Effect of complexing agent concentration on properties of CdZnS thin films in ammonia-thiourea system*

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In this paper, the effects of different concentrations of complexing agent (ammonia) on the surface morphology, composition, structure and photoelectric properties of CdZnS films were studied. The results of X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV-visible spectrum showed that the surface morphology of the films became worse and the content of zinc decreased significantly with the increase of ammonia concentration. The crystalline phase of CdZnS films was not influenced by the ammonia concentration. Because the film has good absorbance, transmittance greater than 70% and band gap width between 3.5 eV and 3.07 eV, it is suitable to be used as a buffer layer for solar cells. CdS, ZnO and $Zn(OH)_2$ were found in the precipitates at the bottom of the solution, and the formation of these precipitates affected the properties of the CdZnS films.

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The research of $Cu(In,Ga)Se_2$ (CIGS) thin film solar cells has attracted extensive attention with relatively high conversion efficiency and low production cost. As II-VI semiconductor, CdS has thermal stability, efficient transport characteristics and a wide direct band gap (2.42 eV)[1], so it is suitable for photovoltaic applications. It is used as a buffer layer in CIGS solar cells. It can prevent the leakage phenomenon caused by the damage of absorption layer film caused by sputtering ZnO, and improve the defect of too large band gap difference between the window layer and the absorption layer. However, CdS films have relatively low transmittance to blue light and can absorb wavelengths below 515 nm[2]. By doping different elements such as Ga[3], Cu[4], Co[5], Ag[6], and Zn[7,8], the optical band gap and blue light transmission can be changed, and the doping gives CdS better performance as a buffer layer for solar cells. In recent years, CdS has high toxicity and serious harm to human body and environment[9]. As a substitute for CdS buffer layer in CIGS thin film solar cells, ZnS thin film has been widely studied[10]. Adopting wide gap material ZnS as buffer layer can reduce window absorption loss and improve the short circuit current of the battery[11]. The maximum efficiency of ZnS deposited by the chemical bath deposition (CBD) method as a buffer layer for CIGS thin film solar cells was 18.6%[12]. However, the much lower efficiency of solar cells using ZnS as buffer layer compared to CdS as buffer layer was attributed to the poor lattice of CdZnS can be made between CdS and ZnS by adjusting the concentration of Zn ions, so that it has good lattice matching and optical transmittance[13], thus improving the efficiency of solar cells. On the other hand, it can reduce the use of toxic substance cadmium. But there are few studies on ammonia, which is not only a complexing agent but also a variable of acid-base balance regulation. There are few studies on the precipitation produced by CdZnS in the film formation process, which has a great impact on the quality of the film. Therefore, in this paper, the effects of ammonia concentration on the surface morphology and photoelectric properties of CdZnS thin films are mainly studied, and the composition and structure of the precipitates are explored.

This experiment used CBD method to deposit CdZnS thin film on glass substrate. Before deposition, the beaker and a 2 cm×2 cm glass substrate required in the experiment are soaked in dilute hydrochloric acid soaked for 10 min to remove surface impurities, and placed in deionized water, ultrasonic cleaning solution, deionized water for ultrasonic cleaning in turn. After washing, the six beakers were labeled A, B, C, D, E, and F in order. The experiment was divided into six independent experimental groups with F for CdS for comparison and reference. A beaker add cadmium sulfate (0.05 M), zinc sulfate (0.2 M), ammonium sulfate (0.1 M) and appropriate amount of deionized water, stir well with a glass rod (stirring for 2 min) placed in the constant temperature water bath, and the washed glass substrate using the holder placed vertically in the beaker, when the temperature of the solution reaches 85 °C to the beaker to add a concentration of 25%

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ammonia 5.6 mL (0.5 M), 1 M thiourea 4.5 mL and start timing. Thereafter, the chemical water bath was kept undisturbed until the end of deposition, and the reaction time was 30 min. The above experimental steps were repeated for the remaining groups B, C, D, E and F. The temperature of the reaction solution remained unchanged, and the concentration of ammonia added was 6.8 mL (0.6 M), 7.9 mL (0.7 M), 9 mL (0.8 M), 10.1 mL (0.9 M) and 5.6 mL (0.5 M) in that order. After 35 min of chemical deposition, the glass substrate was removed, washed with deionized water, and blown dry with nitrogen gas. After taking out the glass substrate, filter the solution in the beaker, filter out the precipitated material and put it into the glassware, put it into the drying oven for 2 h, and set the temperature at 90 °C.

The CdZnS thin film buffer layer prepared by CBD method uses zinc salt and cadmium salt as precursor solution and ammonia as complexing agent to form ammonia-cadmium complex and decompose thiourea to achieve the preparation of buffer layer film. In the process of deposition, the homogeneous reactions and heterogeneous reactions occur simultaneously on the substrate[14]. Heterogeneous reactions generate films on the substrate, while homogeneous reactions generate precipitation in the solution. Therefore, the occurrence of homogeneous reactions should be inhibited in the process of deposition of films. The heterogeneous reaction is further divided into cluster mechanism and ion-ion mechanism[11], where the ion-ion mechanism generates dense, flat films with fewer holes and the cluster mechanism generates films with rough surfaces and more holes. However, it is very difficult to maintain the ion-ion mechanism all the time during the experiments, and a mixed way of growth by ion-ion mechanism first and cluster mechanism later generally occurs. The reaction mechanism is shown in Fig.1.

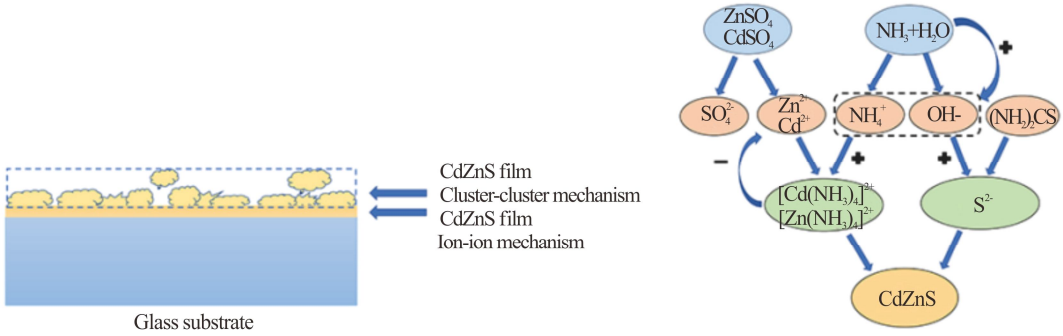

Fig.1 Growth mechanism of CdZnS thin film

Fig.2 shows the X-ray diffraction (XRD) patterns of CdZnS films deposited with different ammonia concentrations. It can be seen that there are one strong diffraction peak and two weak peaks in the five groups of XRD diffraction patterns with different ammonia concentrations, which have the same diffraction pattern. CdZnS films at 2θ=26.7°, 2θ=44.3°, 2θ=52.3° can be classified as (002 H), (110 H), (112 H) of hexagonal CdZnS (JCPDS 20-1235), respectively. From the figure, it can be seen that there are two weak diffraction peaks at 2θ=44.3° and 2θ=52.3°, which are (110 H) and (112 H), and it can be found that the magnitude of the intensity of these two peaks is related to (002 H) at the same ammonia concentration, and the higher the intensity of (002 H) peak, the more obvious the (110 H) and (112 H) peaks are. The above five groups of CdZnS films with different ammonia concentrations are all hexagonal in phase, the conformation and arrangement of the polymer chain in the crystal were not changed, which indicates that the concentration variables of ammonia do not affect the crystalline crystalline phase of CdZnS.

Fig.3 shows the XRD diffraction pattern of the precipitation at the bottom. In the figure, #(002), #(110), #(112) are consistent with the diffraction 2θ angle and crystal of CdZnS film, which are all CdZnS. Through the comparison, JCPDS 36-1451 *(100), *(002), *(101), *(102), *(110), *(103), *(200), *(112), and *(201) are the diffraction peaks of the ZnO. KHURSHEED et al[15] also mentioned the 2θ angle and crystal phase of ZnO in their article about ZnO, and the present experimental study is identical to their findings. A diffraction peak with low amplitude was found at 2θ=32.8°. After comparing JCPDS 38-0385, this diffraction peak was found to be the (211) crystalline phase, which is the diffraction peak of $Zn(OH)_2$. In Ref.[16], $Zn(OH)_2$ begins to decompose into ZnO at 65 °C. Therefore, a part of $Zn(OH)_2$ decomposed to ZnO in the precipitation. The formation of $Zn(OH)_2$ precipitation further confirmed that the mass of CdZnS film was related to the formation of the precipitation. It can be clearly observed in Fig.3 that the diffraction peak of ZnO is much higher when the ammonia concentration is 0.6 M than that when the ammonia concentration is 0.5 M. Therefore, it can be inferred that ZnO is more easily produced when the ammonia concentration increases. Therefore, it can be inferred that an increase in ammonia concentration makes it easier to produce ZnO or $Zn(OH)_2$.

Fig.4(a), (b), (c), (d) and (e) show the scanning electron microscopy (SEM) images of CdZnS films prepared with ammonia concentrations of 0.5 M, 0.6 M, 0.7 M,

0.8 M, and 0.9 M at the same reaction times, respectively. During the increase of ammonia concentration, the solution was always alkaline and the pH value increased from 11.54 to 12.68. It can be seen from the figure that under the condition of 0.5 M ammonia, the CdZnS film is homogeneous distribution and dense with fewer pores, and the film quality is relatively good at 0.5 M, 0.6 M, and 0.7 M concentrations. However, at the concentration of 0.8 M and 0.9 M, large holes begin to appear, and discontinuous "islands" appear. The main reason for the above phenomenon is that with the gradual increase of ammonia concentration, the OH^- in the reaction solution began to gradually increase, the pH value of its solution increased, and the S^{2-} generated by the reaction between thiourea and OH^- also increased, but the OH^- concentration in the solution was much larger than the S^{2-} concentration, and the solubility product constant of $Zn(OH)_2$ was 10—17, which was 7—10 orders of magnitude larger than that of ZnS and CdS, and OH^- was extremely easy to react with the Cd and Zn complexes in the solution. This is the reason why the efficiency of CdZnS grown with CBD is several percentage points lower than that of the CdS buffer layer. During the experiment, it can be clearly found that with the increase of ammonia concentration, the color of the solution gradually turns yellow, and the precipitation at the bottom increases successively. We speculate that the formation of precipitation blocks the formation of CdZnS films, which eventually resulting in the increase of pores and the appearance of "island" phenomenon. Fig.4(f) shows the cross-sectional view of CdZnS thin film, and it can be seen that the cluster growth phenomenon is similar to "cloud-like" in the figure.

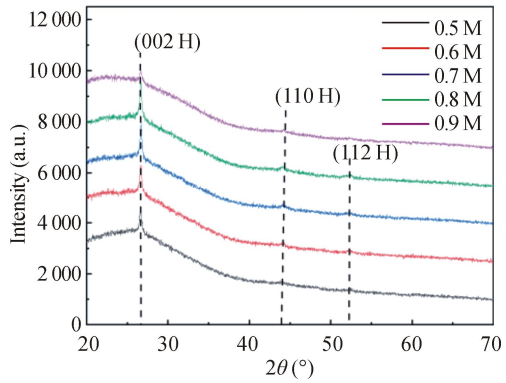

Fig.2 XRD patterns of CdZnS films deposited with different ammonia concentrations

Fig.5 respectively shows SEM images of precipitated substance at the bottom of solution with ammonia concentrations of 0.5 M and 0.6 M. Many hexagonal prismatic particles can be observed in Fig.5(b). Combined with the XRD pattern and articles about ZnO[15], the hexagonal prismatic particles in the precipitation at the bottom are ZnO. It is further confirmed that ZnO is formed in CdZnS thin films.

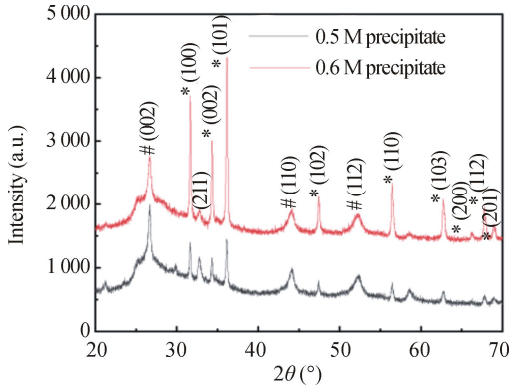

Fig.3 XRD patterns of bottom precipitation

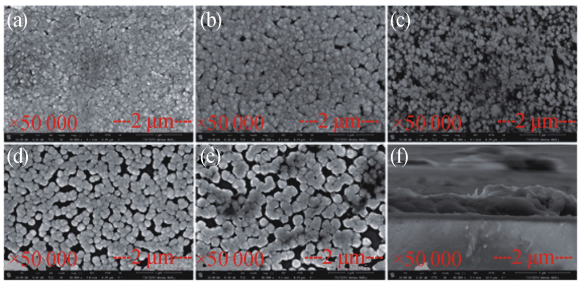

Fig.4 SEM images of CdZnS films deposited with different ammonia concentrations: (a) 0.5 M; (b) 0.6 M; (c) 0.7 M; (d) 0.8 M; (e) 0.9 M; (f) 0.5 M

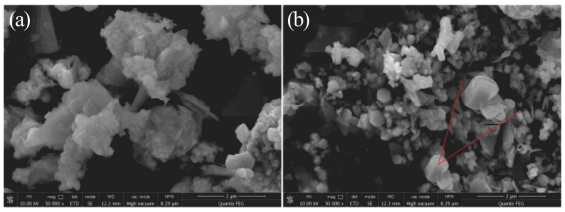

Fig.5 SEM images of precipitated substance at the bottom of solution with different ammonia concentrations: (a) 0.5 M; (b) 0.6 M

Tab.1 shows the CdZnS film thickness measured by the step meter. It can be seen that the film thickness gradually increases with the increase of ammonia concentration. This is because the increase of OH^- leads to the accelerated decomposition rate of thiourea and the increase of S^{2-} in the solution. Therefore, the formation rate of CdZnS film is accelerated.

Tab.1 Thicknesses of CdZnS films with different ammonia concentrations

$CdSO_4$ concentration (M)	Film thickness (nm)
0.5	78.5
0.6	84.3
0.7	89.4
0.8	90.4
0.9	91.6
0.5 CdS	95.4

Tab.2 shows the percentages of sulfur, zinc and cadmium measured by energy dispersive spectrometer (EDS). It can be seen that as the increase of ammonia concentration, the content of zinc atoms decreases, while the content of sulfur and cadmium atoms gradually increases. The reason for this phenomenon is that the production of ZnS and CdS will be accelerated by the gradual increase of ammonia concentration, but the solubility product constant of ZnS is $K_{sp}=10^{-24.7}$ and that of CdS is $K_{sp}=10^{-27}$[17]. Therefore, CdS is easier to obtain supersaturation. This is also the reason why the elemental zinc content in CdZnS films is smaller than that of cadmium. EDS of precipitated at the bottom of the solution was found to contain four elements, S, Zn, Cd and O, confirming the formation of CdS, CdO and ZnO in the XRD analysis.

Tab.2 Atomic percentages of O, Cd, Zn and S in CdZnS films with different ammonia concentrations

Ammonia concentration (M)	Atomic percentage S: Zn: Cd: O
0.5	39.98: 21.08: 38.94: --
0.6	41.15: 16.36: 42.49: --
0.7	43.21: 10.21: 46.58: --
0.8	43.62: 09.71: 46.67: --
0.9	44.56: 07.56: 47.88: --
0.5 CdS	52.43: -------: 47.54: --
0.5 precipitate	6.27: 20.88: 10.87: 61.99
0.6 precipitate	7.30: 27.93: 14.70: 50.07

Fig.6 shows the absorption spectra of CdZnS films. We can obviously see that CdZnS films has good absorption characteristics for electromagnetic waves from 300 nm to 500 nm, and the absorbance gradually increases with the increase of ammonia concentration in the range from 300 nm to 500 nm. Combined with SEM, it can be seen that the absorbance is lower when the film forming quality is better.

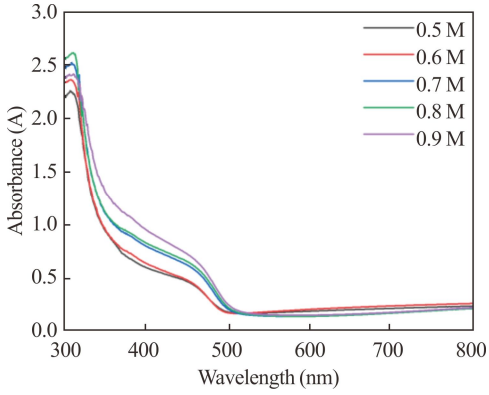

Fig.6 Absorbance plots of CdZnS films deposited with different ammonia concentrations

Fig.7 shows the transmission spectra of the CdZnS film, which can be seen in the band of 300—800 nm, the lower the ammonia concentration, the higher its transmittance. By observing the samples, it was found that the CdZnS films on the glass surface gradually turned yellow with the increase of ammonia concentration. After doping with Zn elements, it can be found that the transmittance increases significantly. The optical transmittance of CdZnS films prepared with ammonia concentrations of 0.6 M, 0.7 M, 0.8 M and 0.9 M can reach more than 70%, which meets the preparation conditions of solar thin film cells. Combined with SEM, it can be seen that the transmittance of the film is higher when the film forming quality is better.

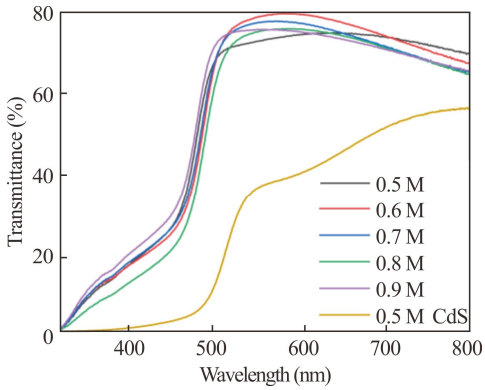

Fig.7 Transmittance plots of CdZnS films deposited with different ammonia concentrations

Fig.8 is the Tauc plot method used to calculate the band gap widths of CdZnS films prepared with five different ammonia concentrations[18]. It can be seen that when ammonia concentrations are 0.5—0.9 M, the corresponding band gap widths are 3.5 eV, 3.47 eV, 3.34 eV, 3.32 eV and 3.07 eV, respectively. Obviously, with the increase of ammonia concentration, the band gap width of CdZnS film gradually decreases. The reason for this phenomenon is that with the increase of ammonia concentration, the content of zinc atoms in the film decreases. In many studies on zinc doping, it is mentioned that the overall band gap width of CdZnS film can be increased after adding zinc[19]. Therefore, combined with EDS data, it can be seen that with the increase of ammonia concentration, the zinc atom content of the film decreases, resulting in a smaller band gap of CdZnS film.

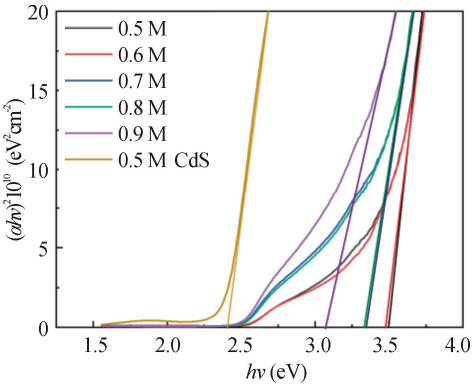

Fig.8 Band gaps of CdZnS films deposited with different ammonia concentrations

In this paper, the effects of ammonia concentration on the surface morphology, crystal phase structure, elemental composition analysis and photoelectric properties of CdZnS films were studied. And with the increase of ammonia concentration, the surface morphology of the film becomes worse. The growth mechanism of CdZnS thin films can be seen through its cross section to change from the ion-ion growth mechanism to the cluster-cluster growth mechanism. XRD showed that the ammonia concentration has not affected the crystalline phase of the CdZnS films, with better crystallinity at concentrations of 0.5 M, 0.6 M, 0.7 M, and 0.8 M. The atomic percentage measured by EDS shows that zinc content in the film has an obvious decreasing trend with the increase of ammonia concentration. Combining with the band gap diagram calculated by Tauc plot, it can be seen that the decrease of the band gap width is closely related to the decrease of zinc content. XRD, SEM and EDS tests on the precipitation at the bottom of the solution proved that the precipitation was a mixture of CdS, CdO, ZnO and $Zn(OH)_2$, and further inferred that CdZnS film was a mixture of CdZnS and Zn(O,OH), but there may be other compounds in the process of film growth.

Statements and Declarations

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

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