Hindawi Publishing Corporation
Advances in OptoElectronics
Volume 2007, Article ID 18619, 5 pages
doi:10.1155/2007/18619

Research Article

Application of CBD-Zinc Sulfide Film as an Antireflection Coating on Very Large Area Multicrystalline Silicon Solar Cell

U. Gangopadhyay,[1,2] K. Kim,[2] S. K. Dhungel,[2] H. Saha,[1] and J. Yi[2]

[1] *IC Design & Fabrication Centre, Electronics & Telecommunication Engineering Department, Jadavpur University, Kolkata 700032, India*
[2] *School of Information and Communication Engineering, Sungkyunkwan University, Suwon-City 440-746, South Korea*

Received 1 April 2007; Revised 18 September 2007; Accepted 20 December 2007

Recommended by Armin Aberle

The low-cost chemical bath deposition (CBD) technique is used to prepare CBD-ZnS films as antireflective (AR) coating for multicrystalline silicon solar cells. The uniformity of CBD-ZnS film on large area of textured multicrystalline silicon surface is the major challenge of CBD technique. In the present work, attempts have been made for the first time to improve the rate of deposition and uniformity of deposited film by controlling film stoichiometry and refractive index and also to minimize reflection loss by proper optimization of molar percentage of different chemical constituents and deposition conditions. Reasonable values of film deposition rate (12.13 $\mathrm{\AA}'$/min.), good film uniformity (standard deviation < 1), and refractive index (2.35) along with a low percentage of average reflection (6-7%) on a textured mc-Si surface are achieved with proper optimization of ZnS bath. 12.24% efficiency on large area (125 mm $\times$ 125 mm) multicrystalline silicon solar cells with CBD-ZnS antireflection coating has been successfully fabricated. The viability of low-cost CBD-ZnS antireflection coating on large area multicrystalline silicon solar cell in the industrial production level is emphasized.

1. INTRODUCTION

Pyramid type surface texturing is a well established process used for monocrystalline silicon solar cell.Unlike monocrystalline silicon (c-Si),multicrystalline silicon (mc-Si) can exhibit poor surface texturing due to its different grains and grain boundaries. Therefore, application of AR coating is one of the challenging issues in the area of mc-Si solar cell research. It has been demonstrated that zinc sulfide (ZnS), a wide direct band gap semiconductor with high-refractive index (2.35), can be used as single AR coating or as part of a double layer AR coating if used in conjunction with a low-refractive index material [1]. Also, ZnS thin film has been proven as one of the promising thin film materials for detector, emitter, and modulators in optoelectronics [2]. ZnS film can be used as a reflector and dielectric filter due to its high value of refractive index as well as high transmittance in visible region [3, 4]. It is used as buffer layers in CuInSe- and $CuGaSe_2$-based solar cells, respectively [5, 6]. Several techniques such as, molecular beam epitaxy [7], H_2 plasma chemical sputtering [8], thermal evaporation [9], MOCVD [7], and MOVPE [10] have been used to produce ZnS thin film with adequate properties. Spray pyrolysis is an interesting technique for preparing thin films [11]. Indeed, this technique is very attractive due to its simplicity and low cost, but uniformity control over a large area is one of the major problems. Another low-cost approach for deposition of ZnS film on semiconductor or glass substrate is the chemical bath deposition (CBD) technique [12–14]. In CBD, deposition of metal chalcogenide semiconducting thin films is done by maintaining the substrate in contact with the solution of chemical bath containing the metal and chalcogen ions. The film formation on substrate takes place when ionic product exceeds solubility product. However, the precipitate formation in the bulk of solution is an inherent problem in CBD technique. This normally results in unnecessary precipitation and loss of materials during CBD-ZnS film deposition on semiconductor or glass substrate and hampers the uniformity of the deposited film. In order to avoid such problem, proper optimization of chemical constituents of bath deposition is necessary.

We have previously reported on the chemical bath deposition of ZnS thin films in the context of their application as an antireflection coating on monocrystalline silicon solar cell [15]. For multicrystalline (mc-Si) silicon large area substrate due to different grain orientation structure, serious nonuniformity has been noticed during experiment. Bath chemical constituent percentage was changed from our previously reported values [16] in order to achieving good uniformity of deposition on the surface of m-Si wafer. This paper reports the key factors involved in proper optimization of CBD technique such as composition of chemical constituents, stoichiometry and refractive index of the deposited film, and deposition time to form uniform and reproducible viable ZnS antireflection coating in batch process by CBD on commercial mc-Si silicon solar cells.

2. EXPERIMENTAL

For the deposition of films, the solution conditions (molar concentrations) and mounting angle of substrates were maintained at 60° for better deposition [16]. During our experiment, the concentrations of different constituent chemicals were taken as zinc sulfate ($ZnSO_4$) 0.08 M, ammonia solution (NH_4OH) 0.784 M, hydrazine monohydrate (N_2H_4, H_2O) 0.003 M, and thiourea CS $(NH_2)_2$ 0.14 M,respectively, for achieving good uniformity of deposited ZnS film on whole area of large mc-Si substrate. Zinc sulfate was added to the required quantity of ammonia solution followed by hydrazine monohydrate in order to improve the dissolution of the $ZnSO_4$. Next CS $(NH_2)_2$ was added to the hot solution (temperature ∼ 80°C). The temperature was maintained at 80°C during deposition, and silicon wafers were withdrawn from the solution after 10, 20, 30, 40, 50, 60, and 75 minutes, respectively, in order to study the variation of thickness of the ZnS film with time of deposition

The films were deposited on multicrystalline silicon substrate, which were cleaned by rinsing in running DI-water bath and subsequently drying. The optical reflectance of ZnS films was carried out using spectrophotometer.The energy dispersive X-ray (EDAX) analysis was used to determine the percentage of zinc and sulfur present in the deposited ZnS film. For large area surface study of the deposited CBD film, we have used scanning electron microscopy (SEM) study. The thicknesses of the films were measured using ellipsometry.

3. RESULTS AND DISCUSSION

A typical SEM micrograph of ZnS film deposited on m-Si silicon wafers by CBD technique had given in Figure 1. This film was prepared at 80°C at a fixed substrate tilting angle of 60° with a deposition period of 1 hour 20 minutes. The scanning electron microscopic (SEM) studies indicated that the coverage of deposited ZnS films on mc-Si surface was considerable uniform over an area 156 cm^2 (approx.). The uniformity is believed to be achieved by our slightly higher concentration of zinc sulfate and hydrazine used for our experiments on mc-Si solar cells compared to that used in our previous experiments on monocrystalline silicon solar cell [16]. In order to explain this, we need to understand that for our CBD technique, ZnS thin film is prepared by the decomposition of thiourea CS $(NH_2)_2$ in an alkaline solution containing

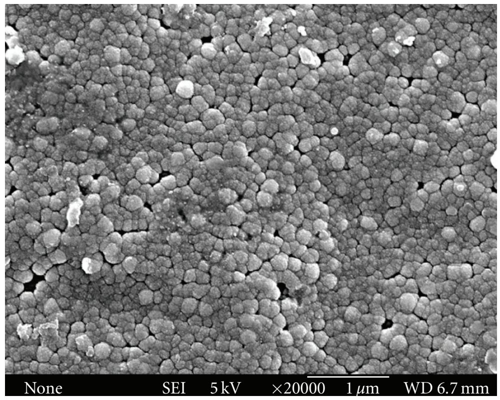

Figure 1: SEM micrograph of CBD-ZnS film on mc-Si substrate.

zinc salt. In our CBD experiment, we have used zinc sulfate and thiourea as source materials. Precipitation control during deposition has to be made by controlling the concentration of free Zn^{2+} ion in the CBD bath.In the solution, $ZnSO_4$ divided into two separate ions of Zn^{2+} and $SO_4{}^{2-}$.

The decomposition of the thiourea is given by [13]

$$\begin{gathered} \mathrm{CS\,(NH_2)_2 + OH^- \longrightarrow SH^- + CH_2N_2 + H_2O}, \\ \mathrm{SH^- + OH^- \longleftrightarrow S^{2-} + H_2O}, \end{gathered} \tag{1}$$

OH^- ions come from hydrazine monohydrate in CBD bath by breaking at 80°C.

Finally, ZnS films are formed according to the relation:

$$\mathrm{Zn^{2+} + S^{2-} \longleftrightarrow ZnS}. \tag{2}$$

Hydrazine (N_2H_4, H_2O) has been added to the reaction bath to promote the ZnS incorporation within the film because at elevated temperature (80°C),it dissociate and supplied necessary OH^- ion for S^{2-} ion formation which in turn formed ZnS film. However, the actual mechanism depending on the film uniformity with different grain size in mc-Si prepared by varying the concentration of Zinc sulfide and hydrazine monohydrate is not clear.

Figure 2 shows the standard deviation of the thickness of the CBD-ZnS film deposited on mc-Si samples at 80°C for a fixed 60° substrate tilt and for different deposition periods. For standard deviation calculation, we have measured the thickness of the deposited ZnS film on silicon wafers (125 mm × 125 mm) at nine different geometrical locations using ellipsometer. It was observed from Figure 2 that the standard deviation of film thickness falls sharply with deposition times. This is probably due to CBD bath used that requires certain amount of time to initiate heterogeneous reaction throughout the bath uniformly. The rapid fall of standard deviation after 20 minutes of deposition may be due to higher rate of film deposition throughout the whole surface of wafer leading to an increase in film uniformity. We conclude that the uniformity of the film improves (standard deviation < 1) with deposition time. The refractive index of a 75 minutes deposition film on m-Si sample was measured to be 2.35 using ellipsometer. The film thickness

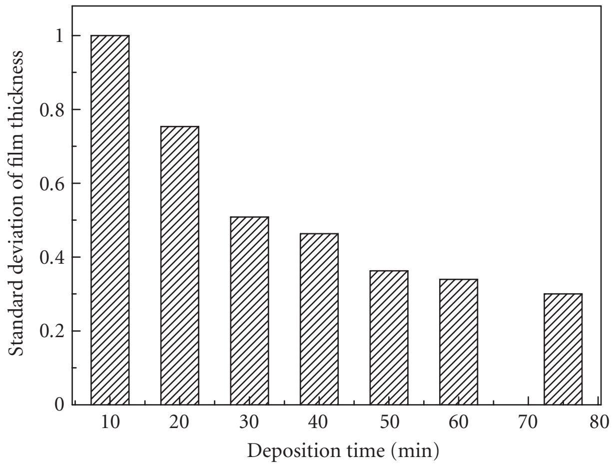

FIGURE 2: Variation of standard deviation of CBD-ZnS film on mc-Si substrate with deposition time at fixed CBD bath temperature of 80°C.

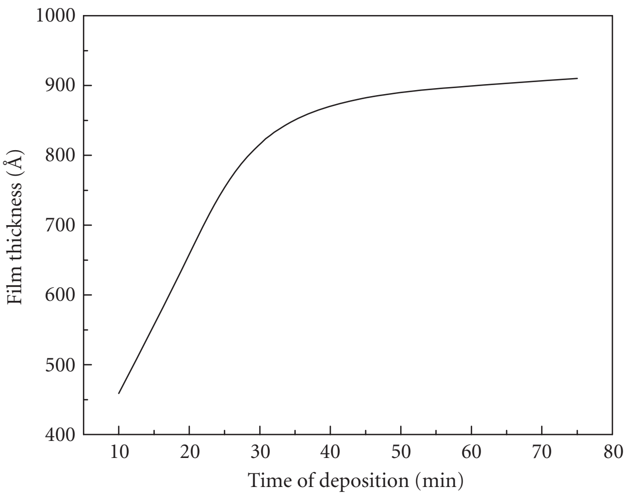

FIGURE 3: Variation of thickness of deposited CBD-ZnS film on mc-Si substrate with deposition time at fixed CBD bath temperature 80°C

verses deposition time of CBD-ZnS at fixed 60° substrate tilting deposited at 80°C is shown in Figure 3. It was observed that the film thickness increases sharply with time in the first 30 minutes of deposition and saturates afterwards. The reflectivity (%) and weighted average reflectance (%) of ZnS (900 Å′) coated,PECVD silicon nitride (746 Å′) coated textured mc-Si samples, and textured mc-Si sample are, respectively, shown in Figures 4 and 5. ZnS coated cells show slightly higher weighted average reflectance (7.1%) than PECVD SiN_x coated cells (6.7%) in general. The presence of higher atomic percentage of oxygen is revealed from the EDAX analysis of the films (see Figure 6). This indicates that the S/Zn ratio (indicates the film stoichiometry) is around 0.71.

The illuminated I-V characteristics (LIV) of the large area (125 mm × 125 mm) solar cell with and without CBD ZnS AR coating are shown in Figure 7. From the curves,

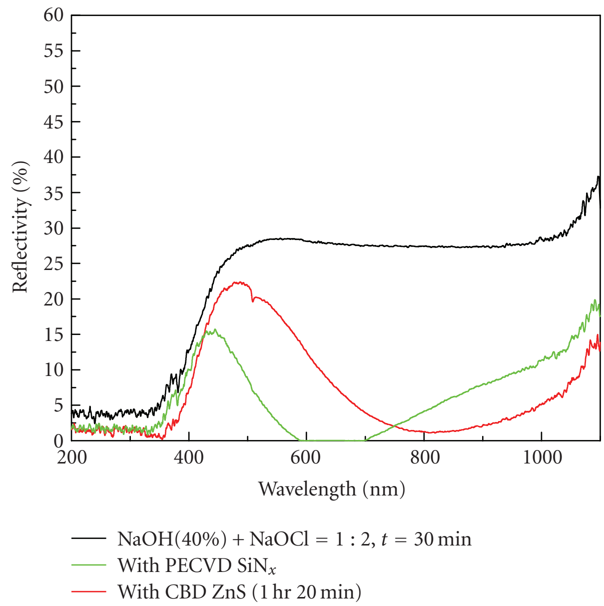

FIGURE 4: Reflectivity of NaOH−NaOCl textured mc-Si surface, CBD-ZnS coated and PECVD SiN_x coated films on NaOH−NaOCl mc-Si substrate.

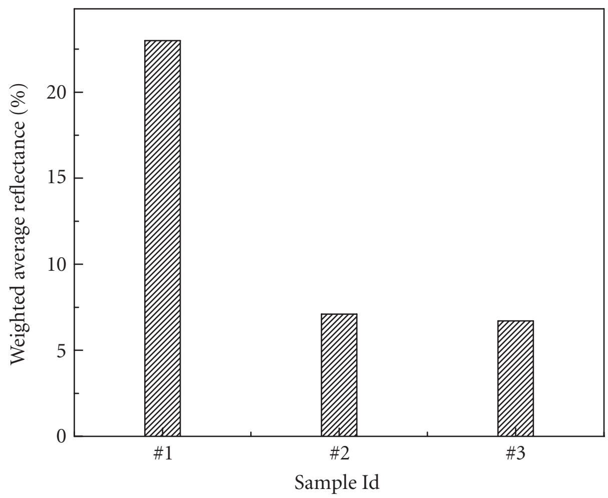

FIGURE 5: Weighted average reflectance (%) of Sample Id no. 1 (NaOH−NaOCl textured mc-Si surface), Id no. 2 (CBD-ZnS coated) and Id no. 3 (PECVD SiN_x coated) films on NaOH−NaOCl textured mc-Si substrate.

it was observed that the short-circuit current of multicrystalline solar cell has increased from 3.93 A to 4.42 A after CBD-ZnS coating representing a 12.5% gain in short-circuit current and 14.9% gain in overall efficiency. It was also observed from Table 1 that except short-circuit current density and conversion efficiency,the performance parameter V_{oc} did not make significant change or degrade after CBD-ZnS coating on the finished solar cell. Spectral response curves from Figure 8 indicate substantial improvement after the application CBD-ZnS coating demonstrating the potential of CBD

Table 1: Performance parameters of large area (125 mm × 125 mm) multicrystalline silicon solar cell with and without CBD-ZnS AR coating, V_{oc} = open circuit voltage, I_{sc} = short circuit current, V_m = voltage at maximum Power Point, I_m = current at maximum Power Point, P_m = maximum Power output, FF = fill factor, Eff = efficiency.

Sample description	V_{oc} (V)	I_{sc} (A)	V_m (V)	I_m (A)	P_m (W)	FF	Eff. (%)
Without AR coating	590.3	3.93	489.34	3.39	1.66	0.72	10.65
With ZnS AR coating	588.8	4.42	491.03	3.89	1.91	0.73	12.24

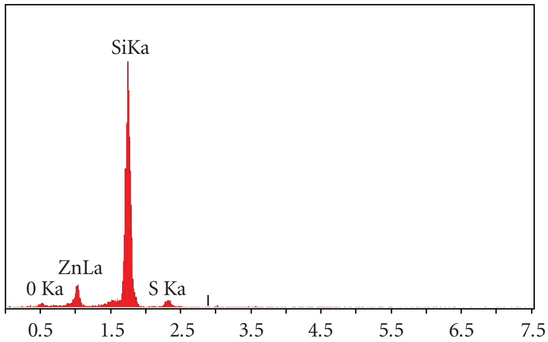

Figure 6: Energy Dispersive X-ray analysis curve of CBD-ZnS film on mc-Si substrate.

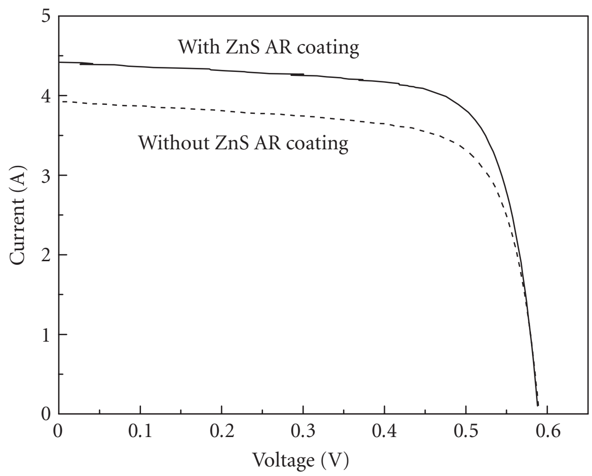

Figure 7: Illuminate current-voltage characteristic of large area mc-Si solar cell with and without ZnS AR coating.

ZnS as ARC on commercial multicrystalline silicon solar cells.

4. CONCLUSION

Film uniformity (standard deviation < 1),good stoichiometry (0.71),high value of refractive index (2.35),and low-percentage weighted average reflection 7.1% were achieved through proper optimization of ZnS bath for depositing ZnS on mc-Si solar cell. Moreover, it has been observed that 12.5% gain in short-circuit current and 15% gain in overall efficiency have been achieved using CBD-ZnS films as AR coating on textured multicrystalline silicon solar cells. 12.24% efficiency on large area (125 mm × 125 mm) multicrystalline silicon solar cells is achieved by using CBD-ZnS antireflection coating on textured surface.

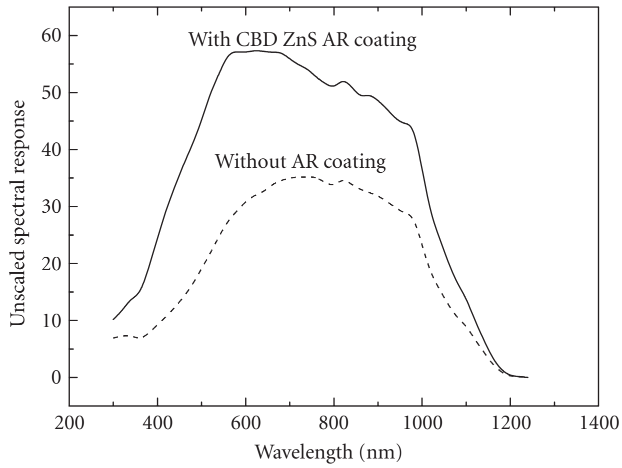

Figure 8: Spectral response of large area mc-Si solar cell with and without ZnS.

REFERENCES

[1] G. Zhang, J. Zhao, and M. A. Green, "Effect of substrate heating on the adhesion and humidity resistance of evaporated MGF_2/ZnS antireflection coatings and on the performance of high-efficiency silicon solar cells," *Solar Energy Materials and Solar Cells*, vol. 51, no. 3-4, pp. 393–400, 1998.

[2] B. Elidrissi, M. Addou, M. Regragui, A. Bougrine, A. Kachouane, and J. C. Bernède, "Structure, composition and optical properties of ZnS thin films prepared by spray pyrolysis," *Materials Chemistry and Physics*, vol. 68, no. 1–3, pp. 175–179, 2001.

[3] J. A. Ruffner, M. D. Hilmel, V. Mizrahi, G. I. Stegeman, and U. J. Gibson, "Effects of low substrate temperature and ion assisted deposition on composition, optical properties, and stress of ZnS thin films," *Applied Optics*, vol. 28, no. 24, p. 5209, 1989.

[4] A. M. Ledger, "Inhomogeneous interface laser mirror coatings," *Applied Optics*, vol. 18, no. 17, p. 2979, 1979.

[5] R. R. Potter and J. R. Sites, "Current-voltage transients in (Cd,Zn)S/$CuInSe_2$ solar cells," *Applied Physics Letters*, vol. 43, no. 9, pp. 843–845, 1983.

[6] K. T. R. Reddy and P. J. Reddy, "Studies of $Zn_xCd_{1-x}S$ films and $Zn_xCd_{1-x}S/CuGaSe_2$ heterojunction solar cells," *Journal of Physics D*, vol. 25, no. 9, pp. 1345–1348, 1992.

[7] Z. Porada and E. Schabowska-Osiowska, "Surface electrical conductivity in ZnS(Cu, Cl, Mn) thin films," *Thin Solid Films*, vol. 145, no. 1, pp. 75–79, 1986.

[8] Y. Tomomura, M. Kitagawa, A. Suzuki, and S. Nakajima, "Homoepitaxial growth of ZnS single crystal thin films by molecular beam epitaxy," *Journal of Crystal Growth*, vol. 99, no. 1–4, pp. 451–454, 1990.

[9] M. Tonouchi, Y. Sun, T. Miyasato, H. Sakama, and M. Ohmura, "Room-temperature synthesis of ZnS:Mn films by H_2 plasma chemical sputtering," *Japanese Journal of Applied Physics*, vol. 2, pp. L2453–L2456, 1990.

[10] P. J. Dean, A. D. Pitt, M. S. Skolnick, P. J. Wright, and B. Cockayne, "Optical properties of undoped organometallic grown ZnSe and ZnS," *Journal of Crystal Growth*, vol. 59, no. 1-2, pp. 301–306, 1982.

[11] O. Briot, N. Briot, A. Abounadi, B. Gil, T. Cloitre, and R. L. Aulombard, "Reflectivity analysis of ZnS layers grown on GaAs and Si substrates by metal organic vapour-phase epitaxy," *Semiconductor Science and Technology*, vol. 9, no. 2, pp. 207–209, 1994.

[12] H. H. Afifi, S. A. Mahmoud, and A. Ashour, "Structural study of ZnS thin films prepared by spray pyrolysis," *Thin Solid Films*, vol. 263, no. 2, pp. 248–251, 1995.

[13] 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.

[14] E. J. Ibanga, C. Le Luyer, and J. Mugnier, "Zinc oxide waveguide produced by thermal oxidation of chemical bath deposited zinc sulphide thin films," *Materials Chemistry and Physics*, vol. 80, no. 2, pp. 490–495, 2003.

[15] J. Vidal, O. de Melo, O. Vigil, N. López, G. Contreras-Puente, and O. Zelaya-Angel, "Influence of magnetic field and type of substrate on the growth of ZnS films by chemical bath," *Thin Solid Films*, vol. 419, no. 1-2, pp. 118–123, 2002.

[16] U. Gangopadhyay, K. Kim, D. Mangalaraj, and J. Yi, "Low cost CBD ZnS antireflection coating on large area commercial mono-crystalline silicon solar cells," *Applied Surface Science*, vol. 230, no. 1–4, pp. 364–370, 2004.