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INVESTIGATION OF Cu(In,Ga)Se2 FILMS FABRICATED BY ONE-STEP ELECTRODEPOSITION

HSIANG CHEN[a*], YIH MIN YEH[b], SHENG TING HUANG[a],WEN JIN YEH[b]
[a]*Department of Applied Materials and Optoelectronic Engineering, National Chi Nan University, Puli, Taiwan*
[b]*Graduate School of Opto-Mechatronics and Materials, WuFeng University, Minsyong, Chiayi*

In this study, CIGS thin films were fabricated on an ITO substrate by one-step electrodeposition with different conditions. The films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscope (AFM), and energy-dispersive X-ray spectroscopy (EDS). In addition, we annealed the as-deposited thin film at 200-350°C for 30 min and then analyzed the crystalline structure and material morphology of the annealed films to observe the effects of annealing on the film composition.

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Keyword: one-step; electrodeposition; Cu(In,Ga)Se_2; thin film solar cell;annealing

1. Introduction

$CuIn_{1-x}Ga_xSe_2$ (CIGS) thin films are considered as one of the most ideal materials for low cost and high-efficiency solar cells because of their high absorptivity (>$10^5 cm^{-1}$) and stability.[1] Among various fabrication methods for preparing CIS(CIGS) absorber layers including co-evaporation, sputtering and selenization, and electrodeposition, co-evaporation is the most successful technique which has the highest conversion efficiency that can reach to 20% in a laboratory scale [2-7]. However, solar cells based on CIGS absorber layers with highest efficiency have been fabricated via complicated and expensive vacuum technology. In contrast, the electrodeposition technique is potentially suitable to obtaining low cost, good quality, large area CIGS thin films because of low temperature, non-vacuum and simple fabrication processes.[8-12] In our experiment, a one-step elecrodeposition for preparing CIGS thin films have been used and followed by annealing at various temperatures from 200 to 350°C to figure out the preferable condition to fabricate a high quality films.

2. Experiment

To fabricate the electrodeposited CIGS film, we first prepared a bath containing $CuCl_2$, $InCl_3$, $GaCl_3$ and H_2SeO_3. The pH value was adjusted from 1.5-2.0 by HCl and NH_4OH. The CIGS thin films were electrodeposited using a classical set-up of the three-electrode potentiostatic system in an electrochemical cell. The set-up comprised of a reference electrode (Ag/AgCl), a counter electrode (Pt), and the working electrode (ITO). During the deposition process, a constant potential of -2.5 V to -3.5 V was applied for 5-40 min at different temperatures from 28-60 °C. In order to enhance the crystallinity of thin film, reduce the defects and appropriately adjust the grain size, we annealed the deposited CIGS thin fim at the temperature from 200-350°C in the tube annealing furnace for 30 min.

*Corresponding author: hchen@ncnu.edu.tw

The as-deposited and annealed films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscop (AFM), and energy-dispersive X-ray spectroscopy (EDS) to analyze the structure, morphology, thickness and composition of the films.

3. Results and discussion

To fabricate the CIGS film, the films are grown in various deposition conditions. To get better quality of the deposited film, it is feasible that we can stir the bath to let ions evenly distribute in the bath. However, the same theory applies to this experiment is infeasible. Table 1 shows the compositions of the films measured by EDS. We can observe that In and Ga do not separate out with stirring, but the four elements separate out in the same condition of depositing without stirring. Therefore, we can speculate that stirring the bath hinders the co-depostion. Moreover, Fig. 1 (a)-(f) present the surface morphology of the film deposited in various conditions in Table 1. As shown in Fig.1, the film surface morphology with stirring the bath is sheet-based, and granular-based without stirring.

Table.1 Result of thin film with or without stirring during the deposition process

sample No.	with stirring	deposited potential	ratio of thin film composition%				Cu/(In+Ga)	X=Ga/(Ga+In)
			Cu	In	Ga	Se		
(a)	yes	-2.8	60.46	0.00	0.00	39.54		
(b)	no	-2.8	34.72	8.75	0.26	56.27	3.8535	0.0289
(c)	yes	-3.0	56.41	0.00	0.00	43.59		
(d)	no	-3.0	28.89	16.68	2.65	52.38	1.4946	0.1371
(e)	yes	-3.2	34.29	0.00	0.00	65.71		
(f)	no	-3.2	28.74	19.39	3.28	48.58	1.2678	0.1447
※Fixed parameters：pH=1.6，deposition time 10 min								

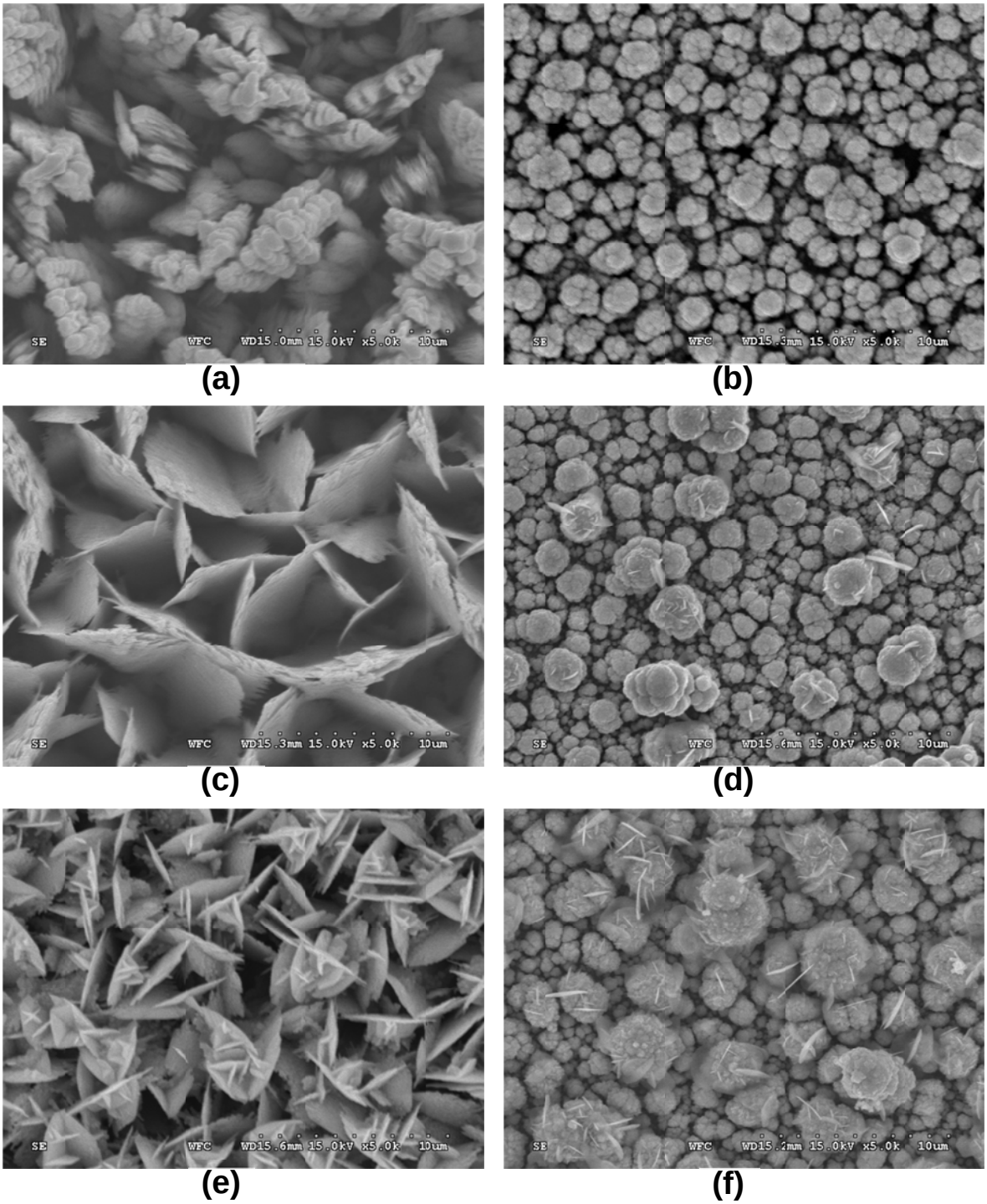

Fig.1 Film surface morphology with or without stirring during the deposition process.

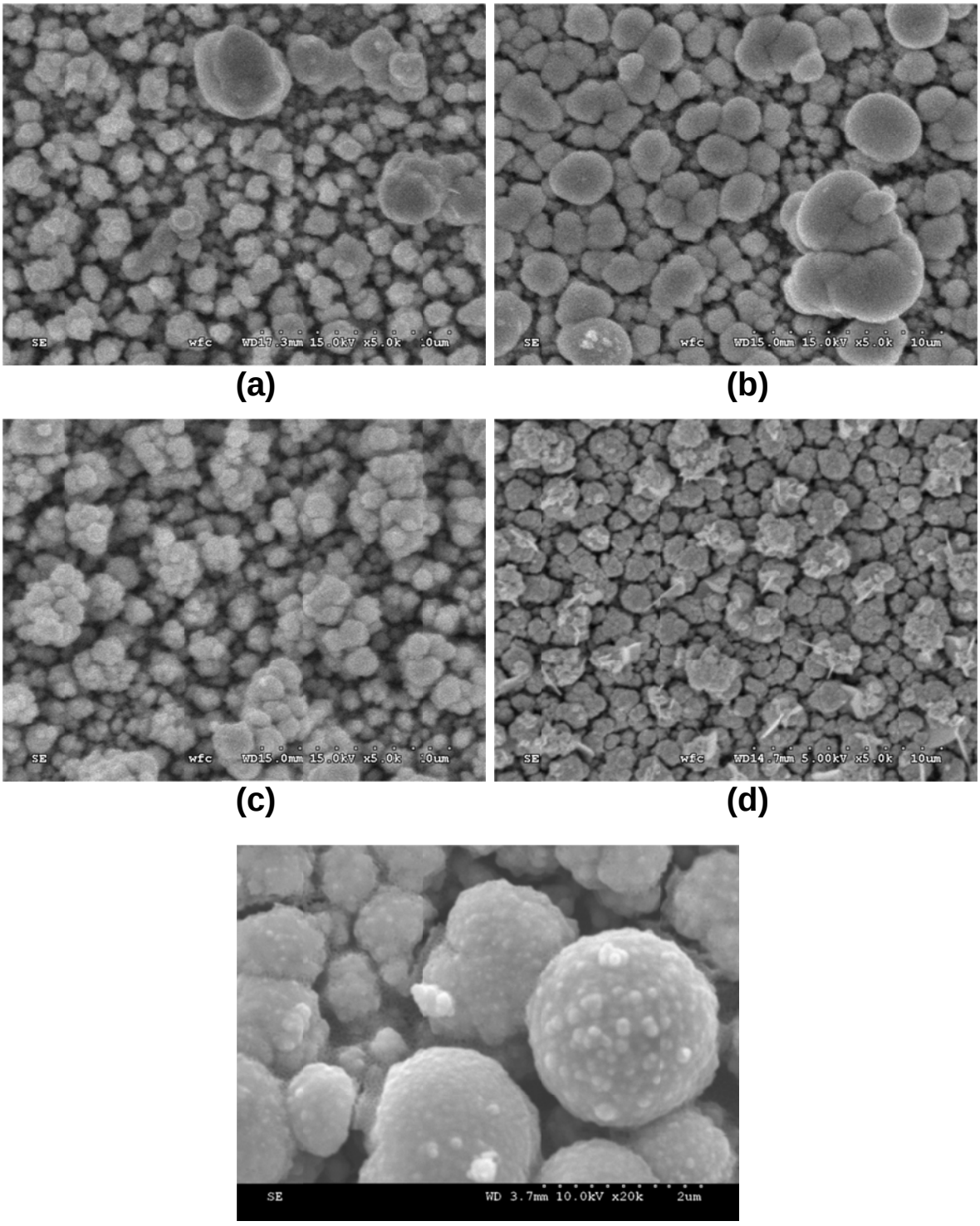

Fig.2 By depositing 10 min, using deposition potential -3.2V, the CIGS thin film surface morphology with different pH: (a)1.6 (b)1.7 (c)1.8 (d)1.9, (e) a larger magnification of fig.2(b)(20K magnification rate)

In addition to stirring, many factors such as electrodeposition time, deposition temperature, and pH value will influence the CIGS surface morphology. Fig. 2(a)-(d) show the pH effects on thin film surface morphology. It is obvious that the higher the pH value is, the smaller the CIGS crystalline particles are. To view the particles with a larger magnification rate as shown in Fig. 2 (e). The large particles consist of many small particles.

Since surface morphology resolution can be generally observed by SEM only in micron meter scale, we use AFM to make further observations on the surface of the samples to understand the surface morphology of $Cu(In_{1-x}Ga_x)Se_2$ thin film in nanoscale. Fig.3(a)-(d) shows the comparison with AFM and SEM image of the $Cu(In_{1-x}Ga_x)Se_2$ thin film. In the observation of the particles in nanoscale, it can be clearly found that the growth direction of $Cu(In_{1-x}Ga_x)Se_2$ crystalline particles is random and the surface of Cu(In1-xGax)Se2 thin film has some pores. By carefully observing, we found that each spherical particle as shown in SEM images of Fig. 3(a) and (b) is composed by clusters of small crystalline particles as shown in AFM images of Fig. 3(c) and (d).

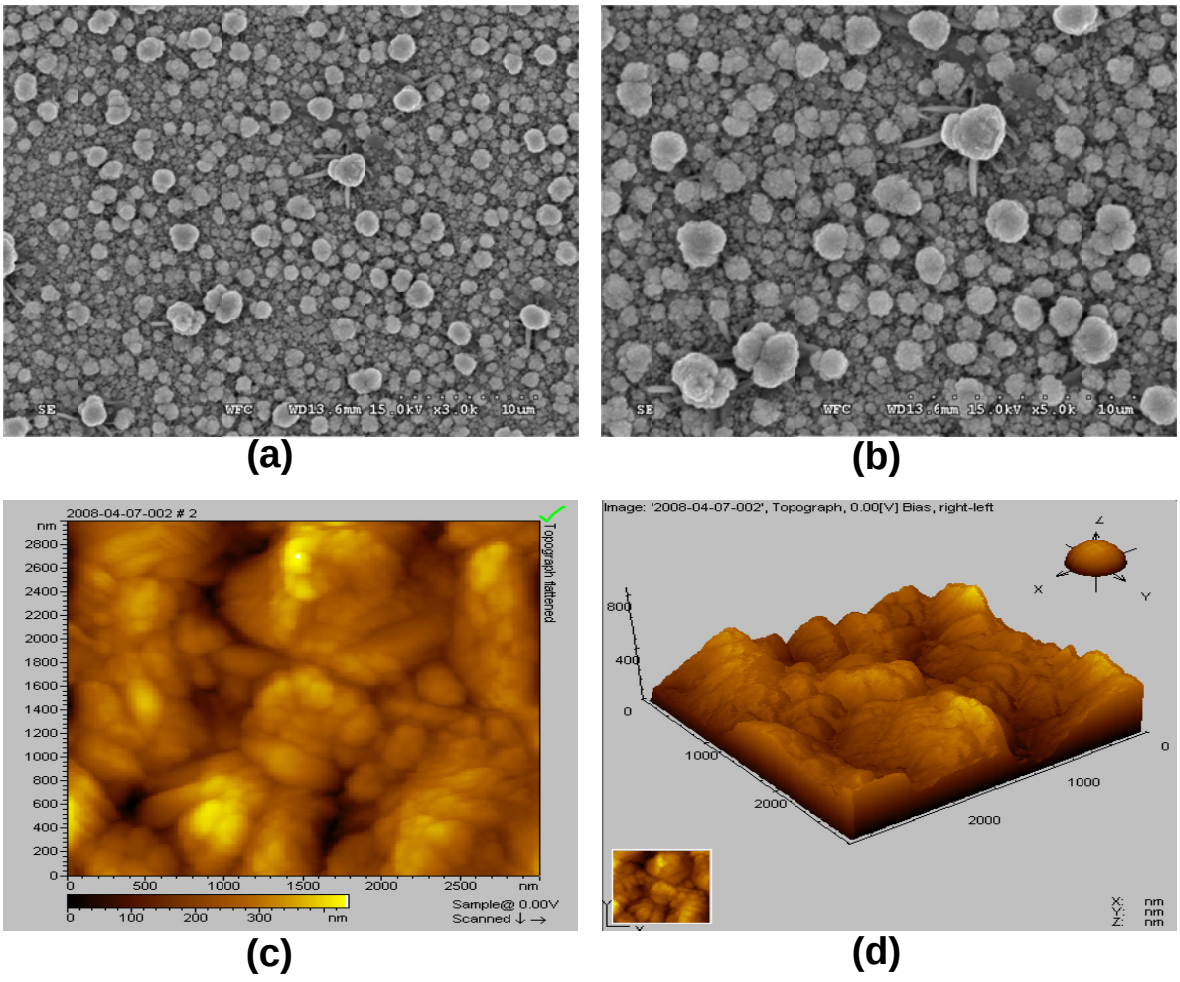

Fig.3 The microscopic image with deposition time 10 min, deposition potential -3.0V, and pH value 1.7: (a)3.0K SEM image (b)5.0K SEM image (c)2D AFM image (d)3D AFM image.

Furthermore, in addition to changing the deposition potential and pH value, heating the deposition bath can helps the precipitation of Ga as shown in Table.2. Though there are many disadvantage of heating the bath including shortening the life of the electrode, accelerating the bath damage, and peeling the plated film especially when the bath heated to 70°C , the film has better compactness and higher Ga concentration as the deposition temperature is increased to 60°C as shown in Fig.4(a)-(d) and Table 2.

Table.2 Result of thin film with different deposition temperatures.

No.	Temperature	ratio of thin film composition %				Cu/(In+Ga)	X=Ga/(Ga+In)
		Cu	In	Ga	Se		
(a)	28°C	29.85	14.32	3.39	52.45	1.6855	0.1914
(b)	40°C	26.79	9.36	5.28	58.57	1.8299	0.3607
(c)	50°C	34.21	12.46	9.02	44.31	1.5926	0.4199
(d)	60°C	31.36	13.09	11.73	43.82	1.2635	0.4726
※Fixed parameters：Deposition potential -3.0V，pH=1.7，deposition time 10 min							

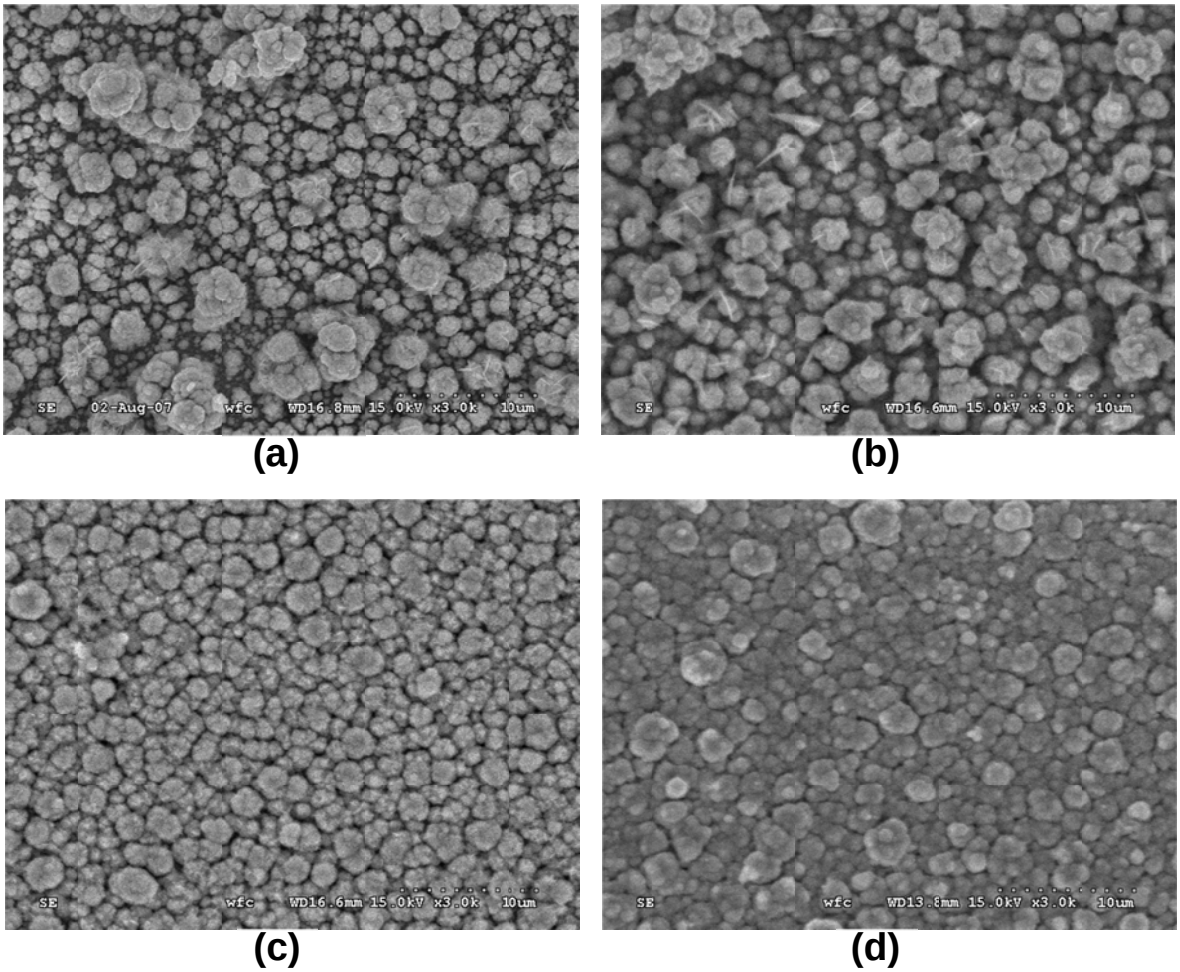

Fig.4 SEM micrographs of thin films deposited at different temperature: (a)28°C, (b)40°C, (c)50°C and (d) 60°C

As shown in Fig.5 (a)-(d), with deposition time increasing, the crystalline particles of CIGS thin film becomes larger, making the big clusters of the thin film surface and the flakes appear.

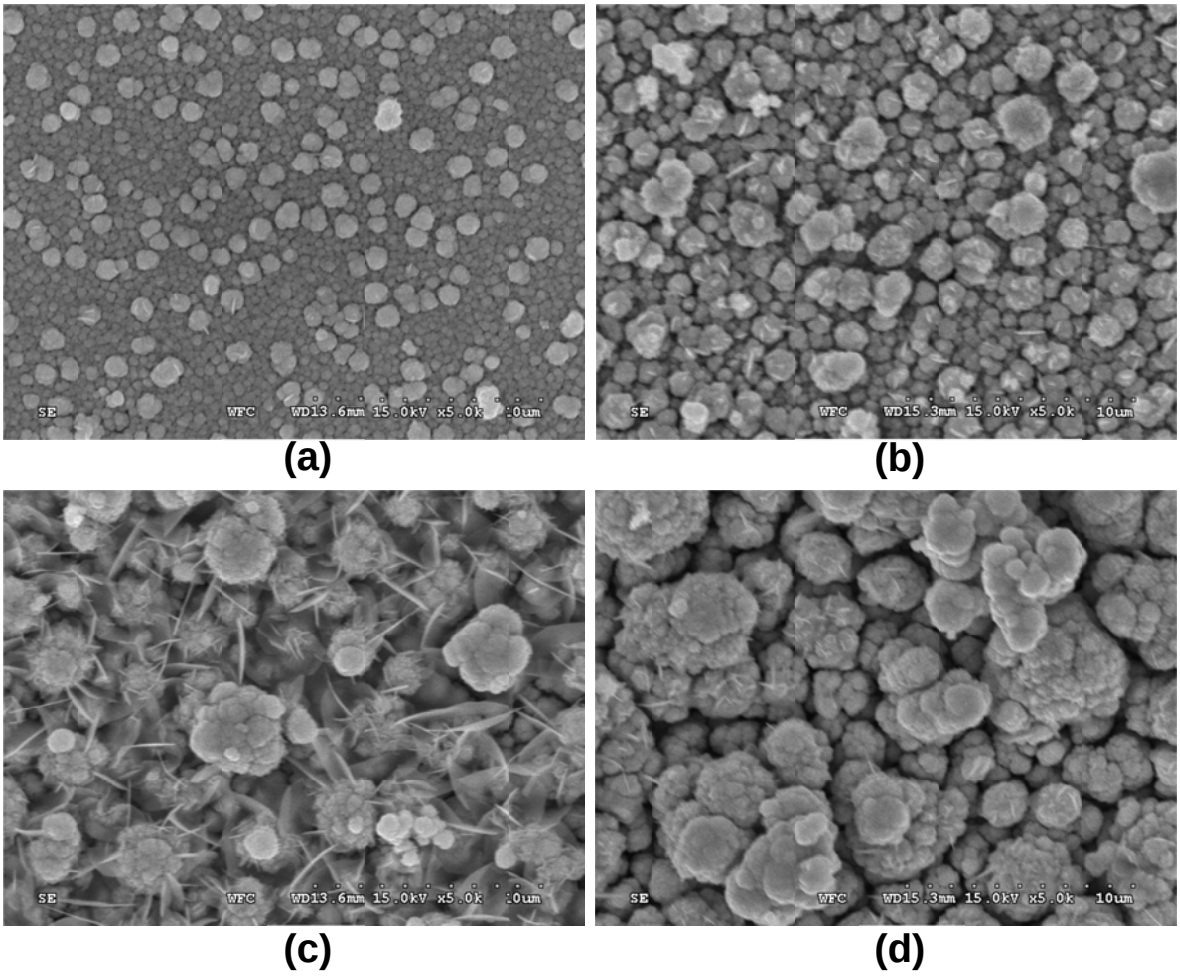

Fig.5 SEM micrographs of CIGS thin films deposited in different time with deposition potential -3.0V, and pH value 1.7: (a)5 min (b)10 min (c)20 min (d)40 min.

Moreover, thin film grows thicker as the depostion time increases by observing the cross-sectional thickness, and the film grows messily when deposition time is longer as shown in Fig. 6 (a)-(d). Since the CIGS solar cell absorber layers just require a thickness of 1-3μm to absorb the sun's energy effectively, the preferable deposition time is 5 min.

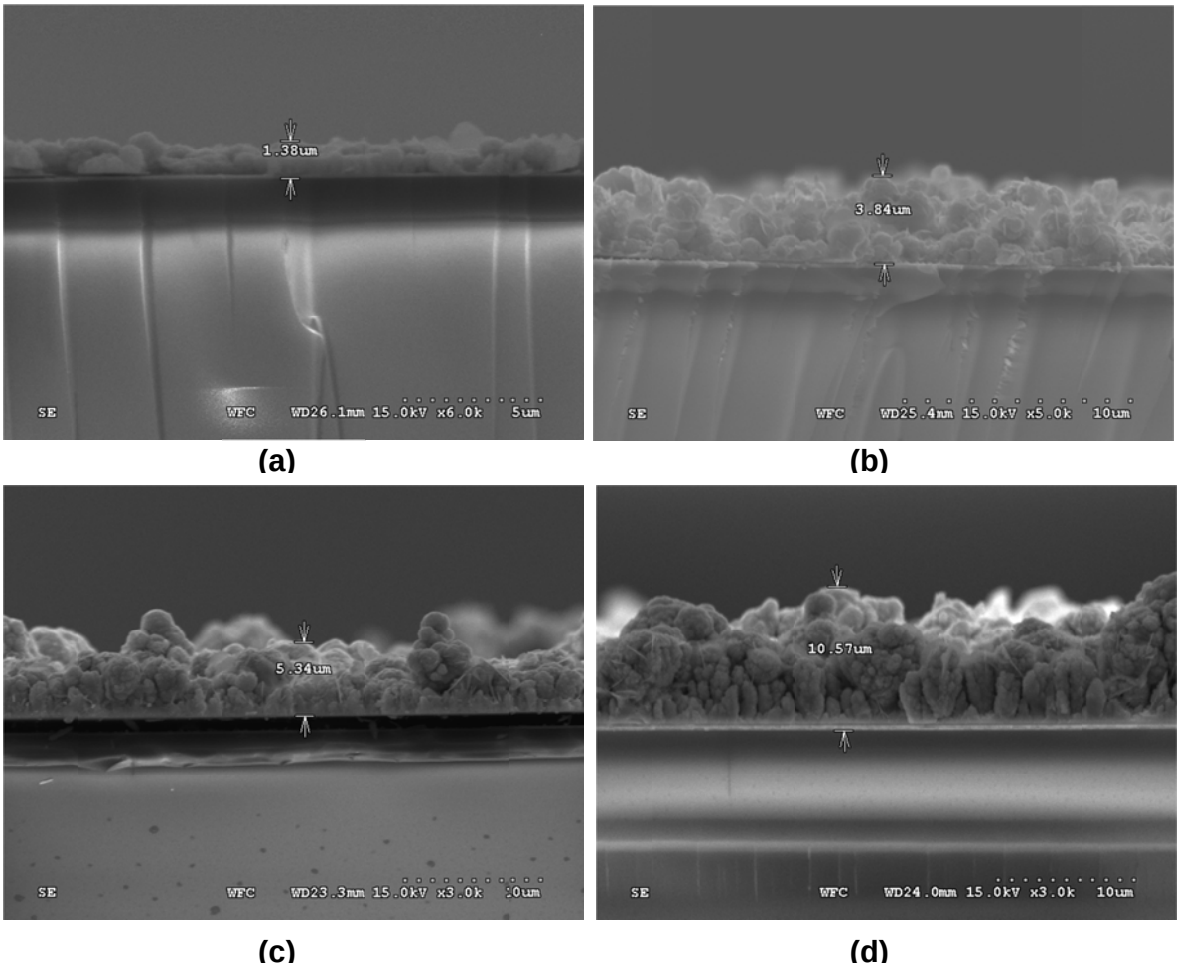

Fig.6 With deposition potential -3.0V, pH value 1.7, the profile morphology and thickness of CIGS thin film deposited in different deposited time: (a)5 min (about 1.38μm) (b)10 min (about 3.84μm) (c)20 min (about 5.34μm) (d)40 min (about 10.57μm)

The uniformity of film composition and crystallinity can be improved by iannealing after the growth of the film, which can diffuse atoms to reduce the concentration gradient so that the composition of film is evenly distributed. The thin film latticecan be rearranged so that the crystallinity becomes better. Based on the XRD diffraction pattern in Fig.7, diffraction peak intensity is strongest for the film annealed at 200°C for 30 min, indicating the film has better crystallinity. From the SEM images in Fig.8(a)-(f), we can find that annealing temperatures higher than 200°C can cause the cracks. By comparing SEM and XRD analyses, we infer that annealing temperature of 200°C is the preferable condition. .

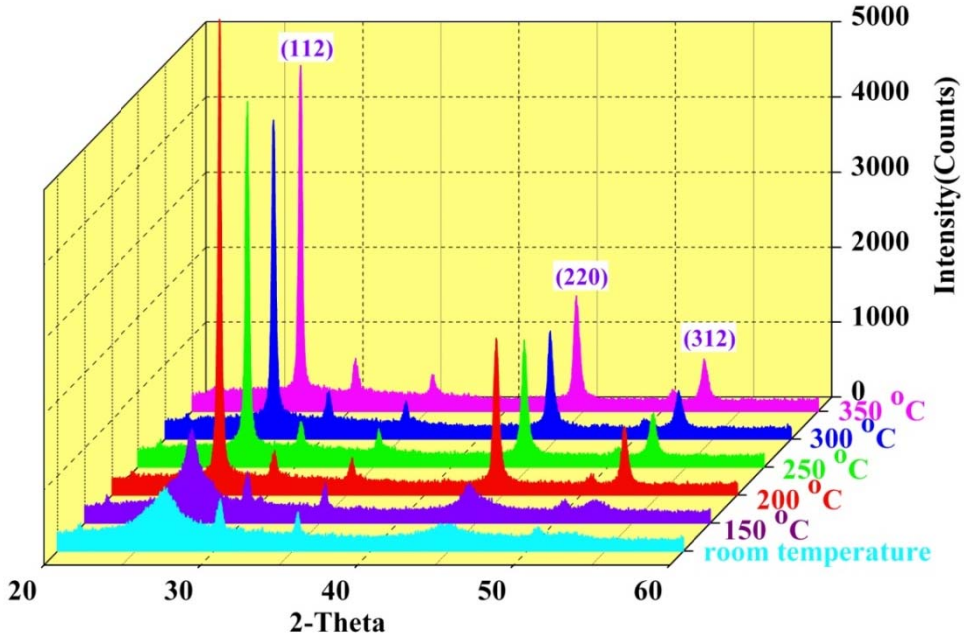

Fig.7 With deposition potential -3.2V, pH value 1.7, the effect on different annealing temperature of CIGS thin film crystal structure

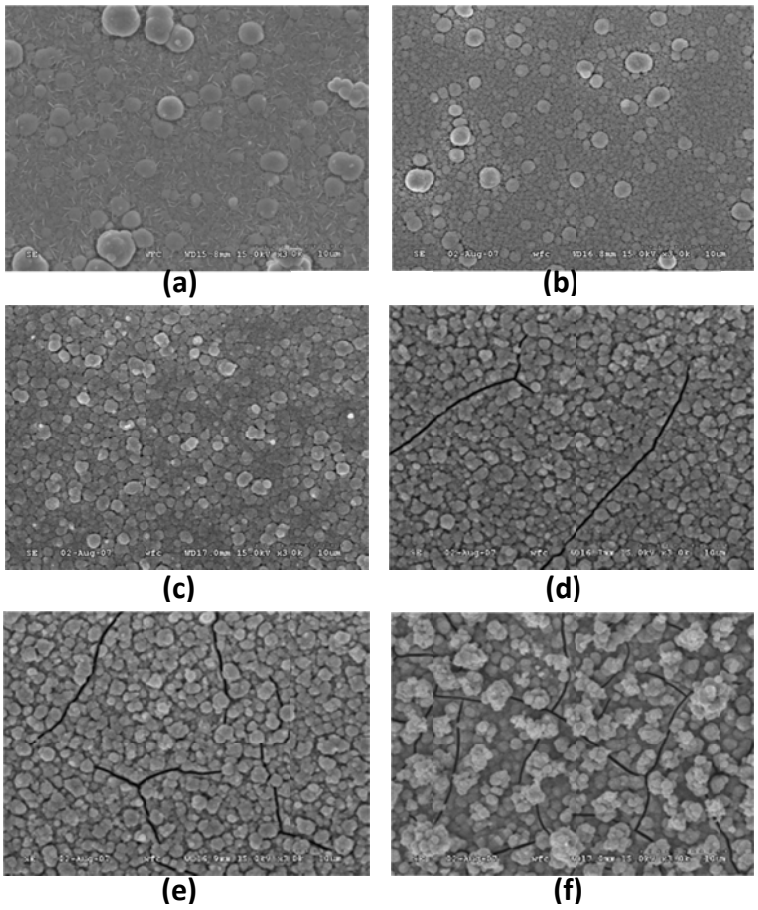

Fig.8 The effect on different annealing temperature of surface of CIGS thin film: (a)as-dep, and annealed at (b)150°C (c)200°C (d)250°C (e)300°C (f)350°C

4. Conclusion

In this research, the CIGS thin films fabricated on ITO glass substrate by the co-electrodeposition technique with annealing has been investigated. In addition to low cost and high efficiency, the advantage of preparing CIGS thin film is the low temperature process, so the applicable range of substrate is wide and it is appropriate for large area deposition. Based on the experimental results, stirring the bath will influence the Ga deposition. In addition, the appropriate pH value is 1.7 and the preferable deposition time is 5 min. Furthermore, Ga is the hardest element to deposit in CIGS thin films. Based on the experimental results, the amount of Ga will increase gradually when the deposited potential reache to -3.0 V. By the analyses of XRD and SEM, the appropriate temperature for annealing the CIGS thin films is 200°C. The one-step electrodeposited film is promising for future solar cell applications.

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