Application of CBD Zinc Sulfide (ZnS) Film to Low Cost Antireflection Coating on Large Area Industrial Silicon Solar Cell

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Zinc sulfide is a semiconductor with wide band gap and high refractive index and hence promising material to be used as ARC on commercial silicon solar cells. Uniform deposition of zinc sulfide (ZnS) by using chemical bath deposition (CBD) method over a large area of silicon surface is an emerging field of research because ZnS film can be used as a low cost antireflection coating (ARC). The main problem of the CBD bath process is the huge amount of precipitation that occurs during heterogeneous reaction leading to hamper the rate of deposition as well as uniformity and chemical stoichiometry of deposited film. Molar concentration of thiorea plays an important role in varying the percentage of reflectance and refractive index of as-deposited CBD ZnS film. Desirable rate of film deposition (19.6 Å / min), film uniformity (Std. dev. < 1.8), high value of refractive index (2.35), low reflectance (0.655) have been achieved with proper optimization of ZnS bath. Decrease in refractive index of CBD ZnS film due to high temperature treatment in air ambiance has been pointed out in this paper. Solar cells of conversion efficiency 13.8 % have been successfully achieved with a large area (103 mm × 103mm) mono-crystalline silicon wafers by using CBD ZnS antireflection coating in this modified approach.

Keywords : Zinc sulfide, Chemical bath deposition, Antireflection, Solar cell

1. INTRODUCION

Texurization of single crystalline silicon substrate of <100> orientation and appropriate antireflection coating (ARC) have become well established methods in photovoltaic industry for minimizing the optical losses[1]. In large area commercial mono-crystalline silicon solar cells, PECVD silicon nitride coating is normally used in batch process but it is relatively costlier process[2]. So, researchers in the field of solar cell are searching for the cost effective antireflection coating for commercial production. Zinc sulfide (ZnS), a wide direct band gap semiconductor with high refractive index (2.35), is a promising material for ARC on silicon solar cells[3]. Also, thin film of ZnS has been proven as one of the promising thin film materials for detector, emitter, and modulators in optoelectronics. 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. It is used as buffer layer in the solar cells made up of the materials such as CuInSe and $CuGaSe_2$ [4]. Several techniques such as, molecular beam epitaxy, H_2 plasma chemical sputtering, thermal evaporation, MOCVD and MOVPE are used to produce thin film of ZnS with adequate properties. Spray Pyrolysis is an interesting technique for preparing thin films[5]. This technique is indeed a very attractive one due to its simplicity and low cost but uniformity control over a large area is one of its major problems. Another low cost approach for deposition of ZnS film on semiconductor or glass substrate is the chemical bath deposition (CBD) technique[6].

In CBD, deposition of metal chalcogenide semiconducting thin films occurs due to substrate maintained in contact with the solution containing the metal and chalcogen ions. The film formation on substrate takes place when ionic product exceeds solubility product. However, this resulted into precipitate formation in the bulk of solution which cannot be eliminated. This leads to the unnecessary precipitation and loss of materials during CBD ZnS film deposition on commercial mono-crystalline silicon solar cells which hamper the uniformity of batch industrial batch process. In order to avoid such a problem, proper optimization of

constituents of CBD is necessary. We are probably the first to report the possibility of CBD ZnS film as a low cost antireflection coating on large area commercial mono-crystalline silicon solar cell. For the viability of CBD ZnS as antireflection coating in batch process for industrial silicon solar cells, this paper reports the key factors involved in proper optimization of CBD technique such as composition of chemical constituents, stoichiometry and refractive index of deposited film, dipping angle, and deposition time. Our approaches will contribute to low cost, high production yield and reliable antireflection coating for commercial silicon solar cells.

The lowering of the refractive index of CBD ZnS film at high temperature (~ 740 °C) firing in air ambiance has been observed. So, fire through ARC contact metallization cannot be effective processing step for this type of ARC on solar cell. It is, therefore, the paper sheds light also on modification of process sequence for CBD ZnS antireflection coating on large area Industrial silicon solar cells.

2. EXPERIMENTAL

In the CBD technique, a soluble salt of the required metal is dissolved in an aqueous solution to release cations. The non-metallic element is provided by a suitable source compound which decomposes in the presence of hydroxide ions, releasing the anions. The anions and cations then react to form the compound. So, ZnS thin film can be prepared by decomposition of thiourea in an alkaline solution containing zinc salt. In our CBD experiment, we have used zinc sulfate and thiourea as source materials. In general, the solubility products of zinc sulfides are very small ($Ksp=10^{-24.7}$) [7]. So, precipitation during deposition has to controlled by the concentration of free Zn^{2+} ion in the CBD bath. In the solution, $ZnSO_4$ divides into two separate ions Zn^{2+} and SO_4^{2-}.

The decomposition of the thiourea is given by

$CS(NH_2)_2 + OH^- \rightarrow SH^- + CH_2N_2 + H_2O$

$SH^- + OH^- \leftrightarrow S^{2-} + H_2O$

Finally, $Zn^{2+} + S^{2-} \leftrightarrow ZnS$

But, due to its low solubility, ZnS produced by this direct reaction precipitates onto exposed surfaces (homogeneous process). This film has low optical transmittance due to rough film topology [8]. This problem can be solved by using suitable complexing agent which releases small concentrations of ions according to the complex ion dissociation and equilibrium constant. In our CBD ZnS bath, the complexing agent used was ammonia solution (NH_4OH). This ammonia solution provides the adequate alkaline medium that helps to form zinc complex ions.

$NH_4^+ + OH^- \leftrightarrow NH_3 + H_2O$

$Zn^{2+} + 4NH_3 \leftrightarrow Zn(NH_3)_4^{2+}$

These complex ions and the sulfide ions migrate to the substrate (mono-crystalline in our case) surface and react to form ZnS (heterogeneous process).

$Zn(NH_3)_4^{2+} + S^{2-} \rightarrow ZnS + 4NH_3$

Hydrazine added to the reaction bath, as done for ZnS thin film deposition, may promote the ZnS incorporation within the film.

Active sites on the silicon surface act as nucleation centre initiating ZnS deposition. Normally, the layers formed by the heterogeneous process have good uniformity as well as high transmittance.

For the first series of depositions, the solution conditions (molar concentrations) and mounting angle of substrate were varied to determine the range over which uniform deposition on large area occurred. The concentrations used were: zinc sulfate 0.07 M; Ammonia 0.784 M; Hydrazine mono-hydrate 150 ml/litre; and thiourea, 0.09 M, 0.14 M, 0.21 M. The mounting angle of the silicon substrate was varied between 30 and 80 degrees.

For the first series of depositions, the solution conditions (molar concentration) were varied, stirred and zinc sulfate was added to the required ammonia solution followed by hydrazine monohydrate. It was found that that process of addition improved the dissolution of the $ZnSO_4$ .The solution was then heated and $CS(NH_2)_2$ was added at the required temperature.

The silicon wafers, mounted at different tilting angle from 30° to 80° on quartz carrier, were then immersed in the solution. Mounting angle (tilting angle) of the wafers is very important for achieving desired amount of ZnS deposition on different silicon surfaces. The temperature was maintained at 80 °C during deposition and silicon wafers were withdrawal at 10, 20, 30, 40, 50 and 60 minutes, respectively, from the carrier. The films deposition on the substrates were then allowed for different duration of times. The films deposited on mono-crystalline silicon substrates were then cleaned by rinsing in distilled water followed by ultrasonic treatment. The optical reflectance of ZnS films were carried out using Spectrophotometer in the UV-visible wavelength range.

The EDAX analysis was used to determine the percentage of zinc and sulfur present in the deposited ZnS film and scanning electron microscope (SEM) was used to observe the surface topology of the deposited film.

The saw damages of mono-crystalline silicon wafers removed by etching about 15 μm each side by wet-chemical etching with NaOH solution at 70 °C. Then, the wafers were texturized by dipping in 1.8% NaOH solution at 82 °C for 30 min, followed by several times di-water rinsing and drying. In this experiment, we have used conventional $POCl_3$ diffusion and screen printed

metallization for silicon solar cell fabrication. The n-type impurity was diffused into textured silicon wafers in open-tube furnace using conventional $POCl_3$ diffusion source at 900 °C as 10 min pre-deposition followed by 30 min drive-in. Then, they were forwarded for edge isolation after which some diffused samples were coated with CBD ZnS film followed by back Ag/Al and front Ag screen printing, baking and co-firing. Other diffused wafers were directly taken for Ag front and Ag/Al back metallization, baking and co-firing followed by CBD ZnS coating. Just before ZnS coating, both front and back contact bars were covered with soldering contact strips for some finished solar cells followed by ZnS coating. Standard Ag-paste (Ferro coductroX3349, Ag-conductor paste) and Ag/Al-paste (product no. 3398, Ferro Electronic Materials) were used in the screen printed metallization technique, which was followed by baking and co-firing at the temperature of 740 °C in a conveyer belt furnace.

3. RESULT AND DISCUSSION

Figure 1 shows a typical SEM picture of ZnS film deposited on textured mono-crystalline silicon wafers by CBD technique. This film was prepared at 80 °C at a fixed substrate tilting angle of 60° with a deposition period of 1 hour.

The concentrations of chemical constituents used were: zinc sulfate 0.07 M, ammonia 0.784 M, hydrazine mono-hydrate 150 ml/litre and thiourea 0.14 M. As can be seen in the figure, the surface morphology of the ZnS film is homogeneous and dense.

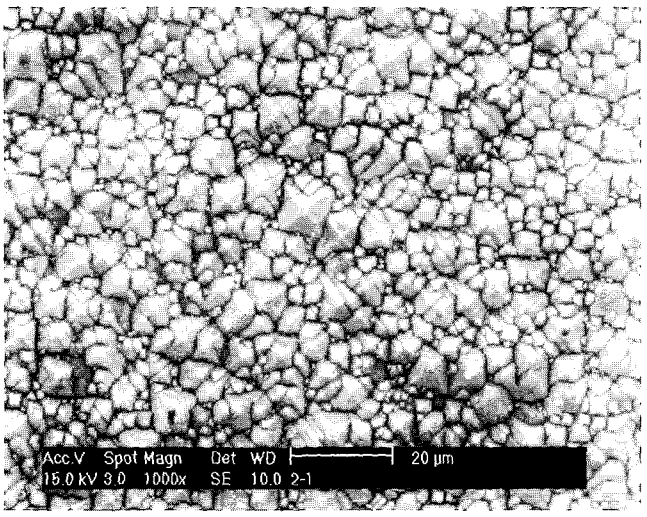

Fig. 1. SEM photomicrograph of a typical as deposited ZnS film on textured silicon wafer.

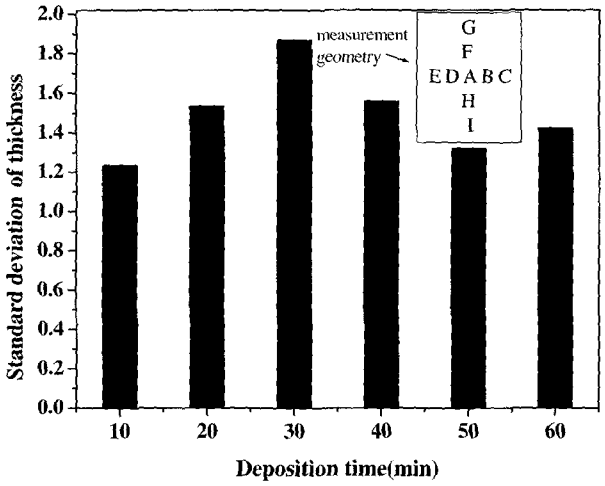

Fig. 2. Standard deviation of thickness of as deposited CBD ZnS film for different time of deposition at fixed 80 °C bath temperature.

Figure 2 shows the standard deviation of the thickness of the CBD ZnS film deposited on mono-crystalline silicon samples at different time durations of deposition, for a fixed angle (60°) of substrate tilting. For the calculation of standard deviation, we have taken the thickness of the deposited ZnS film on silicon wafers (103 mm × 103 mm) at nine different geometrical locations as shown in Fig. 2. Ellipsometer was used to measure the thickness of the films. Low values of standard deviation (<1.8) of the CBD ZnS film thickness indicates the uniformity of the film over full area of the substrate.

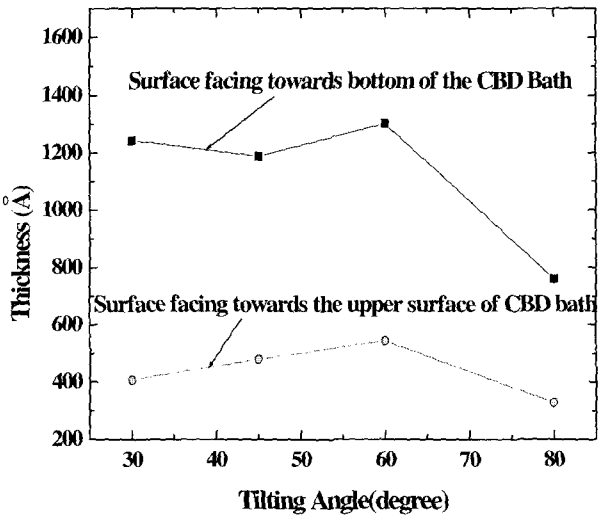

Fig. 3. Variation of thickness of as deposited ZnS films on both surfaces with the tilting angle (mounting angle) of the silicon wafer in CBD ZnS bath at 80 °C for 1 hour.

Figure 3 shows the variation of the thickness of the ZnS films deposited at different tilting angles of the substrate. It is observed from this figure that the thickness of the ZnS depends on the mounting angle of the sample and it is maximum at 45° substrate tilting angle. Moreover, it has been noted from Fig. 3 that the maximum thickness of deposited film is achieved on the downward face of the silicon substrate whose tilting angle (measured from horizontal bottom) is 45°. Deposition of ZnS film on other surface, which is facing towards upper portion liquid surface, is comparatively less due to large angle of contact with bath solution. The present observations show that the substrate tilting angle of 45° could be the optimum angle for desired film deposition by heterogeneous reaction and optimal necessary persistence of precipitation on the surface under deposition by homogeneous reaction. The actual mechanism of this angular dependence of CBD is still not clear. Arfsten et al [9] have studied the angular dependence of the substrate in dip coating technique for the deposition of optical interference filters. In our study, we have chosen substrate tilting angle of 60° for the deposition of ZnS films because the loading and unloading of large number of wafers is much easier at this angle than at tilting angle of 45°.

The variation of thickness of the CBD ZnS film with time of deposition at a fixed tilting angle of 60° of the silicon substrate and at a deposition temperature of 80 °C is shown in Fig. 4.

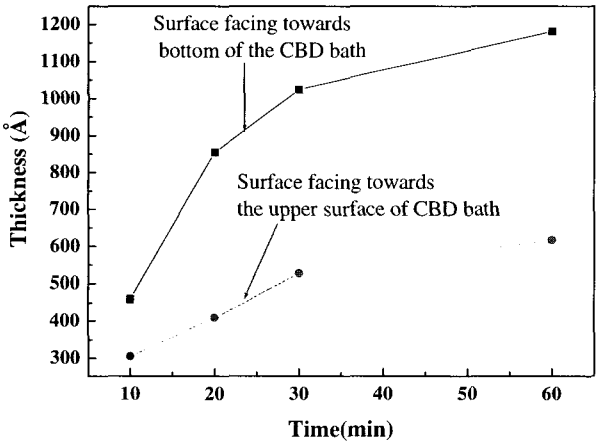

Fig. 4. Variation of as deposited ZnS film thickness with time of deposition at fixed 60° tilting angle in CBD bath and at fixed deposition temperature 80 °C.

It has been observed that the film thickness increases sharply with time up to 30 min and then increases slowly which may be due to more precipitation caused by homogeneous reaction as the times goes on and thus leading to decrease in the growth rate of ZnS film.

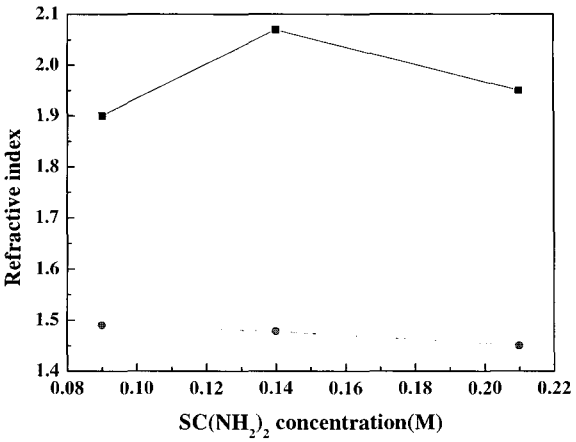

Fig. 5. Variation of refractive index of ZnS films with the concentration of thiourea $\{CS(NH_2)_2\}$ before and after annealing in air at a temperature of 740 °C.

Figure 5 represents the variation of the refractive index of the ZnS films with the concentration of thiourea $\{CS(NH_2)_2\}$ before and after annealing at a temperature of 740 °C. The deposition time was 1 hour for all the films prepared. The films formed with thiourea concentration of 0.14 M and 0.16 M have high refractive indices. The values of refractive indices of all the films reduced to the range of 1.45 to 1.50 after annealing. The reduction is also attributed to the formation of non-stoichiometric oxide phases in the ZnS films. Moreover, the presence of higher atomic percentage of oxygen is revealed from the Energy dispersive X-ray analysis (EDAX) of as- deposited CBD ZnS films (Fig. 6).

This figure indicates the S/Zn ratio of 0.71, which is lower than the value (S/Zn = 0.96) reported in the literature, where thin film of ZnS was prepared by low pressure MOCVD method.

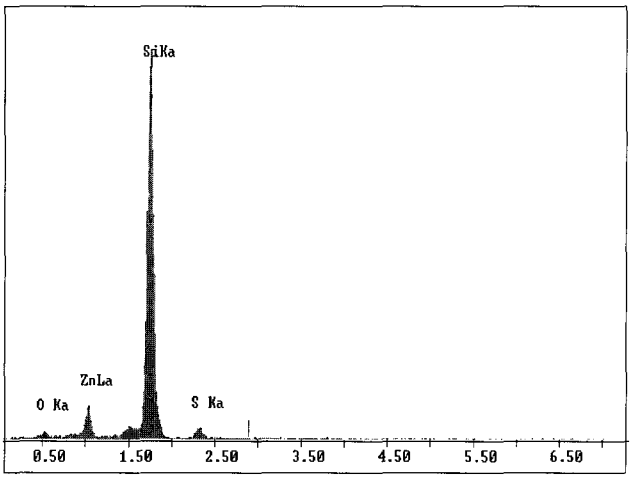

Fig. 6. EDAX spectrum of a typical ZnS film on mono-crystalline silicon surface.

The reflectance dependence on wavelength of CBD ZnS film coated textured mono-crystalline silicon samples are shown in Fig. 7.

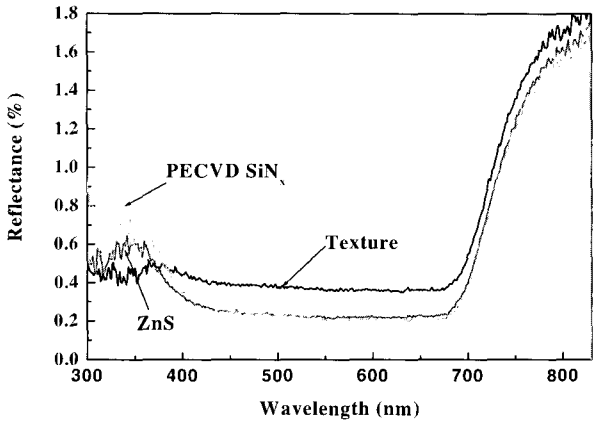

Fig. 7. Reflectance of a typical as-deposited ZnS film along with textured silicon and PECVD silicon nitride coated textured silicon samples respectively.

The reflectance of NaOH textured silicon and PECVD silicon nitride coated silicon samples are also given in this figure for comparison. We have observed that the reflectance of ZnS film, deposited on textured silicon substrate at 0.14 M concentration of thiourea is lower than PECVD SiN_x film at lower wavelength region. This may be due the high refractive index and good chemical stoichiometry of ZnS film.

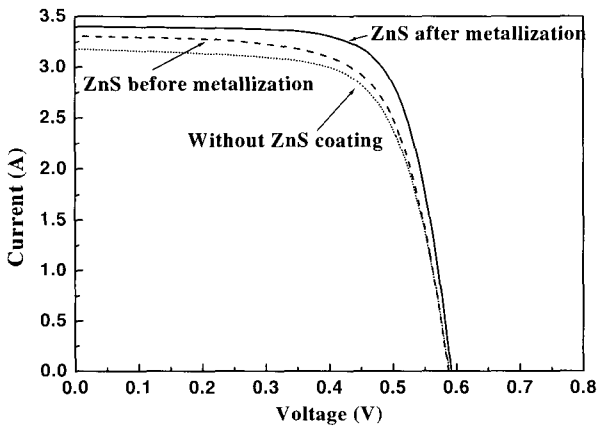

Fig. 8. Illuminated current–voltage (LI-V) characteristics of without and with CBD ZnS ARC using two different coating approach.

From the illuminated I-V (L I-V) characteristic (Fig. 8) and table 1, we have observed that all electrical parameters of the solar cells in which ZnS is deposited after metallization for front and back contacts are better improved than the solar cells with ZnS coating before the metallization and firing in and belt furnace at 740° C .

Table 1. The different electrical parameters of ZnS coating before and after metallization.

Type of Solar cell	V_{OC} (V)	I_{SC} (A)	V_m (V)	I_m (A)	F.F	Eff. (%)
Only textured	0.588	3.20	0.463	2.75	0.68	12.2
ZnS before metallization	0.587	3.35	0.455	2.89	0.67	12.6
Zns after metallization	0.591	3.44	0.476	3.05	0.71	13.9

(V_{OC} = Open circuit voltage, I_{SC} = Short circuit current, V_m = Voltage at maximum power point, I_m = Current at maximum power point, F.F = Fill factor)

Less improvement of all electrical parameters has been noticed in the case of contact made by firing through ZnS ARC film on commercial textured solar cells may be due to the formation of non-stoichiometric ZnO phases during firing. The ZnO, acting as buffer layer for metal penetration, leads to degrade the contact behavior showing the less improvement in electrical performance.

Therefore, we observed a 6.55% gain in short circuit current and 5% gain in overall efficiency by using CBD ZnS films as antireflective coating over large area (103 mm × 103 mm) mono-crystalline silicon solar cell using ZnS film deposited after front and back metal contact formation.

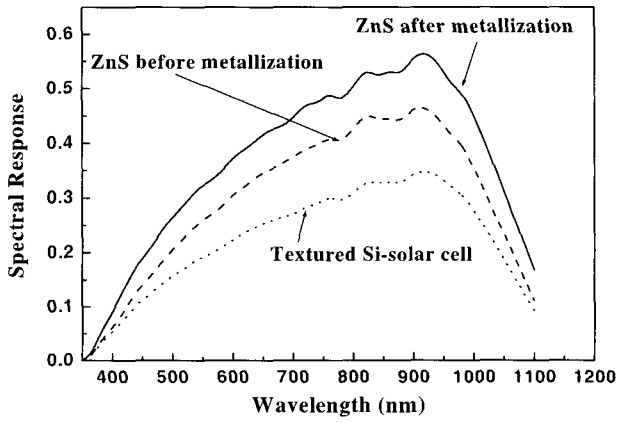

Fig. 9. Spectral response of the fabricated solar cell with and without ZnS ARC using two different CBD ZnS coating approach.

It is seen from the Fig. 9 that the overall spectral response of ZnS coated solar cell (ZnS coating after both metal contacts formation step) has increased substantially, indicating the possibility of CBD ZnS to be used as antireflection coating for large area commercial mono-crystalline silicon solar cell.

4. CONCLUSION

Desirable high rate of film deposition (19.6 Å/min), film uniformity (Std. dev. < 1.8), high value of refractive index (2.35), low percentage of average reflection (0.655) are respectively achieved with proper optimization of ZnS bath. Decrease in refractive index of CBD ZnS film due to high temperature treatment in air ambiance has been pointed out in this paper. We have successfully achieved cells with 13.8% conversion efficiency starting with large area (103 mm × 103 mm) mono-crystalline silicon wafers by using CBD ZnS as antireflection coating on textured surface.

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