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Archives of Physics Research, 2011, 2 (3):29-33
(http://scholarsresearchlibrary.com/archive.html)

ISSN : 0976-0970
CODEN (USA): APRRC7

Wide band gap nanocrystalline CuSCN thin films deposited by modified chemical method

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ABSTRACT

Nanomaterials have immerged as an area of interest motivated by potential applications of these materials in light emitting diodes, solar cells, polarizers, optical sensors, optical data communication, optical data storage etc. We have prepared copper thiocyanate (CuSCN) thin films using modified chemical bath deposition (M-CBD) method which is a modified version of chemical bath deposition (CBD) method, at room temperature in aqueous medium. In this method the glass substrate is immersed in cationic and anionic precursors, alternatively and film growth takes place on the substrate surface. Growth of CuSCN thin films requires the Cu (I) cations as a copper ions source. This is achieved by complexing Cu (II) ions using $Na_2S_2O_3$*. The anion source KSCN as thiocyanate ions. The deposited films were characterized by different characterization techniques to study structural, surface morphological and optical properties. Obtained CuSCN thin films exhibits good crystallinity, high purity, dense and uniform morphology with an average crystallite size 23 nm showing rhombohedral structure with direct band gap 3.9 eV.*

Keywords: Chemical methods; Thin films; Wide band gap; XRD; SEM; Optical properties.

INTRODUCTION

Wide band gap semiconducting thin films attract strong interest due to their capability for applications in electronic devices such as photovoltaic devices, liquid crystal displays or photo-thermal collectors. Further, numerous reports are available for n-type buffer materials for solar cells as CdS, ZnS, ZnSe and In_2S_3 [1–5]. $CuAlO_2$, CuI and CuSCN are wide band gap p-type materials [6–8].

It is well known that CuSCN is a wide-band gap, p-type semiconductor [9, 10]. The CuSCN is a candidate material for realization of dye-sensitized solid-state photovoltaic cells [11–13]. CuSCN was used as window for solar cells and was reported to act as a catalyst for the synthesis

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of organic compounds [14]. O'Regan carried out electrodeposition of CuSCN on SnO_2 and studied photocurrent action spectra as well as current–voltage characteristics [15]. Copper plates were immersed in solution containing KSCN, $Na_2S_2O_3$ and acetic acid to form the CuSCN coating to study the surface states on CuSCN [16]. CuSCN thin films have been prepared by several different methods, such as electrodeposition [17, 18], microcrystal growth [19], alumina template process [20], and chemical deposition methods [21]. The physical properties of CuSCN thin films depend on the deposition conditions and techniques.

In this paper, wide band gap nanocrystalline CuSCN thin films are prepared at room temperature on glass substrate using M-CBD method. The parameters are optimized with final objectives to use this material as window layer for solar cells

MATERIALS AND METHODS

Experimental details:

To deposit CuSCN thin films onto glass substrates, a modified chemical bath deposition (M-CBD) method was used. The glass substrates were washed with detergent (soap solution), rinsed in acetone and finally ultrasonically cleaned with double distilled water before deposition of thin film. All the reagents used for the preparation of CuSCN thin film are of analytical grade (Merk chemicals) and used as it is without further purification. Copper sulphate pentahydrate ($CuSO_4.$ $5H_2O$), Sodium thiosulphate ($Na_2S_2O_3.$ $5H_2O$), and Potassium thiocyanate (KSCN) were used for the preparation of CuSCN thin films. Double distilled water was used throughout the experiment.

We used an aqueous solution bath consisting of 0.1M $CuSO_4$ and 0.1M $Na_2S_2O_3$, which forms thiosulphatocuprate (I) complex. The release of Cu (I) ions is possible via the following reactions $[Cu\ (S_2O_3)]^- \leftrightarrow Cu^+ + S_2O_3^{2-}$, which acts as a source of cations. For this sodium thiosulphate was added to copper sulphate by drop wise in the volumetric ratio (1:4) with constant stirring for 10 min., 0.007 M potassium thiocyanate was used as source of anions. For the deposition of CuSCN film, initially the substrate was immersed in cationic precursor for 20 sec. where adsorption of Cu^+ ions takes place on the surface of substrate then the substrate was manually transferred to the beaker containing double distilled water for 5 sec. to rinse it, so that unabsorbed ions were removed. Next step, the substrate was manually immersed in an anionic precursor for 20 sec. so the SCN^- ions were reacted with the $Cu^{+\ ions}$. Again the loosely bounded ions were removed by rinsing the substrate in double distilled water for 5 sec. This completes one M-CBD cycle. Thus mono layer of CuSCN was formed. Increasing the number of immersion cycles the thickness of the film increases.

RESULTS AND DISCUSSION

X-Ray diffraction (XRD):-

X-ray diffraction patterns of the films were recorded on Bruker D8 advance X-ray diffractometer with scanning angles in the range 10 to 80 degree using CuKα radiation (λ = 1.5406 Å). Fig.1 Shows X-ray diffraction pattern of as deposited CuSCN thin films on glass substrate. Diffraction pattern on glass substrate shows two major peaks (003) and (101). A strong orientation was observed along (003) direction for CuSCN on glass substrate. We observed the crystal structure of CuSCN corresponds to rhombohedral structure with β-phase (JCPDS No.29-0581).

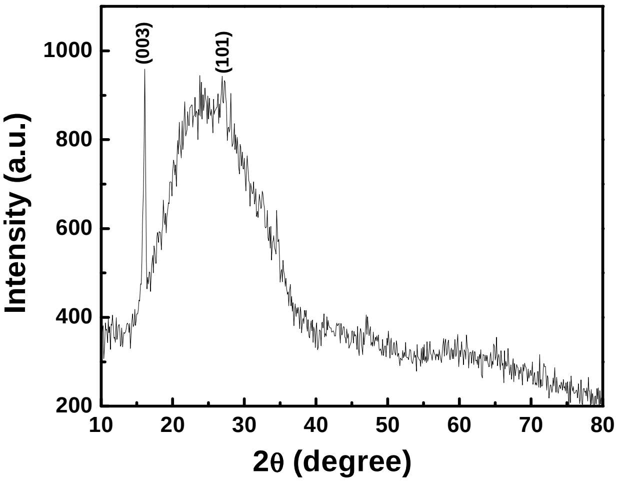

Fig. 1: The X-ray diffraction pattern of as-deposited CuSCN.

An average value of the crystallite size at the (003) plane can be obtained by applying the Debye-Scherrer's formula, neglecting peak broadening due to residual stresses in the films, D = 0.9λ/βcosθ where, λ=1.5406 Å for CuKα, β is the full width at half maximum (FWHM) of the peak corrected for the instrumental broadening in radians and θ is the diffraction/Bragg's angle). The sample CuSCN thin film as deposited resulted in an average crystallite size of approximately 23 nm.

Scanning Electron Microscopy (SEM)

The surface morphology revealed by Scanning electron microscope (SEM), (JEOL-JSM-6360A). Scanning electron microscopy is a convenient method for studying the surface morphology and microstructure of thin films. The scanning electron micrograph of as deposited CuSCN thin films on glass substrate were taken for M-CBD is shown in Fig. 2. The as deposited film of CuSCN shows the dense and uniform structure with agglomeration of tiny particles with average grain size, ranges from 150 to 350 nm.

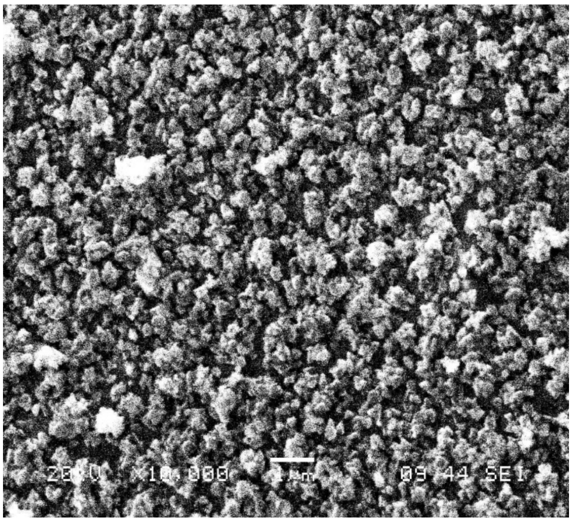

Fig 2: The surface morphology of as-deposited CuSCN on glass substrate

Optical absorption studies: -

The optical absorption spectrum of the film was recorded using an UV-Shimadzu scanning spectrophotometer (UV-1601). The optical absorption of as-deposited CuSCN thin film on glass substrate was studied in the wavelength range 300-800 nm. Fig.3 shows the optical absorption spectrum of as deposited CuSCN thin film.

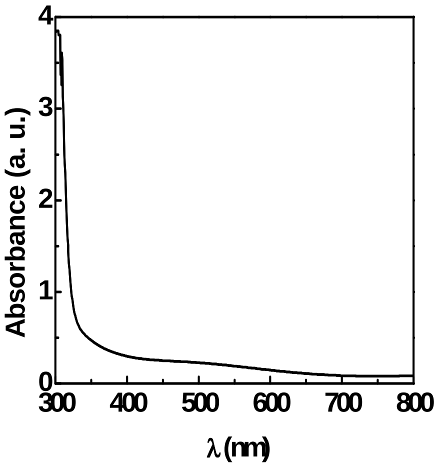

Fig.3 Optical absorption spectrum of as-deposited CuSCN thin film

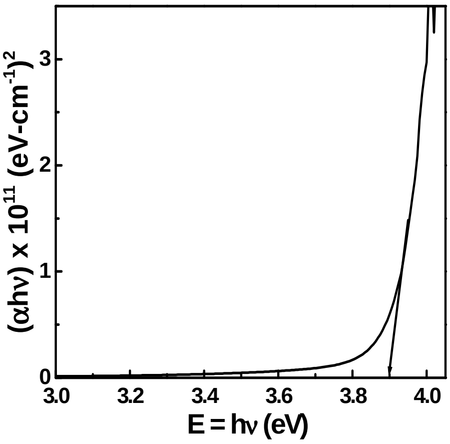

Fig.4 The plot of $(\alpha h\nu)^2$ vs. hν of as deposited CuSCN thin film

The theory of optical absorption gives the relation between the absorption coefficient and the photon energy, for direct allowed transition as:

$$\alpha h\nu = A(h\nu - Eg)^{1/2}$$

where A is the constant, Eg is the band gap, $h\nu$ is the photon energy.

Fig.4. shows the plot of $(\alpha h\nu)^2$ vs. hν for as-deposited CuSCN thin film. The best linear relationship was obtained, indicating that the optical band gap in these films is due to a direct allowed transition. The optical band gap has been determined from the value of the intercept of the straight line at a $(\alpha h\nu)^2 = 0$. The as-deposited CuSCN thin film shows the direct band gap 3.9 eV. From literature survey, the band gap values for CuSCN are 3.6 eV [22], 3.7 eV [23] and 3.8 eV [24] for thin film. The band gap of as-deposited CuSCN nanostructure is estimated to be 3.9 eV which is larger than the direct band gap of listed above. The higher band gap can be attributed to size effect of the present nanostructure. Thus the increase of band gap as compared to above can be understood on the basis of quantum size effect which arises due to very small size of nanostructure.

CONCLUSION

CuSCN thin films was prepared by a simple method namely, modified chemical bath deposition (M-CBD), onto glass substrates. Film quality depends upon the preparative parameters. The structural studies reveal that the CuSCN films have a rhombohedral crystal structure with β-phase. Optical band gap energy of as-deposited CuSCN thin film are found to be 3.9 eV. From the above outcome, our aim is to use wide band gap nanocrystalline CuSCN thin film as window materials for the solar cell.

Acknowledgements

The authors wish to thank Principal, P. S. G. V. P. Mandal's Arts, Commerce and Science College Shahada for his constant support to carry out this research work and also to the Principal, Dr N.O. Girase, S.V.S's Arts and Science College Dondaicha for his encouragement to carry out this research work. One of the authors (PBA) is thankful to the university grants commission, New Delhi for minor research project F. No. 47-1342/10(WRO).

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