Large Area (10 x 10 cm²) Production of CdS Buffer Layer for Solar Cells by Chemical Bath Method

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Abstract—Thin film solar cells (TFSCs) have been attracting great attention to new generation solar cells for the development of the photovoltaic (PV) market globally through the fabrication of cost effective high-efficient device. A cadmium sulfide (CdS) buffer layer, which decouples the absorber layer and window layer for a device, can be synthesized by a simple and cheaper technique naming as chemical bath deposition (CBD). CdS thin films have been synthesized by the CBD technique using ammonium hydroxide as a complexing agent. The deposition was done in a soda lime glass substrate with an area of 10 x 10 cm². The thickness was around 50 nm indicating the homogeneity and uniform growth of material over the substrate. X-ray diffraction (XRD) proved the crystallinity of the CdS thin film with a preferential plane along (002) having the wurtzite hexagonal crystal structure with an average crystallite size of 19 nm. A more uniform and granular structure of the CdS thin film was observed from morphological and topographical analysis with an average grain size of around 47 nm. The formation of pure cadmium sulfide was confirmed by energy dispersive X-ray spectroscopy. Better transmittance response in the visible region along with an energy gap around 2.35 eV of CdS thin film validates the good photoconductivity, wide band gap, and high electron affinity of CdS. The CdS thin film also helps in the passivation of surface states of the absorber layer as well as provides the mechanical protection from sputtered deposition ZnO and removal of surface oxides.

The present work is aimed at the large-area (10 x 10 cm²) production of CdS thin film on soda-lime glass (SLG) substrate using the CBD technique applicable for the buffer layer in CIGSe thin film solar cells. Basic characterizations of the samples were performed considering three different points to check the uniformity and effective deposition of the film throughout the substrate.

II. EXPERIMENTAL DETAILS

A. Materials

Soda lime glass substrates (SLG, corning No 2947, 10 x 10 cm²), extran solution, sodium hydroxide pellets (NaOH, 98.0 %), hydrochloric acid (HCl, 37.0 %), cadmium acetate dihydrate (Cd(CH₃COO)₂·2H₂O, 98.0 %), thiourea (CH₄N₂S, 99.0 %), ammonium hydroxide solution (NH₄OH, 28.0-30.0 %) were purchased from Sigma-Aldrich (chemicals company). Nitrogen (N₂) gas cylinders were bought from Infra group-Mexico. All the reagents were employed as received without further purification, and all the solutions were prepared using deionized water.

B. Substrate cleaning

Before starting the deposition, SLG substrates were, first, completely cleaned ultrasonically in the extran solution, then in 2.5 M of NaOH aqueous solution (45 min), followed by 0.1 M HCl (4 min), and lastly cleaned with ethanol (10 min) and deionized (DI) water. Thus, cleaned substrates were dried by N₂ gas flux, making ready for deposition.
C. Film deposition

CdS thin film on 10 x 10 cm² SLG substrate by CBD techniques. Cadmium acetate dihydrate aqueous solution (0.01 M) as a cadmium source, thiourea aqueous solution (0.29 M) as a sulfur source, and ammonium hydroxide aqueous solution (2.4 M) was used for the precursor materials. The magnetic stirrer was used to sustain the bath temperature during the deposition. The bath temperature was 70 °C, and the deposition duration was chosen for 10 min. The parameters were taken from the optimized results obtained for small scale production [2]. The synthesized CDS thin film was characterized by considering three different points of a substrate, which can be seen in the photograph (Fig. 2).

D. Film characterization

Bruker’s DektakXT stylus profiler was used to estimate the thickness of deposited CdS thin film. To investigate the crystal structure of the CdS thin films, X-ray diffraction (XRD) patterns obtained from X’Pert PRO PANalytical were analyzed using Cu-Kα (λ = 1.5406 Å) radiation at grazing incidence of 0.5° in the 2θ ranges from 20° to 80°. The micro Raman spectra of fabricated films were obtained by the HORIBA Jobin Yvan system with He-Ne laser (632 nm) at room temperature. Field emission scanning electron microscope (FESEM-AURIGA), and atomic force microscope (AFM) (NT-MDT, NTEGRA) was used to reveal the surface morphology and topography of the CdS thin films, respectively. The chemical composition of the CdS films was measured in the wavelength range of 300-1100 nm by JascoV-670 spectrophotometer.

III. RESULTS AND DISCUSSION

A. Growth rate

![Fig. 1. Growth rate of CdS thin film](image)

The deposition was carried out at a different temperature to optimize the appropriate bath temperature. The growth rate was increased with increasing bath temperature from 60 °C to 80 °C in all deposition duration (7-16 min). The highest growth rate (7.7 nm/min) was obtained with the film deposited at 80 °C due to the kinetic enhancement of the involved reaction during the nucleation growth whereas, the lowest growth rate (2.85 nm/min) was observed at 60 °C of bath temperature. The thickness of the buffer layer is more important rather than the growth rate in high-efficient solar cells [6]. Higher bath temperature provided better growth of CdS materials over the substrate because of the activation energy during the reaction kinetics. The activation energy of the film growth and the formation enthalpy of Cd^2+ could be accountable for varying the growth rate of CdS thin film. The growth rate for lower temperature was due to the supremacy of ion by ion reaction mechanism [7]. Elevated temperature means the increment of free ions (Cd^{2+} and S^{2-}) concentration in a bath, which boosts the growth rate and hence film thickness. The parameters (bath temperature: 70 °C, deposition duration: 10 min) were adopted to deposition CdS on 10 x 10 cm² substrate after finding the optimized condition from small scale production.

![Fig. 2. Photograph of CdS thin film deposited on 10 x10 cm² SLG substrate](image)

B. Structural Properties

The structural property of 10x10 cm² CdS thin film was analyzed by XRD and Raman spectra for different point position, as shown in Fig. 3. The XRD pattern (Fig. 3a) revealed the crystalline nature with a preferential orientation along (002) reflection plane having a wurtzite hexagonal crystal structure. Besides the preferential (002) plane, two other planes corresponding to the ((110) and (112) planes of the
hexagonal phase appeared. The phase of CdS thin film can be varied from cubic or hexagonal or mix of two depending upon the bath parameters and chemical precursors used [8]–[10]. The highest peak intensity was almost the same to all the point position signifies the equal crystallinity and well distribution of material over the substrate during nucleation and growth. The average crystallite size was found to be around 19 nm calculated from Scherrer’s equation, considering the preferential reflection plane. The hump around the peaks can be seen in XRD patterns because of the penetration depth of X-ray even from grazing incidence due to an ultrathin thickness appropriate for CIGSe based solar cell as a buffer layer.

C. Morphological properties

Morphology of the CdS thin film (Fig. 4) deposited on a 10 x10 cm² SLG substrate was analyzed by FESEM images on various points position. No significant pinholes can be observed from the morphology of the CdS thin film, indicating a strong adherence of grains to the substrate, which prevents the interdiffusion of elements from adjacent layers, especially from the ZnO window layer, in a photovoltaic device. The distribution of grains was uniform, with granular in nature, conforming to the homogeneity of the CdS film. The average grain size was around 47 nm.

Raman spectroscopy is a powerful technique to analyze the doping concentration, lattice defect identification, and crystal orientation. Nevertheless, it cannot be able to differentiate the two crystal structures of CdS material because of frequency matching between cubic and hexagonal vibrational modes. Fig. 3b illustrates the Raman spectra of CdS films in which two peaks, corresponding to the first and second longitudinal optical phonon modes were detected. The 1LO (301 cm⁻¹) and 2LO (602 cm⁻¹) peaks were strong and weak, correspond to the fundamental and overtone modes, respectively.
The chemical composition of CdS thin film was examined by energy dispersive X-ray spectroscopy (EDS). A typical EDS spectrum is portrayed as a plot of X-ray count (cps/eV) versus energy in KeV. The EDS spectrum of the CdS thin film deposited on 10 x 10 cm² SLG at position one is shown in Fig. 5. The pattern showed that the Cd/S ratio for all the point positions was nearly equal to 1.

![Fig. 5. EDS pattern of CdS thin film](image)

**D. Topographical properties**

The topographical analysis was performed by AFM images and revealed the distinct distribution of the grains, as shown in Fig. 6. The RMS roughness of the films was ranged between 5 and 7 nm, which confirms the high degree of uniformity of the CdS thin films. The surface roughness is also responsible for the optical properties as an effect of electron scattering. The low roughness leads to scattering more electrons, whereby reducing the transmittance value. That is, there is no diffused light through the CdS thin film if the surface structure is quite smooth. The average grain size was around 35 nm estimated from AFM images, which were in close agreement to that of FESEM images.

![Fig. 6. 3D AFM images (2 µm x 2 µm) of CdS thin film deposited on 10 x 10 cm² SLG substrate](image)

**E. Optical properties**

The optical transmittance was taken in the UV-vis region between the wavelength range 300-1100 nm. The average transmittance (Fig. 7) was found to be around 70% (at 550 nm wavelength) exhibit a good transparent film applicable for a buffer layer in solar cell application. A slight difference in transmittance values was obtained in the CdS film taken at different points, which could vary thickness [11]. The value of transmittance increases with decreasing thickness. It was observed that optical absorption coefficient, originated from the transmittance data, is a function of photon energy and the absorption edge, estimated by using the following equation [12]:

$$\alpha = \frac{1}{d} \ln \left(\frac{T}{T_0}\right)$$  \hspace{1cm} (1)

where $d$ is the thickness of the CdS thin films, $T$ is the transmittance value. The value of the absorption coefficient was found to be in the order of $10^5$ cm⁻¹. The value of the optical band gap ($E_g$) was estimated after the determination of the absorption coefficient by using the following Tauc relation

$$a_\nu = A(\nu - E_g)^n$$  \hspace{1cm} (2)

where $E_g$ is the bandgap energy, $\nu$ is the photon energy; $A$ is independent energy constant, $n$ is an exponent that indicates the nature of optical transition states. The value of $n$ is 1/2 and 3/2 for allowed and forbidden direct transitions, respectively. While $n$ is 2 and 3 for allowed and forbidden indirect transitions, and for CdS, a direct bandgap material, $n = \frac{1}{2}$.
The optical band gap energy (Fig. 7 (inset)) of CdS thin films was calculated by extrapolating the straight-line portion of the plot \((ah\nu)^2\) to energy \((h\nu)\) axis and found to be approximately in the range between 2.34 eV and 2.37 eV.

**Fig. 7. Transmittance spectra of CdS thin film deposited on 10 x 10 cm² SLG substrate**

**F. Solar cell fabrication**

Molybdenum thin film (500 nm) as a back contact was deposited on 100 cm² SLG by direct current (DC) magnetron sputtering by varying power of 100 W and 300 W making it bilayer with a working pressure of 5 mTorr. CISe absorber was fabricated by the selenization of metallic precursor layers (CuIn) on Mo-coated SLG substrates. The ramping step selenization technique did recrystallization of the CISe absorber at 550 °C for 60 minutes. 50 nm thick cadmium sulfide (CdS) n-type buffer layer by chemical bath deposition (CBD). Additionally, 50 nm intrinsic zinc oxide (i-ZnO) and 120 nm thick transparent conducting oxide layer (Al: ZnO; 2/98 wt%) were deposited using radio frequency (RF) sputtering. The J-V curve shown in Fig. 8a demonstrates that the best cell efficiency of 4.73% is achieved with the open-circuit voltage \((V_{oc})\) of 398 mV, short circuit current density \((J_{sc})\) of 26.76 mA/cm², and the fill factor (FF) of 44%. The lower value of efficiency could be the reason for the window layer, where Al doped ZnO had the resistivity in the order of \(10^{-2}\ Ω\cdot cm\). RMS roughness of the films were varied from 5 to 7 nm displaying compactness of the grains and distributed uniformly. The optical bandgap was found to be around 2.35 eV calculated from the Tau plot of transmittance data obtained from UV-visible spectroscopy. 4.73% of photoconversion efficiency was obtained from CISe based solar cells, adopting 50 nm thick CdS buffer layer over 100 cm² substrate. It is possible to obtain a photovoltaic device with an effective deposition of CdS buffer layer over a large area by chemical bath method, which can be viable from the aforementioned results.

**Fig. 8. (a) Current-voltage characteristics, and (b) external quantum efficiency of CISe solar cells based on 50 nm thick CdS buffer layer**

**IV. CONCLUSIONS**

Cadmium sulfide (CdS) buffer layer was successfully synthesized by chemical bath deposition technique and then characterized structurally, morphologically, topographically, and optically. A thin film of CdS with a thickness of around 50 nm deposited at 70 °C showed polycrystalline in nature with a dominant peak around 26° of two theta value conforming a wurtzite hexagonal crystal structure from XRD pattern. The Raman spectra verified the formation of CdS thin film with fundamental and overtone modes at 301 cm⁻¹ and 602 cm⁻¹, respectively, closely agreed to the already reported value. A grain size distribution of the synthesized CdS thin film was analyzed by FESEM images with an average grain-sized 47 nm. RMS roughness of the films were varied from 5 to 7 nm displaying compactness of the grains and distributed uniformly. The optical bandgap was found to be around 2.35 eV calculated from the Tau plot of transmittance data obtained from UV-visible spectroscopy. 4.73% of photoconversion efficiency was obtained from CISe based solar cells, adopting 50 nm thick CdS buffer layer over 100 cm² substrate. It is possible to obtain a photovoltaic device with an effective deposition of CdS buffer layer over a large area by chemical bath method, which can be viable from the aforementioned results.
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