Crystalline Structure and Optical Properties of Cd$_{1-x}$Zn$_x$S Thin Films Prepared by CBD

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Abstract. Cd$_{1-x}$Zn$_x$S thin films were deposited on glass substrates by chemical bath deposition. The influence of $x$ on the crystalline structure, surface morphology and optical properties of Cd$_{1-x}$Zn$_x$S thin films were studied by measures of XRD, SEM, and spectrophotometer, respectively. The SEM images indicated that, with the increase of $x$, the particles of Cd$_{1-x}$Zn$_x$S changed from small and compact to larger and sparser, which was thought to be the transformation of two reaction mechanisms in the deposition process, from ion-by-ion process to cluster-by-cluster process. The average transmittance values of Cd$_{1-x}$Zn$_x$S samples in visible spectrum were all above 70%, and the band gaps of the Cd$_{1-x}$Zn$_x$S thin films varied from 2.47 eV to 3.66 eV during the $x$ from 0 to 1.

Introduction

Buffer layer is an important part in copper zinc tin sulfide (CZTS) thin film solar cell, which is connected to ZnO window layer and CZTS absorption layer. It plays the role of reducing the lattice mismatch and optimizing energy band structure$^{[1]}$. Currently, the commonly used buffer layer material is Cadmium sulfide (CdS), which has the appropriate band gap (2.42 eV$^{[2]}$) and high transmittance. At present, the highest conversion efficiency of CZTS thin film solar cell is 12.6%$^{[3]}$, and the buffer layer material used in this solar cell is CdS. However, the heavy metal element Cd tends to bring environmental pollution. Zinc sulfide is a direct-gap semiconductor with a band gap of 3.6–3.8 eV$^{[4]}$. It can improve the spectral response in short wave range, so that it can improve the short circuit current and photoelectric conversion efficiency$^{[5]}$. Unfortunately, the crystallinity of ZnS thin film is not as good as CdS thin film$^{[6,7]}$. The conversion efficiency of thin film solar cell using ZnS buffer layer is not as high as that using CdS buffer layer.

Considering the advantages of CdS and ZnS thin films, a kind of three-element compound Cd$_{1-x}$Zn$_x$S$^{[8]}$ was studied. It has low Cd content and wider band gap compared with CdS, so that it can improve the spectral response in short wave range. Besides, Cd$_{1-x}$Zn$_x$S has better crystallinity and surface morphology than ZnS. Most of all, the energy band gap value of this material is alterable by changing Zn content$^{[9]}$.

The methods of buffer layer preparation are$^{[10–14]}$: chemical bath deposition (CBD), electrochemical deposition, magnetron sputtering, and close space sublimation, metal organic chemical vapor deposition (MOCVD), etc. CBD is applied frequently in preparing CdS and ZnS buffer layers. This method has advantages of simple operation and good film uniformity$^{[15]}$. But there are few reports about Cd$_{1-x}$Zn$_x$S films prepared by CBD method. In this article, CBD method was used preparing Cd$_{1-x}$Zn$_x$S thin films, and the influence of $x$ on the properties of thin films was discussed.
**Experiment**

The Cd$_{1-x}$Zn$_x$S buffer layers were prepared on glass substrates using CBD method. Slide glasses with the size of 25.4 mm×76.2 mm×1.2 mm were used. Cadmium acetate (Cd(CH$_3$COO)$_2$), zinc sulfate (ZnSO$_4$) and thiourea (SC(NH$_2$)$_2$) were used as the source materials of Cd$^{2+}$, Zn$^{2+}$, S$^2-$, respectively. Ammonia (NH$_3$·H$_2$O) and sodium citrate (Na$_3$C$_6$H$_5$O$_7$) were used as complexing agent, ammonium acetate (CH$_3$COONH$_4$) was used as pH stabilizer. Before deposition, the glass substrates were first immersed in dilute hydrochloric acid for 20 minutes, then ultrasonic cleaned in acetone, anhydrous ethanol, deionized water for 20 minutes, respectively. In order to study the effects of Zn aggregation, the mixture ratio x was defined as $x=[\text{Zn}^{2+}]/([\text{Cd}^{2+}]+[\text{Zn}^{2+}])$.

The structural properties of Cd$_{1-x}$Zn$_x$S thin films were examined by X-ray diffraction (XRD) (Rigaku ultima IV) with the glancing angle mode. The system operates with Cu Kα ($\lambda=0.15406$ nm), scanning speed was 6° per minute, scanning range was from 20° to 80°. The thickness of Cd$_{1-x}$Zn$_x$S thin films were examined by profile meter (KLA Tencor P-6). The surface morphologies and elemental composition were obtained by scanning electron microscopy (SEM) (Hitachi S4800) and EDX system. The optical band gaps of the films were calculated from the transmission spectra obtained with a UV/VIS spectrophotometer (Shimadzu UV-3600) in the wavelength range of 300~900 nm.

**Results and Discussion**

The X-ray diffraction patterns of Cd$_{1-x}$Zn$_x$S samples were shown in Figure 1. The XRD pattern of CdS has six diffraction peaks on the crystal planes of (100), (002), (101), (110), (103), (112), which shows a hexagonal structure without any secondary phases. Similarly, the XRD pattern of ZnS films has three main diffraction peaks on the crystal planes of (111), (220), (311), which shows a cubic structure without any secondary phases. The crystal form of the samples gradually changes from hexagonal to cubic structure with increase of the mixture ratio x. A change in the preferential growth orientation is observed from a decrease on the intensity of the (002) peak and an increase of the (101) peak, which is caused by the formation of stress produced by the lower ionic radii of Zn$^{2+}$ (0.74 Å) substituting Cd$^{2+}$ (0.97 Å) sites in the crystalline lattice and their segregation in the grain boundaries$^{[16]}$.

![Figure 1. X-ray diffraction patterns of the Cd$_{1-x}$Zn$_x$S thin films.](image)

The atomic percentages of the films obtained from the EDX analysis were shown in Table 1. The Zn content increases with the increase of x, but the actual ratios of Cd:Zn in films have almost no
quantitative relationship with the ratios in solutions, especially the Zn content is not as much as initial content in the solution. This may be due to the discrepancy of the deposition rates between CdS and ZnS. In addition, the solubility products \(^{[17]}\) of CdS \((K_{sp}=2 \times 10^{-28})\) and ZnS \((K_{sp}=1.2 \times 10^{-23})\) are different by several orders of magnitude, so that the CdS is easier to be deposited than ZnS.

Table 1. Elemental content of Cd\(_{1-x}\)Zn\(_{x}\)S thin films.

<table>
<thead>
<tr>
<th>x</th>
<th>Molar concentration (mmol/L)</th>
<th>Elemental content (at%)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cd(CH(_3)COO)(_2)</td>
<td>ZnSO(_4)</td>
<td>SC(NH(_2))(_2)</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>0.2</td>
<td>4</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>0.5</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>0.8</td>
<td>1</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

All the samples were uniform and transparent. The color of Cd\(_{1-x}\)Zn\(_x\)S films changed from orange to light yellow with the increase of x. The CdS films were composed by some small spherical granules and aggregates, as shown in Fig 2(a). These aggregates were formed in solution and moved to the substrate, so their size was larger. Besides, the surface morphologies of ZnS films were similar to CdS, but the particles of ZnS were larger and sparser than CdS, as shown in Figure 2(e). When Zn\(^{2+}\) was added in the reaction solution, the surface morphologies of Cd\(_{1-x}\)Zn\(_x\)S films gradually tend to ZnS, the particles became larger and sparser, as shown in (b), (c) and (d) of Fig 2.

We think that this phenomenon may be due to the two reaction mechanisms in the deposition solution. The first is an ion-by-ion process, in which ions condense on the reacting surface to form a film via a heterogeneous reaction. The second is a cluster-by-cluster process, in which colloidal particles (e.g., Cd\(_{1-x}\)Zn\(_x\)S, CdS, ZnS, Zn(OH)\(_2\) and Cd(OH)\(_2\)) preformed in solution via a homogeneous reaction agglomerate and then adsorb on the substrate to form a film. According to Yubo Duan et al. the CdS thin films they prepared by CBD was compact and smooth, but the grain size was small, which was attributed to the heterogeneous reaction\(^{[18]}\). The morphology of their CdS thin film is very similar to Figure 2(a) of this study, therefore, it can be concluded that the CdS thin film we deposited was formed via heterogeneous reaction. Seen from Figure 2(e), it is obvious that the ZnS thin film we prepared consists of large particles and exhibits poor compactness which is in good agreement with the result of Aixiang Wei et al. and their ZnS film growing on the substrate involves cluster-by-cluster mechanism and thus the film comprises of large particles formed by aggregation of ZnS colloid particles in solution\(^{[19]}\).

![Image](a)

![Image](b)
To our knowledge, there has been no reports about the increase of grain size with increasing the Zn$^{2+}$ concentration for preparing Cd$_{1-x}$Zn$_x$S thin film, while in this paper, the grains of Cd$_{1-x}$Zn$_x$S became larger and sparser with increasing the mixture ratio x, which can be inferred that when the solution only contains Cd$^{2+}$, the first progress is dominated, namely heterogeneous reaction. However, the homogeneous reaction gradually becomes the main mechanism with increasing Zn$^{2+}$ concentration in the same solution environment, this phenomenon may be because Zn$^{2+}$ is more electronegative than Cd$^{2+}$ and easier to absorb anions to form colloidal particles in the solution and then deposit on the substrate.
Figure 4. Plot of the \((a\nu)^2\) versus photon energy for the optical band gap determination of the deposited Cd\(_{1-x}\)Zn\(_x\)S films.

The transmission spectra of Cd\(_{1-x}\)Zn\(_x\)S films with different components were shown in Figure 3, which indicates that the average transmittance values in visible spectrum of samples were all above 70\%, and the absorption edge of the films shows an obvious blue shift with the increase of Zn content, which implies a variation of the energy band gap.

As for direct-gap semiconductor thin films, the relationship between band gap and absorption coefficient is \(^{[20]}\):

\[
\alpha h\nu = A(h\nu - E_g)^{1/2}
\]

Where \(\alpha\) is the absorption coefficient, \(E_g\) is the optical band gap, and \(h\nu\) is the photon energy. The values of absorption coefficient are calculated by the following equation:

\[
\alpha = -\frac{\ln T}{d}
\]

Where \(T\) is the transmittance of Cd\(_{1-x}\)Zn\(_x\)S thin films, and \(d\) is the thickness of films. \((a\nu)^2\) is plotted as a function of \(h\nu\), as shown in Figure 4. The band gap is obtained by extrapolating the straight portion of the curve to zero absorption coefficients \(^{[21]}\).

The calculated band gap value was shown in Table 2. The energy band gap shifts from 2.47 eV to 3.66 eV with ratio \(x\) changing from 0 to 1. By means of second order approximation, the calculated relationship between band gap and the ratio \(x\) of Cd\(_{1-x}\)Zn\(_x\)S thin films can be expressed by the following equation:

\[
E_g = 2.5 + 0.83x + 0.33x^2
\]

In ref. [22], the relationship between band gap and the ratio \(x\) of Cd\(_{1-x}\)Zn\(_x\)S body material is:

\[
E_g = 2.42 + 0.9x + 0.3x^2
\]

<table>
<thead>
<tr>
<th>Mixture ratio (x)</th>
<th>Band gaps of Cd(_{1-x})Zn(_x)S thin films (eV)</th>
<th>Band gaps of Cd(_{1-x})Zn(_x)S body materials (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.47</td>
<td>2.42</td>
</tr>
<tr>
<td>0.2</td>
<td>2.68</td>
<td>2.61</td>
</tr>
<tr>
<td>0.5</td>
<td>3.0</td>
<td>2.95</td>
</tr>
<tr>
<td>0.8</td>
<td>3.38</td>
<td>3.33</td>
</tr>
<tr>
<td>1</td>
<td>3.66</td>
<td>3.62</td>
</tr>
</tbody>
</table>

The band gaps of Cd\(_{1-x}\)Zn\(_x\)S thin films and Cd\(_{1-x}\)Zn\(_x\)S body materials were shown in Table 2. At
the same ratio \( x \), the band gap of \( \text{Cd}_{1-x}\text{Zn}_x\text{S} \) thin film shows a small blue shift compared with \( \text{Cd}_{1-x}\text{Zn}_x\text{S} \) body material. This can be due to the quantum confinement effect, which means electronic states near the Fermi level changes from in continuous variable to the quasi-discrete level, the band gaps broaden when the particle size is reduced to a certain value.

**Conclusion**

\( \text{Cd}_{1-x}\text{Zn}_x\text{S} \) thin films were prepared by chemical bath deposition. The results show that, as the increase of the mixture ratio \( x \), the Zn content increased, the crystal structure gradually changed from hexagonal to cubic structure, and more importantly, the particles became larger and sparser, which was caused by the change of thin film growth mechanism (from ion-by-ion process to cluster-by-cluster process). The average transmittance values in visible spectrum of samples were all above 70%. The energy band gap values of the films shifted from 2.47 eV to 3.66 eV, and they showed a small blue shift compared with \( \text{Cd}_{1-x}\text{Zn}_x\text{S} \) body materials.

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**References**


