Hindawi Publishing Corporation
International Journal of Photoenergy
Volume 2014, Article ID 861249, 6 pages
http://dx.doi.org/10.1155/2014/861249

Research Article

Synthesis and Characterization of CZTS Thin Films by Sol-Gel Method without Sulfurization

Xiaoqi Yu, Aobo Ren, Fogen Wang, Ci Wang, Jingquan Zhang, Wenwu Wang, Lili Wu, Wei Li, Guanggen Zeng, and Lianghuan Feng

College of Materials Science and Engineering, Sichuan University, Chengdu 610064, China

Correspondence should be addressed to Jingquan Zhang; zjq100@hotmail.com and Wenwu Wang; 93319189@qq.com

Received 10 February 2014; Revised 28 May 2014; Accepted 28 May 2014; Published 22 July 2014

Academic Editor: Sudhakar Shet

One process of layer-by-layer sol-gel deposition without sulfurization was developed. The CZTS films with 1.2 μm and the sulfur ratio of ~48% were prepared and their characteristics were measured. The as-deposited and annealed films are of Kesterite structure. The as-deposited films do not present obvious electric conduction type. However, the annealed 9-LAY-ANN film is p-type conduction and has sheet resistance of 4.08 kΩ/□ and resistivity of 4.896×10^{-1} Ω·cm. The optic energy gap is 1.50 eV for as-deposited films and is 1.46 eV after being annealed. The region deposited by using Lo-Con solution is more compact than that by the Hi-Con solution from SEM morphology images.

1. Introduction

Great attention is paid to the earth-abundant and nontoxic CZTS (Cu_2ZnSnS_4) as a potential candidate for a light absorbing layer in thin film solar cell devices. The theoretical conversion efficiency of single-junction CZTS solar cell is 32.2% [1], because of its high absorption coefficient over 10^4 cm^{-1} and a suitable direct band gap of 1.4–1.5 eV. In general, the methods of fabricating CZTS films consist of the vacuum-based and the liquid-based techniques. The deposition systems are so expensive that they possibly increase the manufacturing cost for the vacuum-based technology, such as thermal evaporation [2] and Magnetron sputtering [3, 4]. However, the low-cost manufacturing system and process can be adopted by liquid-based technology, such as screen printing [5, 6], chemical bath deposition [7], electro-deposition [8], and sol-gel method [9–15].

The optical and electronic properties of CZTS films are dependent on their composition. So the sulfurization process is an indispensable step for vacuum-based techniques in order to obtain the stoichiometric film, because sulfur is apt to be deficient in the vacuum ambiance owing to its high saturation vapor pressure. On the other hand, the toxic H_2S was often used for the liquid-based deposition techniques to avoid S-deficiency during the annealing process [5, 9–13]. So the liquid-based techniques without intentional sulfurization were developed by some research groups [6–8, 14, 15]. Park et al. reported the CZTS film of 563 nm thickness with the ratio of S being about 50%, which was prepared by using sol-gel technology, by adding excess thiourea into the solution [15]. Yeh et al. reported the CZTS film of 2.9 μm with the ratio of S below 40%, which was prepared by layer-by-layer sol-gel technology in air with the synthetizing temperature of 593 K [14].

Usually, the thickness of CZTS thin film used as solar cell absorbing layer should be more than 1 μm with the purpose of absorbing the light sufficiently and the ratio of sulfur should be about 50%, in order to ensure optical and electronic properties of the film.

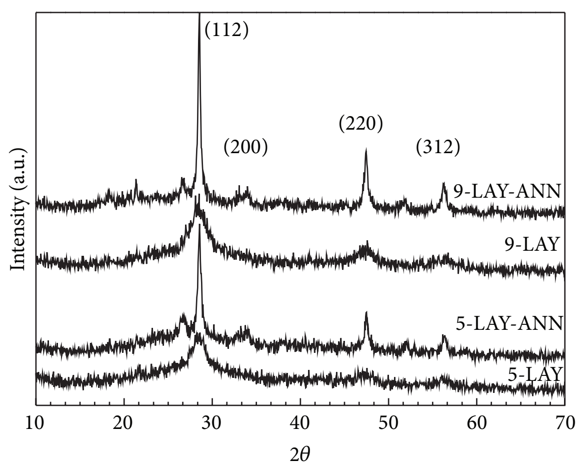
In this work, one process of layer-by-layer sol-gel (LBLSG) deposition without sulfurization was developed. The CZTS films with 1.2 μm and the sulfur ratio of ~48% were prepared and their characteristics were measured.

2. Experiment

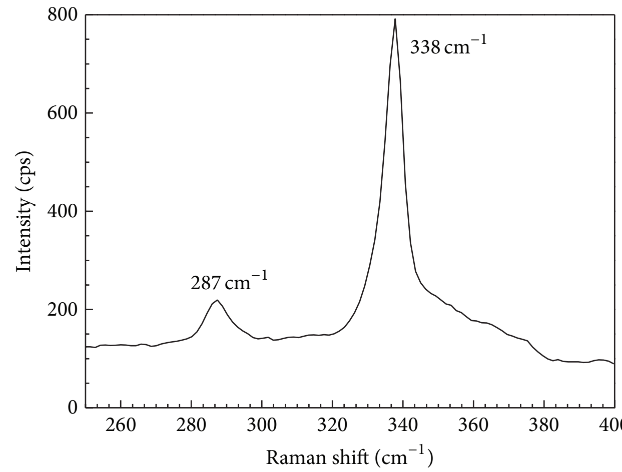
The sol-gel solutions for CZTS precursors were prepared by dissolving $CuCl_2{\cdot}2H_2O$, $Zn(CH_3COO_2)_2{\cdot}2H_2O$, $SnCl_2{\cdot}2H_2O$, and CH_4N_2S into 2-methoxyethanol (2-metho) and

Table 1: The amount of starting materials in the two solutions.

Solution	$CuCl_2 \cdot 2H_2O$ (mmol)	$Zn(ac)_2 \cdot 2H_2O$ (mmol)	$SnCl_2 \cdot 2H_2O$ (mmol)	CH_4N_2S (mmol)	2-metho (mL)	MEA (mL)
Hi-Con	14.4	9.6	8	64	10	1
Lo-Con	3.6	2.4	2	16	10	1



(a)



(b)

Figure 1: (a) XRD patterns of the CZTS films. (b) Raman spectrum of 9-LAY-ANN CZTS thin film.

monoethanolamine (MEA). The 2-metho and MEA were used as the solvent and the stabilizer, respectively. Two types of sol-gel solutions, named as Hi-Con and Lo-Con, were prepared by the recipe shown in Table 1. Each solution was stirred for 20 min at 300 K. The vicious yellow solution Hi-Con was used to make the film thick enough and the pale yellow solution Lo-Con aimed to make the film surface smooth and compact.

CZTS films were deposited on the borosilicate glass. The procedures to deposit each layer in the LBLSG included spin-coating, drying, and baking. Firstly the solution was dropped and rotated for 60 s at 3000 rpm; secondly the spin-coated films were dried at 393 K for 2 h in air on the hot plate; thirdly the dried samples were baked at 523 K for 10 min under nitrogen atmosphere in the quartz tube to prevent O_2 affecting the film. Three samples were prepared. The sample 3-LAY was deposited up to three layers on the borosilicate glass, using solution Lo-Con by LBLSG process. The sample 5-LAY was deposited up to 5 layers, which was deposited with two layers by using solution Hi-Con on the sample 3-LAY. The sample 9-LAY was deposited up to 9 layers, which was deposited with four layers by using solution Lo-Con on the sample 5-LAY. The as-deposited samples of 5-LAY and 9-LAY were annealed at 773 K for 60 min under N_2 atmosphere, named as 5-LAY-ANN and 9-LAY-ANN, respectively.

The structure and phase were characterized by X-ray diffraction (XRD) by using a DX-2500 XRD diffractometer from Dandong Fangyuan Instrument LLC, China. The Raman spectrum was recorded by using a LabRAM-HR Raman Spectrometer from Horiba-Jobin Yvon Ibh Ltd. The film morphologies of surface and cross section were observed by a Hitachi S-4800 scanning electron microscope (SEM), and the compositions were determined by energy dispersive spectrometer (EDS) attached to SEM. X-ray photoelectron spectroscopy (XPS) was measured in order to analyze the element chemical valence state of films via an X-ray photoelectron spectroscope (KRATOS, AXIS Ultra DLD). The transmittance was measured using a UV-VIS-NIR spectrophotometer PerkinElmer Lambda 950 with 150 mm integrating sphere. The film thickness was determined by a surface profiler (XP-2, Ambios Technology, Inc.). The sheet resistance was measured by RTS-9 four-probe test system from Guangzhou 4Probes Tech. Inc., China. And the conductive type was determined using cold-hot probe method by a PN-12 conductive type measure system from Guangzhou 4Probes Tech. Inc., China.

3. Results and Discussion

The XRD patterns of films are shown in Figure 1(a). The as-deposited thin films, 5-LAY and 9-LAY, were poorly crystalline, while the annealed films, 5-LAY-ANN and 9-LAY-ANN, are well crystalline which match well the Kesterite structure of CZTS (JCPDS card 26-0575). The refined tetragonal lattices parameters for 9-LAY-ANN are $a = b = 5.42$ Å, $c = 10.83$ Å, and $V = 318.24$ Å^3, analyzed by Jade5.0 software; however, for sample 5-LAY-ANN, the refined tetragonal lattices parameters were not figured out because of the major error. The crystallites size of 5-LAY-ANN and 9-LAY-ANN was calculated as 24.9 nm and 31.8 nm, respectively, using Debye-Scherrer formula by Jade5.0 software.

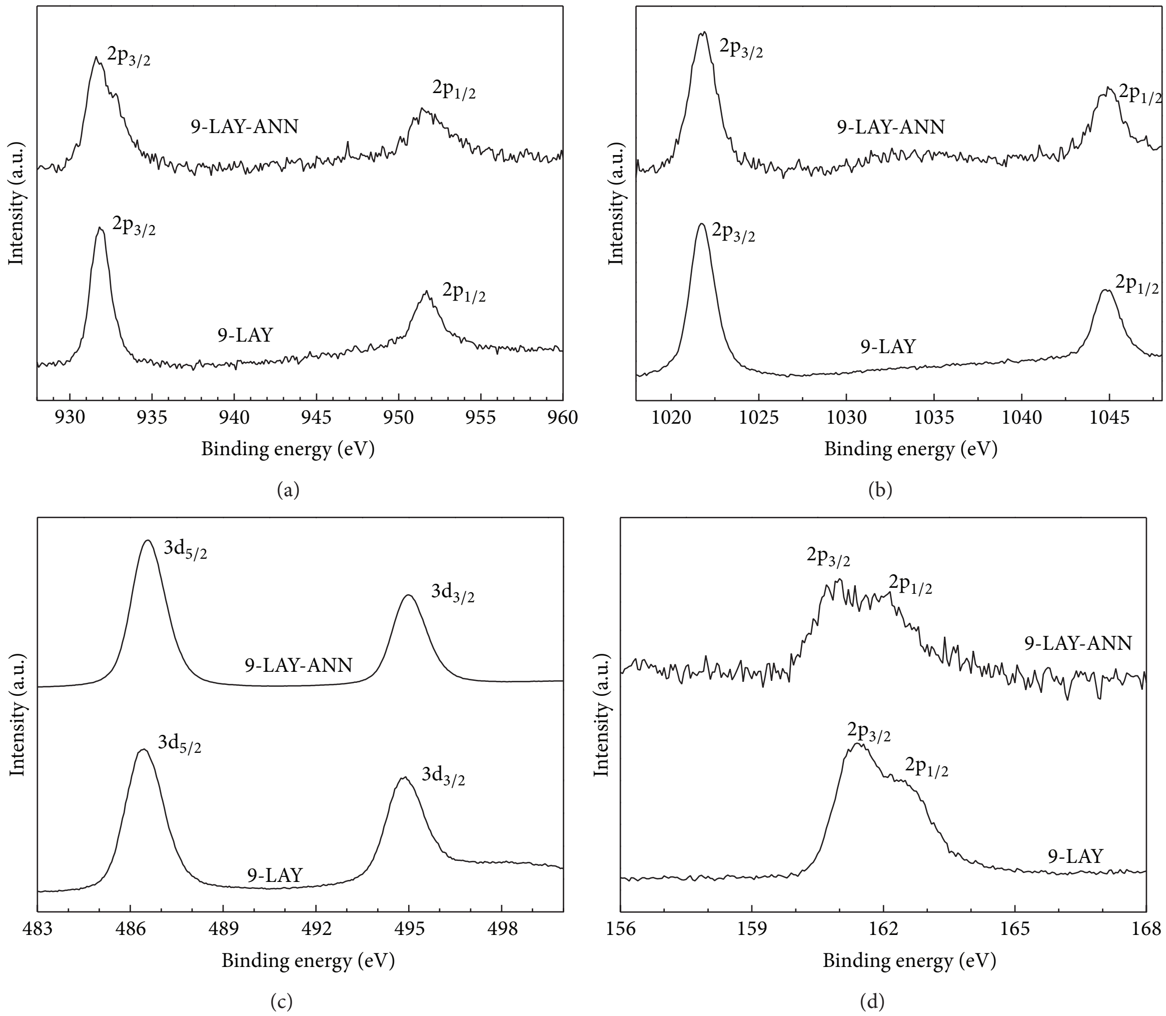


Figure 2: XPS spectra of 9-LAY and 9-LAY-ANN CZTS thin films: (a) Cu 2p, (b) Zn 2p, (c) Sn 3d, and (d) S 2p.

Table 2: Element binding energy values of CZTS films' XPS spectra.

Sample	Cu $2p_{3/2}$ (eV)	Cu $2p_{1/2}$ (eV)	Zn $2p_{3/2}$ (eV)	Zn $2p_{1/2}$ (eV)	Sn $3d_{5/2}$ (eV)	Sn $3d_{3/2}$ (eV)	S $2p_{3/2}$ (eV)	S $2p_{1/2}$ (eV)
9-LAY	932.0	951.4	1021.8	1044.7	486.5	494.9	161.5	163.0
9-LAY-ANN	931.7	951.7	1021.8	1044.9	486.6	495.0	161.0	162.5

Since the (112), (200), (220), and (312) peaks of Cu_2ZnSnS_4 XRD pattern are very close to the (111), (200), (220), and (311) of ZnS XRD pattern (JCPDS card 65-5476), it is necessary to identify further the phases by Raman spectroscopy [16]. The Raman spectrum of 9-LAY-ANN is presented in Figure 1(b). The Cu_2ZnSnS_4 Raman peaks are observed at 287 cm^{-1} and 338 cm^{-1}, while the ZnS Raman peak is not observed at 351 cm^{-1}, demonstrating a single-phase Kesterite CZTS.

XPS spectra of 9-LAY and 9-LAY-ANN CZTS thin films are shown in Figure 2. The element binding energy and the spin-orbit splitting values are listed in Tables 2 and 3, respectively, which are consistent with those reported in the literatures [3, 6, 17]. The almost same characteristics of XPS spectra between 9-LAY and 9-LAY-ANN demonstrate that the CZTS phase began to grow in the LBLSG process, which is consistent with XRD measurements, in which the broad and weak peaks of (112), (220), and (312) are observed for as-deposited samples.

Table 3: Spin-orbit splitting values of CZTS films' XPS spectra.

Sample	Cu 2p (eV)	Zn 2p (eV)	Sn 3d (eV)	S 2p (eV)
9-LAY	19.4	22.9	8.4	1.5
9-LAY-ANN	20.0	23.1	8.4	1.5

The transmittance curves of the CZTS thin films are shown in Figure 3(a), and the Tauc curves calculated from the transmittance curves are shown in Figures 3(b)–3(e). The

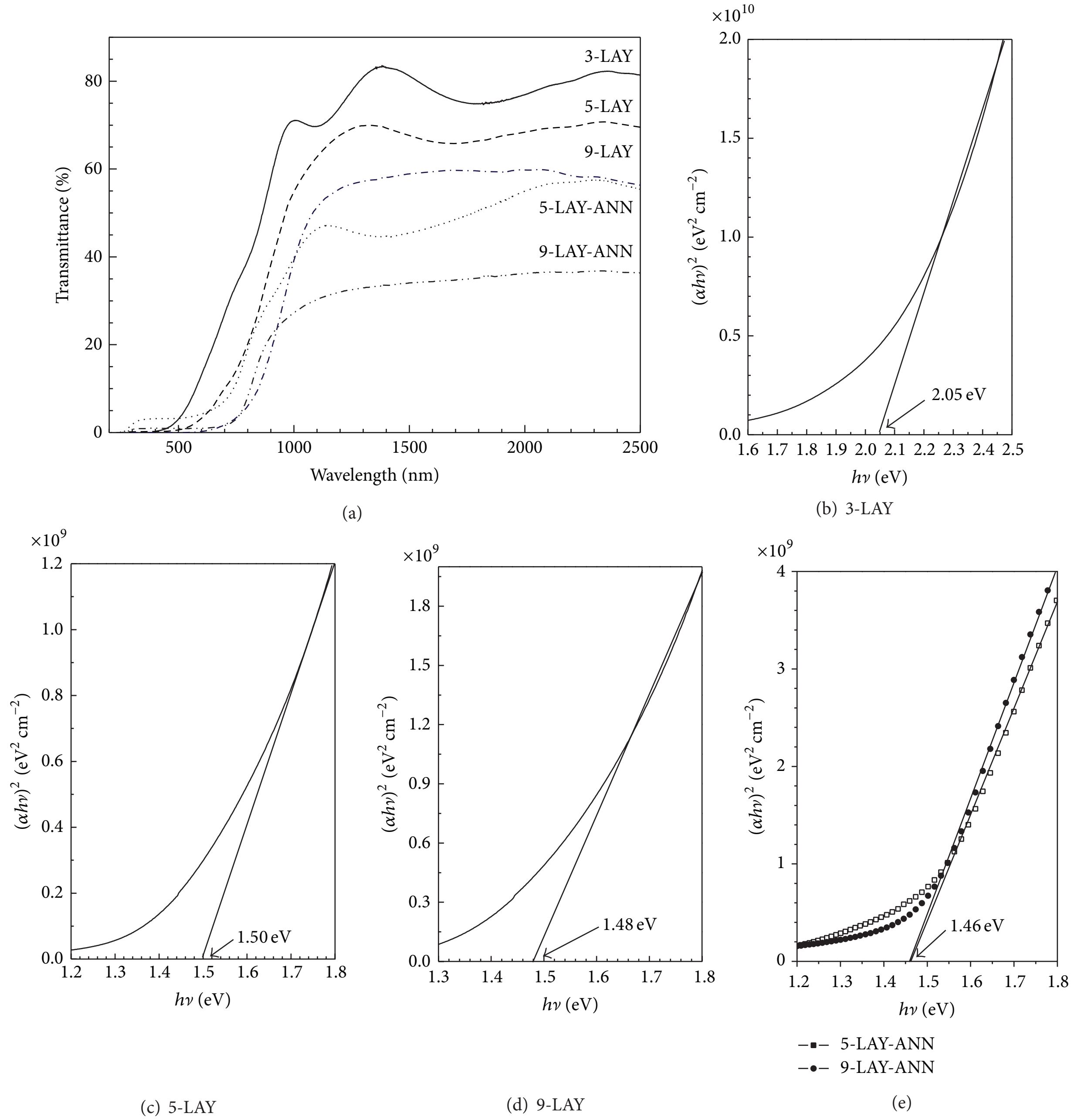
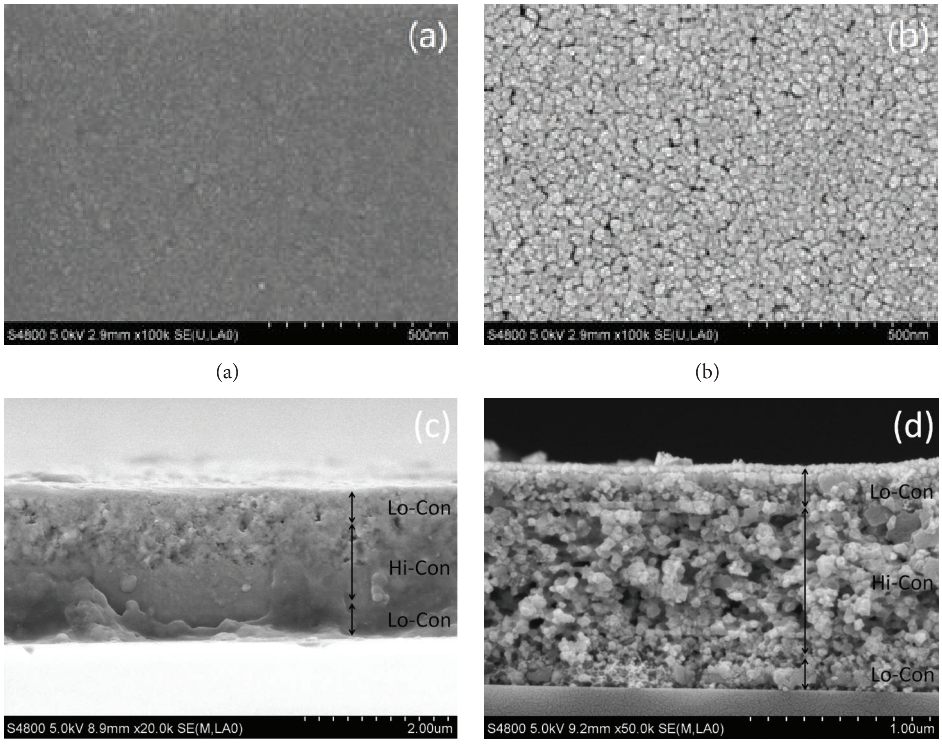


Figure 3: (a) Transmittances of CZTS films. (b)–(e) Tauc curves of CZTS films.

absorption band-edge blue shift of sample 3-LAY transmittance is observed compared with 5-LAY. And the absorption band-edge blue shift of sample 5-LAY transmittance is observed compared with 9-LAY. The absorption band-edge is dependent on the material energy band structure, which is determined by the atom arrangement and crystallization degree. So 9-LAY film should have higher crystallinity than 5-LAY and 3-LAY. The optic energy gap from Tauc curves are listed in Table 4. The annealed samples of 5-LAY-ANN and 9-LAY-ANN have lower optic energy band gap compared with the as-deposited samples of 5-LAY and 9-LAY, which indicates that the annealed films present higher crystallinity. That is consistent with the XRD measurements.

Figure 4 shows SEM photographs concerning surface and cross section morphology of 9-LAY and 9-LAY-ANN CZTS films. There are no obvious grain characteristics for as-deposited 9-LAY film, while about 30 nm grains can be observed for the annealed 9-LAY-ANN film (see Figure 4). Besides, the as-deposited film is compact according to Figure 4(c), while the holes and bigger grains are observed for annealed film as shown in Figures 4(b) and 4(d). The region deposited by using the Lo-Con solution is more compact than



(a) (b) (c) (d)

Figure 4: SEM photographs of CZTS films. (a) and (c) Surface and cross section of 9-LAY. (b) and (d) Surface and cross section of 9-LAY-ANN.

Table 4: Characterizations of the CZTS films.

Sample	Thickness (μm)	Sheet resistance ($\Omega/\square$)	Conduction type	Eg (eV)
3-LAY	0.4	\	\	2.05
5-LAY	1.3	\	\	1.50
5-LAY-ANN	0.9	5.25×10^3	P	1.46
9-LAY	1.7	\	\	1.48
9-LAY-ANN	1.2	4.08×10^3	P	1.46

Table 5: The compositions of the CZTS thin films.

Sample	Cu%	Zn%	Sn%	S%	Cl%	Cu/(Zn + Sn)	Zn/Sn
9-LAY	19.44	15.11	10.64	46.44	8.37	0.75	1.41
9-LAY-ANN	23.49	16.04	12.35	48.12	\	0.83	1.30

that deposited by using the Hi-Con solution, as shown in Figures 4(c)-4(d).

Table 5 is the chemical compositions of CZTS films obtained by EDS measurement. There is Cl in the as-deposited sample, 9-LAY, but Cl is not detected from the annealed 9-LAY-ANN film. The ratio of S/(Cu + Zn + Sn) is 1.028 for 9-LAY and decreases to 0.928 after being annealed. The ratio of metal elements, Cu/(Zn + Sn) and Zn/Sn, is 0.83 and 1.30, respectively, for the annealed 9-LAY-ANN, which is Cu-poor and Zn-rich.

The as-deposited films did not demonstrate obvious conduction type and their sheet resistances were too high to be measured by four-probe test system. The sheet resistances of 5-LAY-ANN and 9-LAY-ANN are 5.25 k$\Omega/\square$ and 4.08 k$\Omega/\square$, respectively, and their resistivity is 4.725×10^{-1} Ω·cm and 4.896×10^{-1} Ω·cm, respectively. The film crystallinity change and Cu-poor will promote the formation of copper vacancy in the annealing process, which is the reason that the conduction type and sheet resistance of the annealed films could be detected.

4. Conclusion

CZTS films were prepared by LBLSG technology without specific sulfurization. The CZTS phase began to form in the LBLSG process. And the grains grew up to ~30 nm after being annealed. The optic energy gap is 1.50 eV for as-deposited film and is 1.46 eV after being annealed. The as-deposited and annealed films are both of Kesterite structure. The as-deposited films do not present obvious electric conduction type. However, the annealed film is p-type conduction and has sheet resistance of 4.08 kΩ/□ and resistivity of 4.896×10^{-1} Ω·cm for 9-LAY-ANN film. The region deposited by using Lo-Con solution was more compact than that by the Hi-Con solution from SEM morphology images.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

This work was supported by the National High Technology Research and Development Program (no. 2011AA050515) and Sichuan Province Science and Technology Support Program (no. 2013GZX0145).

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