INFLUENCE OF Ga COMPOSITION ON CuInGaSe$_2$ FILMS USING ONE-STEP ELECTROCHEMICAL DEPOSITION METHODS

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CIGS film was formed using one-step electrochemical deposition at various deposition potential voltages in solution with diverse pH values. Multiple material analyses such as X-ray diffraction (XRD) analysis, scanning electron microscope (SEM) images, energy dispersive spectroscopy (EDS), and electron probe micro-analyzer (EPMA) images were used to examine the electro-deposition parameters. UV spectrometer was performed to measure the bandgap of the CIGS thin film. A highest Ga composition could be obtained at the most negative voltage of -3.3V and the smallest pH value of 1.6 in our experiment. However, an inferior material property and worse crystalline phase might come with a high Ga concentration. The band gap of the electro-deposited CIGS film with Cu:In:Ga:Se ratio of 1:0.52:0.30:1.98 could achieve 1.16 eV. The electrodeposited CIGS film shows promises for future solar cell applications.

1. Introduction

Among the thin film solar cells, Si-based thin film solar cells, CIGS, CdTe and Dye-Sensitized solar cells have received high emphasis and are believed to be future promising commercialized solar cells. CIGS is a compound of Cu-In-Ga-Se$_2$ with great optical absorption properties due to its compound properties[1] andCIGS thin-film solar cells possess high efficiency, stability, and are eco-friendly. Due to these characteristics, the CIGS thin film has been regarded as a promising photovoltaic component. Based on the NREL reports, the conversion efficiency of a solar cell fabricated in a lab is enabled to reach around 20% [2]. Unfortunately, for the vacuum deposition processes such as MBE, sputtering, and evaporation,expansive instruments are required to synthesize CIGS thin film due to the fact that the CIGS thin film is a ternary or quaternary compound thin film, making it hardly to be popularized [3]. By contrast, electro-deposition as a non-vacuum fabrication method probably has become one of the most popular ways to prepare solar cells in the future because of its advantages of cheap, fast, and suitable for large-scale production. In the preparation process, it can effectively control the film thickness, porosity, and structure with less investment in equipment and easy preparation[4].

CIGS is a compound thin film solar cells with high photoelectric conversion efficiency, and its composition can be represented as the form of Cu (In1-xGax) Se$_2$, providing with a chalcopyrite structure which is a fused semiconductor of CuInSe$_2$ and CuGaSe$_2$[5]. The main absorbing layer of the fused semiconductor isathin filmofcopper indiumgallium selenium (CuInGaSe2), and the quality of the film also affects the overallefficiency of the thin film solar

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cells. Previous studies presents that multi-step processes are necessary to form the quaternary CIGS compound. For example, CIS compound was first fabricated and Ga was doped into the CIS film to form the CIGS compound. The energy band gap of CuInSe2 (CIS) materials is 1.02eV [6]. In order to widen thewidth of the energy band gap, a certain proportion ofGa was doped the CuInSe2 with to produce the CuInGaSe2(CIGS) absorber layer[7].   By contrast, we formed the CIGS compound by one-step electro-deposition. Furthermore, to characterize the film material properties, multiple material analyses such as X-ray diffraction (XRD) analysis, scanning electron microscope (SEM) images, energy dispersive spectroscopy (EDS) and electron probe micro-analyzer (EPMA) images were used to examine the electro-deposition parameters. UV spectrometer was performed to measure the bandgap of the CIGS thin film.

2. Experimental

In this experiment, the Copper Indium gallium selenide (CIGS) thin films are formed on the ITO glass substrate by the co-deposition (electro-deposition) method. The three-electrode electro-deposition system consisted of the referenceelectrode of silver / silver chloride (Ag / AgCl), the counter electrode made of platinumwire(Pt), and the working electrode of ITO glass[8].

During deposition,AUTOLABPGSTAT320 Potentiostat Galvanostat was used to controlthe potential during the deposition process. The electro-depositionsolutioncompositions andelectro-depositionoperating conditions of CIGS thin filmsare shown in Table 1.0.012mole ofcopper chloride(CuCl$_2$), 0.025 mole of indium chloride(InCl$_3$), 0.028mole ofgallium chloride(GaCl$_3$), and 0.025 mole ofselenious Acid(H$_2$SeO$_3$) were used to compose theelectro-deposition solution [9]. Then, the deionized water was used to prepare 160mLdeposition solution, and the pH value of the deposition solution was varied from 1.6 to 1.9 by adding HCl and NH$_4$OH[10]. During the electro-deposition process, stirring was not required[11]and constant potential was maintained within the range from -2.5V to -3.3V. The electro-deposition was performed at room temperature for ten minutes. To characterize material properties of the film, XRD was applied to analyze the crystalline structure and SEM was used to observe the surface topology and the thickness of the CIGS thin film. Furthermore, the distribution of the composition of Cu, In, Ga, and Se of CIGS thin films were analyzed by EPMA. Eventually, UV spectrometer was conducted to measure the optical characteristics of the CIGS thin film.

Table 1. The electro depositionsolution compositionsandelectrodepositionoperating conditions of CIGS thin films

	CuCl$_2$	12mM
	InCl$_3$	25mM
	GaCl$_3$	28mM
Composition and Condition	H$_2$SeO$_3$	25mM
	pH	1.6~1.9
	Deposition voltage	-2.5V~-3.3V
	Deposition temperature	room temperature
	Deposition time	10 min

3. Results and Dicsussion

Compared with the ideal Stoichiometry ratio of CIGS films of   1：0.7：0.3：2 (CuIn$_{0.7}$Ga$_{0.3}$Se$_2$), the element compositions of the deposited and annealed CIGS film with various deposition potential voltages and pH values measured by EDS are shown
in table 2(a) and 2(b).From the table 2 (a), the CIGS thin film in our system was formed under

various potential voltages in a solution at a fixed pH value of 1.7. Since Ga is the most difficult to be deposited during the electro-deposition process, the highest Ga composition could be obtained at the most negative voltage of -3.3V[13]. Moreover, table 2(b) shows the CIGS thin film deposited at a fixed voltage of -3.2V in solutions with varied pH values from 1.6 to 1.9. The results show that precipitation of Ga increased gradually as the pH value increased. Thecomposition of CIGS can be expressedas Cu (In1-xGax)Se$_2$. To satisfy the future optimal conversion efficiency requirements, "X=Ga/(Ga+In)=0.25~0.30" could be achieved .
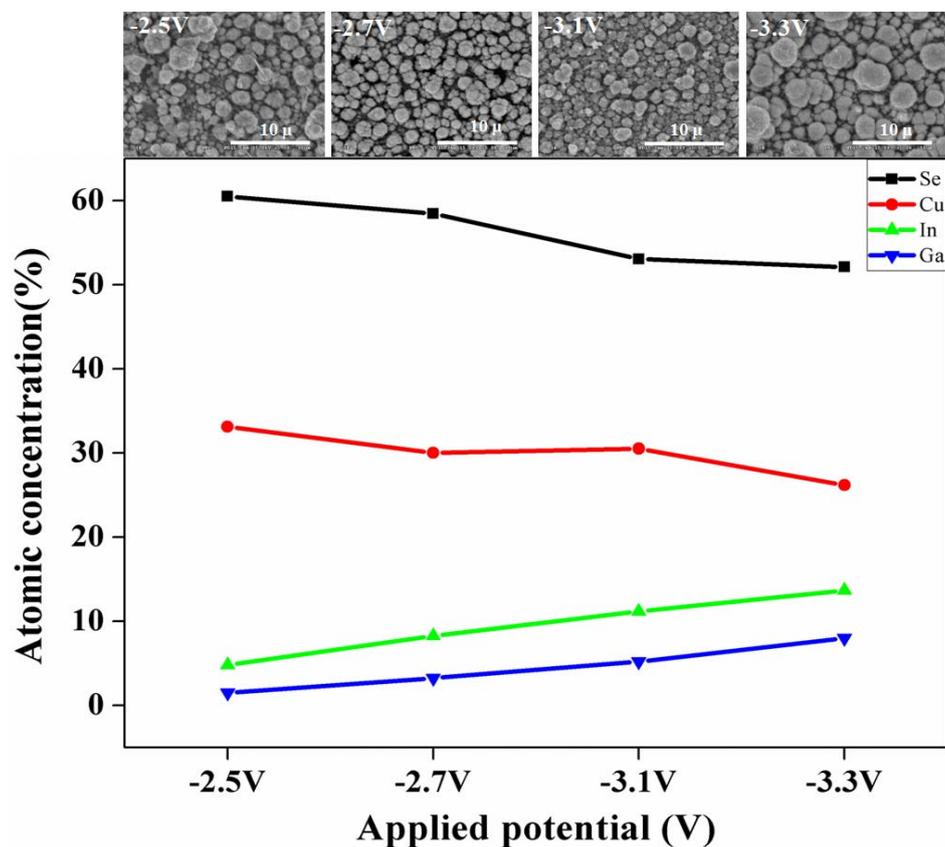

Fig. 1.a. Atomic concentrations of Cu, In, Ga, and Se and SEM images of the deposited

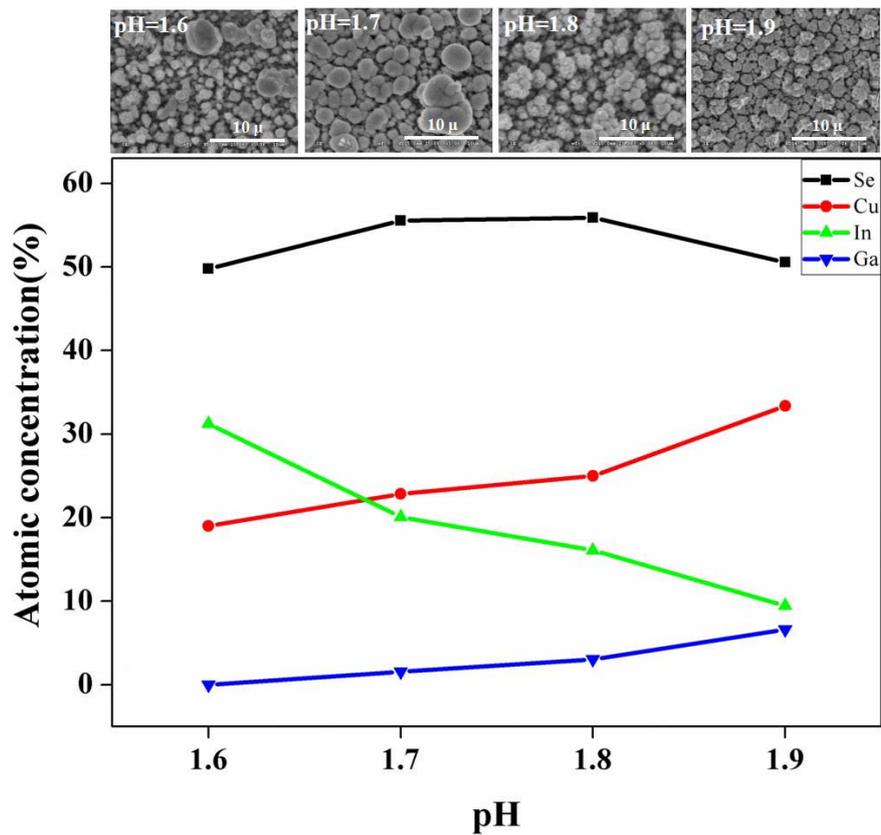*CIGS film with various deposition potential voltages*

Fig. 1.b. Atomic concentrations of Cu, In, Ga, and Se and SEM images of the deposited CIGS film with pH values.

Table 2 Element compositions of the deposited and annealed CIGS film with various deposition potential voltages and pH values

No	V	Proportion(%)				Cu/(In+Ga)	X=Ga/(Ga+In)
		Cu	In	Ga	Se		
(a)	-2.5	33.14	4.81	1.52	60.52	5.2354	0.2401
(b)	-2.7	30.04	8.26	3.26	58.45	2.6076	0.2830
(c)	-3.1	30.53	11.18	5.22	53.06	1.8616	0.3183
(d)	-3.3	26.20	13.69	8.01	52.10	1.2074	0.3691

No	pH	Proportion(%)				Cu/(In+Ga)	X=Ga/(Ga+In)
		Cu	In	Ga	Se		
(e)	1.6	18.99	31.23	0.00	49.78	0.6081	0
(f)	1.7	22.85	20.07	1.55	55.53	1.0569	0.0717
(g)	1.8	24.98	16.08	3.05	55.90	1.3058	0.1594
(h)	1.9	33.36	9.47	6.62	50.55	2.0733	0.4114

To investigate the connections between surface morphology and CIGS compositions, atomic concentrations of Cu, In, Ga, and Se and SEM images under in various deposition voltages are juxtaposed as shown in Fig. 1 (a). Apparently, the Ga and In concentrations increased and the Cu and Se concentrations decreased as the deposition voltage became more negative[14]. By contrast, the film became less compact and the grains were more randomly distributed as the voltage became more negative. Therefore, the increase of Ga concentration may imply the inferior film quality. Similarly, decrease of grain size in SEM images and increase of Ga concentration can be observed as the pH value of the deposition solution increased from 1.6 to 1.9 as shown in Fig. 1 (b).

To investigate the crystalline phase of the deposited film, XRD analyses of the deposited film under various voltages are shown in Fig. 2(a) and XRD analyses of the deposited film in solution with various pH values are shown in Fig. 2(b). Consistent with the SEM images, the deposited film under the most negative voltage in Fig. 2(a) and the smallest pH value of 1.6 exhibited the strongest crystallized structures. The results imply that a low Ga concentration in the film related to an inferior crystallized structure. A high Ga concentration can cause a higher CIGS band gap but an inferior crystallized and compact film can also result in a low conversion efficiency[15]. Therefore, according to the experimental results, it is a trade-off to achieve a high Ga concentration and a better quality film or crystallized phase.

To build connections between Ga distribution and CIGS film deposition,EPMA was performed as shown in Fig. 3. Fig. 3 shows that Ga atoms were distributed in large-size clusters and Se atoms were distributed in small-size particles . Therefore, a high Ga concentration might form clusters randomly distributed on the film and inferior crystalline phased or worse quality film might be formed because of these clusters.
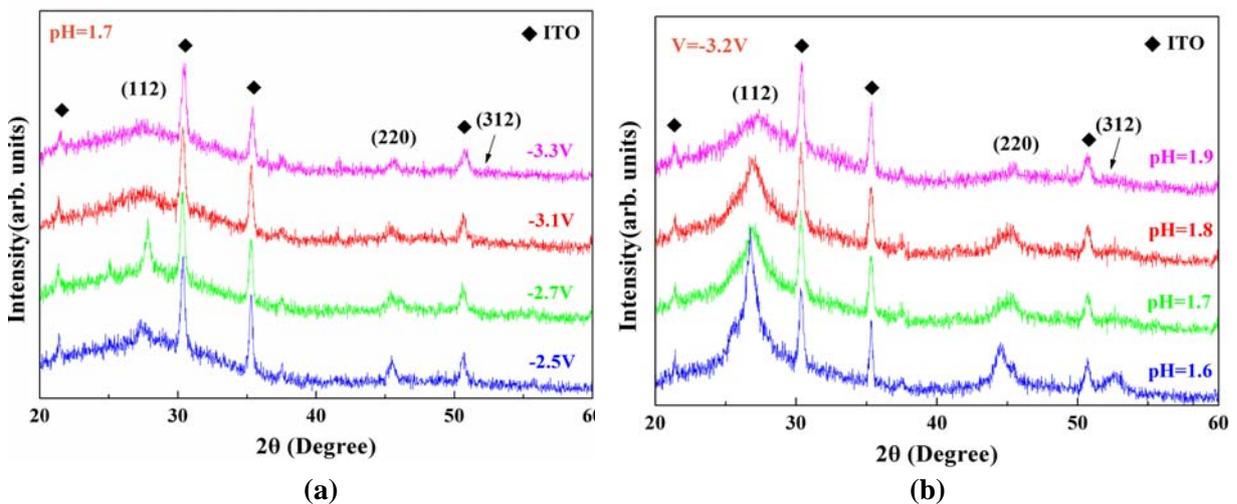

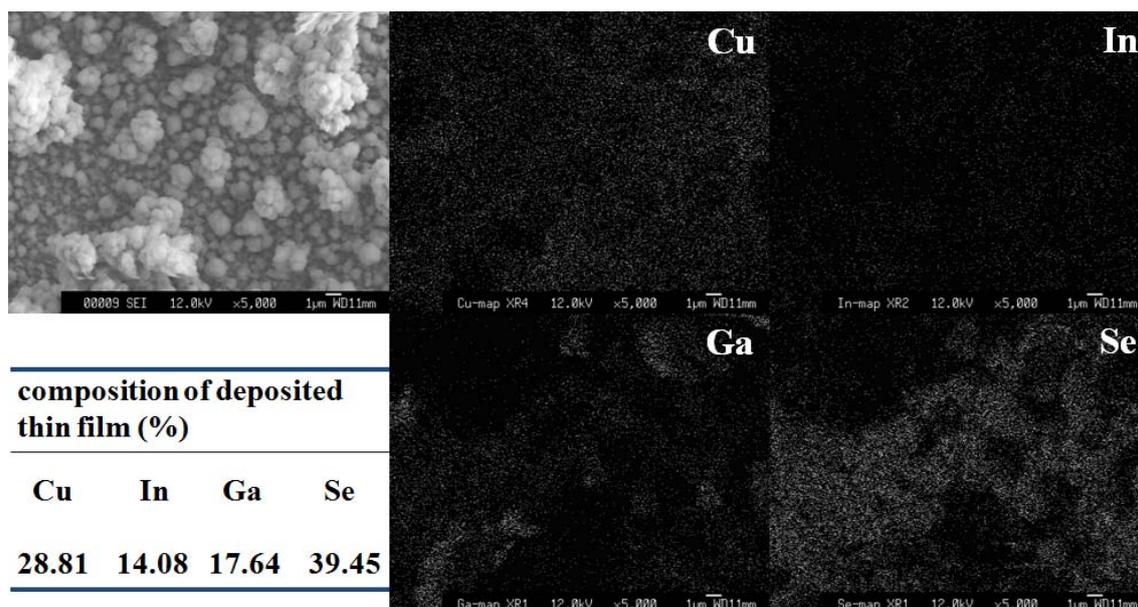*Fig. 2XRD analyses of the deposited CIGS film with (a) various deposition potential voltages and (b) pH values.*

Fig. 3 Atomic distribution of Cu, In, Ga, and Se and SEM images of the CIGS film measured by analysis.

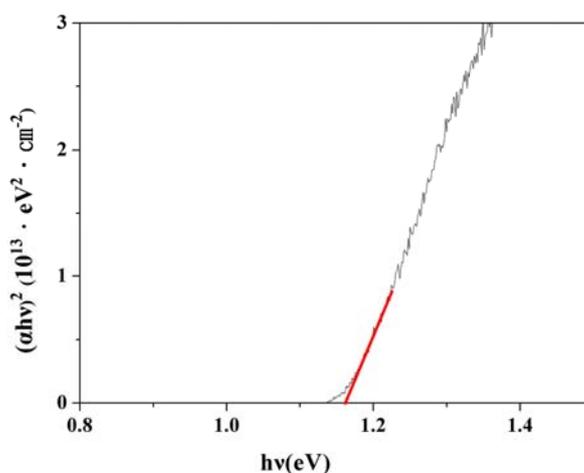| composition of deposited thin film (%)			
Cu	In	Ga	Se
28.81	14.08	17.64	39.45

Fig. 4 UV-VIS measurement of the CIGS film deposited at -3.3 V in solution with a pH value of 1.7

Finally, UV-VIS was used to measure the band gap of the film deposited at -3.3 V in solution with a pH value of 1.7. The element composition ratio of Cu:In:Ga:Se was 1:0.52:0.30:1.98 close to the ideal CIGS film ratio of 1:0.7:0.3:2. The band gap was 1.16 eV extracted from Fig. 4.

4. Conclusion

In this research, CIGS film was formed using one-step electrochemical deposition at various deposition potential voltages in solution with diverse pH values.

To characterize material properties of the film, multiple material analyses techniques such as EDS, SEM, XRD, and EPMA were use to study the relationship between Ga atom concentrations and the deposited film under distinct deposition parameters. The results show that a high Ga distribution would cause inferior crystallization and film properties. The band gap of The

CIGS film with Cu:In:Ga:Se ratio of 1:0.52:0.30:1.98 can achieve 1.16 eV. The electrodeposited CIGS film shows promisesfor future solar cell applications.

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