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Fabrication, Structural, Optical, Electrical Properties and Influence of Complexing Agents on Ternary $CuZnS_2$ Thin Film

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In the present work, copper zinc sulphide ($CuZnS_2$) thin films with and without complexing agents using glass plate as substrate were prepared. Chemical bath deposition method was employed to deposit the thin films. Powder X-ray diffraction (PXRD) patterns of the prepared films indicate the crystalline nature of $CuZnS_2$ with cubic phases. The SEM and AFM images illustrate that the deposited films were highly influenced on the polyhedral morphology by the complexing agents. The influence of complexing agents on absorbance and band gap of the $CuZnS_2$ thin films were characterized using UV-Vis absorption studies. Hall effect measurements indicate the $CuZnS_2$ thin film without surfactant belongs to p-type semiconductor and become n-type after adding the complexing agents EDTA and Leishman stain. From the I-V curve, all the samples having slow conducting nature was found for changing the voltage with the current from -32 nA to +30 nA using solar stimulator.

Keywords: Copper zinc sulphide, Thin film, Leishman stain, EDTA, Absorbance studies.

INTRODUCTION

The solar cell is used to convert sunlight as electricity must be reliable and high efficient with cost effective compared to conventional sources. Several solar technologies including wafer, thin film and organic have been materialized by various researchers to achieve reliability, cost-effectiveness and high efficiency [1]. Recent reports proved that researchers working in the field of solar cells are seeking novel materials to enhance the conversion efficiency of existing solar cells [2]. Among the reported so many materials, sulphide-based materials attracted the materials scientists because of its non-toxic nature [3] and potential characteristic in the field of optoelectronic device fabrication [4]. Presently, researchers show their interests mainly on thin film materials having wide applications in photovoltaics and solar cell [5]. Recently, materials such as copper iodide (CuI) [6,7], $CuAlS_2$ [8,9], $BaCu_2S_2$ [10], CuSCN [11,12] are reported as in the form of thin film. Among them, sulpho salts are efficient material as an absorber for the solar cell fabrication. Especially, copper zinc sulphate (CZS) thin film attracts many researches due to its unique semiconducting property, less toxicity and available abundantly. Also possess excellent conductivity due to p-type transparent semiconductor nature [8,9,13-23].

Thin film can be developed in the form of crystalline or amorphous state by various physical and chemical methods. Thin films may be used as an effective transducer for the trapping of solar energy. For achieving significant energy conversion, solar cells need more surface area so that maximum amount of solar energy can be trapped. More surface area can be obtained by developing the material as thin films, since total energy received by the thin films is directly proportional to the surface area. Ternary compounds are found to be suitable material for opto-electronic device applications and good material for window layer solar cells [17]. Thin film can be developed as multi-component, alloy/compound or multi-layer coatings on the substrate of different shapes and sizes.

Semiconductor materials in the form of thin films has more attraction among the researchers because of its expanding variety of applications in various electronic and optoelectronic devices and low production cost [17]. Formation of uniform film coating is an important factor for the device fabrication [24]. Various materials have been deposited using spray pyrolysis [25], chemical bath deposition [26], sputtering [27], chemical vapour deposition [28], successive ionic layer and reaction (SILAR) [29], electrodeposition [30], *etc*. In the present report, $CuZnS_2$ thin films were prepared using chemical bath deposition method with and without effect of complexing agents EDTA and Leishman's stain. Comparative analyses such as optical, electrical and magnetic properties of the developed thin films are reported.

EXPERIMENTAL

The chemicals *viz*. zinc sulphate, copper sulphate, sodium sulphide, disodium salt of ethylenediaminetetraacetic acid [$Na_2(C_{10}H_14N_2O_8)$], Leishman stain (methanolic solution of methylene blue) for the deposition of $CuZnS_2$ thin films were purchased as analytical grade (99.97%) and all the required solutions were prepared from deionized water (Alpha-Q Millipore).

Preparation of substrate: The glass substrate (25 mm × 75 mm) was used for film fabrication. Initially, the substrates were heated in the concentrated chromic acid bath for 1 h and then cooled at room temperature. Then, the glass plates were degreased with acetone for 10 min and ultrasonically cleaned with distilled water for 10 min and dried in desiccator.

Preparation of precursor solution: The chemical deposition of $CuZnS_2$ thin films onto the glass substrates was carried out using a mixture of 20 mL of 0.05 M zinc sulphate, 20 mL of 0.05 M copper sulphate solution and 10 mL of 0.1M sodium sulphide solution taken in a 100 mL beaker. The above solutions were continuously stirred for 0.5 h with the help of magnetic stirrer at room temperature to obtain a homogeneous mixture of bath solution.

Deposition of thin films: The degreased and cleaned glass slides were vertically positioned inside the beaker containing the above bath solution. Then the beaker was kept undisturbed for about 2 h for deposition process. After the completion of thin film deposition, the glass plates coated with $CuZnS_2$ was washed several times with deionized water and then dried in desiccator for characterization.

The same procedure was repeated for coating the thin films of $CuZnS_2$ with 5 drops of each EDTA and Leishman stain solutions. The addition of EDTA and Leishman stain solution as complexing agents increase the time for the deposition of zinc and copper ions on the substrate. The chemical reaction involved during the deposition processes are presented below:

$$ZnSO_4 + 2H_2O \longrightarrow Zn(OH)_2 + H_2SO_4 \quad (1)$$

$$CuSO_4 + 2H_2O \longrightarrow Cu(OH)_2 + H_2SO_4 \quad (2)$$

$$Na_2S + 2H_2O \longrightarrow H_2S + 2NaOH \quad (3)$$

The above three reactions are combined to form $ZnCuS_2$ deposition.

$$Zn(OH)_2 + Cu(OH)_2 + 2H_2S \longrightarrow ZnCuS_2 + 4H_2O \quad (3)$$

Characterization: The structural studies of $CuZnS_2$ thin films prepared on glass substrates was done by powder X-ray diffraction (PXRD) studies using Ultima3 theta-theta gonio X-ray diffractometer with Cu*K*α radiation (λ = 1.5406 Å) with a scan rate of 4º min^{-1} for 2θ from ~20º to 60º. The surface morphology was analyzed using scanning electron microscopy (SEM) technique. The prepared thin films were placed in the sample holder of VEGA3 TESCAN unit for the SEM analysis. The topographic features of the surface can be obtained from Park XE-100 atomic force microscopy (AFM). Optical absorption studies were performed using UV–Vis–NIR spectrophotometer (Agilent Ultraviolet Spectrum) for the wavelength range of 300-900 nm. The nature of the semiconducting materials can be obtained from hall measurement effect. The photo sensor properties can be obtained from I-V measurement by solar simulator.

RESULTS AND DISCUSSION

XRD studies: Fig. 1 shows the XRD patterns of $CuZnS_2$ thin films with and without EDTA and Leishman stain added. From Fig. 1, the observed peaks at 2θ = 22.05º, 23.50º, 29.06º, 30.99º, 31.88º, 52.01º. All the diffraction peaks were well agreed with the JCPDS standard file No. 65-7736 for CuS and 65-5476 for ZnS with cubic structure [31].

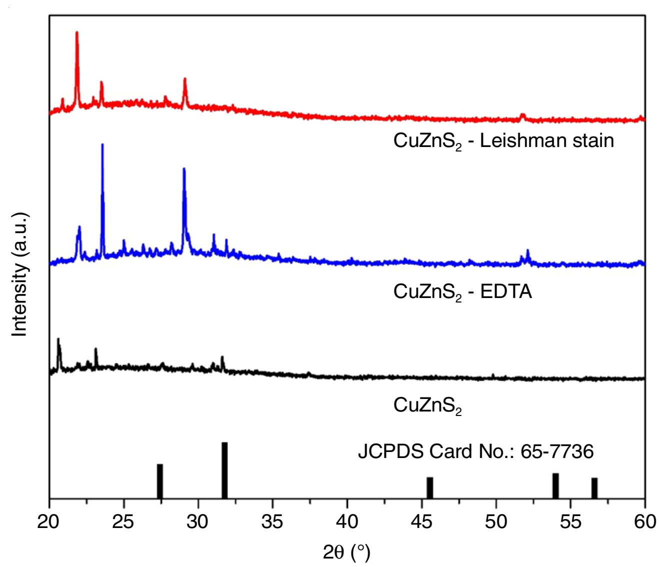

Fig. 1. X-ray diffraction patterns of as-grown $CuZnS_2$ films, $CuZnS_2$ with EDTA and Leishman stain added

Crystallite size (D) of the developed thin films was calculated from the diffraction peaks. The mean particle size was computed by using Scherer formula [32,33]:

$$D = \left(\frac{0.9\times\lambda}{\beta\cos\theta}\right) \quad (5)$$

where λ is the wave length of X-Ray (0.1541 nm), β is full width at half-maximum (FWHM), θ is the diffraction angle and D is crystallite diameter.

The broad nature of the obtained diffraction peaks suggests the crystallite size of the samples is of the order of 5.55 nm, 5.86 nm and 6.21 nm, respectively for $CuZnS_2$ thin films without, with EDTA and Leishman stain added.

SEM studies: The microstructure of $CuZnS_2$ films without, with EDTA and Leishman stain added is shown in Fig. 2. It is understood from the images, the as-deposited films are

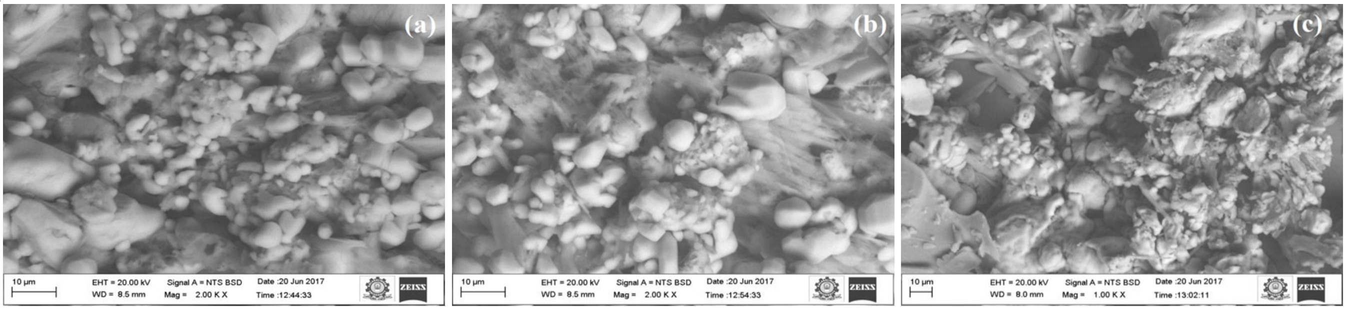

Fig. 2. Scanning electron microscopic images of as-grown films (a) $CuZnS_2$, (b) $CuZnS_2$ with EDTA added and (c) $CuZnS_2$ with Leishman stain added

highly uniform, without pinholes and cracks and are having uniform coating to the substrates [34]. The surface morphology of the deposits is varying with the complexing agents to the reacting materials. Each entity has a non-porous structure. Generally, proliferated grains are occurred in the surface morphology when the complexing agents were added to the parent material.

AFM studies: Surface roughness, size and height of the grains were analyzed using AFM on a scanned area of 5 µm × 5 µm of the film. The AFM images of the 3D and 2D results of $CuZnS_2$ with and without complexing agents added thin films are shown in Fig. 3a-c and Fig. 4a-c, respectively. The AFM image shows the polycrystalline morphology with large number granules of the developed thin films. Also, the substrate surfaces are surrounded by densely packed circular or elliptical particles with all the complexing agents used in the present study. The films were comprised of highly aggregated sharp boundaries. Surface roughness value of without and with EDTA and Leishman stains added $CuZnS_2$ were calculated and found to be 65.47 nm, 65.88 nm and 151.56 nm. From the result, $CuZnS_2$ thin film with Leishman stain has a higher rough surface when compared to other films.

Optical studies: The optical characteristics of $CuZnS_2$ thin films without and with complexing agents added are shown in Fig. 5. The absorbance spectral measurements are recorded for the wavelength between 300 and 900 nm. The maximum absorbance at 298 nm for $CuZnS_2$ thin film without complexing agent added, 295 and 293 nm, respectively for $CuZnS_2$ with the addition of EDTA and Leishman stain is observed. The absorption edge is getting shifted towards lower wavelength with the different complexing agents [35]. Fig. 5 also revealed that the UV region possesses higher absorbance properties

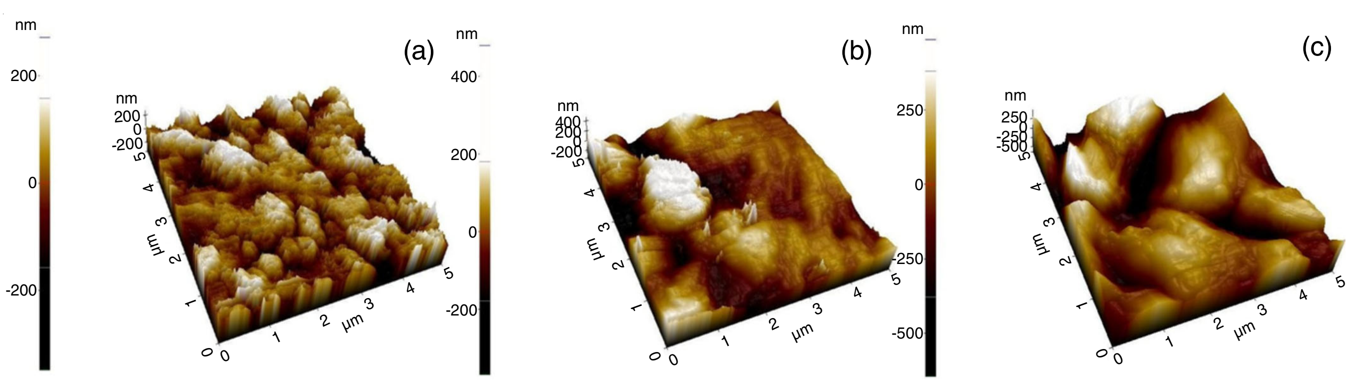

Fig. 3. AFM 3D images of the as deposited films (a) $CuZnS_2$, (b) $CuZnS_2$ with EDTA added and (c) $CuZnS_2$ with Leishman stain added

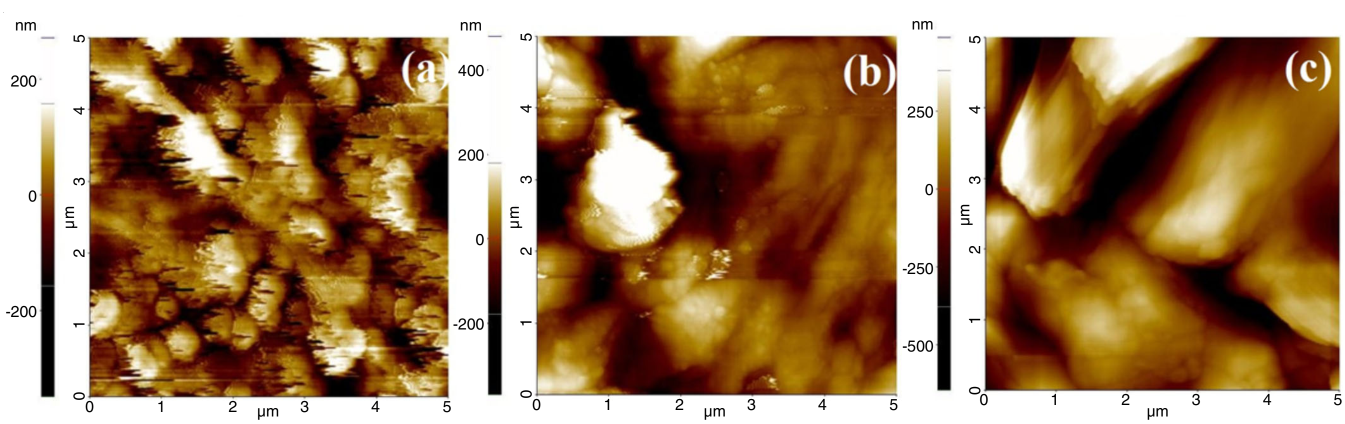

Fig. 4. AFM 2D images of the as grown films (a) $CuZnS_2$, (b) $CuZnS_2$ with EDTA added and (c) $CuZnS_2$ with Leishman stain added

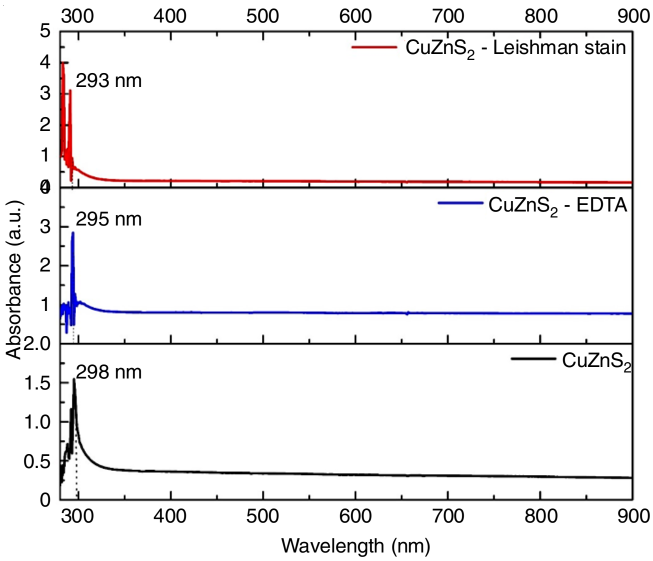

Fig. 5. Optical absorbance (A) of the as deposited films $CuZnS_2$, $CuZnS_2$ with EDTA added and $CuZnS_2$ with Leishman stain added

compared to visible and NIR region, which shows that the proposed material could be used as a potential material for the construction of photovoltaic cells.

Tauc's plot drawn between $(Ah\nu)^2$ and $h\nu$ to obtain the band gap of the prepared samples; where A is absorbance, h is the Planck's constant, ν is the frequency. Here, the absorbance of the materials can be calculated using eqn. 6 [36]:

$$\left(A = \frac{k(h\nu - E_g)^{n/2}}{h\nu} \right) \quad (6)$$

where ν is frequency, k is constant and n carries the value of either 1 or 4, in which 1 for a direct band gap and 4 for indirect band gap materials, respectively. Fig. 6 shows the Tauc's plot of the prepared thin films. For a direct band gap semiconductor (n = 1), the $(Ah\nu)^2$ against hν is directed to be a straight line with an intercept yielding the band gap value [37]. The intercept of the tangent line meets at $x = 0$ gives the band gap energy of the materials. From the plot, E_g values were found to be 3.92 eV, 4.00 eV and 4.21 eV for $CuZnS_2$ films without, with EDTA and Leishman stain added, respectively. The band gap values are getting increased due to decrease in gran size with different complexing agents.

Hall effect measurement: Hall properties of the prepared thin films were studied and the results are given in Table-1. From Table-1, it is evident that the $CuZnS_2$ thin film belongs to n-type semiconductor because of more number of electrons as a carrier type. Addition of complexing agents such as EDTA and Leishman stain increase the hole concentration of $CuZnS_2$ thin film and hence the material becomes p-type semiconductor. So, in this type acceptor energy level is closed to valence band and far away from the conduction band.

I-V Characteristics: Fig. 7 shows the I-V characteristics of sample C ($CuZnS_2$), C1 ($CuZnS_2$ with EDTA), C2 ($CuZnS_2$ with Leishman stain) is obtained from the observations. I-V plots illustrate that current is positive function with forward voltage and current is negative function with reverse voltage. All the samples under investigation show the voltage increasing from -1.25 volt to +1.25 volt along with the changing of the current. The samples C, C1, C2 were slow conducting nature for the changing voltage with the current was found in -30 nA to +30 nA. The sample C series nature was investigated in I-V characteristics by solar simulator.

Conclusion

Thin films of $CuZnS_2$ were deposited without and with EDTA and Leishman stain as complexing agents by chemical bath deposition method. The PXRD patterns results the crystalline nature of the films with cubic phases and with no impurities. SEM images depicted the highly uniform coating and higher particle structure of the thin films. Also, the surface morphology of the films is greatly dominated by the complexing agent. From the topographical studies, it is known that the average grain size and roughness values were clearly observed. The UV-Vis studies illustrated the effect of complexing agents on the optical absorbance. The proposed material could be used

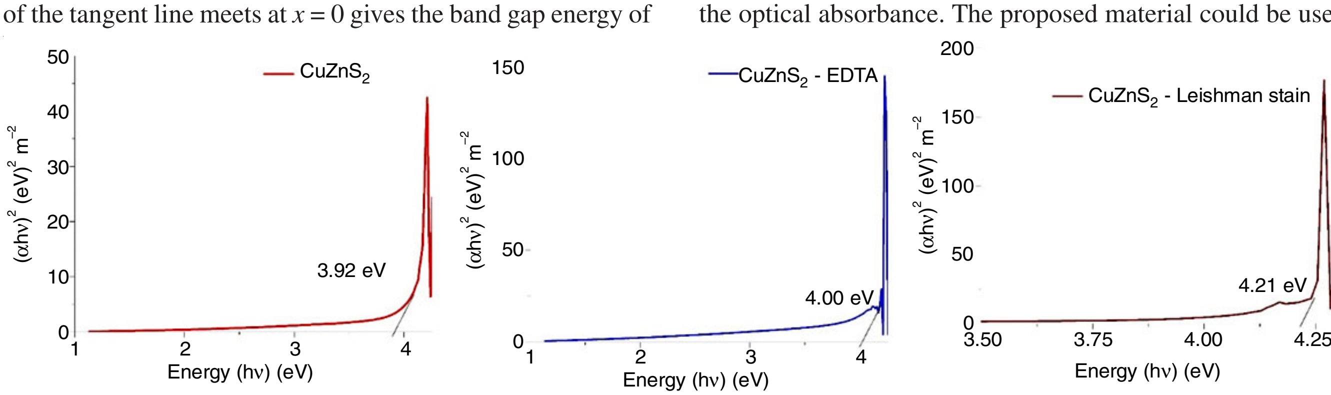

Fig. 6. Band gap of the prepared films $CuZnS_2$, $CuZnS_2$ with EDTA added and $CuZnS_2$ with Leishman stain added

TABLE-1
HALL EFFECT MEASUREMENT RESULTS OF $CuZnS_2$, $CuZnS_2$ WITH EDTA AND $CuZnS_2$ WITH LEISHMAN STAIN

Materials	Resistivity (ρ)	Hall coefficient (RH)	Conductivity (Sigma)	Carrier concentration (Ns)	Mobility (μ)	Carrier type
$CuZnS_2$	2.47×10^{-1}	-1.28×10^{3}	4.05×10^{0}	-2.72×10^{11}	5.17×10^{3}	Electrons
$CuZnS_2$ with EDTA	1.11×10^{4}	3.99×10^{3}	8.98×10^{-5}	8.70×10^{10}	3.58×10^{-1}	Holes
$CuZnS_2$ with Leishman stain	1.114×10^{4}	3.991×10^{3}	8.976×10^{-5}	8.695×10^{10}	3.583×10^{-1}	Holes

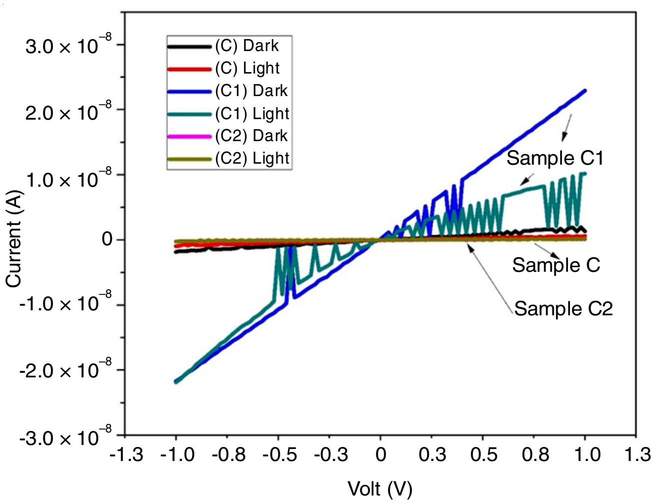

Fig. 7. I-V characteristics for the samples C, C1, C2 films for $CuZnS_2$, $CuZnS_2$ with EDTA added and $CuZnS_2$ with Leishman stain added

as direct band gap semiconductor and the values of band gap were found to be 3.92 eV, 4.00 eV and 4.21 eV. Hall measurements suggested that addition of complexing agents convert the n-type nature of $CuZnS_2$ thin film to p-type nature. From the I-V curve, all the samples having slow conducting nature was found for changing the voltage with the current from -32 nA to +30 nA using solar stimulator. Thus, these films would be deposited readily and are effectively used for solar cell applications.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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