Dynamic scaling and optical properties of Zn(S, O, OH) thin film grown by chemical bath deposition*

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The scaling behavior and optical properties of Zn(S, O and OH) thin films deposited on soda-lime glass substrates by chemical bath deposition method were studied by combined roughness measurements, scanning electron microscopy and optical properties measurement. From the scaling behaviour, the value of growth scaling exponent β, 0.38±0.06, was determined. This value indicated that the Zn(S, O, OH) film growth in the heterogeneous process was influenced by the surface diffusion and shadowing effect. Results of the optical properties measurements disclosed that the transmittance of the film was in the region of 70%–88% and the optical properties of the film grown for 40 min were better than those grown under other conditions. The energy band gap of the film deposited with 40 min was around 3.63 eV.

Keywords: roughness, growth behaviour, Zn(S, O, OH), optical properties

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1. Introduction

ZnS is one of the important semiconductor materials. It has been used as the buffer layer in the $Cu(In,Ga)Se_2$ (CIGS) solar cell because of its potential properties.[1−4] ZnS can not only increase the response in the short wavelength region, but also reduce the band offset between the buffer layer and ZnO layer in the CIGS solar cell. In order to avoid the CIGS film to be destroyed from the ion sputtering during the film growth, ZnS film is generally deposited by chemical bath deposition (CBD).[5−10] Up to now, ZnS film fabricated by this method has been used as the buffer layer of the CIGS thin film solar cell successfully with an efficiency of 18.6%.[11]

In order to further improve the solar cell efficiency, ZnS film with good physical properties should be obtained. It is reported that the electrical, optical and mechanical properties of a thin film depend on to an extent the surface morphology. [12,13] Therefore, a systematic understanding of the film growth behaviour is a good approach for predicting film properties and allowing a better control of the film properties. Scaling concept, relating the thin film growth behaviour to the scaling exponents, can be used to describe the dependence of the surface roughness on the film thickness and lateral length scale. Theoretical and experimental studies have been carried out to describe and predict the statistical properties of the morphology of the films grown under conditions far from the equilibrium.[14] Up to now, this concept has been successfully used to explore the films growth behaviours, including inorganic and organic materials.[15−17] However, the growth behaviour of ZnS film grown by CBD method is less investigated despite the key role of ZnS film in CIGS solar cells. Hence, an understanding of the factors which determine the film morphologies during kinetic growth is necessary, for both the fundamental and technological properties.

In this paper, we apply the scaling theory to characterize the growth behaviour of ZnS film obtained by CBD method. After revealing the growth behaviour, optical properties of the ZnS films are studied.

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2. Experiment

ZnS films were grown onto soda-lime glass by CBD method. The films were prepared from aqueous solutions, composed of analytical-grade reagents zinc sulfate, thiourea and 25% ammonia at 81 °C, and stirred by a stirrer at 375 rpm. The concentrations of solutes were 0.025, 0.27, and 2.9 mol/L for zinc sulfate, thiourea and ammonia, respectively. The soda-lime glass substrates were cleaned by deionised water in an ultrasonic cleaner and dried with N_2 for ZnS film deposition.

After the substrate was taken out from the solution, it was cleaned with deionised water and dried with N_2. The film thickness and roughness were measured using an AMBLOS XP-2 profilometer (since the film is transparent, we use profilometer to measure roughness but not AFM). X-ray fluorescence (XRF) spectrometer was used to characterize the film composition. The film surface was characterized by XL30 S-FEG scanning electron microscope (SEM) systems. The surface structure was studied with grazing-incident X-ray diffraction (GIXRD) on the Panalytical X'Pert Pro diffractometer with Cu K_α radiation ($\lambda = 1.5416$ Å). The transmission measurements were made by UV-IR spectrophotometer Varian.

3. Results and discussion

3.1. Film phase and structure

The film composition is measured by XRF (Fig. 1). Because oxygen and other light atoms cannot be measured by XRF accurately, only the contents of S and Zn are measured and reported here. The S/Zn ratio increases with increasing deposition time, but it is much lower than 1, i.e., the film is not the exact ZnS and more Zn exists in the deposited film. Chen *et al.*[18] claimed that before ZnS formation on the substrate, $Zn(OH)_2$ would be formed first by $Zn^{2+}+2OH^- \rightarrow Zn(OH)_2$ because of its large solubility. Nakada *et al.*[19] thought that oxygen atoms in the ZnS film deposited by CBD method might exist in the compounds of ZnO and $Zn(OH)_2$. In our study, the solution used for film deposition is alkaline. Therefore, according to our XRF results, the film grown in this study should also contain oxygen and OH^-. The phase in the film is most possibly Zn(S,O,OH).

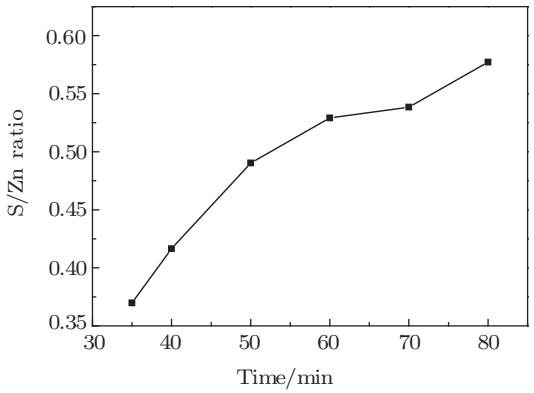


Fig. 1. S/Zn ratio of the Zn(S,O,OH) films.

The surface structures of Zn(S,O,OH) films grown by CBD method are characterized by GIXRD, which is sensitive to the penetrating depth in the film and can disclose the surface structure. The grazing incident angles for all the films are 0.3°. Figure 2 is the corresponding X-ray patterns. With the increasing deposition time, the very weak Bragg peaks of cubic ZnS phase could be detected in the films. This indicates that the Zn(S,O,OH) will transform from an amorphous film grown for a short deposition time to a partially crystallized cubic ZnS film grown for a longer deposition time.

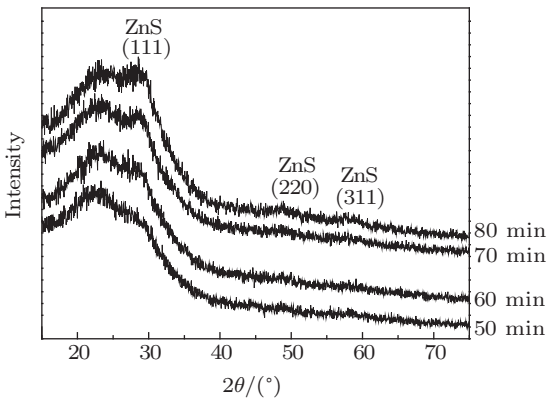


Fig. 2. Selected GIXRD patterns of Zn(S,O,OH) films deposited with different deposition time.

3.2. Dynamic scaling of Zn(S,O,OH) films

The film thickness as a function of deposition time for the Zn(S,O,OH) thin films on glass substrate is shown in Fig. 3. In our experiment, if the substrate is dipped into the solution just a short time, Zn(S,O,OH) film obtained is thin and discontinuous. Thus, only those films deposited over 35 min are characterized. It can be seen from Fig. 3 that two different growth regions exist in the whole growth process, which is

the same as that in our former research.[17] The quasi-linear region I depicts the film growth in the heterogeneous process, in which the film is grown ion-by-ion on the substrate surface; and the saturation region II is the homogeneous growth process in which the film is mostly grown in the cluster-by-cluster manner. This is also shown in the changes of roughness (Fig. 3(a)). In region I, the film roughness changes slowly because of ion-by-ion growth on the substrate. When the growth goes through region I into region II, the film roughness goes up rapidly because of cluster-by-cluster adsorption on the Zn(S,O,OH) film.

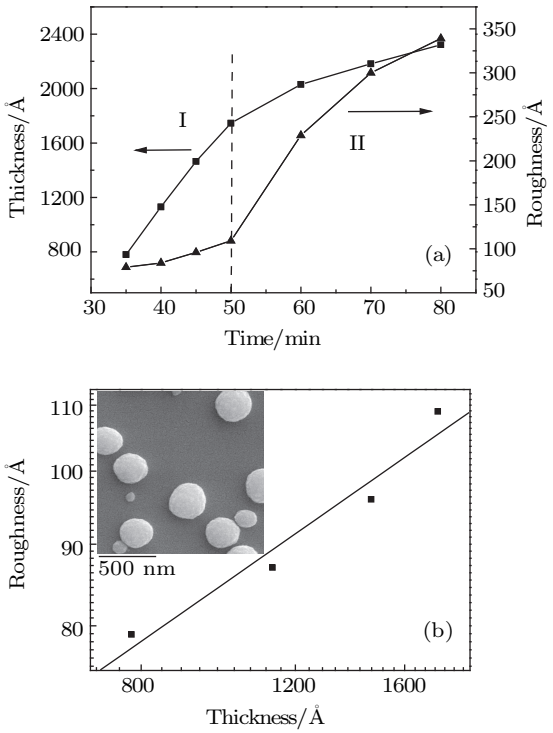


Fig. 3. (a) Thickness and roughness of Zn(S,O,OH) films versus deposition time, and (b) plot of film roughness in region I versus thickness (from the slope of this plot, the growth scaling exponent β of 0.38 ± 0.06). The insert in (b) is the SEM topographic image of Zn(S,O,OH) grown with 40 min.

According to the correlation between the roughness σ and thickness D for the self-affine growth,[14] we have

$$\sigma \sim D^{\beta}, \tag{1}$$

where β ($\beta < 1$) is the growth scaling exponent. The surface roughness scaling characteristic, which is related to the electro-optical properties of photonic devices, [20] could be determined by the power law expressed by Eq. (1). The growth scaling exponent β of Zn(S,O,OH) grown in region I can be determined as 0.38 ± 0.06 from Fig. 3(b). This value is smaller than that of random deposition, 0.5,[14] and larger than that of the process depicted by KPZ equation.[21] Thus, the growth of Zn(S,O,OH) cannot be carried out by random deposition or described by KPZ nonlinear function.

As for the film deposited from solution, very less reports on its growth behaviour are available. Recently, Lafouresse *et al.* have studied the growth of thick electrodeposited film.[22] The β value in their study is 0.29 ± 0.05 when the solution is stirred, but they do not discuss it further. Maybe we could perform the similar research in which the film is deposited in vacuum to analyse the scaling behaviour of Zn(S,O,OH) film grown by CBD method.

Roennow *et al.*[23] proposed that the roughness growth was the sum of three processes: (a) additive roughness from the deposition process, (b) smoothing effects due to surface diffusion, and (c) shadowing effects, which cause preferential growth of surface roughness at a specific length scale. Theoretical and experimental studies indicate that the value of β is larger than 0.5 when the shadowing mechanism dominates the growth process.[24,25] However, without shadowing, i.e., surface diffusion dominates the growth process, the growth exponent value is 0.25.[26,27] In this study, the β value is 0.38 ± 0.06, which is larger than the value from the process without shadowing, but smaller than that with shadowing. Therefore, the growth mechanism cannot be simply described by either shadowing effect or surface diffusion.

It is accepted that the surface diffusion is thermally activated and depends on the deposition potential.[14,28] Surface diffusion will receive benefit from a high substrate temperature. The growth temperature of 81 °C in this study is in favour of the surface diffusion, which will decrease the deposition potential of the ions and the absorbed ions can experience a good surface diffusion before they collide with each other. However, stress will be developed during the film growth even with such surface diffusion. In addition, the lattice mismatch between the glass substrate and Zn(S,O,OH) film will also lead to the stress. Hayakawa *et al.*[29] conclude that the stress from the film and substrates will have a great influence on the film growth mode and the film growth mode will change from layer-by-layer to layer-island. Therefore, stress formed in the Zn(S,O,OH) film will affect the film growth and some ions will collide with each other in advance. It needs to indicate that though the Zn(S,O,OH) film is grown in heterogeneous process in

Region I, some colloids formed in the solution will be absorbed onto the flat surface, as shown in the insert in Fig. 3(b), which is the SEM topographic image of the film deposited for 40 min. Such an adsorbed species can also affect the surface transport of the deposited atoms as a shadow.[28] Thus, the shadowing effect from the stress and absorbed colloids cannot be neglected. Recently, Dolatshahi-Pirouz *et al.* studied the growth of Pt film by oblique angle deposition.[30] They found that shadowing effects cannot be ignored and the growth is affected by both surface diffusion and shadowing effects based on the β value changing from 0.26 ± 0.01 to 0.49 ± 0.04. From the above discussion and the value of the growth scaling exponent in this study, we conclude that the most plausible growth process observed in Region I is the combination of surface diffusion and shadowing effect for the film deposited by CBD method.

As for the growth in Region II, Zn(S,O,OH) film is grown in the homogeneous process and it is not self-affine. Thus, Eq. (1) cannot be used to depict the growth scaling characteristics. The growth mechanism in Region II needs to be studied further.

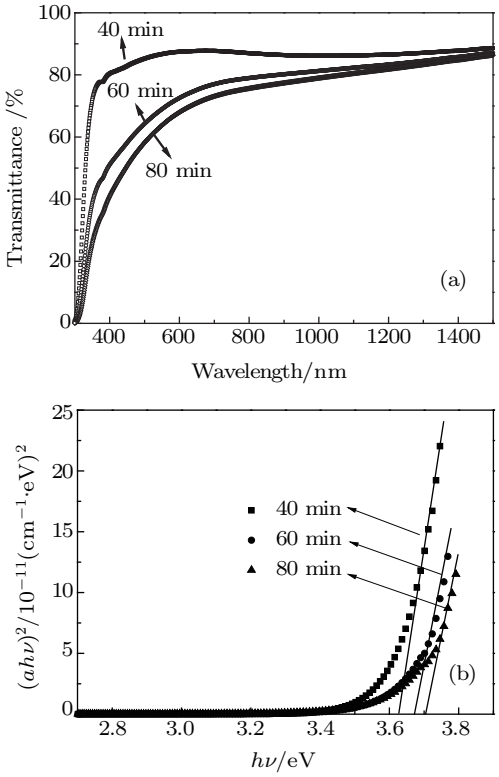


Fig. 4. (a) Optical transmission spectra of the selected Zn(S,O,OH) films, and (b) plot of $(\alpha h\nu)^2$ versus photo energy $h\nu$ for the corresponding Zn(S,O,OH) thin films.

3.3. Optical properties

Figure 4(a) shows the optical transmittance of Zn(S,O,OH) films deposited on glass substrates at 81 °C with the deposition time changing from 40 min to 80 min. It can be seen that the samples' transmittance increases rapidly at $\lambda = 320$ nm. This optical property is nearly the same as that of ZnS film. In our study, the as-grown film is Zn(S,O,OH). Besides ZnS, other phase, such as ZnO, will also contribute to the optical properties of the films. However, the main phase of the film is cubic ZnS, as shown in Fig. 2. This is why the optical properties of the as-grown films are nearly the same as that of ZnS film. Besides, it can be seen that the transmittance is 70%–88% when the wavelength is larger than 620 nm. In addition, the value we obtained is a distinctive result. The optical properties of the films grown in the heterogeneous region are better than those grown in the homogeneous region in the short wavelength range, especially for the film deposited for 40 min, its absorption edge becomes upright and the transmittance in long wavelength region is close to 90%.

In the heterogeneous process, the film forms in the ion-by-ion way and it is compact, which is good for optical transmittance. In addition, the growth by this heterogeneous process is influenced by the surface diffusion and the shadowing effect. When deposited for a short time, surface diffusion is predominant and a film with good quality can be formed. With increasing deposition time, the shadowing effect will increase gradually for the film growth, especially for the film grown by the homogeneous process (deposition time is larger than 50 min). And the film surface is covered by lots of colloids and roughening. This will deteriorate the optical properties of the film, as shown in Fig. 4(a).

The band gap of a semiconductor could be obtained from the optical data. For a direct band gap material, the absorption coefficient α is related to the incident photon energy $h\nu$ by the relation

$$\alpha h\nu = A(h\nu - E_{\mathrm{g}})^{1/2}, \tag{2}$$

where A is a constant, E_{g} is the band gap of the semiconductor. The band gap is determined from the intercept of the straight-line portion of the $(\alpha h\nu)^2$ versus the incident radiation energy $h\nu$. The band gap values determined from Fig. 4(b) increase slightly with

the increasing deposition time. For the film deposited for 40 min, the band gap is 3.63 eV, which is nearly the same as that of the bulk ZnS (3.6 eV). The band gap of ZnO is 3.25 eV. In a previous study on ZnOS,[31] with increasing oxygen content, the band gap decreased. In this study, the energy band gap value increases slightly, so ZnO will not bring much more effect on the band gap.

4. Conclusion

Growth of Zn(S,O,OH) films deposited onto soda-lime glass substrates by using the CBD method has been studied. The roughness of the film changes largely when the film growth changes from heterogeneous to homogeneous process because of the colloidal particles absorbed onto the compact film. By analysing the correlation between roughness and thickness of the films in the heterogeneous process, a β value of 0.38 ± 0.06 is determined, indicating that the film growth in this region is affected by a combination of the surface diffusion and shadowing effect. Though the film composition is expressed by Zn(S,O,OH), its optical property is still the same as that of ZnS. The optical properties of the film show that when grown in the heterogeneous process (transmittance is 70%–88% in the visible region), it is much better than the film grown in the homogeneous process because the growth is influenced by surface diffusion and shadowing effect in the former process. The energy band gap of Zn(S,O,OH) is around 3.63 eV.

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