ELECTRO-DEPOSITED $CuInSe_2$ FILMS FOR FLEXIBLE OPTOELECTRONIC APPLICATIONS

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In this research, one-step electro-deposition was applied to fabricate $CuInSe_2$ films on top of Polyethylene terephthalate (PET) substrate. Proper ion concentration ratios, suitable pH values, appropriate deposition time and current density will enhance the formation of the well-crystallized $CuInSe_2$ film on top of the PET substrate. Compositions of the film were examined by energy dispersive spectrometer (EDS) analysis. Material properties were investigated by X-ray diffraction (XRD), scanning electron microscope (SEM) images, and. Atomic force spectroscopy (AFM). Experiment results indicate that plating solution with a pH value of 1.5, current density of 0.2 or 0.3 ASD, and deposition time of 15 minutes are preferable parameters for high-quality $CuInSe_2$ film fabrication. The flexible $CuInSe_2$ film shows great promises for future flexible solar optoelectronic devices.

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1. Introduction

Development of solar cells is a potential source for alternative energies [1]. In recent years, many manufacturers replace traditional Si-based solar cells with compound-material-based solar cells. Among those solar cells, $CuInSe_2$ solar cells with high abosroption efficiency, broad spectrum absorption, and high thermal stability show great promises for future commercial applications. Therefore, various dry semiconductor processing techniques including evaporation [2], molecular beam epitaxy [3], sputtering [4, 5], spray pyrolysis [6, 7], and selenization [8] have been demonstrated to fabricate high-quality $CuInSe_2$ film for solar cell devices. In addition to dry processing techniques, wet processing fabrication such as electrochemical deposition has been proposed to produce low cost, fast production, and large area $CuInSe_2$ solar cells. In 1983, R.N. Bhattacharya et al. deposited $Cu_{0.9}In_{1.0}Se_{2.1}$ in $InCl_3$, $CuCl_2$, SeO_2, TEA, and, NH_3 solutions [9]. Since then, various deposition conditions and techniques have been used to form high quality $CuInSe_2$ film. For example, two-step $CuInSe_2$ film fabrication process including electrodeposition and selenization has been performed by Y. Li et al. to form high-quality $CuInSe_2$ film [10]. In this research, we deposited the film directly in one-step deposition. Different from previous studies, various deposition conditions have been used to deposit the $CuInSe_2$ film on PET flexible substrate. Various factors including PH values of the plating solution, deposition time, and deposition current has been investigated with multiple material analysis techniques.

2.Experimental

The electrochemical deposition system consisted of two electrodes.Pt was for the counter electrode and conductive PET was for the working electrode. To manufacture $CuInSe_2$ thin film, we used co-deposition processes on PET substrate. After the substrate was cleansed solvant, and deionized water, the substrate was deposited with CuInSe2 film. The compositions of the plating solution were $[CuSO_4]$=1~3mM, $[InSO_4]$=2~10mM, and $[SeO_2]$=2~5mM.

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In addition, H_2SO_4 and NH_4OH were incorporated to adjust the pH values (between 1.5 to 2.0) of the solution after remixing plating solution. Furthermore, the deposition current ranged from 0.1 to 0.3 ASD. After the deposition was completed, the film was rinsed with solvent. Then, the processed film was dried at 80 ℃ to enhance the contact between the CuInSe2 film and the PET substrate. In addition, pH values of the plating solution would also affect adhesiveness of the thin film. Through experiments, the pH value around 1.5 exhibited the best adhesion between the two layers. After the $CuInSe_2$ film on top of the PET substrate was deposited, compositions of the film were examined by energy dispersive spectrometer (EDS) analysis. Moreover, material properties were investigated by X-ray diffraction (XRD), scanning electron microscope (SEM) images, and atomic force spectroscopy (AFM).

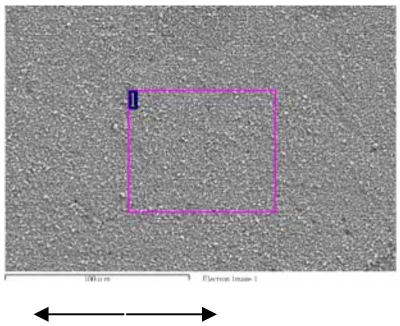
3.Results and discussion

To study the influence of [$CuSO_4$], [$InSO_4$], [SeO_2] ratio, and pH values of the plating solution, the composition of the $CuInSe_2$ thin film deposited in various deposition conditions are shown in Table 1. Obviously, higher concentration of [$CuSO_4$] resulted in higher composition of Cu, higher concentration of [$InSO_4$] resulted in higher composition of In, and higher concentration of [SeO_2] resulted in higher composition of Se.

Table 1. Composition of the $CuInSe_2$ thin film deposited in various deposition conditions.

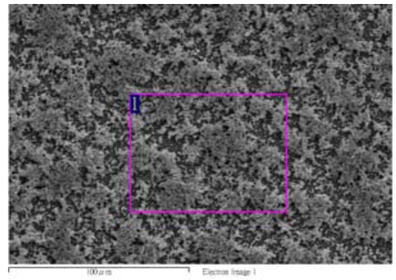
Concentration (mM)				Composition(%)					
[$CuSO_4$]	[$InSO_4$]	[SeO_2]	pH	Cu	In	Se	Cu/In	J(ASD)	t(min)
2	5	5	1.5	21.88	15.17	62.95	1.44	0.3	10
2	5	5	1.7	19.55	11.07	69.38	1.76	0.3	10
2	5	5	1.9	39.45	5.01	55.54	7.87	0.3	10
2	5	3	1.5	36.08	8.37	55.55	4.31	0.3	10
2	5	3	1.7	28.47	20.14	51.39	1.41	0.3	10
2	5	3	1.9	35.12	12.86	52.02	2.73	0.3	10
1	7	3	1.5	19.41	20.15	53.48	0.96	0.3	10
1	7	3	1.7	17.72	28.79	53.48	0.62	0.3	10
1	7	3	1.9	22.03	24.76	53.21	0.89	0.3	10

Then, SEM images could also reveal the difference of the film of various compositions. The In-rich surface morphology in a SEM image is shown in Fig. 1(a), the Cu-rich surface morphology in a SEM image is shown in Fig. 1(b), and the Se-rich surface morphology in a SEM image is shown in Fig. 1(c). On the other hand, the surface morphology with the normal ratio of Cu, In, and Se close to 1:1:2 in a SEM image is shown in Fig. 1(d).

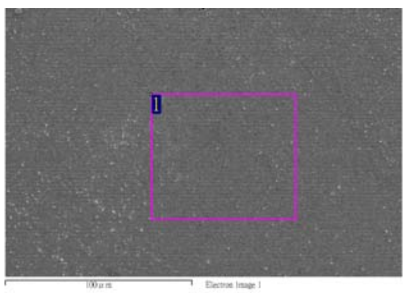


100μm

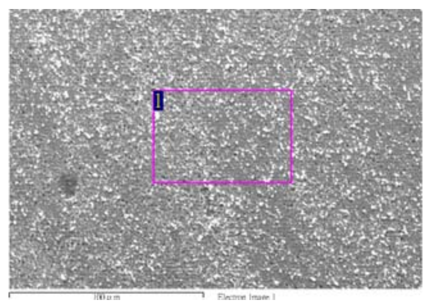
(a)



(b)



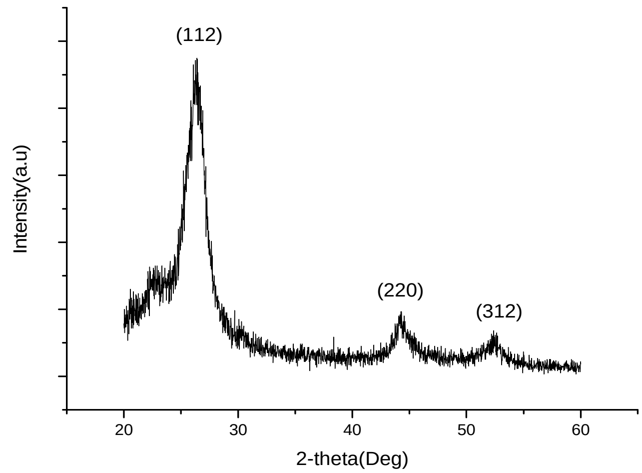
(c)



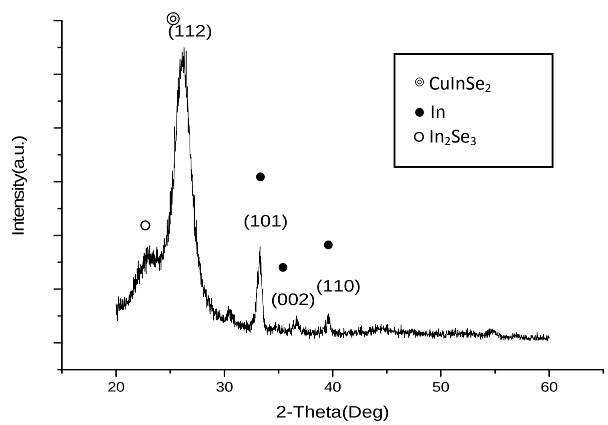
(d)

Fig. 1 Surface morphology of (a) Cu-rich film (b) In-rich film (c) Se-rich film (d) The $CuInSe_2$ film with Cu, In, and Se ratio close to 1:1:2.

Compared with the SEM images, the XRD spectrum of the $CuInSe_2$ film with Cu, In, and Se ratio close to 1:1:2 and the In-rich film can be seen in Fig. 2(a) and (b). The surface morphology of Fig. 2(b) reveals uneven surface and irregular flakes. In the XRD spectrum, In_2Se_3 and In peaks can be observed In-rich $CuInSe_2$ film as shown in Fig. 2(a). In addition to the $CuInSe_2$ main diffraction peak (112), we may see indium (101), (002), and (110) three diffraction peaks.



(a)



(b)

Fig. 2 The XRD spectrum of (a) the $CuInSe_2$ *film with Cu, In, Se close to the ration of 1:1:2 and (b) the In-rich film.*

Furthermore, the relation between the deposition time, the pH value and the Cu/In ratio in the $CuInSe_2$ film is shown in Fig. 3. Apparently, a shorter deposition time and lower pH values of 1.5 and 1.7 have a tendency to form In-rich film as shown in Fig. 3. As the deposition time became longer than 15 minutes and the pH value became larger, the In composition became smaller and the Cu composition became larger. On the other hand, as the deposition current as low as 0.1 ASD, the unconsolidated or loose deposited film might be formed due to a low current density. At the same time, the Cu-over rich film might be observed. For example, Cu/In ratio could be as high as 5.4 when the pH values 1.9 at 0.1 ASD deposition current. The film deposited at a low current of 0.1 ASD was easy to be cracked during deposition as shown in Fig. 4. Instead, proper current densities of 0.2 and 0.3 ASD would tend to form the film with a preferable composition and good quality.

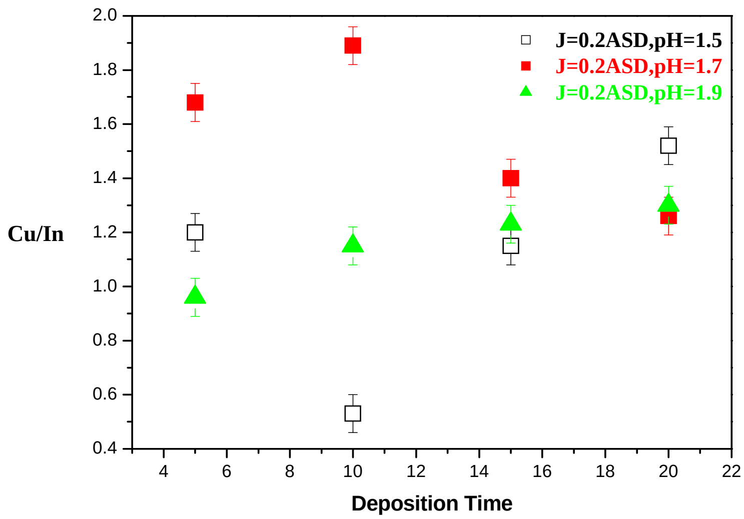
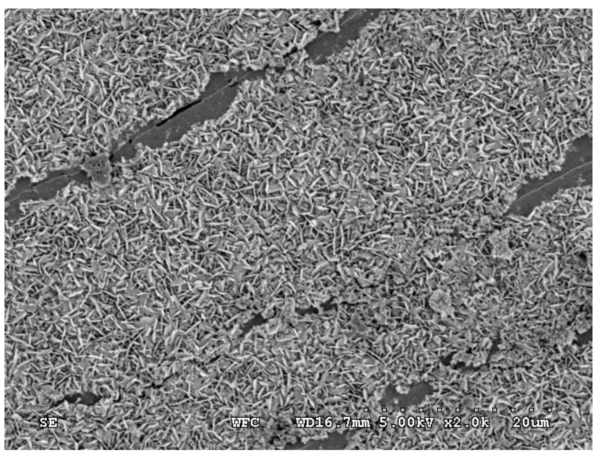


Fig. 3 The deposition time and the pH value versus Cu/In ratio in the $CuInSe_2$ film.

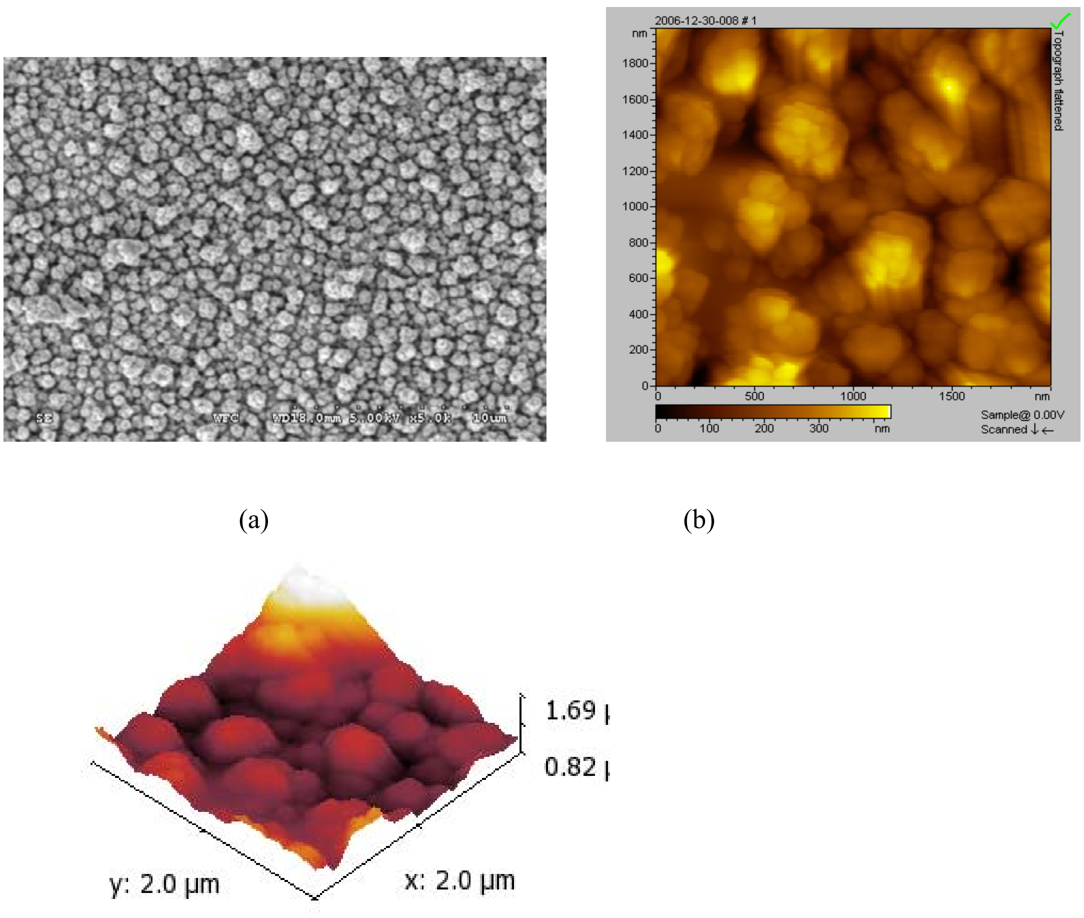


(a)

(b)

Fig. 4 (a) The SEM image and (b) the photo of the deposited $CuInSe_2$ film on top of PET at a low current density of 0.1 ASD.

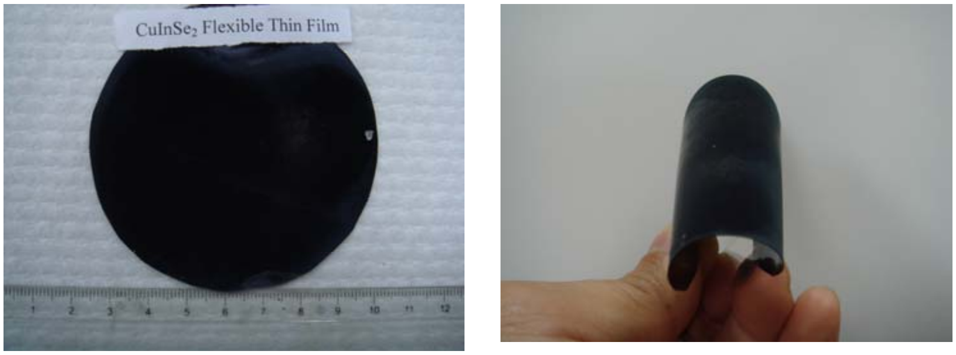
Finally, we zoom into the $CuInSe_2$ film with the ratio of $CuInSe_2$ close to 1:1:2. Compared with the SEM image with smaller resolution as shown in Fig. 2(d), the SEM image with higher solution is shown in Fig. 5(a). The well crystallized-film exhibited grain structures, indicating the crystallization of the $CuInSe_2$ in grains as shown in a high-resoltuion SEM image of Fig. 5(a). To gain insight to the grain, AFM analysis was performed on the $CuInSe_2$ grain as shown in Fig. 5 (b) and(c) . Many small raised areas can be seen in the AFM images, showing the crystallized structures on the $CuInSe_2$ grain. For future flexible optoelectronic applications, we successfully deposited the on the PET substrate. To maintain reliability of the product, the deposited $CuInSe_2$ required to have good adhesiveness on top of the flexible PET substrate. As shown in Fig. 6(a) and (b), the $CuInSe_2$ film has been uniformly deposited of top of the PET substrate. In addition, the good adhesion between the two layers cause that the PET can be bent well without damaging the $CuInSe_2$ film on top



(a) (b)

(c)

Fig. 5 (a) A high resolution SEM image, (b) 2D AFM image , and (c) 3D image of the $CuInSe_2$ film with Cu, In, and Se close to the ratio of 1:1:2.



(a) (b)

Fig. 6 (a) The top- view photo of the $CuInSe_2$ flexible thin film (b) The bending of the flexible film.

4.Conclusion

In this research, an electrodeposited $CuInSe_2$ film on top of a PET substrate has been fabricated. To relate the deposition condition, material properties, and composition of the film, various material analyses including XRD, SEM, EDS, and AFM has been performed. Proper ion concentration ratios, suitable pH values, appropriate deposition time and current density will enhance the formation of the well-crystallized $CuInSe_2$ film on top of the PET substrate. The flexible $CuInSe_2$ film shows great promises for future flexible solar optoelectronic devices.

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