

离子液体电沉积 $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ 薄膜

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摘要: 采用循环伏安法(CV)对离子液体 Reline 中三元 $\text{CuCl}_2+\text{InCl}_3+\text{SeCl}_4$ 体系和四元 $\text{CuCl}_2+\text{InCl}_3+\text{GaCl}_3+\text{SeCl}_4$ 体系的电化行为进行了研究。研究表明, In^{3+} 并入三元 CIS(Cu-In-Se) 薄膜体系和 Ga^{3+} 并入四元 CIGS(Cu-In-Ga-Se) 薄膜体系均有两种途径: 一是发生共沉积, 二是直接还原。利用电感耦合等离子体发射光谱(ICP)和扫描电镜(SEM)对沉积电势、镀液温度和主盐浓度对 CIGS 薄膜组成、镀层表面形貌的影响进行了测试, 结果表明通过工艺参数的选择可以控制 $\text{Ga}/(\text{Ga}+\text{In})$ 和 CIGS 薄膜组成并得到化学计量比为 $\text{Cu}_{1.00}\text{In}_{0.78}\text{Ga}_{0.27}\text{Se}_{2.13}$ 的薄膜。

关键词: 离子液体; 电化行为; 电沉积; CIGS 薄膜

中图分类号: TM914.4²; O614.121; O614.37²; O614.37¹

文献标识码: A

文章编号: 1001-4861(2014)02-0466-07

DOI: 10.11862/CJIC.2014.036

Fabrication of $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ Thin Films via Electrodeposition Method with Ionic Liquid Electrolytes

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Abstract: The electrochemical behavior of $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ (CIGS) was investigated by cyclic voltammetry (CV) in ionic liquid Reline. The insertion of indium (In) into the CIS thin films involved two routes: co-deposition with Cu^{2+} and Se or trivalent indium ion (In^{3+}). The insertion of gallium (Ga) into the quaternary solid phase (Cu-In-Ga-Se) utilized two routes: co-deposition (with Cu^{2+} , In^{3+} , Se^{4+}) and Ga^{3+} directly added to Ga. The effects of electrodeposition potential, bath temperature and main salt concentration on CIGS thin films were researched. $\text{Cu}_{1.00}\text{In}_{0.78}\text{Ga}_{0.27}\text{Se}_{2.13}$ thin films were obtained and satisfactory control of film composition and $\text{Ga}/(\text{Ga}+\text{In})$ was achieved by the choice of process parameters. The standard CIGS sample was calibrated by an inductively coupled plasma optical emission. The morphological properties were detected by scanning electron microscopy. The XRD result shows that the incorporation of Ga into CIS phase and forms CIGS phase.

Key words: ionic liquid; electrochemical behavior; electrodeposition; CIGS thin films

0 Introduction

$\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ (CIGS, where x ranges between 0.6 ~0.8) materials have a high absorption coefficient ($1 \times 10^5 \text{ cm}^{-1}$) that results from the direct energy gap and

permits 1 ~2 μm thin films to absorb a sufficient amount of light^[1-3]. The CIGS absorbed layer plays the decisive role in CIGS thin film solar cell preparation^[4-5]. The band gap of the CIGS alloyed with gallium can be adjusted to 1.05~1.67 eV. CIGS-based film solar cells

收稿日期: 2013-09-03。收修改稿日期: 2013-10-14。

黑龙江省自然科学基金重点(No.ZD201107)资助项目。

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have recently reported power conversion efficiencies of 20% in laboratory devices and 13% in modules^[6]. Several methods of CIGS fabrication based on vacuum techniques, such as multi-step physical vapor deposition and conventional sputtering techniques, have been developed^[7-12]. The factors limiting the application of CIGS thin film solar cells are high manufacturing costs and poor reproducibility. Therefore, practicality demands the development of a new low-cost, continuous and reliable technology to produce CIGS thin films. In 1998, the efficiency of $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ (CIGS) based devices was 14.1% with the addition of a small amount of gallium^[13]. In 2004, devices with laboratory cell efficiency of 11.3% prepared via an electrochemical route were reported^[14]. In 2010, Kwak et al electrodeposited CIGS crystals on the high-density CdS nanowire arrays and subsequently selenized the materials at 400 °C to form photovoltaic cells, which demonstrated a light energy conversion efficiency of 6.18%^[15]. Compared to the traditional aqueous solutions, ionic liquid electrolytes offer a better thermal stability and wider electrochemical windows^[16-17]. Furthermore, the wide potential window and high thermal stability might generate higher deposition efficiencies for electronegative species; additionally, these materials might tolerate the higher deposition temperatures necessary to promote in-situ crystallization and possibly avoid the need for post-deposition heat treatments. Shivagan et al prepared Cu-In, Cu-In-Se and Cu-In-Ga-Se precursor films in Reline ionic liquids that were selenized in a tube furnace at 500 °C for 30 min to form CIS and CIGS films with band gaps of 1.0 eV and 1.09 eV, respectively^[18]. Harati M et al electrodeposited a stoichiometric CIGS thin film in one pot without post-deposition thermal sintering, but they received a film conforming to the stoichiometric ratio only during the first deposition. The Se/Cu ratio will decline to 0.9 from 2.2 if the same solution is used for the second deposition^[19]. The electrodeposition of gallium and silicon in ionic liquid electrolytes are more advantages than aqueous solution electrodepositions^[20]. The large electrochemical window of this ionic liquid allows the direct electrodeposition of selenium,

indium and copper at variable temperatures in a one-step reaction^[21].

All the CIGS samples for compositional analysis were grown on a bare Nickel substrate. Reline, consisting of choline chloride/urea eutectic mixture, is a cost-effective medium that avoids technical problems described above. To obtain stoichiometric, high performance CIGS thin films, the electrochemical behavior of the metal ions and technological parameters of this system were investigated.

1 Experimental

Choline chloride (Aladdin 99%) and urea (Aladdin 95%) were mixed in 1:2 molar ratio at 80 °C to prepare the ionic liquid. The Reline was dried under vacuum for 24 h at a temperature of 80 °C^[22]. CuCl_2 (Aladdin, 99.99%), InCl_3 (Aladdin, 99.99%), GaCl_3 (Sigma-Aldrich, 99.99%) and SeCl_4 (Aladdin, 99.5%) were used without further purification. All of the electrochemical measurements were performed using a CH Instruments 660B. Platinum sheets and Pt wires were used as reference and counter electrodes, respectively. The deposition processes were produced in stirred solutions for 2 h, and the rotational speed was 400 $\text{r} \cdot \text{min}^{-1}$.

A glassy carbon electrode (GCE) with a working surface of 7.1 mm^2 ($\phi=3$ mm) was used as the working electrode when cyclic voltammetry was performed. The cyclic voltammograms were initially swept in the negative direction at a scan rate of 10 $\text{mV} \cdot \text{s}^{-1}$.

All the CIGS samples for compositional analysis were grown on a bare Nickel substrate. The deposits were analyzed by Inductively Coupled Plasma Optical Emission (ICP, Perkin Elmer 5300DV). The morphological properties were detected by scanning electron microscopy (SEM, Quanta 200F). The selenized CIGS thin films were investigated by X-ray diffraction (XRD, D/max-rB 12 kW).

2 Results and discussion

2.1 Electrochemical behavior of Cu(In,Ga)Se_2

Fig.1 shows the cyclic voltammograms for Reline containing the following (Reline is electrochemically

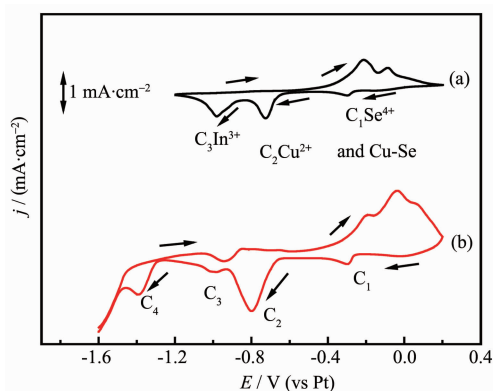
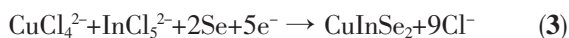


Fig.1 Cyclic voltammograms of (a) ternary Cu-In-Se system and (b) quaternary Cu-In-Ga-Se system; scan rates $10 \text{ mV} \cdot \text{s}^{-1}$

stable in this potential range): (a) $7.5 \text{ mmol} \cdot \text{L}^{-1} \text{ CuCl}_2 + 35 \text{ mmol} \cdot \text{L}^{-1} \text{ InCl}_3 + 70 \text{ mmol} \cdot \text{L}^{-1} \text{ SeCl}_4$, (b) $7.5 \text{ mmol} \cdot \text{L}^{-1} \text{ CuCl}_2 + 35 \text{ mmol} \cdot \text{L}^{-1} \text{ InCl}_3 + 30 \text{ mmol} \cdot \text{L}^{-1} \text{ GaCl}_3 + 70 \text{ mmol} \cdot \text{L}^{-1} \text{ SeCl}_4$. The temperature was 70°C and the scan rate was $10 \text{ mV} \cdot \text{s}^{-1}$. Curve (a) is the cyclic voltammogram of the ternary Cu-In-Se system. The reduction of Cu^{2+} to Cu^+ (Eq.(1)) appears at a potential of -0.1 V and the formation of Cu_2Se obtains at -0.3 V (Eq.(2)), respectively. The cathodic peak at -0.75 V is related to the formation of CuInSe_2 (Eq.(3)). The co-electrodeposition of Cu, In and Se occurs at a positive potential that is higher than the In^{3+} reduction potential due to the large formation energies. The cathodic peak at about -1.0 V corresponds to the In^{3+} direct reduction to In (Eq.(4)). So the assimilation of In into the solid film involves two different routes: co-deposition with Cu^{2+} forms CuInSe_2 and In^{3+} directly restores into In. In (Curve (b)), the peak at approximately -0.3 V is likely associated with the simultaneous reduction to form ternary Cu-In-Se system.



The second cathodic peak (c_2) at -0.8 V is related to the Cu, In, Ga, Se co-deposition. There are two reasons to demonstrate this hypothesis: (1) Comparing with the ternary Cu-In-Se system, the cathodic current at the potential range notably

increased. (2) The electrodeposition of CIGS in Reline containing $0.028 \text{ mol} \cdot \text{L}^{-1} \text{ CuCl}_2 + 0.06 \text{ mol} \cdot \text{L}^{-1} \text{ InCl}_3 + 0.06 \text{ mol} \cdot \text{L}^{-1} \text{ GaCl}_3 + 0.14 \text{ mol} \cdot \text{L}^{-1} \text{ H}_2\text{SeO}_3$ was studied. A stoichiometric $\text{Cu}_{1.00}\text{In}_{0.92}\text{Ga}_{0.40}\text{Se}_{0.58}$ thin film was obtained by setting a constant deposition potential of -0.8 V at 45°C . The peaks at about -1.0 V and -1.37 V correspond to the reduction reactions of In^{3+} and Ga^{3+} , respectively. Hence, Ga^{3+} insertion into the solid films also involves two routes: co-deposition with Cu^{2+} , In^{3+} , Se and Ga^{3+} directly converted into Ga. SEM morphology of the CIGS film (Fig.2) appears to show that the overall surface of thin film is uniform and compact.

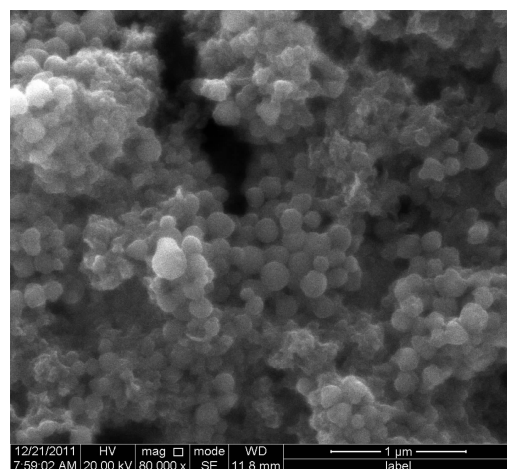


Fig.2 Morphology of deposited CIGS film from Reline

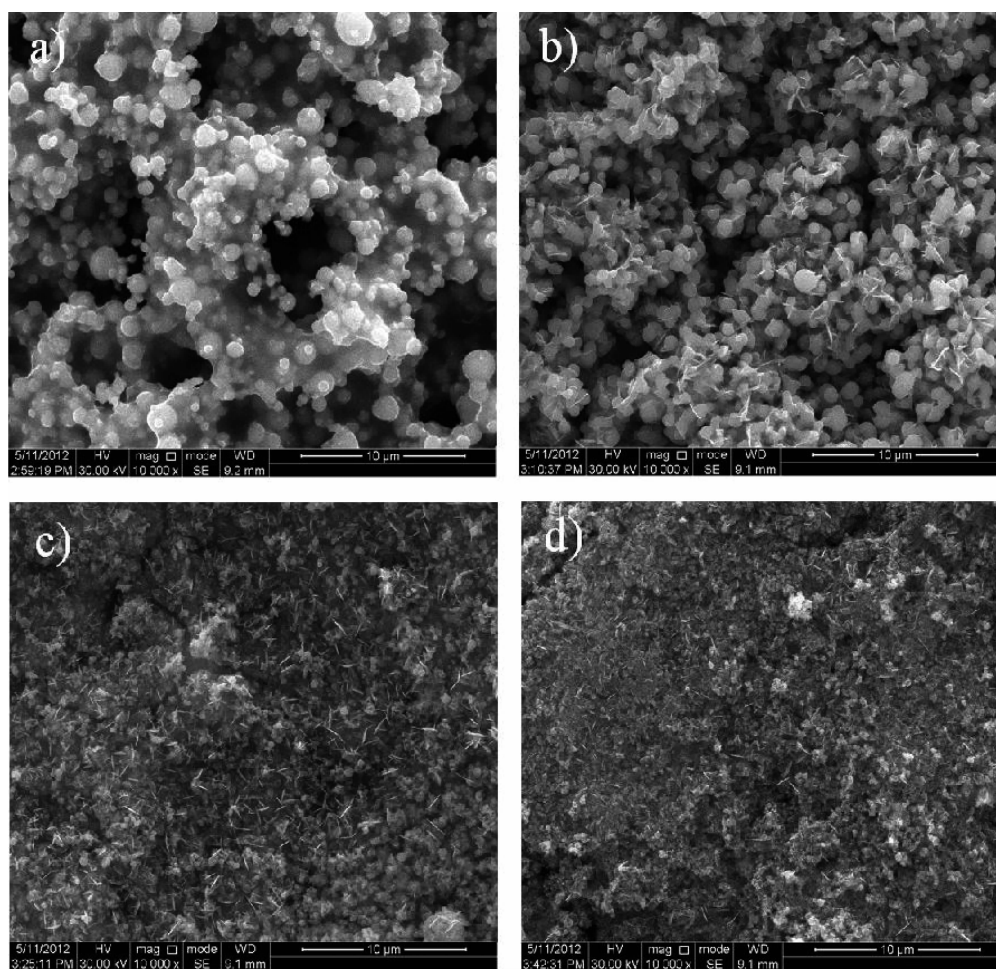
2.2 Effects of electrodeposition processes

2.2.1 Effect of deposition potential

Table 1 presents the effects of deposition potential on the composition of the CIGS thin films. The content of In and Ga increases with the negative shift of the deposition potential. This is because the reduction potential of In and Ga is more negative than Cu and Se, we can also know that the negative shift of deposition potential has less effect on the reduction of Cu and Se. The deposition potential not only determines whether the In^{3+} , Ga^{3+} deposit on the electrode surface but also concludes the composition of CIGS thin film. Stoichiometric CIGS thin films are obtained according to the ICP results under the deposition bath contains $7.5 \text{ mmol} \cdot \text{L}^{-1} \text{ CuCl}_2$, $35 \text{ mmol} \cdot \text{L}^{-1} \text{ InCl}_3$, $30 \text{ mmol} \cdot \text{L}^{-1} \text{ GaCl}_3$, $70 \text{ mmol} \cdot \text{L}^{-1} \text{ SeCl}_4$, which results in a thin film composition of $\text{Cu}_{1.00}\text{In}_{0.78}\text{Ga}_{0.27}\text{Se}_{2.13}$ (normalized by

Table 1 Composition of CIGS thin films electrodeposited at various potentials

Potential / V	Content / at%				Composition
	Cu	In	Ga	Se	
-0.9	20.63	5.25	1.44	72.68	$\text{Cu}_{1.00}\text{In}_{0.25}\text{Ga}_{0.06}\text{Se}_{3.52}$
-1.1	29.37	17.64	2.55	50.42	$\text{Cu}_{1.00}\text{In}_{0.60}\text{Ga}_{0.08}\text{Se}_{1.72}$
-1.3	21.47	20.53	5.63	52.36	$\text{Cu}_{1.00}\text{In}_{0.96}\text{Ga}_{0.26}\text{Se}_{2.44}$
-1.5	19.37	37.96	7.41	35.27	$\text{Cu}_{1.00}\text{In}_{1.96}\text{Ga}_{0.38}\text{Se}_{1.82}$

**Fig.3** Morphology of deposited CIGS films at various deposition potentials: (a) -0.9 V, (b) -1.1 V, (c) -1.3 V and (d) -1.5 V

taking Cu equal to 1.00). Fig.3 is the SEM morphology of the CIGS films deposited at various deposition potentials.

It can be seen from Fig.4, The surface of the CIGS thin film is porous with uneven spherical grains at -0.9 V. The holes diminish and spherical grains become more homogeneous when the potential increases to -1.1 V. With further increase of the deposition potential, the surface of the thin film becomes compact and uniform. The SEM morphology of the CIGS film deposited at -1.3 V shows some

needle-like structure corresponds to Cu-Se phase which can be eliminated by annealing process. If the deposition potential is more negative than -1.5 V, the ionic liquid will decompose. So the deposition potential for constant potential deposition should be higher than -1.5 V.

2.2.2 Effect of bath temperature

Table 2 compares the composition of the CIGS thin films on different bath temperatures. The contents of In and Se increase while the content of Cu decreases for the higher temperature. This means that

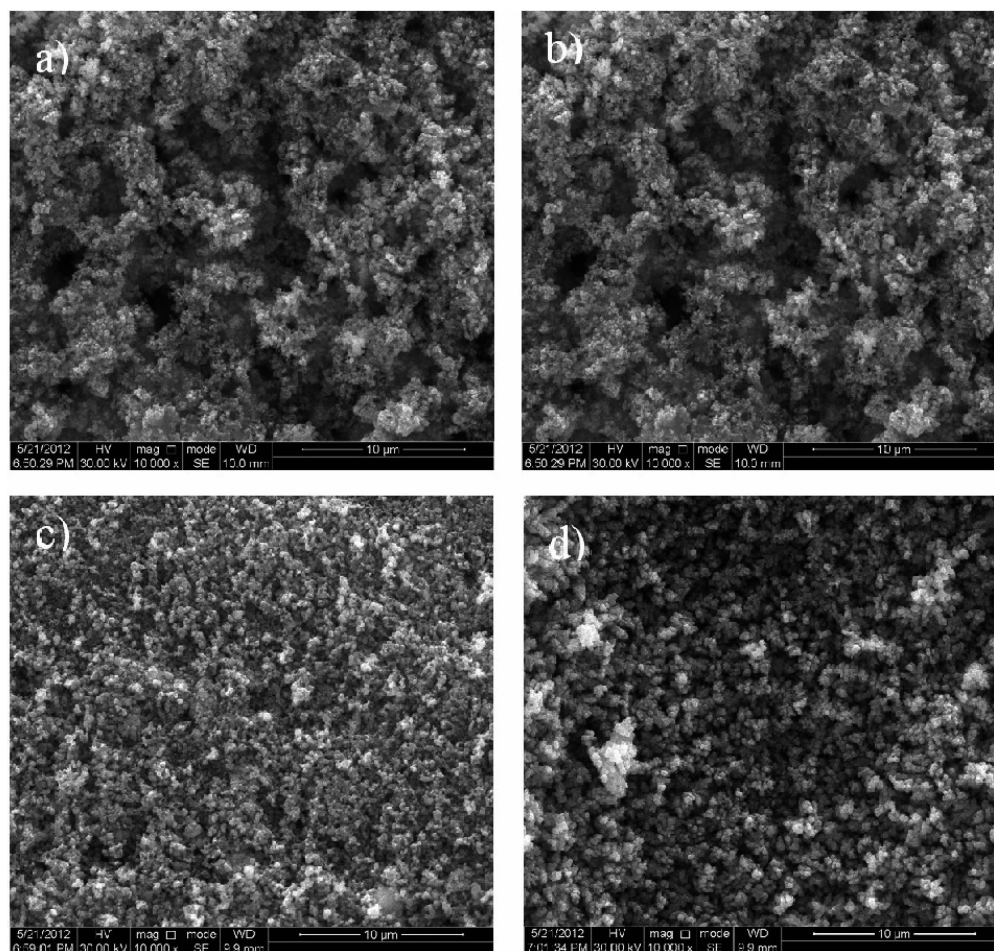


Fig.4 Morphology of deposited CIGS films at various bath temperatures: (a) 40 °C, (b) 50 °C, (c) 60 °C and (d) 70 °C

Table 2 CIGS thin film composition at various bath temperatures

Temperature / V	Content / at%				Composition
	Cu	In	Ga	Se	
40	44.21	18.96	3.25	33.57	$\text{Cu}_{1.00}\text{In}_{0.43}\text{Ga}_{0.07}\text{Se}_{0.76}$
50	34.98	26.24	2.38	36.40	$\text{Cu}_{1.00}\text{In}_{0.75}\text{Ga}_{0.07}\text{Se}_{1.04}$
60	24.51	34.24	2.29	38.96	$\text{Cu}_{1.00}\text{In}_{1.39}\text{Ga}_{0.09}\text{Se}_{1.59}$
70	21.23	29.49	4.03	45.24	$\text{Cu}_{1.00}\text{In}_{1.39}\text{Ga}_{0.19}\text{Se}_{2.13}$

the bath temperature plays an important role to promote the electrodeposition of In and Se.

Fig.4 is the SEM morphology of the CIGS films deposited at various bath temperatures. The overall surface of thin film become uniform and dense with the temperature rising. And higher temperature is also propitious to improve the crystallinity, which is good for fabricating high quality solar cells.

2.2.3 Effect of main salt concentration

Fig.5 illustrates the effects of the composition of CIGS thin films with different concentration of main

salts.

It was shown from Fig.5 that the atomic composition (at%) of various components in CIGS thin films is proportional to corresponding main salt concentration ($\text{mmol} \cdot \text{L}^{-1}$) in the solution. When the InCl_3 concentration increased, the content of Cu decreases while the content of Ga remains almost the same. We can obtain the stoichiometric $\text{Cu}_{1.00}\text{In}_{0.78}\text{Ga}_{0.27}\text{Se}_{2.13}$ (normalized by taking Cu equal to 1.00) thin film by setting a constant deposition potential of -1.3 V , at $70 \text{ }^\circ\text{C}$, and $\text{Ga}/(\text{Ga}+\text{In})$ atomic ratio is 0.26. It is most

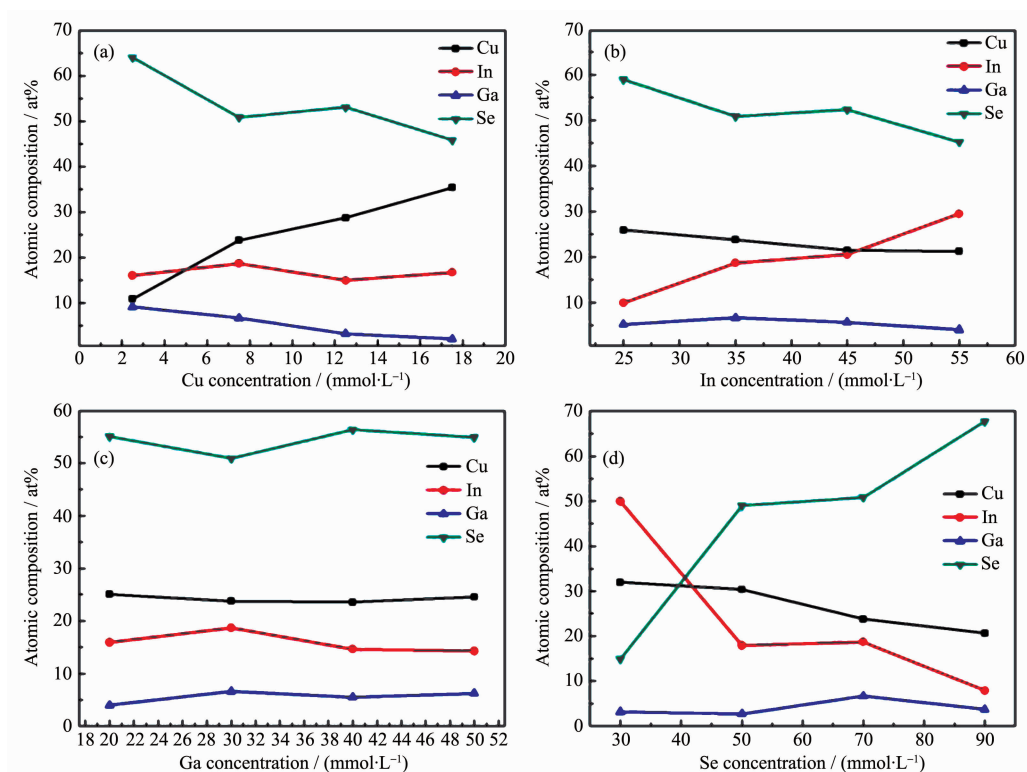


Fig.5 Composition of CIGS thin films with different concentration of main salts: (a) Cu concentration (b) In concentration (c) Ga concentration and (d) Se concentration

important to notice that the $\text{Ga}/(\text{Ga}+\text{In})$ decreases from 0.34 to 0.12, and we can obtain the desired band-gap value by controlling the InCl_3 concentration. Further work is in progress to achieve the actual formation mechanism of deposited $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ thin films and the annealing process which can be used to produce efficient cells absorber layers.

From the XRD pattern in Fig.6(b), it is observed that a small positive shift in 2θ value of (112)

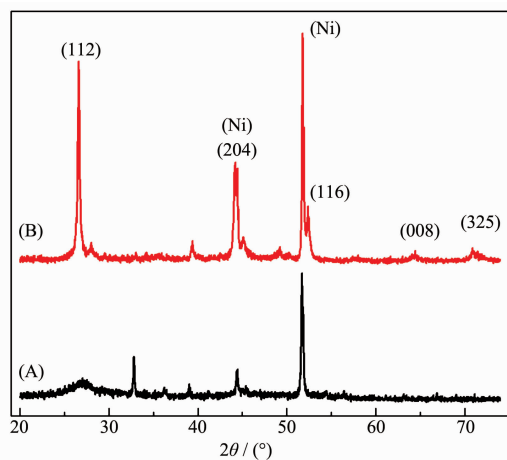


Fig.6 XRD patterns of CIGS films for: (a) unannealed and (b) 400 °C annealed

diffraction peak (ICDD 00-40-1 487) with $2\theta=26.76^\circ$. This indicates the incorporation of Ga into CIS phase and forms CIGS phase.

2.2.4 Effect of deposition times

The electrodeposition was conducted by setting a constant potential of -1.3 V , at $70\text{ }^\circ\text{C}$. CIGS thin film composition results measured by ICP when using one solution bath for 8 consecutive electrodepositions is presented in Table 3. The deposition bath contains $7.5\text{ mmol}\cdot\text{L}^{-1}\text{ CuCl}_2+40\text{ mmol}\cdot\text{L}^{-1}\text{ InCl}_3+40\text{ mmol}\cdot\text{L}^{-1}\text{ GaCl}_3+50\text{ mmol}\cdot\text{L}^{-1}\text{ SeCl}_4$. We can clearly see that the composition of the CIGS thin films remains the same in the first five depositions. Ionic liquid electrolyte has a good stability in consecutive electrodeposition. The CIGS thin film has stoichiometric composition with $\text{Ga}/(\text{Ga}+\text{In})$ equal to 0.18 and Se/Cu of about 1.5. If we use the same solution for the sixth deposition the selenium to copper ratio drops quickly. From the seventh deposition, Se/Cu drops below 1.0. We are investigating adjusting the solution in order to obtain a film of optimal stoichiometric ratio on subsequent depositions.

Table 3 CIGS thin film composition when using one solution bath for 8 times

Deposition times	Composition
1	Cu _{1.00} In _{0.70} Ga _{0.15} Se _{1.50}
2	Cu _{1.00} In _{0.70} Ga _{0.15} Se _{1.50}
3	Cu _{1.00} In _{0.70} Ga _{0.15} Se _{1.50}
4	Cu _{1.00} In _{0.70} Ga _{0.15} Se _{1.50}
5	Cu _{1.00} In _{0.70} Ga _{0.15} Se _{1.50}
6	Cu _{1.00} In _{0.70} Ga _{0.15} Se _{1.20}
7	Cu _{1.00} In _{0.70} Ga _{0.15} Se _{0.90}
8	Cu _{1.00} In _{0.70} Ga _{0.15} Se _{0.80}

3 Conclusions

Electrodeposition of CuIn_xGa_{1-x}Se₂ thin films on bare nickel substrate in the ionic liquid Reline has been investigated. Firstly, the cyclic voltammograms of the two systems in Reline were described. It was shown that In³⁺ and Ga³⁺ inserts into the solid films involve two ways: co-deposition and directly reduction. Secondly, the electrodeposition of the CIGS thin films in Reline at variable deposition potentials, bath temperatures and deposition times were described. The effect of simple combinatorial variation in bath composition on film properties was studied. We can see that the stoichiometric composition of the film is Cu_{1.00}In_{0.78}Ga_{0.27}Se_{2.13}, which was obtained by setting a constant deposition potential of -1.3 V, at 70 °C, and Ga/(Ga+In) atomic ratio is 0.26.

Acknowledgement: This work was supported by the National Science Foundation of Heilongjiang Province in China (No.ZD201107).

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