received May 22, 2017; **Accepted** May 24, 2017; **Published** May 26, 2017

Citation: Vidya Patil S, Neha Desai D, Suvarta Kharade D, Rahul Mane M, Poatrao Bhosale N (2017) Room Temperature Synthesis of Nanocubic $CuInSe_2$ Thin Films. J Adv Chem Eng 7: 171. doi: 10.4172/2090-4568.1000171

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Results and Discussion

Growth and reaction mechanism of $CuInSe_2$ thin films

The controlled and slow release of ions is the main beauty of APT. Hence we have used a TEA as complexing agent. The Na_2SeSO_3 solution added to the cationic alkaline reaction mixture play dual role as a source of Se^{2-} ions as well as a reducing agent due to presence of excess Na_2SO_3. At alkaline pH, Na_2SeSO_3 hydrolyses into Na_2SO_4, follows base catalyzed reaction and release Se^{2-} ions into the solution as per the reactions (1) and (2)

$$Na_2SeSO_3+OH^- \rightarrow Na_2SO_4+HSe^- \quad (1)$$

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

The excess Na_2SO_3 oxidises into Na_2SO_4 and releases electrons concomitantly, which are responsible for the reduction of Cu^{+2} into Cu^{+1} states during the deposition of $CuInSe_2$ and according to reactions (3) and (4)

$$Na_2SO_3+2OH^- \rightarrow Na_2SO_4+H_2O+2e^- \quad (3)$$

$$Cu^{2+}+e^- \rightarrow Cu^+ \quad (4)$$

The APT is based on the principle of Ostwald ripening law. Initially, there is a formation of seed nuclei take place. These nucleation centres form a monolayer on a substrate by ion by ion condensation. The number of smaller crystallites comes together to form a larger crystallites in accordance with the Ostwald ripening law.

Following chemical reactions (5) and (6) are proposed for the formation of $CuInSe_2$ thin films in this investigation:

$$(NH_4)_5\ [Cu2N(CH_2\text{-}CH_2\text{-}O)_3]+(NH_4)_3\ [In\ 2N(CH_2\text{-}CH_2\text{-}O)_3]+2\ Na_2SeSO_3+10\ H_2O$$

(Cu-TEA Complex) (In- TEA Complex)

↓pH 9.5 R. T. (300 K)

$$\mathbf{CuInSe_2}+4\ [N(CH_2\text{-}CH_2\text{-}OH)_3]+2\ Na_2SO_4+8\ NH_4OH$$

Optical study

The absorption spectra of $CuInSe_2$ thin films are recorded in the range of 300 nm to 1100 nm on a UV-Vis spectrophotometer. The absorption spectra and band gap is shown in the Figure 1. The absorption is in the visible range of solar spectrum. The band gap of a thin film is determined by using the following equation,

$$\alpha h\nu = A(h\nu - E_g)^n \quad (7)$$

Where, 'h' is Planck's constant, 'E_g' is Band gap of the material, 'A' is Parameter depends on the transition probability, 'n' is exponent. Exponent 'n' may have values such as 1/2, 3/2, 2 and 3 depending on the nature of electronic transition responsible for the absorption of light. The value of n=1/2 for allowed and direct transition, n=3/2 for direct forbidden transition n=2 for indirect allowed transition, n=3 for indirect forbidden transition. The nature of obtained data confirms that $CuInSe_2$ thin films shows a direct allowed type of transition with a band gap 1.38 eV. Such a band gap is highly beneficial for the solar cell applications.

Structural study

XRD spectra of $CuInSe_2$ thin films show the peaks of $CuInSe_2$ with mixed phases of Cu_2Se_3 and In_2Se_3 phases. The XRD pattern of $CuInSe_2$ thin film is shown in Figure 2. The observed peaks corresponding to the (101), (111), (210), (211), (002) and (311) planes are of Cu_2Se_3 phase, whereas (101), (205), (021) planes in the XRD belong to In_2Se_3. The peak observed (112), (103), (211), (105), (220), (301), (312), (323) and (316) are corresponds to $CuInSe_2$ (JCPDS file No.81-1936). $CuInSe_2$ have tetragonal crystal structure with lattice constants a=5.781 Å and c=2.0139Å. The crystallite size of $CuInSe_2$ thin film samples calculated from well-known Scherer's formula.

From calculated values of crystallite size the dislocation density (δ) and microstrain (ε) for all the samples were determined by using equation 8 and 9 respectively.

$$\delta = \frac{1}{D^2} \quad (8)$$

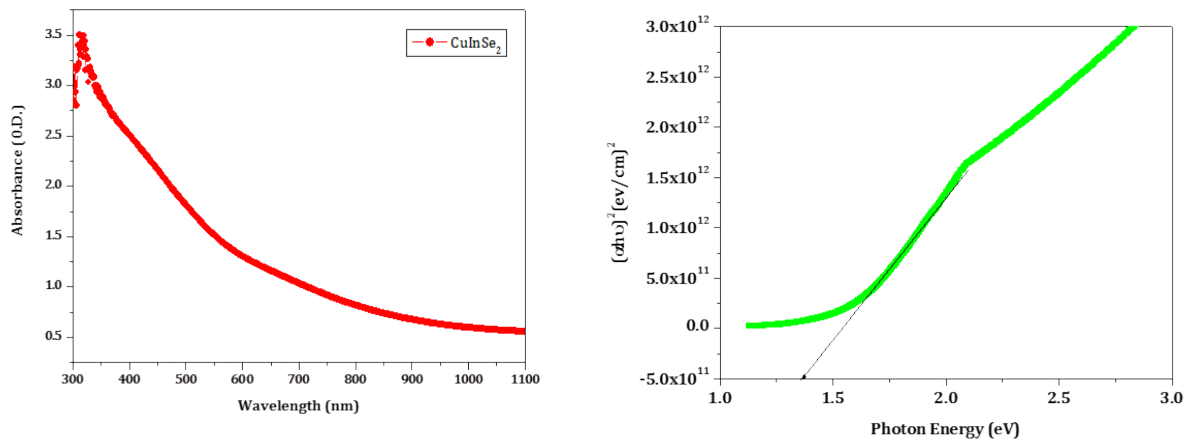

Figure 1: TEM and SAED images of Chitosan magnetite nanocomposites CMN particles.

Sample	Optimized preparative parameters			
	Bath composition	pH	Temperature (K)	Deposition time (h)
$CuInSe_2$	5.0 ml 0.05 M Cu -TEA complex solution+2ml 0.05 M In-TEA complex solution+10ml 0.25 M Na_2SeSO_3 solution, total volume made to 40 ml by adding double distilled water	9.5 ± 0.5	Room temperature (300 K)	3

Table 2: Optimized preparative parameters for the deposition of $CuInSe_2$ thin films.

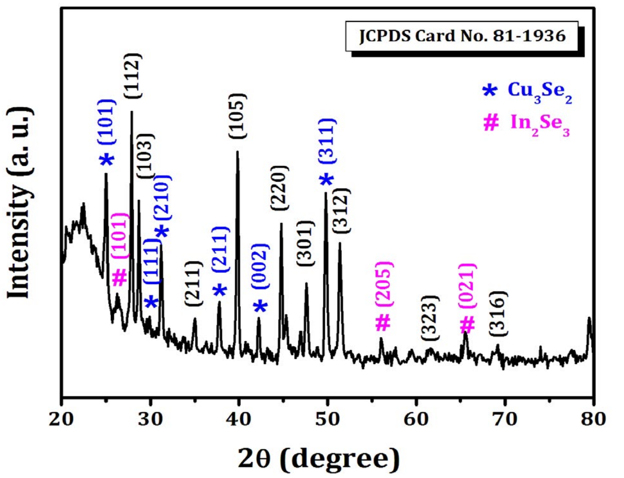

Figure 2: a) Optical Absorption spectra of $CuInSe_2$ thin film. **b)** Optical band gap from Tauos plot.

$$\varepsilon = \frac{\beta \cot \theta}{4} \quad (9)$$

Where, D is crystallite size, θ is Bragg's diffraction angle and β is full width at half maximum (FWHM). The obtained values of (δ) and () of $CuInSe_2$ thin film given in Table 3.

Morphological study

In order to study the morphological aspects of $CuInSe_2$ thin films, FESEM analysis is carried out. The low resolution and high resolution SEM images show a uniform, adherent, pin hole free thin film formation. The SEM images reveal nanocubic structure for thin films. Such a nanocubic structures are interconnected with each other. The interconnected nanocubic structure provides a better pathway for the conduction of electrons. Hence it is beneficial for the solar cell applications. The Figure 3 shows SEM images of $CuInSe_2$ thin films.

Compositional study

The quantitative analysis of $CuInSe_2$ thin films is done using EDS analysis. The EDS spectrum shows a three principle peaks for Cu, In and Se respectively. The observed atomic percentage of $CuInSe_2$ thin films is in well agreement with the expected atomic percentage. Hence the presence of Cu, In and Se in the synthesized thin film is confirmed by EDS. The EDS spectrum is shown in the Figure 4.

Conclusions

The nanostructured $CuInSe_2$ thin films are successfully synthesized by APT at room temperature. The opt structural, morphological, compositional properties of $CuInSe_2$ thin films are studied. The optical study reveals a band gap 1.38 eV. The X-ray diffraction study confirms nano crystalline nature of $CuInSe_2$ thin films. The SEM images reveal uniform nanocubic thin film formation. The presence of Cu, In and Se in the synthesized thin film is also confirmed by EDS. All these parameters reveal that $CuInSe_2$ thin films are beneficial for the solar cell applications.

Summary

Today scientists all over the world are working on the solar cell technology. The chalcopyrite and chalcogenide thin films are considered as potential candidates for the solar cell applications. The chalcopyrite thin films possess characteristic properties such as high absorption coefficient, tunable band gap, high stability etc. Considering all these facts we are interested in the synthesis of $CuInSe_2$ thin films. Here we have used a simple and low cost arrested precipitation technique for the synthesis of $CuInSe_2$ thin films. $CuInSe_2$ thin films is the most widely studied material for their optostructural and optoelectronic properties. Hence, we have done the characterization of $CuInSe_2$ thin films to know their optical, structural, morphological and compositional properties.

Sample Code	Crystallite Size (D) nm	Dislocation Density (δ) × 10^{-3} lines/nm^2	Microstrain (ε) × 10^{-3}
$CuInSe_2$	60.6	2.7149	0.1405

Table 3: Variation of crystallite size (D), dislocation density (δ) and microstrain (ε) $CuInSe_2$ thin film.

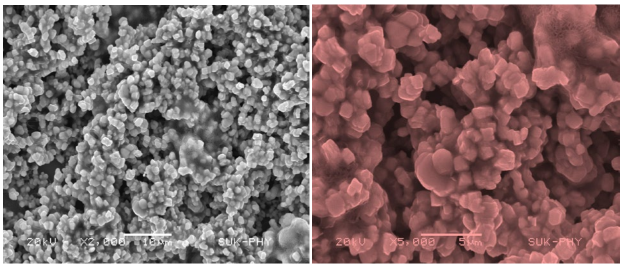

Figure 3: SEM images of $CuInSe_2$ thin films.

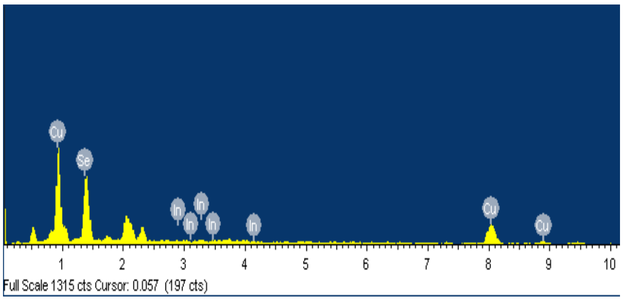

Figure 4: EDS spectrum of $CuInSe_2$ thin films.

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