Conference Paper

Substrate Rotation Chemical Bath Deposition of Cadmium Sulfide Buffer Layers for Thin Film Solar Cell Application

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A method for deposition of cadmium sulfide (CdS) buffer layer thin films on fluorine-doped tin oxide (FTO) glass, by chemical bath deposition (CBD), has been modified. For achieving relatively uniform and pin-hole-free CdS films, substrate rotation, concentration of CdS salts, and deposition time were optimized. The deposited films were characterized by UV-Vis-NIR spectroscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD), and atomic force microscopy (AFM). Band gap of ~2.4 eV was measured by UV-Vis-NIR spectroscopy, CdS phase was confirmed by XRD, and film uniformity and roughness (~15–20 nm) were measured by SEM and AFM, respectively.

1. Introduction

In past three decades, photovoltaic (PV) industry has moved from mere concepts to a full-fledged industry. Silicon- (Si-) based technology for harnessing solar energy being the main contributor to this commercialization accounting for over 93% market share. This conventional Si technology is now constrained by the shortage, high prices, weight, and fragility of Si. These problems have been addressed by thin film technologies developed in last decade.

Thin film solar cells (TFSCs) have shown great potential to be future of PV industry. CuInGaSe₂- (CIGS-) based TFSCs have demonstrated efficiencies comparable to Si technology. Recently, Jackson et al. [1] reported 20% efficient solar cell with thin film of CIGS as absorber layer and CdS buffer layer. Commercially available thin film solar cell modules integrate p-type CIGS or cadmium telluride (CdTe) absorber layer with n-type CdS buffer layer to form the junction. P-type absorber layer with thickness of around 2 μ m is usually

deposited by coevaporation technique for commercial applications. The chemical bath deposition (CBD) technique is used for deposition of CdS on absorber layer. This method is a low temperature method and relatively inexpensive which makes it suitable for large area industrial processes. Various other materials like ZnS, In₂S₃, and In(OH)₃ have also been used as substitute for CdS [2, 3]. However, efficiencies achieved with these materials have not been as high as CdS. Different methods for deposition of CdS have also been studied [4]. Although efficiencies achieved by these methods have been comparable to CBD technique, their processing is difficult.

Generally, a wide band-gap material to maximize the transmission and photocurrent is desired for buffer layer. CdS having a band-gap of ~2.4 eV, corresponding to 517 nm, is preferred buffer material for TFSC. It transmits photons with energy lower than 2.4 eV to pass through it and reach absorber layer to generate photocurrent. The other important requirement for efficient buffer layer is thin and

uniform deposition. A thin layer of thickness less than 100 nm is required to minimize the recombination of generated electron-hole pairs. Any nonuniformity or pin holes in the buffer layer can lead to shorting of device, localized electronic aberrations, and increased tunneling. Layer thickness can be increased to prevent pin holes; however, a thick coating can reduce the transmission of light through the layer. Therefore, an optimum buffer layer thickness (<100 nm) must be selected to avoid pinholes and increase transmission of the layer. Highly resistive buffer layer is preferred to reduce the possibility of shunting of the junction. Efficiency of a TFSC also depends on matching of lattice constants of buffer layer and absorber layer and conduction band offset (CBO) at the interface [5]. Hence, method of deposition influences the performance of cell by modifying interfacial properties.

In conventional CBD method used for CdS deposition, solution of chemical precursors is constantly stirred by a magnetic bar for distribution of precursors uniformly throughout the solution. However, films obtained by this method are not very uniform and have pin holes due to the formation of swirls and air bubbles. To maintain uniformity and prevent pinholes formation in such a thin layer, substrate rotation chemical bath deposition (SRCBD) was used. A linear increase in deposition rate and higher Cd/S ratio with increase in rotation energy during SRCBD has been reported earlier [6]. In this contribution, we have discussed about the effect of rotation energy on morphology of CdS films and effect of annealing on band edge of CdS films.

2. Experimental Details

CdS films were grown on FTO-coated soda-lime glass (SLG) slides and bare soda lime glass substrates by SRCBD and conventional CBD method. Substrates were cleaned by sonication in propan-2-ol, rinsed with deionized (DI) water and clamped vertically in the bath solution with the help of Teflon clamps attached to a controlled motor. 150 mL of cadmium sulfate [CdSO_4] solution of variable (0.01 M to 0.2 M) concentrations and 60 mL of 28–30% w/w ammonium hydroxide [NH_4OH] were heated to a temperature of 70°C. 150 mL of thiourea [$\text{SC}(\text{NH}_2)_2$] (0.1 M to 0.4 M) was slowly added to the bath solution and solution was constantly stirred. A constant rotation of around 20 rpm was provided to the substrate in SRCBD method to avoid air bubbles to settle on the substrate. After 10 minutes of deposition, 50–80-nm-thin n-type CdS layers were deposited on both side of substrate. Depositions on back side were cleaned with HCl and washed with DI water ultrasonically to remove any loosely adhered particles. Consequently, they were annealed at 180°C in nitrogen atmosphere for 30 minutes.

Deposited films were optically characterized UV-Vis-NIR spectroscopy in energy range of 1.1 eV to 3.3 eV corresponding to wavelength range of 380 to 1200 nm. Absorption spectra were recorded before and after annealing to study the effect of annealing. XRD spectrum of the film was recorded in 2 theta range of 10° to 80°. Film surface morphology was imaged using a surface electron microscopy (SEM) with electron gun operating at 20 kV. Surface roughness was measured by atomic force microscopy (AFM).

FIGURE 1: X-ray diffraction spectrum of annealed CdS film deposited on FTO coated soda lime glass by SRCBD.

3. Results and Discussion

Recorded XRD spectrum of CdS film deposited by SRCBD method is shown in Figure 1. It shows the peaks at two theta values of 26.7° and 44°, indicating cubic CdS phase in the film. Since thickness of deposited film is very less, a large hump was present in XRD spectrum due to diffractions obtained from glass.

Optical absorbance spectra were recorded for the CdS/FTO/SLG samples without annealing and after annealing the sample at 180°C for 30 minutes in nitrogen atmosphere. Annealing improved the optical properties of CdS film. It was observed that band edge of absorption spectra becomes sharp and moves towards lower wavelength after annealing as shown in Figure 2. Hence, greater number of high energy photons pass through annealed CdS layer and reach absorber layer. By using absorption spectra, band gap of annealed CdS/FTO/SLG film was calculated to be 2.4 eV.

Surface morphology of deposited films was compared by top view SEM images of CdS on FTO/SLG. Figure 3 shows the uniform deposition of CdS on FTO/SLG by SRCBD technique at 25kx magnification; however, the deposition using conventional CBD had few pinholes which could shunt the p-n junction. A uniform film was obtained by rotating the substrate at 20 rpm. The rotation of substrate served two purposes. It churned the solution and distributed heat and chemical precursors uniformly in the solution. Also, it did not allow air bubble to settle on the surface of substrate and hence prevented pin-hole formation. At higher rotation speeds, thickness of deposited film was more at edges and less at centre. At lower rotation speeds, air bubbles produced during heating of bath solution settled on the surface of substrate and prevented the contact of substrate with bath solution at that point. This caused pin-hole defects in the deposited film. Surface roughness of CdS film was found to be around 15–20 nm using AFM, not shown here.

Quality of deposited films also varied with change in order of addition of chemical precursor to bath. Scotch tape test showed that immersion of substrate in CdSO_4 and

FIGURE 2: Optical absorbance spectra of SRCBD deposited CdS film in range of before and after annealing.

FIGURE 3: Top view SEM images of CdS films grown by SRCBD and conventional CBD at 25kx magnification.

NH_4OH solution during heating of solution and addition of $\text{SC}(\text{NH}_2)_2$ on reaching of desired temperature produced good adhesive films. Preheating of CdSO_4 and NH_4OH with substrate leads to the formation of $[\text{Cd}(\text{NH}_3)_4]^{2+}$ in solution [7] and on surface of substrate as shown in reaction (2). Cd complex formed on surface of substrate might act as active site for deposition of CdS film. On the addition of $\text{SC}(\text{NH}_2)_2$ at deposition temperature, CdS deposition initiates at the active sites on substrate and uniformly covers the entire substrate. The reaction for formation of films can be summarized as follows:

4. Conclusion

A uniform, adhesive CdS layer was deposited on FTO/SLG substrate by SRCBD method. SEM images suggest that a slow rotation provided to substrate prevented pinhole formation and produced defect-free CdS film. However, film deposited by conventional CBD method was found to have few pinholes due to the formation of air bubbles on the substrate during deposition. Annealing of CdS film improved its optical properties and increased its band gap allowing more photons to reach absorber layer and contribute to photocurrent.

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References

- [1] P. Jackson, D. Hariskos, E. Lotter et al., "New world record efficiency for $\text{Cu}(\text{In,Ga})\text{Se}_2$ thin-film solar cells beyond 20%," *Progress in Photovoltaics*, vol. 19, no. 7, pp. 894–897, 2011.

- [2] Y. Tokita, S. Chaisitsak, A. Yamada, and M. Konagai, "High-efficiency Cu(In,Ga)Se₂ thin-film solar cells with a novel In(OH)₃:Zn²⁺ buffer layer," *Solar Energy Materials and Solar Cells*, vol. 75, no. 1-2, pp. 9-15, 2003.
- [3] D. A. Johnston, M. H. Carletto, K. T. R. Reddy, I. Forbes, and R. W. Miles, "Chemical bath deposition of zinc sulfide based buffer layers using low toxicity materials," *Thin Solid Films*, vol. 403-404, pp. 102-106, 2002.
- [4] D. Hariskos, S. Spiering, and M. Powalla, "Buffer layers in Cu(In,Ga)Se₂ solar cells and modules," *Thin Solid Films*, vol. 480-481, pp. 99-109, 2005.
- [5] T. Nakada, M. Hongo, and E. Hayashi, "Band offset of high efficiency CBD-ZnS/CIGS thin film solar cells," *Thin Solid Films*, vol. 431-432, pp. 242-248, 2003.
- [6] A. I. Oliva-Avilés, R. Patino, and A. I. Oliva, "CdS films deposited by chemical bath under rotation," *Applied Surface Science*, 2010.
- [7] M. A. Mahdi, S. J. Kasem, J. J. Hassen, A. A. Swadi, and S. K. J. A l-Ani, "Structural and optical properties of chemical deposition CdS thin films," *International Journal of Nanoelectronics and Materials*, vol. 2, pp. 163-172, 2009.