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INFLUENCE OF SODIUM CITRATE ON DEPOSITION AND PROPRETIES OF $Cd_{1-x}Zn_xS$ BUFFER LAYERS BY CHEMICAL BATH DEPOSITION

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$Cd_{1-x}Zn_xS$ buffer layers were prepared by chemical bath deposition using solutions containing cadmium acetate, zinc acetate, thiourea, sodium citrate and ammonia hydroxide. The influence of sodium citrate on the morphology, composition, micro-structure, electrical and optical properties of the $Cd_{1-x}Zn_xS$ layers are investigated. The characterization results of the films reveal that the sodium citrate in the deposition solution facilitate the formation of bigger cluster in $Cd_{1-x}Zn_xS$ films and make the films smoother. The sodium citrate in the deposition solution prevents the incorporation of Zn into the buffer layers, thus decreasing the content of Zn in the deposited layers. The sodium citrate also influences the chemical environment of Cd in the films, i.e., more CdS exist in the film when sodium citrate was added. Due to the changes in composition and structure, the E_u energy of the $Cd_{1-x}Zn_xS$ film decreases when sodium citrate was added in the deposition solution, indicating that the degree of the structure disorder in the films are reduced by adding sodium citrate. About the electrical properties, we find the conductivity of the films are decreased but the photo-sensitivity are increased by the addition of sodium citrate.

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1. Introduction

CdS is an important II-VI semiconductor material that widely used for photo-detector, thin-film solar cells, photo-catalyst [1], etc. CdS buffer layers by chemical bath deposition have already become the standard process for $Cu(In,Ga)Se_2$ (CIGS) [2] and CdTe [3] solar cell fabrication. However, the band-gap energy of CdS (~2.5 eV) is relatively low. When CdS is used as buffer layers for CIGS or CdTe solar cell, the absorption of the incident light by CdS layer will cause the loss of the photo-current [4-5], which is harmful for solar cell efficiency [6]. In this condition, people tried to enlarge the band-gap of the CdS buffer layers by Zn-alloying (i.e., $Cd_{1-x}Zn_xS$) [7-9].

For the chemical bath deposition of $Cd_{1-x}Zn_xS$, normally the Zn-alloying is achieved by adding Zn salt into the deposition solution of CdS layer. The composition of $Cd_{1-x}Zn_xS$ could be adjusted by changing the concentration of Cd or Zn ions in the deposition solution. On the other hand, the composition of $Cd_{1-x}Zn_xS$ layer could be changed by adding additional complex agent in the solution containing Cd and Zn ions. In principle, the complex agent will form complex compound with Cd and Zn ions. But the stability constants of complex compounds should be different. Therefore, the concentration of free Cd^{2+} and Zn^{2+} ions and their ratio in the solution can be adjusted by the complex agent, which will further influence the composition of the deposited layer. Furthermore, the change of the concentration of free Cd^{2+} and Zn^{2+} ions, or the complex agent itself may modify the deposition mechanism of the buffer layer, which can influence the properties of the buffer layer. Since the properties especially the electrical properties of the buffer

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layer are important for chalcogenide solar cells, the usage of additional complex agent during the buffer deposition could be an effective way to modify the solar cell performances. But firstly, the influence of the complex agent on the properties of buffer layers should be investigated.

In this paper, we added sodium citrate into the deposition solution of $Cd_{1-x}Zn_xS$ layer. We found that the addition of such chemical could significantly adjust the composition of the deposited $Cd_{1-x}Zn_xS$ layer. We further investigated the influence of the sodium citrate concentration on the morphology, composition, electrical and optical properties of the $Cd_{1-x}Zn_xS$ layers. The results and the discussion about the deposited $Cd_{1-x}Zn_xS$ layers are shown below in this paper.

2. Experimental details

Cadmium acetate, zinc acetate, thiourea, sodium citrate and ammonia hydroxide are used as raw chemicals for the deposition of $Cd_{1-x}Zn_xS$, glass slides are used as substrates. Firstly, glass slides are successively cleaned by acetone, ethanol and pure water in a supersonic cleaner. For the deposition of $Cd_{1-x}Zn_xS$, the deposition solution is prepared by mixing the solution of cadmium acetate, zinc acetate, thiourea, sodium citrate and ammonia hydroxide. The concentration of cadmium acetate, zinc acetate, thiourea and ammonia hydroxide are fixed at 0.003 M, 0.009 M ,0. 25M and 1 M, respectively. The concentrations of sodium citrate are 0 M, 0.01 M, 0.02 M and 0.04 M for different deposition. After the preparation of the solution, the glass slides are put into the solutions and transfer to a water bath with the temperature of 75°C, the deposition last for different times to achieve similar thicknesses of 80nm. Finally, the glass slides are removed from the solution, cleaned by water and collected.

The morphologies of the deposited layers are measured by a FEI Scanning Electron Microscopy (SEM) (using an acceleration voltage of 15 kV). The composition of the film is measured by Orbis X-ray fluorescence (XRF) setup. The phases of the deposited layer are analyzed using a JY LabRAM HR Raman spectrometer equipped with 325 nm laser. XPS spectra of the buffer layer are measured using a ESCALAB250Xi setup. The transmittance and reflectance spectra of the films are measured using a PerkinElmer WinLab V6 UV spectroscopy. The conductivity of the $Cd_{1-x}Zn_xS$ layers in dark and under illuminations are measured under AM1.5 illumination by an Agilent B1500A Semiconductor Device Analyzer.

3. Results and discussion

3.1. Surface morphologies and compositions

Fig 1 shows the SEM images of the deposited layers. All the films are compact that fully cover the substrate. The films are composed of nano-sized clusters. This is probably the deposition of the layers follow the cluster-to-cluster mechanism [10]. By comparison, it is clear that the addition of sodium citrate increases the size of the cluster in the deposited films. Moreover, the films become smoother by using the sodium citrate additive. Table 1 shows the compositions of the deposited films. The results clearly prove that Zn is incorporated into the deposited layers, and the addition of sodium citrate significantly alter the composition of the deposited layers. By adding sodium citrate into the deposition solution, the Zn content in the layers are obviously reduced. This could be caused by the formation of a rather stable complex compound between Zn ion and citrate ions, the free Zn^{2+} ions in the solution would be decreased thus less Zn^{2+} ions can react with S^{2-} ion to incorporate into the deposited layer. However, when the concentration of sodium citrate changes, the Cd/Zn ratio in the deposited films does not change significantly, probably because the concentration of sodium citrate only changes from 0.01 M to 0.04 M. Actually, when the concentration of sodium citrate increases further, the deposition speed of the layer will be quite slow. So we don’t use higher concentration of sodium citrate in this paper.

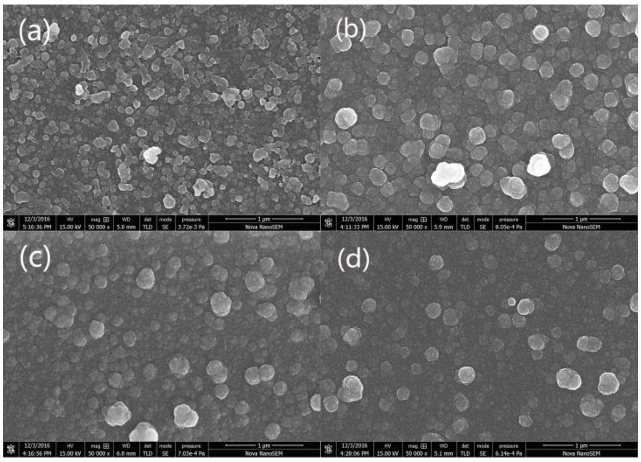

Fig 1. SEM images of the $Cd_{1-x}Zn_xS$ layers prepared with sodium citrate of (a) 0 M; (b) 0.01 M; (c) 0.02 M and (d) 0.04M

Table 1 XRF results of the $Cd_{1-x}Zn_xS$ layers prepared with different concentrations of sodium citrate

Concentration of sodium citrate	0 M	0.01 M	0.02M	0.04M
Atomic concentration of Cd	34.66	36.79	38.48	37.05
Atomic concentration of Zn	2.37	0.72	0.68	0.81
Cd/Zn ratio	14.62	51.10	56.59	45.74

3.2. Raman spectroscopy analysis

Fig 2 shows the Raman spectra of $Cd_{1-x}Zn_xS$ layers in the region of 300-800 cm^{-1}. For all the layers, two prominent Raman peaks can be seen which could be assigned to the 1-LO and 2-LO mode of $Cd_{1-x}Zn_xS$. By comparing with the 1-LO mode of CdS (located at ~297cm^{-1}) [11-13], the main Raman peaks of the $Cd_{1-x}Zn_xS$ (~299cm^{-1}) films prepared here are slightly shifted to the higher wavenumber. This could be caused by the incorporation of Zn into the lattice of CdS. For the $Cd_{1-x}Zn_xS$ layer prepared without sodium citrate, the main peak shift to the higher wavenumber due to higher Zn incorporation. Moreover, the ratio between the signal to noise for this sample seems smaller than the other samples, indicating that the micro-structure in this sample is more disordered than other samples. For the samples prepared with sodium citrate, there is no obviously difference found among their Raman spectra, indicating that the concentration of sodium citrate does not change the micro-structure of the $Cd_{1-x}Zn_xS$ layers too much.

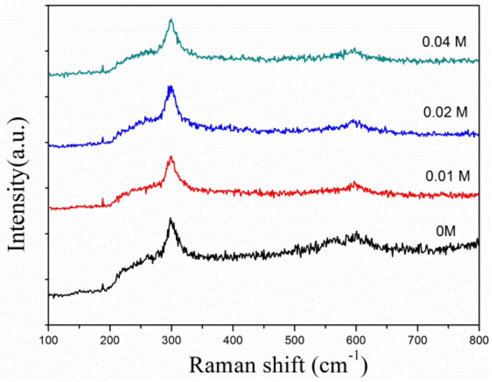

Fig 2. Raman spectra of the $Cd_{1-x}Zn_xS$ layers prepared with different concentrations of sodium citrate

3.3. XPS spectra analysis

To investigate the micro-structure of the $Cd_{1-x}Zn_xS$ layer, XPS measurement was deployed. Fig.3(a) shows the XPS spectra of the $Cd_{1-x}Zn_xS$ layers and Table 2 exhibits the composition of the buffer layers by XPS measurement. Since the XPS measurement only detect the surface are of the sample. The composition measured by XPS is the surface composition. By comparing Table 1 and Table 2, it can be seen the Zn content at surface is much higher than the Zn content in the bulk (especially for the layer prepared without sodium citrate). Because all the depositions of the buffer layers are terminated by removing from the deposition solution and rinsed by water, the deposition reaction at the surface may not fully finished. This may be the reason that the surface composition is different with the bulk composition. Moreover, the higher Zn content at the surface indicate that the Zn-related ions or compound real take part in the deposition of the buffer layer. Fig.3 shows the enlarged Cd $3d_{5/2}$ and Cd $3d_{3/2}$ peak for different $Cd_{1-x}Zn_xS$ layers[14]. It can be seen that the Cd 3d peaks shift to higher binding energies for the layer prepared with sodium citrate. To clarify this phenomenon, we fit the original XPS peaks of Cd $3d_{5/2}$ with three peaks at 404.6 eV (corresponds to CdO), 405.2 eV (corresponds to CdS) and 405.8 eV (corresponds to $Cd(OH)_2$). The fitting result of the peaks can be seen in Fig.3. For the $Cd_{1-x}Zn_xS$ layers prepared without sodium citrate, Cd element main exist as CdO at the surface. But for the $Cd_{1-x}Zn_xS$ layers prepared with sodium citrate, the CdS component increases. The sodium citrate also induces the formation of $Cd(OH)_2$ at the surface, and the quantity of this component is influenced by the concentration of the sodium citrate. As we mentioned, the deposition reaction was stopped when the sample was removed from the deposition solution, so the chemical environments of the elements at the surface may be not identical to the chemical environments of the elements in the bulk. However, the differences of the composition and chemical environments of elements between the surfaces of $Cd_{1-x}Zn_xS$ layers indeed indicate the deposition process or the deposition mechanism of the $Cd_{1-x}Zn_xS$ layers are modified by the addition of sodium citrate. Therefore, the properties of the $Cd_{1-x}Zn_xS$ layers may be changed by using sodium citrate in the deposition solution, so we investigated the optical and electrical properties of the $Cd_{1-x}Zn_xS$ layers.

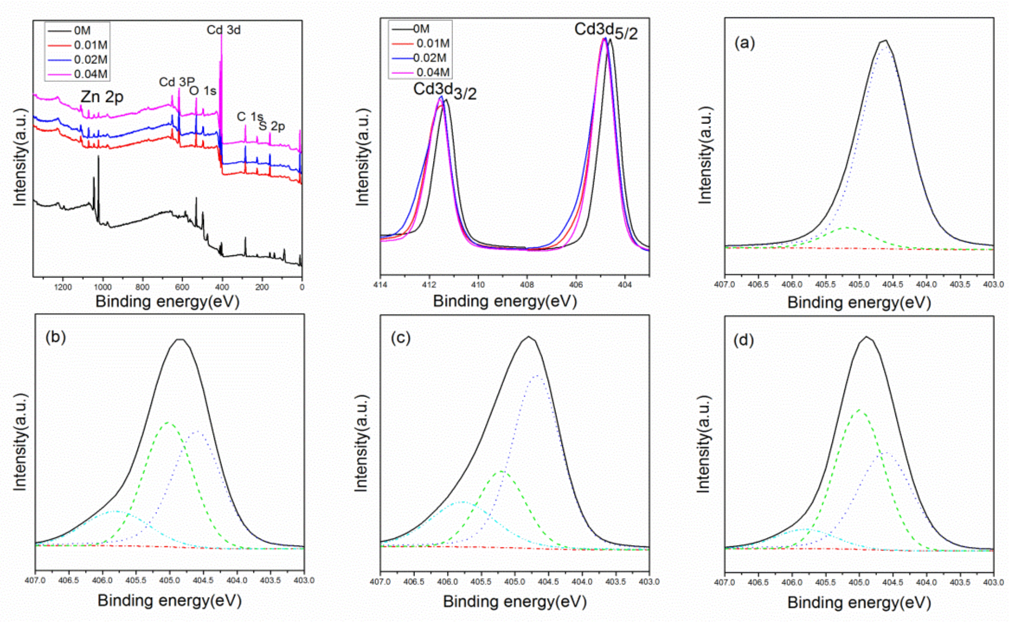

Fig.3 XPS spectra of the $Cd_{1-x}Zn_xS$ layers, enlarged Cd 2d peaks and their fitting results with sodium citrate of (a) 0 M; (b) 0.01 M; (c) 0.02 M and (d) 0.04M.

Table 2 Compositions of the $Cd_{1-x}Zn_xS$ layers prepared with different concentrations of sodium citrate by XPS

Concentration of sodium citrate	0 M	0.01 M	0.02M	0.04M
Atomic concentration of Cd	6.66	39.42	40.8	41.64
Atomic concentration of Zn	64.9	6.7	5.77	4.47
Cd/Zn ratio	10.26	5.88	7.07	9.32

3.4 Optical properties

Fig 4 (a) shows the transmittance and reflectance spectra of the deposited layers. It can be seen that the average transmittance of the films is around 75% for the light with wavelength above 500 nm. The relatively low transmittance is because of the high reflectance of the films (~ 25% at high wavelength region). From the transmittance and reflectance data, the absorption coefficient and the band-gap energy of the films can be calculated according to the Tauc formula [15]:

$$(\alpha h\upsilon)^2 = A(h\upsilon - E_g) \tag{1}$$

here α is the absorption coefficient of the material, $h\upsilon$ is the energy of the photon and E_g is the band-gap energy of the material. Fig. 4 (b) shows the Tauc plot of the films prepared with different concentration of sodium citrate. Due to the low content of the Zn in the films, the band-gap energies of the films are almost the same (i.e., all are around 2.5eV).

Based on the absorption coefficient, the Urbach energy (E_u) of the material can be calculated which indicates the degree of film with tail static disorder by valence band tail and conduction band tail states within the local area of electronic state transition. In principle, small E_u energy means small disorder of the end state. For the $Cd_{1-x}Zn_xS$ film prepared without sodium citrate, the E_u energy is 112 meV. For the $Cd_{1-x}Zn_xS$ film prepared with 0.01M, 0.02M and 0.04M sodium citrate, the E_u energies of the films are 88meV, 83meV, 82meV and 78meV, respectively. Therefore, we can conclude that the addition of sodium citrate in the deposition decrease the disorder of the structure in the $Cd_{1-x}Zn_xS$ films. This would benefit the electrical properties of $Cd_{1-x}Zn_xS$ films.

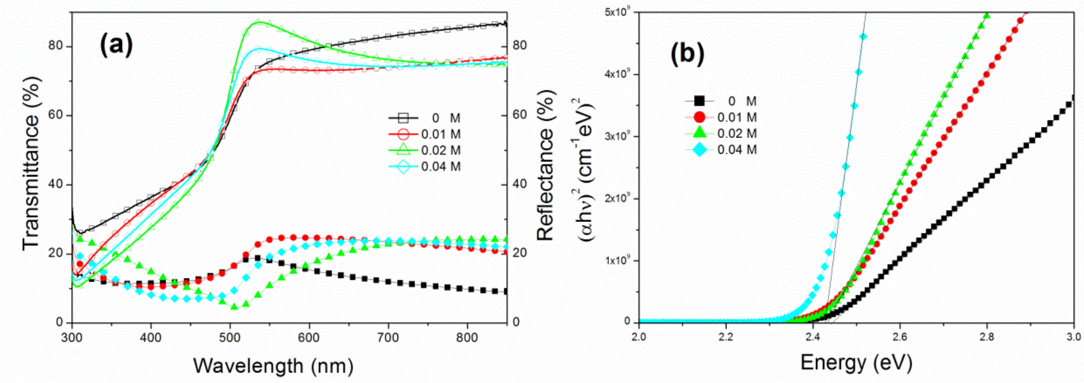

Fig 4. (a) Transmittance and reflectance spectra of the deposited layers (b) Tauc plot of the $Cd_{1-x}Zn_xS$ layers prepared with different concentrations of sodium citrate

3.4. Electrical properties of the $Cd_{1-x}Zn_xS$ films

The photo and dark conductivity of the $Cd_{1-x}Zn_xS$ films prepared using different concentration of sodium citrate are measured. The results of the measurement can be seen in Table 3 By comparing the data, we found that the addition of sodium citrate greatly decreases the conductivity of the $Cd_{1-x}Zn_xS$ films (decrease by 1-3 order of magnitude). For the $Cd_{1-x}Zn_xS$ films prepared with sodium citrate, $Cd_{1-x}Zn_xS$ films prepared by 0.01M of additive has relatively higher photo and dark conductivities than that of the other $Cd_{1-x}Zn_xS$ films. If more sodium citrate is added, the photo and dark conductivities of the $Cd_{1-x}Zn_xS$ films decrease significantly and do not change too much as the concentration of sodium citrate changes. The reason for the experimental above may be that the addition of sodium citrate changes the intrinsic or extrinsic electrical defects in the $Cd_{1-x}Zn_xS$ films (e.g., O, H and related complexes can be shallow donor in CdS[16]). Furthermore, we find that the addition of sodium citrate increases the ratio between the photo conductivity and dark conductivity, this is probably because that sodium citrate can decrease the disorder of the structure in $Cd_{1-x}Zn_xS$ films. Because the buffer layer with low conductivity could increase the series resist of the solar cell, $Cd_{1-x}Zn_xS$ films prepared by 0.01 M of sodium citrate would be suitable for solar cell fabrication due to the lower E_u energy and relatively high conductivity.

Table. 2 Photo and dark conductivities of the $Cd_{1-x}Zn_xS$ films prepared with different concentrations of sodium citrate

Concentration of sodium citrate (M)	Dark conduction $(\Omega\cdot cm)^{-1}$	Photoconduction $(\Omega\cdot cm)^{-1}$	Photosensitivity
0	6.33E-04	7.97E-03	1.26E+01
0.01	1.12E-05	9.11E-03	8.10E+02
0.02	1.72E-07	1.97E-04	1.14E+03
0.04	1.63E-07	2.33E-04	1.43E+03

4. Conclusions

In this paper, we prepared $Cd_{1-x}Zn_xS$ films by adding sodium citrate in the deposition solution containing Cd and Zn ions. The influence of the sodium citrate on the properties of $Cd_{1-x}Zn_xS$ films are investigated. The $Cd_{1-x}Zn_xS$ films should follow the cluster-to-cluster deposition mechanism, the addition of sodium citrate increases the size of the clusters in the $Cd_{1-x}Zn_xS$ films and make the films smoother. The Cd/Zn ratio in the $Cd_{1-x}Zn_xS$ films is greatly increased by the adding of sodium citrate.

The micro-structure, e.g., the chemical environment of Cd in the film, is changed by the addition of sodium citrate. Due to the low content of Zn in the $Cd_{1-x}Zn_xS$ films, the addition of sodium citrate does not change the optical band-gap of the $Cd_{1-x}Zn_xS$ films obviously. However, sodium citrate can decrease the E_u energy of the $Cd_{1-x}Zn_xS$ films, indicating that the degree of the structure disorder in the films are reduced. Finally, we find the conductivity of the films are decreased but the photo-to-dark conductivities are increased by the addition of sodium citrate.

The influence of the sodium citrate concentration on the properties of $Cd_{1-x}Zn_xS$ films are also investigated in this paper, however, the results show the properties of $Cd_{1-x}Zn_xS$ films do not change too much when the concentration of sodium citrate changes from 0.01 M to 0.04 M.

Acknowledgements

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