Shallow chemical bath deposition of ZnS buffer layer for environmentally benign solar cell devices

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Abstract
Zinc sulfide (ZnS) thin film was grown by a shallow chemical bath deposition (SCBD) technique. In this technique a highly conducting hot plate was used to heat the substrate, while higher thermal gradient was achieved by a shallow bath of the ZnS solution. Consequently, homogeneous nucleation is reduced and quality of ZnS thin films can be improved by shaking. The main advantage of this technique over a traditional one is that the use of solution can be reduced greatly, which is crucial for cost reduction in practice. The effects of shaking on growth kinetics and film properties were investigated by characterizing the as-grown ZnS thin films by x-ray diffraction, transmittance and scanning electron microscopy (SEM).

Keywords: zinc sulfide, shallow chemical bath deposition, optical properties, structural properties
Classification numbers: 4.10, 5.01, 5.03

1. Introduction

Currently, the photovoltaic market is growing continuously and cost reduction to meet the grid parity is an essential issue due to the shrinking of government subsidies. Thin-film based solar cells, mainly those prepared from CdTe and Cu(In, Ga) Se₂ (CIGS), are believed to be a good solution to meet the grid parity target. In these cells, n-type buffer layer materials play a very important role and affect the efficiency as well as the production cost. Conventionally, CdS buffer layers are used in thin-film solar cells to obtain high conversion efficiency. But the use of CdS thin films in solar cell production causes environmental problems due to a high amount of Cd compounds waste and toxic hazards [1, 2]. Hence, investigations to replace these toxic Cd compounds are still ongoing. One possible substitute of CdS may be ZnS. It has a wider energy band gap than CdS, which results in transmission of more high-energy photons to the junction [3]. ZnS with its large band gap is also an important semiconducting material which has vast potential use in thin-film devices, such as photoluminescent and electroluminescent devices. Besides, ZnS could also be used as an important material in short wavelength emitting diodes.

There are several techniques available to deposit ZnS films, for example, thermal evaporation [4], spray pyrolysis [5], sputtering [6], chemical bath deposition (CBD) [7–10], chemical vapor deposition (CVD) [11], successive ionic layer adsorption and reaction (SILAR) [12] and the metal–organic vapor phase epitaxy (MOVPE) [13]. Among them, the CBD method is enormously attractive since this technique acquires several advantages over conventional thin-film deposition methods. The main advantages of the CBD method are low cost, low evaporation temperature, good large area uniformity and coverage [14–16]. In addition, many intrinsic problems associated with high-temperature techniques, including increased point defect concentrations, evaporation and
decomposition of ZnS thin films [17] might also be avoided. The buffer layer deposition by CBD method follows two mechanisms: (i) ion-by-ion (heterogeneous reaction) and (ii) cluster-by-cluster (homogeneous reaction) deposition [18]. The homogeneous deposition leading to powdery and non-adherent films is highly undesirable. However, films deposited by such a process also feature scattering centers and peeling [19]. For a better film quality, the homogeneous process is desirable, in which cation and anion adsorptions take turns to form the semiconductor thin film and yield better film quality. For large-area production there are a few key requirements such as better uniformity, good coverage, no homogeneous nucleation and low cost. The major drawback of CBD technique is the use of the large amount of chemical solution, which drastically increases the product cost. To reduce the homogeneous nucleation, sequentially adding the reactants has been proposed by Bhattacharya [19]. The use of heated substrate has also been used in production [20]. Thin-film deposition using continuous CBD has also been proposed [21]. Recently, we have deposited CdS thin films by shallow CBD technique and found the qualities of the as-grown films are quite good [22]. In the industrial manufacturing of CIGS solar modules, both the low material yield and the relatively high amount of waste cause high production costs as well as environmental problems. To resolve these problems, works have been done by several authors [23–26].

In the present work we proposed the deposition of n-type ZnS buffer layer by a simple process i.e. shallow CBD. In this technique a heated substrate with the highly-conductive metal is used at the bottom to maintain thermal uniformity. On the other hand, due to the use of the shallow depth of the solution, only a small amount of solution was used. Hence the cost for the post treatment is greatly reduced. Another important advantage of this technique is that it is rather fast as compared to traditional CBD. To observe the effect of shaking we have prepared ZnS thin films using both conditions i.e. with and without shaking conditions. The structural, surface morphological and optical properties of the prepared films are also studied.

2. Experimental

Before developing ZnS films on glass substrates, a cleaning process was applied to the substrates. First, the glass substrates were put into a cup of distilled water and kept there for 10 min to remove contaminants such as dust on their surfaces. Then they were taken from the cup and dried. To remove the remaining contaminants all substrates were ultrasonically cleaned with acetone and rinsed with deionized water, and subsequently dried. After completing the cleaning processes of the substrates, solutions were used for forming ZnS films on the surface of the substrates. ZnS films were prepared using the solution of analytical grade with purity over 99.9% of 0.7 M thiourea (CS(NH$_2$)$_2$) as S ion source, (0.3 M) ZnSO$_4$ as Zn ion source in the presence of 7 M ammonium hydroxide (NH$_4$OH). The prepared solution was first homogenized by stirring with a small magnetic bar, and the pH value was kept at 10–11. The solution temperature was kept nearly 80 °C, where the temperature was measured by a thermocouple. Films were then deposited on 60 mm×60 mm×1 mm glass substrates using the apparatus shown in figure 1. A highly conducted hot plate made of copper was used to heat the substrate, and this ensured the temperature uniformity for the substrate. Because the cooling is from the top due to evaporation and convective heat transport, higher thermal gradients could be obtained with the shallow bath. Consequently, the homogeneous nucleation could be reduced. After that the glass substrates were kept horizontally on the Cu plate. On the glass substrate we used an O-ring to define the growth zone. Then, the solution was added up to about 2 mm in depth. This technique has the following advantages: higher thermal gradients can be obtained with the shallow bath, consequently homogeneous nucleation could be abridged and wastage of a large amount of solution can stop. After deposition, the ZnS films were washed ultrasonically to remove the loosely adhered ZnS particles on the film and finally dried in air.

The structural characterization of the films was carried out by the x-ray diffraction (XRD) technique using a M21X-SRA (MAC Science Co. Ltd, Kanagawa, Japan). The operating conditions were as follows: target Cu, voltage 50 kV, current 100 μA, scan range: 10–70°, scan size: 0.03°, and count time: 0.4 s/point. The transmission spectra were recorded in the range of 300–600 nm by a Shimadzu UV-Vis spectrophotometer. The surface morphology of the ZnS films was analyzed by scanning electron microscopy (Jeol, Japan: JSM-6390 LV).

3. Results and discussion

It is well known that the growth of thin films by CBD occurs mainly through two processes: (i) ion-by-ion (heterogeneous reaction) or (ii) cluster-by-cluster (homogeneous reaction) deposition [18]. The homogeneous deposition leading to powdery and non-adherent films is highly undesirable. For a better film quality, the heterogeneous process is desirable. In CBD process, ZnS thin films can be prepared by decomposition of thiourea in an alkaline solution containing zinc salt and a suitable complexing agent (NH$_3$) which allows for obtaining a soluble species of ZnS in this medium. The deposition process is based on the slow release of Zn$^{2+}$ and S$^{2-}$ ions into solution which then condense on an ion–ion basis on the substrate. In our experiment we have used zinc sulfate and thiourea as source materials. Precipitation control
during deposition has to be done by controlling the concentration of free Zn$^{2+}$ ion in the shallow bath. In the solution, ZnSO$_4$ was divided into two separate ions of Zn$^{2+}$ and SO$_4^{2-}$.

The decomposition of the thiourea is given by [2]:

\[
\text{CS(NH$_3$)$_2$ + OH}^- \rightarrow \text{SH}^- + \text{CH$_3$N$_2$ + H$_2$O},
\]

\[
\text{SH}^- + \text{OH}^- \leftrightarrow \text{S}^{2-} + \text{H$_2$O},
\]

\[
\text{Zn}^{2+} + \text{S}^{2-} \leftrightarrow \text{ZnS}.
\]

This direct reaction of ZnS preparation is called homogeneous reaction and films produced in this way have a rough topology and low optical transmittance. To diminish this process, ammonia is used to form complex ions with the metal ions:

\[
\text{NH}_3^+ + \text{OH}^- \leftrightarrow \text{NH}_4^+ + \text{H}_2\text{O},
\]

\[
\text{Zn}^{2+} + 4\text{NH}_3 \leftrightarrow \text{Zn(NH$_3$)$_4}^{2+}.
\]

These complex ions and the sulfide ions migrate to the substrate surface, where they react to form ZnS (heterogeneous process).

\[
\text{Zn(NH$_3$)$_4}^{2+} + \text{S}^{2-} \leftrightarrow \text{ZnS} + 4\text{NH}_3.
\]

Due to large temperature gradients in the shallow CBD system, the homogeneous nucleation was minimized. On the other hand, one major problem in the traditional CBD system, where the solution and the substrates are heated homogeneously, is that the efficiency of the deposition process is low due to the homogeneous precipitation and deposition on the reactor walls. Again, this problem could be resolved by the shallow CBD with the heated substrate at the bottom; the direct heating of the CBD substrate limits the undesirable homogeneous reactions. The films obtained by this method were uncolored, smooth, homogeneous and adherent.

The structures of the ZnS films grown on glass substrates were determined by x-ray diffraction (XRD) with Cu-K$_\alpha$ radiation. Generally, ZnS exists in two forms, cubic and hexagonal. The cubic form is stable at room temperature, while the less dense hexagonal form is stable at high temperatures. Figure 2 shows reordered XRD patterns of ZnS films deposited by shaking and without shaking conditions. The diffraction peaks at 28.5°, 47.5° and 56.3° were assigned to the (111), (220), and (311) planes of the cubic zinc blend structure. The high noise content of the XRD graph did not allow identification of other phases, e.g. Zn(OH), ZnSO$_3$.

Recently, Kang et al [27] and Limei et al [28] have also observed the high noise content of the XRD in ZnS thin films. In the XRD patterns the peaks are wider, which indicate that the films were basically amorphous or microcrystalline. Our observed results (position of diffraction peaks) are in good agreement with the previous reports [27, 28].

The optical transmittance spectra of ZnS films deposited with and without shaking conditions, in the wavelength range of 300–600 nm, are shown in figure 3. As can be seen from figure 3, both the films are highly transparent in the visible region and present a steep absorption edge at a wavelength of about 300 nm. It can also be easily noticed that under shaking condition the transmission was increased and reached in the
range of 80 to 85% of transmittance, while in the without shaking condition the transmission range was observed in the range of 70 to 75%. In other words, the films deposited under shaking condition have high transmission in the visible region, which is desirable for enhancing the short-circuit current. Hence, these films could be used as the buffer material in solar cells. Furthermore, the absorption coefficient $\alpha$ of the thin films was calculated from the transmittance spectra using Beer–Lambert’s law and was analyzed using the following expression for near-edge optical absorption of semiconductors:

$$\alpha \nu = k \left( h \nu - E_g \right)^{n/2},$$

where $k$ is constant, $E_g$ is the band gap, and $n$ is a constant that is equal to 1 for direct band gap semiconductors. The band gap ($E_g$) of the films, calculated by plotting the square of the product of absorption coefficients and photon energy $(\alpha \nu)^2$ versus photon energy $(h \nu)$ are shown in figure 4. Accordingly, the band gap is obtained by extrapolating the straight portion of the curve to zero absorption coefficient and the values are found to be 3.58 and 3.67 eV for the ZnS thin films deposited under without shaking and shaking conditions, respectively. The values of band gap for the films are very close to that of bulk cubic ZnS (3.54 eV) and smaller than that of hexagonal ZnS (3.91 eV). This confirms that the deposited films belong to cubic zinc blend structure. However, a higher band gap value of deposited thin films, as compared to bulk ZnS, is probably due to the quantum size effect and are found in good agreement with earlier reports [8].

Figure 5 illustrates the scanning electron microscopy (SEM) micrographs of the surfaces of the deposited ZnS films. To achieve better uniformity we have also deposited the films by shaking condition. A complete substrate coverage and better uniformity, which is very important for the devices, has been achieved by shaking condition in the deposited ZnS thin film. The film thickness of the deposited films is found to be in the range 35–50 nm.

4. Conclusion

In this study, good quality ZnS thin films were grown on glass substrates by a shallow CBD technique under both shaking and without shaking conditions. The problems of low materials yield as well as the production of a large amount of waste solution could be greatly reduced. The results of ZnS thin films grown by the shallow CBD technique agreed well with the reported results indicating the shallow CBD is a promising tool for thin-film deposition. The morphology and optical properties of ZnS thin films deposited under shaking condition are found to be improved. Both the films grown by shallow CBD at different temperatures had very good transmittance, hence these films could be used as the buffer material in solar cells.

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