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Effects of ammonia concentration on morphology, composition and optical properties of $ZnO_{1-x}S_x$ thin films of Cu(In, Ga)Se_2 solar cells[*]

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$ZnO_{1-x}S_x$ films were prepared by chemical bath deposition (CBD) on glass substrate. The effects of ammonia concentration on the structure characteristics of $ZnO_{1-x}S_x$ films were studied. The results of scanning electron microscope (SEM) show that the film has good density when the concentration of ammonia is 0.4 M. Because more S^{2-} ions are involved in the reaction and less precipitates are generated, the film is relatively dense. The distribution of the film element shows that the growth rate of the film first accelerates and then slows down as the concentration of ammonia increases. X-ray diffraction (XRD) study shows that the diffraction peak is obvious when the ammonia concentration is 0.4 M, and the crystallinity of the film is good. Ultraviolet (UV) spectrophotometer test results show that the ratio of S content (x) and optical band gap (E_g) satisfies $E_g(x)=3.325\,7x^2-2.718\,7x+4.357\,6$. Increasing S content can increase the optical band gap of the film, and increasing ammonia concentration can improve the absorbance of the film, but both have good transmittance. At the ammonia concentration of 0.4 M, the absorbance of the film is good in the wavelength range of 300—900 nm, the transmission rate reaches 80%, and the band gap is 3.75 eV, which is suitable for the buffer layer of solar cells.

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There are lattice defects between Cu(In, Ga)Se_2 (CIGS) window layer and absorption layer, which limits the photovoltaic conversion rate of solar cells. This problem can be solved by adding $ZnO_{1-x}S_x$ film between the window layer and the absorption layer as a buffer layer[1]. $ZnO_{1-x}S_x$ film has the advantages of adjustable band gap, non-toxic, easy preparation, etc. CIGS solar cells, which are used as buffer layer, have been widely studied in recent years[2]. ZnS is an N-type semiconductor compound with an optical band gap of 3.72 eV[3]. It also has good transmission for short wave, and is non-toxic and environment friendly. It is suitable for being used as a buffer layer for heterojunction solar cells. However, the CIGS band gap is 1.02—1.67 eV, and the gap between the two is quite different. The direct contact leads to the band mismatch of the absorption layer of the solar cell[4], which affects the photoelectric conversion efficiency of the cell. In general, ZnO binding with equivalent anions (S, Se, Te) can significantly adjust the band gap structure[1], and the size difference between S and O is the smallest[5]. When $ZnO_{1-x}S_x$ film is formed by doping ZnO, the band gap of the film can be adjusted between 3.6 eV and 3.95 eV by adjusting the proportions of elements in the film[6], which can make the band gap of the buffer layer and the absorption layer match, increase the absorbance of the film, and improve the photoelectric performance of the film. The $ZnO_{1-x}S_x$ thin film can be prepared by sputtering method, and its efficiency reaches 23.35% when applied to CIGS module. By changing the sputtering conditions, it is found that the sputtering power will affect the composition of the film, and then affect the crystallization of the film and even its properties[7]. When the $ZnO_{1-x}S_x$ film was grown by three-step method, the band gap of the film would change with the change of S content[2]. When the $ZnO_{1-x}S_x$ film was deposited by electroplating, the concentration of the reagent (tartaric acid) would affect the transmittance and composition of the film, thus affecting the band gap and related properties of the film[6]. $ZnO_{1-x}S_x$ film could be deposited by sol-gel spin coating method, and it was found that the concentration of the reaction reagent ($SC(NH_2)_2$) would affect the performance of the film, and then the performance of the components. It was found that when S/(S+O)=0.44 in the film, the corresponding band gap was the minimum (3.72 eV)[8]. Among them, chemical bath deposition (CBD) method is easy to operate and suitable for industrialization of film deposition. The efficiency of $ZnO_{1-x}S_x$ film prepared by

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CBD method can reach 23.35% when applied to CIGS module. In recent years, $ZnO_{1-x}S_x$ thin films with an optical band gap of 3.65 eV were also prepared according to the formula volume. After being applied to components, the efficiency reached 11.65% without a subtracting reflection layer[9]. Although the study on the use of buffer on $ZnO_{1-x}S_x$ film has been widely reported, most of the buffers use hydrogen peroxide and other toxic substances, but the effects of ammonia water as a buffer on $ZnO_{1-x}S_x$ film are less[10]. In this paper, the effects of ammonia concentration on the morphology, structure and optical properties of $ZnO_{1-x}S_x$ films were studied to improve the optical and electrical morphology of the films, and to reduce the lattice defects of the window layer and the absorption layer. By adjusting the band gap of $ZnO_{1-x}S_x$ films, the window layer and the absorption layer could be better matched.

Some of the ions of insoluble substances will enter the solution and some will be deposited on the solid surface. When the two rates are the same, they reach the dissolution equilibrium, and the equilibrium constant is the solubility product[11]. However, the materials prepared by CBD process generally have a very small solubility product, so once Zn^{2+}, S^{2-} and OH^- exist in the solution, precipitates will be rapidly generated, affecting the growth of the film. Therefore, the CBD method usually adds complexing agent to reduce the release rate of metal ions, and usually chooses ammonia as the complexing agent and $(NH_4)_2SO_4$ as the buffer. NH_4^+ reacts with Zn^{2+} to form a stable Zn complex, which can effectively control the deposition rate and improve the film growth quality.

Fig.1 shows the experimental device diagram. In the preparation stage, weigh the required amounts of $ZnSO_4$, $SC(NH_2)_2$, and $(NH_4)_2SO_4$, and mix them with ultrapure water to obtain the corresponding solution ($ZnSO_4$: 0.2 M; $(NH_4)SO_4$: 0.2 M; $SC(NH_2)_2$: 1 M; ammonia: 0.2—0.7 M), clean the 2 cm×3 cm substrate with cleaning solution, then rinse it with ultrapure water, and dry it with nitrogen. The solution was added to the beaker in the order of $ZnSO_4$ and $(NH_4)SO_4$. In this experiment, $ZnSO_4$ and $SC(NH_2)_2$ were used as the Zn source and S source, ammonia water was used as the complexing agent, and $(NH_4)_2SO_4$ was used as the buffering agent. When the water bath is heated to 80 °C, add 25% ammonia and $SC(NH_2)_2$ in sequence, start timing, and stir them every 5 min. A white precipitate gradually formed in the beaker. After reacting for 80 min, remove the beaker, wash and dry the sample. In the process of the experiment, 2 cm×3 cm glass substrate washed by deionized water and ultrasonic cleaning solution should be put into the beaker, and $ZnSO_4$, $(NH_4)_2SO_4$ and appropriate amount of deionized water should be successively added into the beaker. When the water bath is heated to 80 °C, ammonia water with 25% concentration and 1 M $SC(NH_2)_2$ should be successively added, and time should be started, stirring every 5 min. White precipitate was gradually formed in the beaker. After reacting for 80 min, the beaker was removed, and the sample was washed and dried.

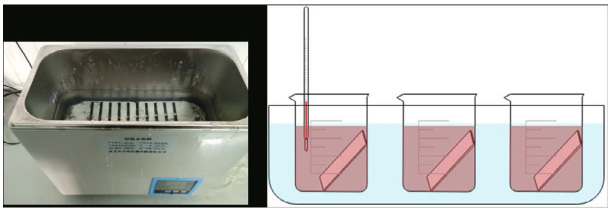


Fig.1 Experimental device diagram

The following chemical reactions occur during the deposition of the film.

1. $ZnSO_4$ provides Zn^{2+} to react with ammonia to form complex ions:

$$ZnSO_4 \rightarrow Zn^{2+} + SO_4^{2-}. \tag{1}$$

2. Ammonia water hydrolysis:

$$NH_3 \cdot H_2O \rightarrow NH_4^+ + OH^-, \tag{2}$$

$$Zn^{2+} + 4NH_3 \rightarrow [Zn(NH_3)_4]^{2+}. \tag{3}$$

3. Zn^{2+} and OH^- produce $Zn(OH)_2$ precipitate and ZnO:

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2, \tag{4}$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O. \tag{5}$$

4. Hydrolysis of $SC(NH_2)_2$ yields S^{2-}:

$$SC(NH_2)_2 + OH^- \rightarrow HS^- + CO_3^{2-} + 2NH_3, \tag{6}$$

$$HS^- + OH^- \rightarrow S^{2-} + H_2O. \tag{7}$$

5. $ZnO_{1-x}S_x$ is formed by the reaction of Zn and ammonium complex ions with S^{2-} formed by OH^- resulting from the hydrolysis of $SC(NH_2)_2$ and ammonia water:

$$[Zn(NH_3)_n]^{2+} + SC(NH_2)_2 + 2OH^- \rightarrow ZnO_{1-x}S_x + \text{waste}. \tag{8}$$

When Eq.(4) occurs in the solution, the precipitate is formed and the colloid is formed, or the reaction Eq.(4) occurs on the surface of the substrate and the wall of the container respectively to form a film. Therefore, in the process of deposition of $ZnO_{1-x}S_x$ film by CBD method, there are two competing chemical reactions, homogeneous reaction in solution and heterogeneous reaction on the substrate and the surface of the vessel wall. The homogeneous reaction will form a large number of colloidal particles in the solution, which will make the performance of $ZnO_{1-x}S_x$ film bad. Therefore, the deposition of high quality $ZnO_{1-x}S_x$ thin films must try to inhibit the occurrence of homogeneous reactions.

The surface roughness of the film was studied by scanning electron microscope (SEM 460l03040702). The composition and element content of the film were analyzed by energy dispersive spectrometer (EDS 460l03040702) on SEM with field emission gun (Quanta-Feg250). The crystalline structure of the films was measured by X-ray diffraction (XRD uitimaiv) with Cu rotating target, step size of 0.02, voltage of 40 kV and current of 200 mA. The film thickness was measured using a step height gauge (Veeco Dektak 150). The absorptivity and transmittance of the film in the wavelength range of 300—900 nm were measured by UV-Vis-NIR TP720.

As shown in Tab.1, with the increase of ammonia concentration, the thickness of the film first increases, then decreases and then increases, indicating that the growth rate of the film first accelerates, then slows down and then accelerates. As the S content of the film decreases at first and then increases and decreases again, the release rate of S^{2-} ions in the solution is accelerated, resulting in the formation of precipitation rate faster than that of $ZnO_{1-x}S_x$ film generated by Zn-ammonia complex ion and S^{2-}. The increase of pores in the film also reduces the growth rate of the film, and the film becomes thinner.

Tab.1 Thicknesses of $ZnO_{1-x}S_x$ films under different ammonia concentrations

Ammonia concentration (M)	Thickness of the thin film (nm)
0.2	138
0.3	122
0.4	147
0.5	142
0.6	115
0.7	98

Fig.2 shows the surface morphology of $ZnO_{1-x}S_x$ films deposited at different ammonia concentrations. In terms of film density, (c) and (d) look more flatter and have better density. Because there are more Zn^{2+} ions in the solution, due to the addition of complexing agent, the release rate of metal ions is slowed down, so that Zn^{2+} reacts with OH^- to produce less $Zn(OH)_2$ precipitation. At the same time, complex ions react with S^{2-} produced by the hydrolysis of $SC(NH_2)_2$ and ammonia to produce $ZnO_{1-x}S_x$. The film growth rate is accelerated, the thickness is increased, there are fewer holes, and the film density is better. With the increase of ammonia concentration, there is too much ammonia in the solution, the release rate of metal ions is too slow, the precipitation of $Zn(OH)_2$ formed by the reaction of Zn^{2+} ions with OH^- produced by hydrolysis increases, the film growth rate decreases, the alkaline value of the solution increases, resulting in more holes. When the ammonia concentration is 0.4 M, because the complexing agent slows down the release rate of Zn^{2+} ions and makes the release rate of Zn^{2+} ions close to that of S^{2-} ions, there is little precipitation, the film growth rate is accelerated and the density is increased. Because holes will increase the probability of carrier recombination and reduce the photoelectric conversion efficiency, films with fewer surface holes and better density are more suitable for thin film buffer layers.

The distribution diagrams of Zn, S and O elements in $ZnO_{1-x}S_x$ thin films deposited under six ammonia concentrations are shown in Fig.3. The ZnO particles in the films decrease with the increase of ammonia concentration. Under the condition of 0.4 M ammonia, there are both ZnO particles and ZnS particles in the film, and the growth of the film is more uniform and dense than other conditions, which is also consistent with the results of XRD pattern. It can be seen that the element distribution is relatively uniform as a whole. Combined with the EDS results, it can be roughly determined that the acicular grain is ZnO. With the increase of ammonia concentration, the larger spherical grains correspond to ZnS. In addition, according to the EDS results, some smaller grains were grown on the substrate surface, corresponding to ZnS.

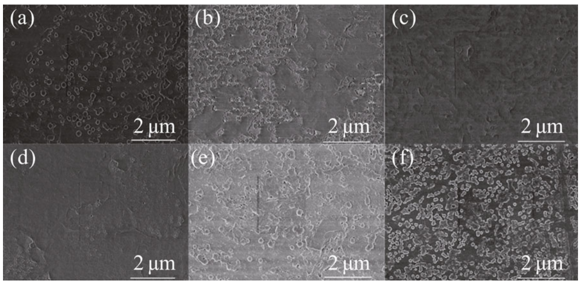


Fig.2 SEM images of $ZnO_{1-x}S_x$ films deposited with different ammonia concentrations: (a) 0.2 M; (b) 0.3 M; (c) 0.4 M; (d) 0.5 M; (e) 0.6 M; (f) 0.7 M

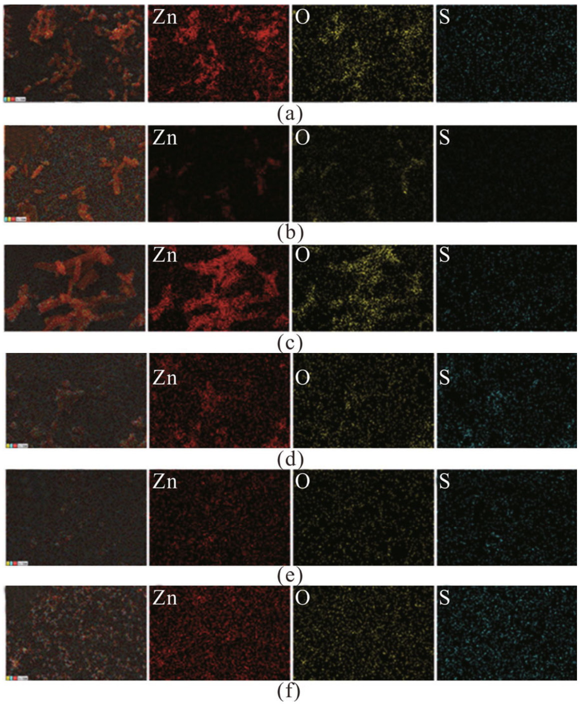


Fig.3 EDS spectra of $ZnO_{1-x}S_x$ films deposited with different ammonia concentrations: (a) 0.2 M; (b) 0.3 M; (c) 0.4 M; (d) 0.5 M; (e) 0.6 M; (f) 0.7 M

Tab.2 Atomic percentages of Zn, O and S in $ZnO_{1-x}S_x$ films with different concentrations of ammonia

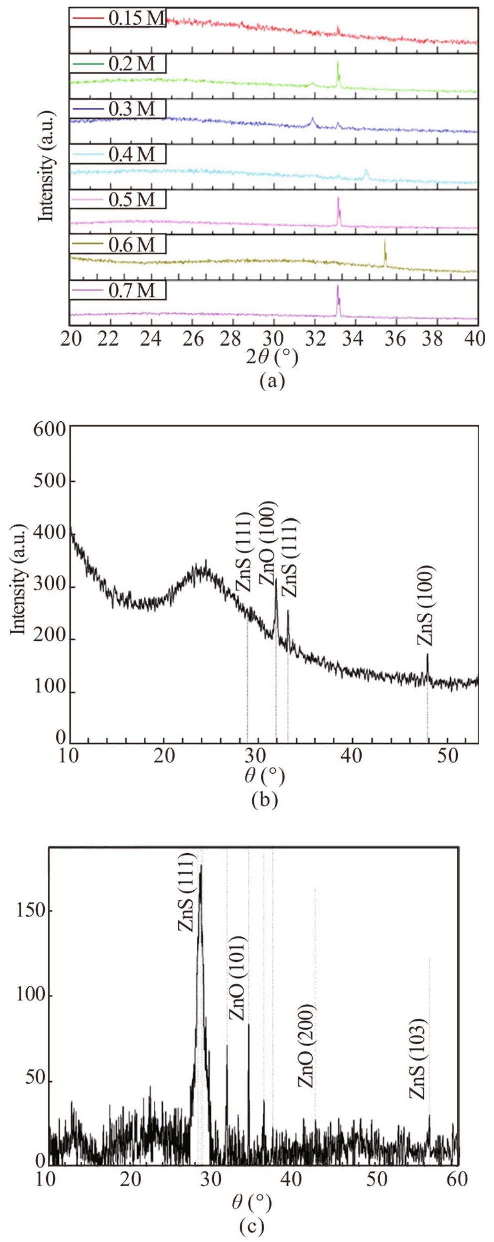
Ammonia concentration (M)	Atomic percentage Zn: O: S	S/(Zn+S)
0.2	22.12: 60.33: 20.25	0.478
0.3	27.72: 60.43: 20.16	0.421
0.4	27.06: 67.97: 55.97	0.674
0.5	26.63: 50.99: 52.41	0.663
0.6	23.05: 77.12: 21.81	0.486
0.7	25.08: 54.38: 23.87	0.488

When the concentration of ammonia is increased to 0.4 M and 0.5 M, the number of complex complexes formed by $ZnSO_4$ and ammonia increases, and the complex ions react with S^{2-} produced by the hydrolysis of $SC(NH_2)_2$ and ammonia to form $ZnO_{1-x}S_x$. As the addition of ammonia, the complexing agent increases the release rate of metal anions, resulting in less precipitation, and increases the growth rate of the film and the film is relatively flat. EDS results show that the atomic percentage of S increases significantly and that of Zn increases slightly, indicating that the S content is related to the growth rate of the film. When the concentration of ammonia increases to 0.6 M, the hydrolysis of S^{2-} ions is inhibited due to the high acidity of the solution. Although the complexing agent was added, the release rate of metal ions is faster than the growth rate of the film, and the growth rate of the film is slowed down, holes increases, and the atomic percentage of S begins to decrease. However, when the ammonia concentration continues to increase to 0.7 M, due to the excessive consumption of S^{2-} involved in the reaction, there is less S^{2-} in the solution, the precipitation of $Zn(OH)_2$ from Zn^{2+} and OH^- increases, and the growth rate of the film slows down. It is proved that the increase of ammonia concentration leads to the change of Zn content in the film, the growth rate of the film changes accordingly, and the decrease of S content can inhibit the growth of the film.

By changing the concentration of ammonia, the corresponding samples were obtained and tested by XRD. The diffraction angle was 20°—80°. As shown in Fig.4, the diffraction peak of 33° is the glass peak of the substrate, and other diffraction peaks also appear in some samples between 28°—32°.

Through the deposition of different substrates and XRD analysis, the crystallinity of the film was determined. As shown in Fig.4, the diffraction peak at 31.88° corresponds to ZnO(100). (b), (c) and (d) in Fig.4 are the test results of thin films deposited on Si(100), Si(111) and glass under the condition of 0.3 M ammonia. After the XRD patterns of the glass deposition samples were analyzed without the influence of the substrate diffraction peaks, as shown in Fig.4(d), diffraction peaks corresponding to ZnO(100) and ZnS(111) appear in the XRD patterns of the films. Compared with ZnO, the diffraction peak corresponding to ZnS is not obvious, because S compounds are easy to form amorphous state.

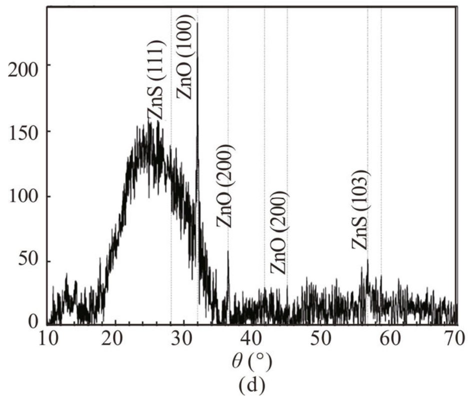
The diffraction of the sample at the concentration of 0.15 M ammonia is weak, indicating that the film deposition effect is poor and the film crystallization is not very good at this concentration. When the ammonia concentration is too high, the diffraction peak of ZnO also weakens. This is because the increase of the pH value of the solution promotes the decomposition of $SC(NH_2)_2$, increases the anions, and reduces the concentration of cations. In the initial stage of pH value increasing, the final results of these two processes increase the concentration of anions and cations that can participate in the reaction in the solution at the same time, so the growth rates of ZnO and ZnS are accelerated and the diffraction peak becomes obvious gradually. Subsequently, although the increase of pH value increases the concentration of S^{2-} and O^{2-} more and more, the concentration of Zn^{2+} becomes smaller and smaller. As a result, the concentration of anions and cations that can participate in the reaction in the solution decreases, so the growth rate of $ZnO_{1-x}S_x$ film is also reduced, and then the film thickness is reduced. Therefore, the growth rate of $ZnO_{1-x}S_x$ thin films can be controlled by the pH value of the solution. The above three reactions also lead to that with the increase of the pH value of the solution, the anion ratio of the film increases, but the electron concentration and resistivity have no specific change trend with the specific reaction conditions.



(a)

(b)

(c)



(d)

Fig.4 (a) XRD patterns of the samples corresponding to 0.15—0.7 M ammonia water; XRD patterns of (b) Si (100), (c) Si (111), and (d) glass substrate deposition samples under the condition of 0.3 M ammonia, respectively

The optical properties of the film were studied by UV-Vis-NIR spectrophotometer. The absorbance curves of the film are shown in Fig.5. From the overall perspective, the absorbance of the film less than 500 nm is higher than that of the film more than 500 nm, and the absorbance of the film drops sharply between 300 nm and 350 nm. From the perspective of ammonia concentration, the absorbance of the film gradually increases with the increase of the concentration. When the ammonia concentration increases to 0.6 M and 0.7 M, the absorbance begins to decrease.

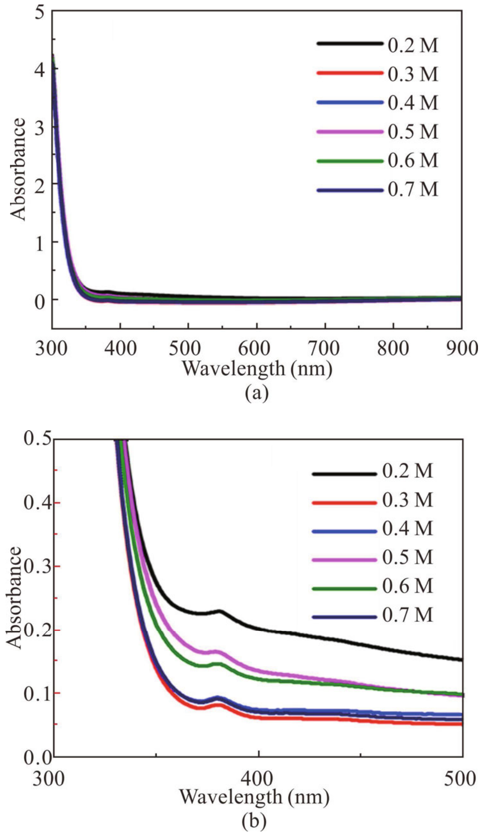


Fig.5 Relationship between absorbance and wavelength of ZnO$_{1-x}$S$_x$ films deposited with different ammonia concentrations in the wavelength ranges of (a) 300—900 nm and (b) 300—500 nm

The transmittance curves of the films are shown in Fig.6. When the incident wavelength is less than 400 nm, the transmittance of the film increases sharply with the increase of wavelength. When it exceeds 400 nm, the transmittance increases slowly. The transmittances of the films at five ammonia concentrations have a certain difference, and the best transmittance is close to 80%. When the ammonia concentration reaches 0.4 M, the transmittance of the film exceeds 85%, indicating superior optical performance.

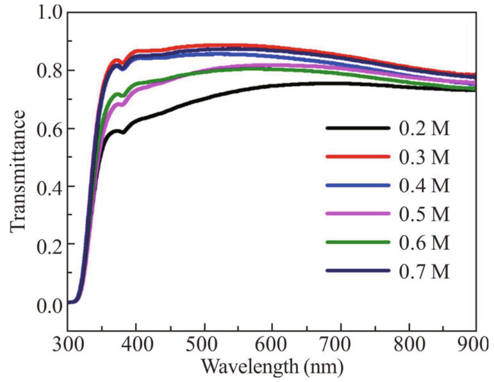


Fig.6 Relationship between transmittance and wavelength of ZnO$_{1-x}$S$_x$ films deposited with different ammonia concentrations

The transmittance of the film was detected by UV spectrophotometer, and the band gap value of the corresponding sample was calculated according to the formula. The measured wavelength range is 300—900 nm. It is known that when the film reflectance (R) is extremely small, the relationship between its transmittance (T) and its corresponding absorption coefficient (α) is

$$T=(1-R)^2\exp(-\alpha d). \tag{9}$$

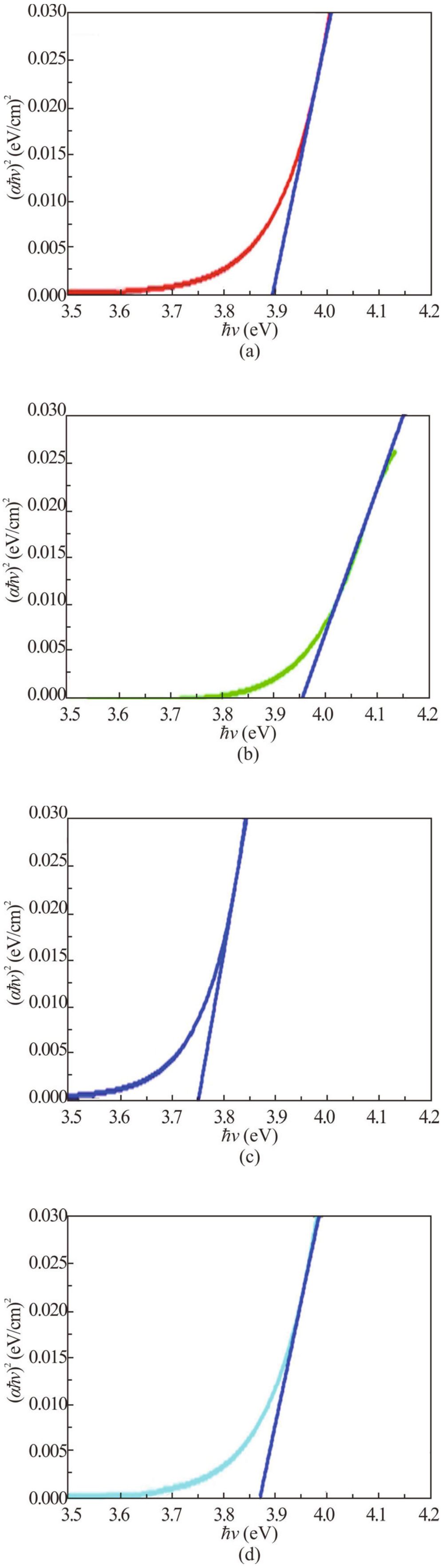
Since its reflectivity is extremely small, the formula can be simplified as

$$T=\exp(-\alpha d), \tag{10}$$

where d represents the thickness of the film. The film absorption coefficient and its corresponding optical band gap are related as follows according to Tauc formula:

$$\alpha\hbar v=A(\hbar v-E_g)\ n, \tag{11}$$

where A represents a constant, $\hbar v$ represents the photon energy, $\hbar$ is Planck's constant, v represents the photon frequency, and E_g represents the optical band gap of the film. Since both ZnS and ZnO are direct band gap semiconductors that allow dipole transitions, the value of n is 1/2. In the relationship between $(\alpha\hbar v)^2$ and $\hbar v$, the slope of the linear fitting domain is taken. The intercept of the x-axis corresponds to the band gap value of the film (E_g), as shown in Fig.7.



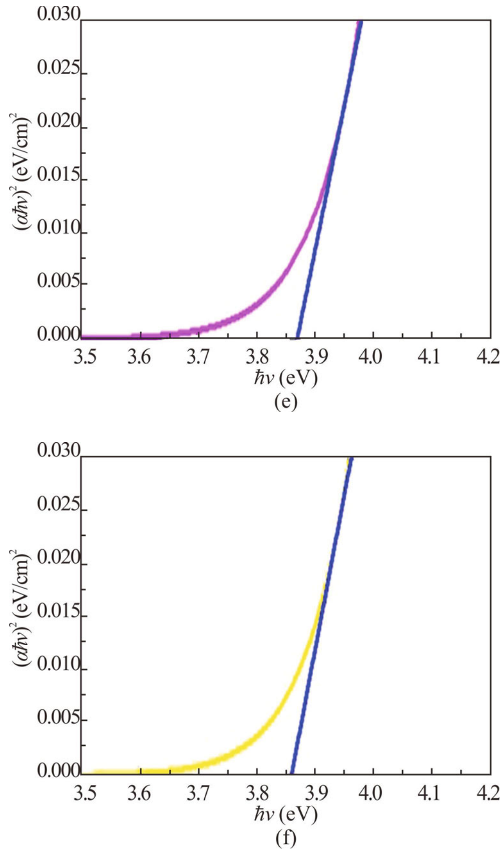


Fig.7 $(\alpha\hbar v)^2$-$\hbar v$ curves of corresponding samples under the ammonia concentrations of (a) 0.2 M, (b) 0.3 M, (c) 0.4 M, (d) 0.5 M, (e) 0.6 M, (f) 0.7 M

It can be seen that the band gap of the sample is larger than that of ZnS (3.6—3.9 eV). The band gap of nanocrystalline ZnS is as high as 4.3 eV, which is much higher than that of pure ZnS. It is indicated that the ZnS part in the grown film exists in the form of nanocrystalline grains. The band gap of semiconductor is related to grain size, surface defect and dangling bond. Therefore, the increased band gap may be due to the reduction of the size of ZnS nanoparticles.

The band gap of the samples grown in 0.4 M ammonia environment is the smallest (3.75 eV). Under the condition of appropriate ammonia concentration, Zn^{2+} ions will quickly react with ammonia. After adding $SC(NH_2)_2$, S^{2-} ions are more likely to precipitate in alkaline environment, and $ZnO_{1-x}S_x$ is then reacted with complex complexes.

The band gap of samples grown in 0.3 M ammonia environment is the largest, which is about 3.95 eV. This is because the concentration of ammonia is too low, which is not conducive to the polymerization between ions, making the film growth poor. When the ammonia concentration is 0.2 M, the band gap value is 3.89 eV, as shown in Fig.7.

The band gap of $ZnO_{1-x}S_x$ film varies from 3.89 eV to 3.75 eV at different ammonia concentrations. Fig.8 shows the band gap of $ZnO_{1-x}S_x$ film at $0.2 \le x \le 0.6$, which is a nonlinear change. Further study shows that there is a functional relationship between the two. With the increase of x

(S/(S+O)), the absorption edge of $ZnO_{1-x}S_x$ is blue shifted. The intrinsic absorption is caused by the transition from valence to conduction band, and the blue shift of absorption edge indicates the increase of band gap width, so the quadratic function relation is used to fit this law, which can be expressed by the dielectric model and the pseudopotential model. The relationship between band gap value and x satisfies the equation of

$$E_g(x)=3.325\,7x^2-2.718\,7x+4.357\,6. \tag{12}$$

Tab.3 Element contents, Zn content ratios and band gap values of the films

Zn (at.%)	O (at.%)	S (at.%)	S/(O+S)	E_g (eV)
22.12	60.33	20.25	0.251 3	3.89
27.72	60.43	20.16	0.250 1	3.95
27.06	67.97	55.97	0.451 5	3.75
26.63	50.99	52.41	0.506 8	3.87
23.05	77.12	21.81	0.220 4	3.86
25.08	54.38	23.87	0.305 0	3.85

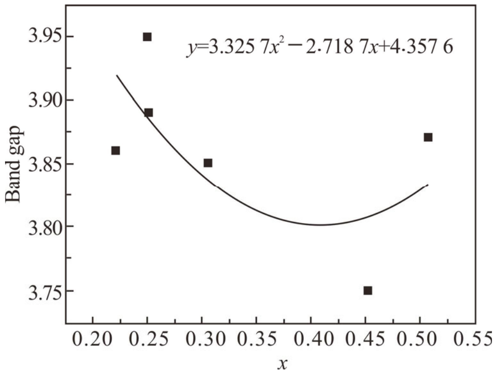


Fig.8 Variation trend of band gap of $ZnO_{1-x}S_x$ film with x

$ZnO_{1-x}S_x$ thin films were prepared by CBD method. The characterization analysis of the film samples prepared at different ammonia concentrations shows that the deposition effect is poor when ammonia concentration is too low (0.15 M, 0.2 M), and the main composition is ZnO with a large band gap. When the ammonia concentration increases to 0.3 M and 0.4 M, ZnO(100) diffraction peak appears in the XRD pattern, and ZnS(111) diffraction peak also appears near 28°. EDS characterization results also confirm that at 0.3 M, the film components are mainly ZnO and ZnS. In addition, with the increase of ammonia concentration, the content of S in the film also increases, and the ratio of S/(S+O) increases. The band gap value first decreases and then increases. The lowest band gap value is 3.75 eV at 0.4 M, and the transmittance of the film is also the best. The spectrophotometer test shows that the ratio (x) of S/(O+S) in the film is related to the optical band gap value E_g. With the increase of ammonia concentration, the hydrolysis of $SC(NH_2)_2$ is accelerated to produce more S^{2-} ions, which can inhibit the occurrence of homogeneous reaction. However, with more hydrolysis of $SC(NH_2)_2$ by ammonia, due to excessive consumption of S^{2-} involved in the reaction, there are less S^{2-} ions in the solution, the precipitation of $Zn(OH)_2$ generated by Zn^{2+} and OH^- increases, and the film growth rate slows down.

Statements and Declarations

The authors declare that there are no conflicts of interest related to this article.

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