

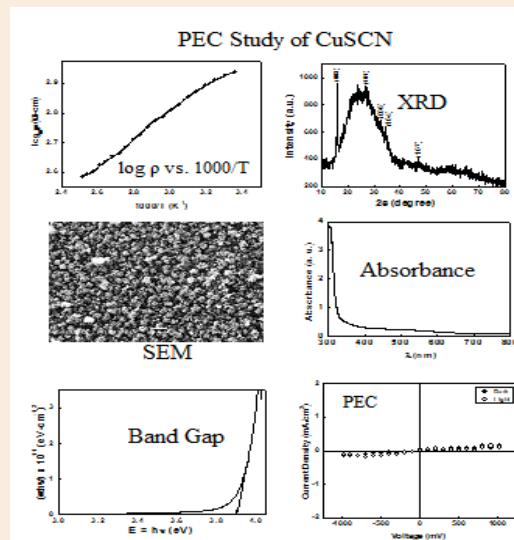
Research Article

Photoelectrochemical (PEC) Studies on Chemically Deposited CuSCN Thin Film by Simple Chemical Route

P B Ahirrao¹, M S Shinde^{2,*}, I. J. Patil³ and R S Patil³¹S.V.S's Dadasaheb Rawal College, Dondaicha, 425408, (M. S.) India²Dept. of Physics, M.J.M. Arts, Commerce & Science College Karanjali (Peth), Dist-Nashik - 422 208 (M. S.) India³P.S.G.V.P. Mandal's Arts, Commerce and Science College, Shahada, 425409, (M. S.) India**Abstract**

Chemical deposition method, namely, modified chemical bath deposition (M-CBD) has been used to deposit copper thiocyanate (CuSCN) thin films. The CuSCN thin films were deposited onto glass and FTO coated glass substrates from an aqueous medium at room temperature. To obtain good quality of thin films, preparative conditions such as concentration, pH of precursor solution and adsorption, reaction and rinsing time durations were optimized at room temperature. The structural, morphological, optical, electrical and photoelectronchemical (PEC) properties of the films were investigated. X-ray diffraction (XRD) patterns of CuSCN thin films reveals that the films have a rhombohedral structure. The band gap was found to be 3.9 eV. The PEC studies showed that the material is a wide band gap. **PACS:** 81.15.-z; 68.55.-a; 78.20

Keywords: Thin films; Chemical synthesis; Optical properties; X-ray diffraction (XRD); and PEC properties

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Introduction

The research on photoelectrochemical cell has been very active, as it offers a novel way of photovoltaic energy conversion because of low cost and with high flexibility in design and color. 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. The electronic properties of semiconducting films are usually related to their crystalline structure and surface morphology [1, 2]. Wide band gap semiconductors are electronic materials in which the energy of the band-to-band electronic transitions exceeds approximately 2 eV [3]. Wide band gap materials are often utilized in applications in which high temperature operation is important. Various reports are available for n-type buffer materials for solar cells as CdS, ZnS, ZnSe, ZnO, In₂Se₃ and CuInS₂ [4-10]. But very few p-type wide band gap materials CuI, CuSCN, CuAlO₂ and Cu₂O were identified in the preparation of semiconducting thin films [11-15]. Thin film solar cells based on wide band gap semiconductors are promising for the next generation of photovoltaic modules [16]. A wide band gap CuSCN is a promising hole-transporting material due to its transparency in the visible light spectrum range, reasonable hole conductivity ($\geq 5 \times 10^{-4}$ mho cm⁻¹) [17] and chemical stability [18]. A p-CuSCN is a good hole-transporting material for realization of dye-sensitized solid-state photovoltaic cells [19, 20] and employed to fabricate the ZnO nanorods-based p-n heterojunctions [21, 22]. CuSCN thin films have been prepared by several different methods, such as electrodeposition [23, 24], microcrystal growth [25], alumina

template process [26] and Chemical deposition methods [27]. The physical properties of CuSCN thin films depend on the deposition conditions and techniques. Recently, much attention has been focused to study properties of CuSCN.

In this paper, we mainly focus onto the study of structural, optical, electrical and photoelectrochemical (PEC) properties of CuSCN thin films deposited at room temperature on glass and FTO coated glass substrate using modified chemical bath deposition [M-CBD] method. Our aim was to achieve CuSCN thin films having a wide band gap, by low cost chemical route to use these materials as window/buffer layer for solar cells.

Experimental

All materials used in this work were of Merck-analytical reagent grade. The materials copper sulfate (CuSO_4), sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) and potassium thiocyanate (KSCN) were used.

To deposit the CuSCN thin film we used an aqueous medium. The double distilled water is used for the preparation of the solution. For the optimization of concentration of copper ions, the Cu in CuSO_4 is in oxidation state 2+ while for deposition of the CuSCN thin film, the Cu should be in oxidation state 1+. $\text{Na}_2\text{S}_2\text{O}_3$ acts as a reducing as well as complexing agent as it contains the thiosulphato ligands (S_2O_3)²⁻. The reduction reaction (Cu^{2+} to Cu^+) and complex formation reaction in the equimolar solution of the CuSO_4 and $\text{Na}_2\text{S}_2\text{O}_3$ produced the thiosulphatocuprate complex $[\text{Cu}(\text{S}_2\text{O}_3)]^-$ which releases Cu^+ ions by the dissociation equilibrium $[\text{Cu}(\text{S}_2\text{O}_3)]^- \leftrightarrow \text{Cu}^+ + \text{S}_2\text{O}_3^{2-}$ [28]. For the 4:1 volumetric ratio of the CuSO_4 : $\text{Na}_2\text{S}_2\text{O}_3$, a uniform and good quality films are obtained. For the deposition of CuSCN thin films, a cationic precursor solution consists of a mixture solution of 0.1 ML^{-1} copper sulfate and 0.1 ML^{-1} sodium thiosulfate in a volumetric ratio 4:1 in a first beaker and a potassium thiocyanate 0.007 ML^{-1} in a second beaker as an anionic precursor.

Initially the substrate was immersed in cationic precursor for 20 sec, where adsorption of Cu^+ ions takes place on the surface of substrate and the unadsorbed ions were removed by rinsing the substrate in double distilled water for 5 sec. For the reaction with SCN^- ions this substrate was immersed in an anionic precursor for 20 sec. Again the substrate was rinsed in double distilled water for 5 sec; the loosely bounded ions of CuSCN were removed. Thus one layer of CuSCN is formed. This completes one M-CBD cycle. Such cycles were repeated until the desired film thickness was reached. Thickness of films was found to be 230 nm; for the deposition of 20 cycles, this was determined by using gravimetric weight difference method. The complete deposition was carried out at room temperature (300 K).

Characterizations

The CuSCN films were characterized by means of X-ray diffraction (XRD), SEM, Optical absorption, Electrical resistivity measurement technique and the PEC properties.

The phase purity of the samples was characterized by x-ray diffraction (XRD) using an x-ray diffractometer with $\text{CuK}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$). The surface morphology revealed by scanning electron microscope (JEOL-JSM-6360A). The optical absorption spectrum of the film was recorded using an UV Shimadzu scanning spectrophotometer. The electrical resistivity measurement was carried out using a DC two-point probe method. The PEC properties was carried out by using Electrochemical Workstation (Super-1000S, supplied from SAP Instrument, India) with exposed area of 0.5 cm^2 under dark and illumination at 35 mW/cm^2 light intensity.

Results and Discussion

The crystallinity and phase purity of the products were examined by X-ray diffraction (XRD) as shown in **Figure 1**. The five diffraction patterns (16.10, 26.90, 32.60, 34.5 and 47.20), corresponding to the (003), (101), (006), (104) and

(107) planes respectively are observed. The peak at 16.10 indicates that the films are highly oriented along (003) direction.

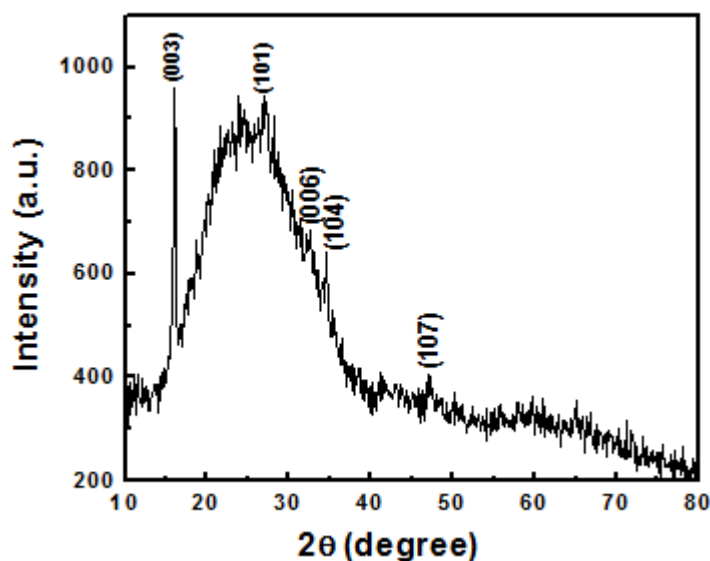


Figure 1 XRD pattern of as-deposited CuSCN thin films

By comparison of observed interplaner distance 'd' and standard, 'd' values, it is concluded that the formed compound is CuSCN with the rhombohedral crystal structure of β -phase, which is in good agreement with the JCPDS data card [29]. An average value of the crystallite size (D) was calculated at (003) plane by applying the Debye-Scherrer's relation [30].

$$D = \lambda / \beta \cos \theta$$

where, λ is the wavelength of X-ray, β is the angular line width at half maximum intensity in radians and θ is the Bragg's angle. The as-deposited CuSCN thin film is resulted in an average crystallite size of approximately 23 nm indicates the film is nanocrystalline.

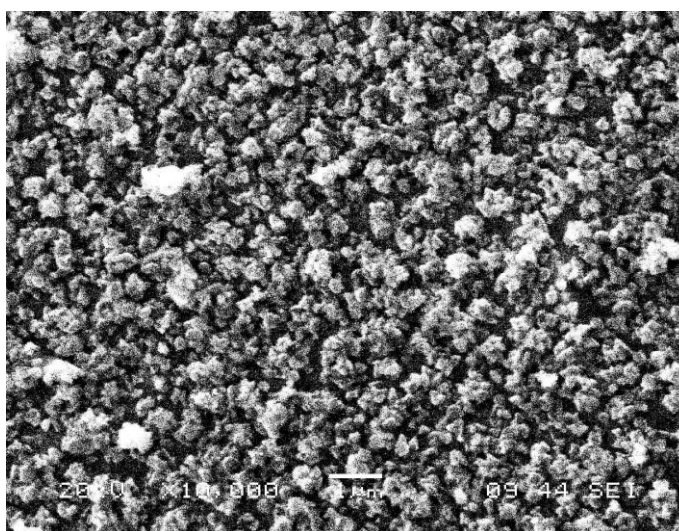


Figure 2 SEM of as-deposited CuSCN thin films

Scanning electron microscopy is a convenient method for studying the surface morphology and microstructure of thin films. The morphology of the material depends on the substrate, deposition method, temperature, and way of substrate cleaning. In the M-CBD method, the film growth takes place by ion-by-ion adsorption and reaction. The CuSCN thin film deposited onto amorphous glass substrate with 230 nm thickness by M-CBD method was used to study the surface morphology using scanning electron microscope (SEM). **Figure 2** shows a Scanning electron micrograph of CuSCN thin film as deposited onto amorphous glass substrate at 10,000 X magnification. The scale bar length is 1 μm .

It is observed that the as deposited thin film of CuSCN shows the dense and well covered uniform structure with agglomeration of small size nanoparticles gathers to form a bigger size grains. The average particle size, ranges from 150 to 350 nm.

The optical absorption of as-deposited CuSCN thin film on glass substrate was studied in the wavelength range 300-800 nm as shown in **Figure 3**.

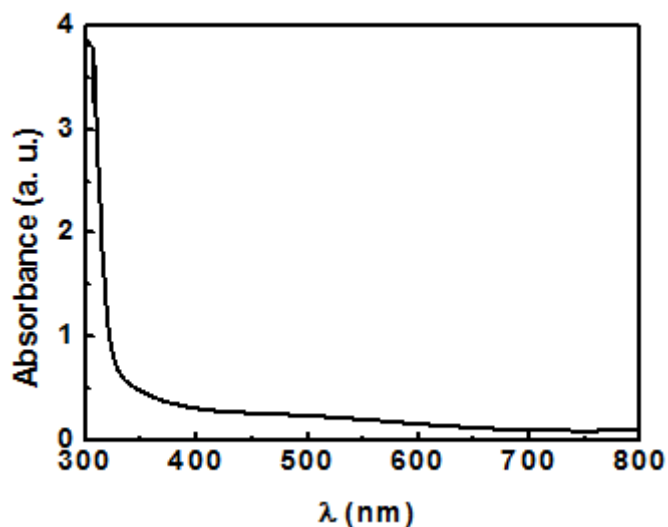


Figure 3 Plot of Absorption vs. Wavelength of as-deposited CuSCN thin films

The figure shows that absorbance decays exponentially with an increase in wavelength. The absorbance is large in the UV regions but decays very sharply within the UV-Vis boundary extending into the Vis region. The decay becomes relatively slower in the VIS and NIR regions.

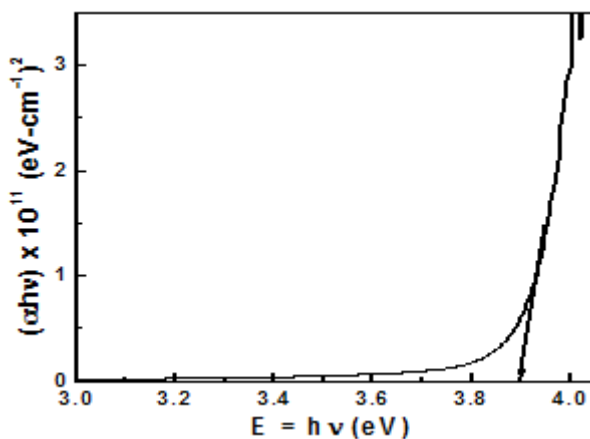


Figure 4 Variations of $(\alpha h\nu)^2$ vs. energy $(h\nu)$ for CuSCN thin film

To obtain the optical band gap of as-deposited CuSCN thin film, a variation of $(\alpha h\nu)^2$ vs. $h\nu$ is shown in **Fig. 4**. The best linear relationship was obtained, indicating that the optical band gap in the film 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 thin films are, 3.6 eV [31], 3.7 eV [32], 3.8 eV [33] and 3.88 eV [34]. The band gap of as-deposited CuSCN nanostructure is estimated to be 3.9 eV from the UV-visible absorption spectrum, 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.

The dark electrical resistivity of the thin film was measured using a DC two-probe method for the temperature range 300–400 K in air atmosphere. The electrical resistivity of as-deposited CuSCN film on glass substrate was found to be 872 Ω -cm, which matches with the reported value [33]. These films with low resistivity values are required for photo-electrochemical solar cell applications.

A plot of inverse absolute temperature verses \log (resistivity) for a cooling cycle is shown in **Figure 5**. The dependence is almost linear indicating the presence of only one type of conduction mechanism in the film. Since, the experimental data fit into the relation,

$$\rho = \rho_0 \exp(-E_a/kT)$$

In this case, activation energy was calculated from linear portion of the graph and was found to be 0.089 eV.

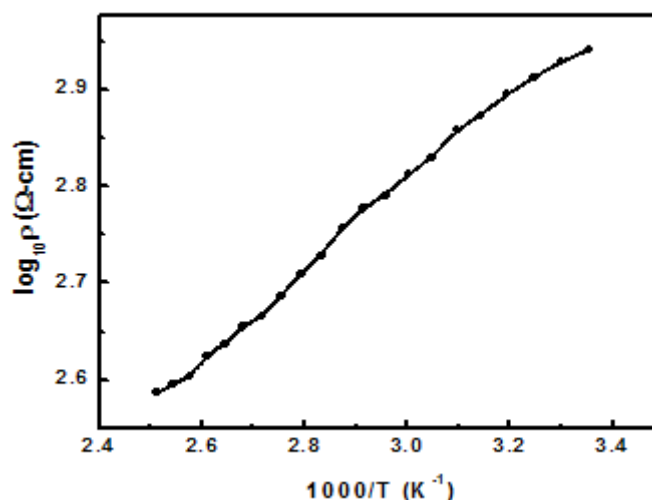


Figure 5 Plot of $\log \rho$ vs. $1000/T$ for CuSCN thin films

The activation energy of as-deposited CuSCN is much less than the reported value [35]. The conductivities in these materials are extrinsic showing p-type conductivity. The decrease in resistivity with increase in temperature confirms the semiconducting behavior of the CuSCN thin film.

The CuSCN thin films were deposited onto FTO coated glass substrate using optimized conditions given in section 2, by M-CBD method. The basic requirements of a good thin film electrode for PEC cells are low resistivity. The low resistivity photoelectrode is required to minimize the series resistance of the PEC cell. The as-deposited CuSCN thin films were used in the PEC cells as a photoelectrode and their performance was tested. An electrolyte solution composed of a mixture of 10^{-2} ML⁻¹ potassium iodide (KI) and 10^{-4} ML⁻¹ iodine (I₂) dissolved in double distilled water at room temperature (300 K) [36]. The colour of final solution was light brown.

By using CuSCN thin films grown onto FTO coated glass substrate as photoelectrode (anode), the KI/I₂ as an electrolyte and Platinum (Pt.) as a counter electrode (cathode). The photoelectrode and platinized FTO counter electrodes were sandwiched together with 3 μ m thick Tixo Tape over thin film as spacers. The liquid electrolyte was introduced between the photoelectrode and counter electrode by capillary action. A black-painted mask was used to create an exposed area of 0.5 cm² for thin films.

The PEC properties of CuSCN thin films were carried out by using Electrochemical Workstation (Super-1000 S, supplied from SAP Instrument, India) with exposed area of 0.5 cm² under dark and illumination at 35 mW/cm² light intensity.

Figure 6 represents typical current density versus applied voltage (I-V) characteristics measured in the voltage range from -1000 mV to +1000 mV under dark (closed circles) and light illumination (open circles) using standard AM 1.5 condition with 100 mW/cm² for structure FTO/ CuSCN /Electrolyte/Platinum.

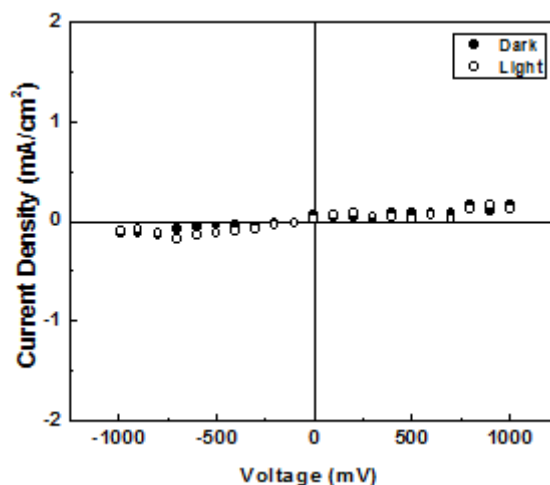


Figure 6 PEC characteristics of CuSCN thin film in dark and under light

From figure it is observed that, the I-V curve, for dark as well as for illuminated are overlap with each other, i.e. there is no shifting of curve. This implies that there is no generation of electron-hole pairs. Hence the obtained efficiency is ideally zero. Suggest that the material is a wide band gap material. Also from optical absorption studies the calculated value of band gap for CuSCN thin film was 3.9 eV which is too high to absorb the visible part of solar spectrum, so that there was no absorption of light in visible region of solar spectrum.

Thus, from above results, we conclude that all the visible light falls on material (CuSCN) is directly transmitted through it. Therefore, the as-deposited CuSCN thin film grown using modified chemical bath deposition (M-CBD) method can be used as buffer layer for solar cells below 3.9 eV.

Conclusion

A simple method namely, modified chemical bath deposition (M-CBD), was employed to deposit CuSCN thin films onto glass and FTO coated glass substrates. Film quality depends upon the preparative parameters. An XRD study reveals that the films have a rhombohedral structure. The band gap was found to be 3.9 eV. and activation energy 0.089 eV for the thickness 230 nm. Also from I-V characteristics studies, it is seen that the CuSCN deposited by M-CBD method gives zero efficiency, which means, all the visible light falls on materials (CuSCN) are directly transfer through it and there are no electron-hole pair generations. The results suggest that the material is wide band gap. Thus we conclude that the as-deposited material CuSCN can be used as a prominent candidate in solar cells application as a window/ buffer layer.

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