Effects of Saccharin Addition on Surface Morphology and Microstructure of Electrodeposited Cu-In Alloy

Hsiang Chen[a]*, Yih-Min Yeh[b], Ching-Pang Chen[c]

***Abstract*—In this research, material quality of electrodeposited Cu-In alloy has been investigated. We study effects of saccharin addition in various concentrations under different bias current. To characterize the film quality under various current and saccharin concentration, XRD and SEM are used to analyze thin film orientation, composition and surface morphology. Based on multiple material analyses, we confirm that a proper amount of saccharin additive can enhance well-crystallized microstructure of electrodeposited Cu-In alloy and limit the growth of Cu-rich phase.**

Keywords: CIS, Thin Film, Electrodeposition, Saccharin, Crystallization

I. Introduction

Over the past decade use of CIS (Cu-In-Se) thin film for the absorption layer of solar cells has attracted growing attention due to its high efficiency, low cost, and long life [1]. To fabricate high quality CIS film, various methods have been proposed, including evaporation [2], molecular beam epitaxy [3], sputtering [4, 5], spray pyrolysis [6, 7], and selenization [8]. In contrast to expensive dry deposition methods in vacuum conditions, wet processing of electrodeposition has also been investigated due to its low cost, fast production, and large area fabrication [9, 10]. Until now, two methods have been used for CIS film electrodeposition, one-step [11] electrodeposition and two-step electrodeposition. During the two-step CIS deposition process, Wang et al. [12] used $CuCl_2$ and H_4Cit electrolytes for electrodeposition of Cu-In alloy and then obtained Cu-In alloy using selenium processing for CIS film fabrictation. To fabricate high-performance CIS thin film for the absorption layer, the Cu-In precursor film quality is crucial to the overall quality of CIS film solar cell applications. We propose adding saccharin in plating solutions to obtain high-quality, good crystalline phase Cu-In film. In previous reports [13][14], saccharin additive has been shown to suppress metal precipitate and mitigate film stress in alloy electrodeposition. However, addition of saccharin in electrodeposition process to fabricate Cu-In alloy for potential CIS solar cells applications has not been clearly reported. In this study, we investigate potential improvements in film quality with the addition of saccharin of various concentrations. Furthermore, the influence of bias current has been examined to find better conditions to deposit the Cu-In alloy for future CIS cell applications.

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II. Experimental

This study examines the fabrication of electrodeposited Cu-In Alloy. The electrodepositing system consists of two electrodes: Pt for the counter electrode and ITO for the work electrode. Using co-electrodeposition, the system can grow Cu-In thin film on ITO. The compositions of electrolyte and operation conditions of electrodeposition are shown in Table 1. During the deposition process, the system uses constant current to electrodeposit Cu-In thin film with power supply unit AUTOLAB potentiostat / galvanostat model PGSTAT320. Details of the experiment procedure are as follows. The compositions of the plating solution were [CuCl2]= 0.008M, [InCl3]= 0.02M, [H3Cit]= 1.142M, and [TEA]= 0.4M. The concentration of saccharin varied from 0 to 0.082M. After mixing the plating solution, HCl was used to adjust the pH of the solution. Then, ITO (the work electrode) was put into the electrodeposited solution and deposited by constant current for 1800 s. Finally, the Cu-In film samples were cleansed with deionized water and kept in a moisture-proof box after drying. To analyze film quality under various currents and saccharin concentrations, XRD was used to analyze thin film orientation, composition and microstructure, and SEM was used to observe surface morphology.

III. Results and Discussion

In order to determine the preferable condition for electrodeposition, this experiment used plating solution from co-deposition with various current densities and different additive concentrations of saccharin. XRD and SEM analyses were used to study film composition, deposition orientation, and surface morphology.

Investigation into the effect of saccharin addition was begun with a fixed current density of 1.0 $mAcm^{-1}$. For comparison, a Cu-In alloy film in a plating solution without saccharin was deposited for 30 minutes. An XRD result of Cu-In thin film deposited in this solution is shown in Fig. 1.

Table I Plating solution compositions and operation conditions of electrodeposited Cu-In alloy

Cu-In plating solutions	
$CuCl_2$	0.008M
$InCl_3$	0.02M
H_3Cit	1.142M
TEA	0.4M
pH	2.0
Current densities	1.0 ~2.0 $mAcm^{-2}$
Saccharin concentration	0~0.082M

Among all the Cu-In alloy diffraction peaks, a single element in diffraction peak appeared at 2θ=32.96˚ and $Cu_{16}In_9$ diffraction peaks appeared at 35.45˚, 55.33˚, 69.28˚. Moreover, the diffraction peaks of element Cu appeared in three locations, at 43.29˚, 53.43˚, 74.12˚ with orientations (111), (200), and (220). Then, Cu-In thin film with differing saccharin concentrations was deposited at a fixed current density of 1.0 $mAcm^{-1}$. To compare the XRD spectra before and after saccharin addition, the spectra of the Cu-In alloy electrodeposited in plating solutions with various saccharin concentrations are shown in Fig. 2. After adding saccharin with a concentration of 0.002M, the Cu-In phase (200) peak noticeably increased with a diffraction peak at 34.5˚, while the diffraction peak of Cu at 50.43˚ decreased. When the saccharin concentration was increased to 0.004M, the CuIn (200) peak rose, while the Cu element peaks at 50.43˚ nearly disappeared. However, after saccharin concentrations were further increased to 0.054M and 0.082M, the peak intensity at (200) decreased. Based on these results, adding saccharin with a proper concentration not only reduces Cu precipitate but also enhances the Cu-In thin film crystalline phase to the preferred orientation (200). Nevertheless, increasing the amount of saccharin concentration to more than 0.054M may result in decreases in the concentration of Cu and In ions [15]. Moreover, oversaturation may occur, so that the excessive amounts of saccharin near the electrode may suppress the formation of well-crystallized Cu-In alloy. As a result, the Cu-In (200) peak decreases instead. From the above analysis, it can be concluded that saccharin addition with a proper amount can enhance well-crystallized microstructures in electrodeposited Cu-In alloy thin film orientation and limit the growth of the Cu-rich phase.

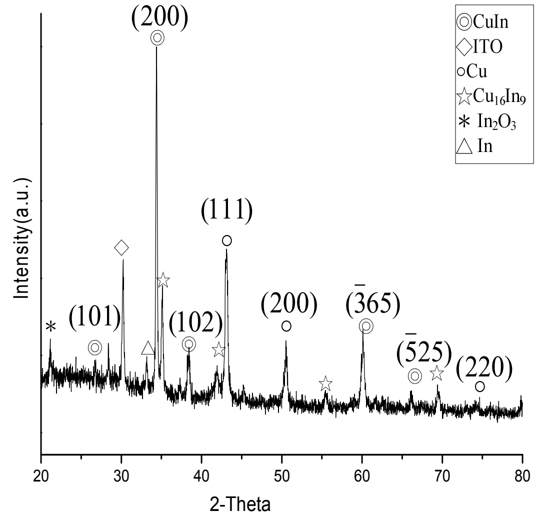


Fig. 1. XRD results of Cu-In thin film without saccharin

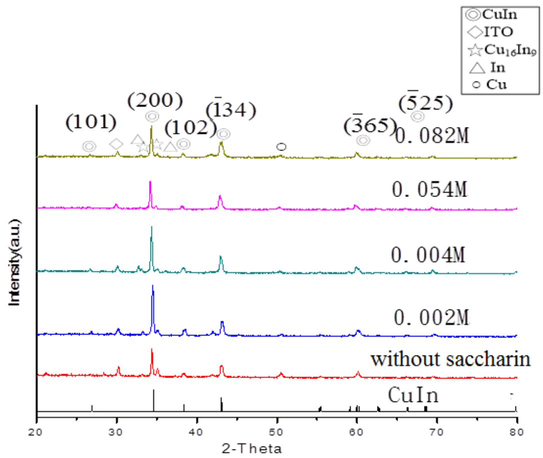
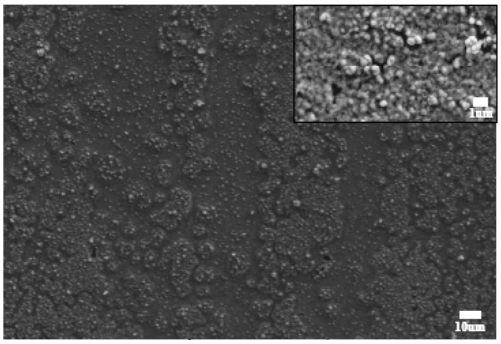
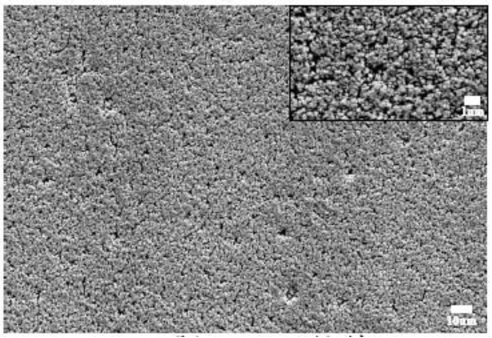


Fig. 2. XRD results of electrodeposited Cu-In thin film with differing saccharin concentrations

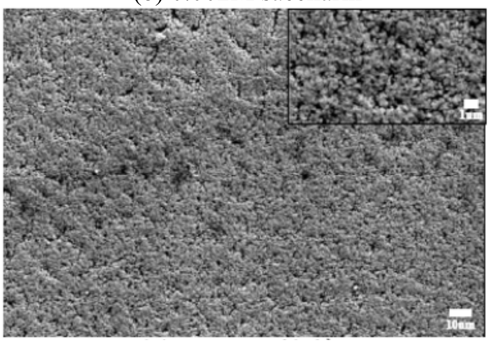
To reveal surface morphology of the Cu-In alloy film deposited with and without saccharin, SEM images of Cu-In thin film deposited with different amounts of saccharin are shown in Fig. 3(a), (b), (c), (d), and (e). Consistent with XRD analysis, film without saccharin has a poor crystalline structure with a scattered and discontinuous surface, as shown in Fig. 3(a). After adding saccharin with concentrations of 0.002M and 0.004M, the film surface in the images became smoother and more compact, as shown in Fig. 3(b) and (c). If the saccharin concentration is increased to 0.054M and 0.082M, the excess amount of saccharin in the solution may block the Cu-In formation in the film surface and cause the film surface to become rougher again, as shown in Fig. 3(d) and (e). According to SEM analysis, adding an appropriate amount of saccharin can enhance the film compactness and improve film quality. Since saccharin can enhance metal ion adherence to electrode surfaces in the galvanization process and enhance the efficiency of deposition, the film deposited with saccharin obtains a smoother crystalline surface and displays less film stress. However, when too much saccharin is added, the saccharin interferes with the uniformity of surface reactions, and a crustal structure with cracks and clusters may be formed, as shown in Fig. 3(d) and (e).



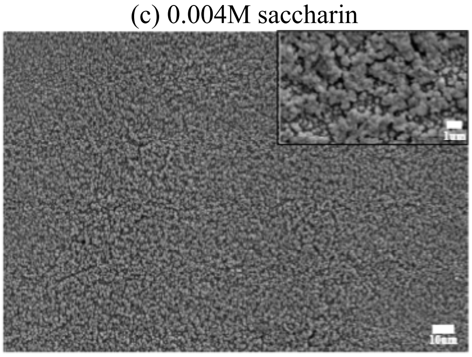
(a) without saccharin



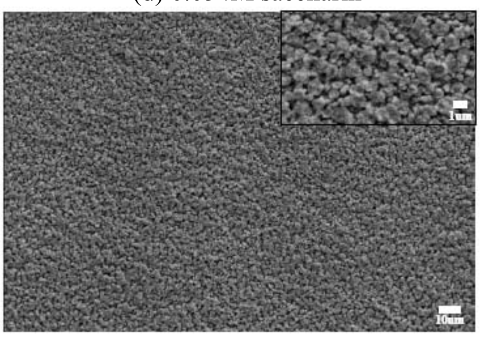
(b) 0.002M saccharin



(c) 0.004M saccharin



(d) 0.054M saccharin



(e) 0.082M saccharin

Fig. 3. Morphology of Cu-In thin film with saccharin recruitment (a) 0.002M (b) 0.004M (c) 0.054M (e) 0.082M

In addition to the influence of saccharin addition, current density during film deposition may also impact film quality. Therefore, an investigation into the influence of current density on the Cu-In film without saccharin, with a low concentration of saccharin, and with a high concentration of saccharin was conducted. Results of XRD analysis are shown in Figs. 4 and 5. For Cu-In film deposited without saccharin or with a low concentration of saccharin at 0.001M in a plating solution, the higher the current density, the stronger the Cu-In peak intensity in the XRD spectra, indicating that a higher current can result in a better crystallized Cu-In thin film. After the addition of a high concentration of saccharin of 0.082M in the plating solution, the trends changed. As shown in Fig. 6, the maximum peak intensity of Cu-In (200) and (134) occurred at a current density of 1.5 $mAcm^{-2}$. As the current further increased to 2.0 $mAcm^{-2}$, the intensity of Cu-In (200) and (134) peaks decreased. According to previous research [16], reduction of Cu with mass transfer control at low current densities. However, as the current density increased in the high concentration solution, other intermediate saccharin reaction products and absorption of saccharin molecules near the cathode electrode potentially block the diffusion of Cu ions, hindering Cu-In deposition. Therefore, an inferior-crystallized phase is formed in the XRD spectrum.

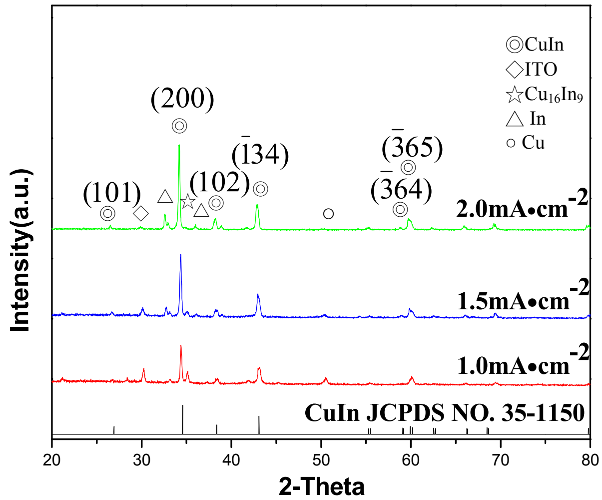


Fig. 4. XRD results of different current densities without saccharin

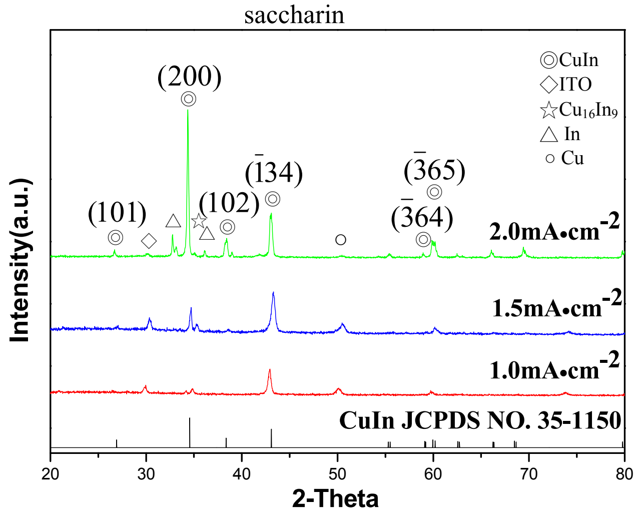


Fig. 5. XRD results of different current densities with addition of 0.001M saccharin

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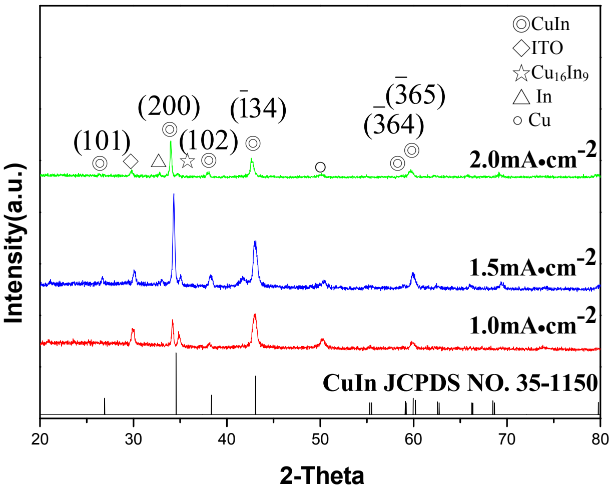

Fig. 6. XRD results of different current densities with addition of 0.082M saccharin

To analyze surface morphology of electrodeposition Cu-In thin film for 30 minutes at different current densities in various concentrations of saccharin, Fig. 7(a) (b), and (c) shows SEM images of the surface of the Cu-In alloy deposited without saccharin under 1 mAcm^{-2}, 1.5 mAcm^{-2}, and 2 mAcm^{-2} current densities. Additionally, Fig. 8(a), (b), and (c) shows the surface of the Cu-In alloy deposited with a low level of saccharin at 0.001 M under current densities of 1 mAcm^{-2}, 1.5 mAcm^{-2}, and 2 mAcm^{-2}. Inferior crystallized phases can be observed on the surface of the Cu-In alloy deposited without saccharin under 1 mAcm^{-2}. As the current intensities increased to 1.5 mAcm^{-2} and 2 mAcm^{-2}, Cu-In film was formed with a larger grain size, as shown in Fig. 7(a), (b), and (c). A similar trend can be observed in the SEM images the surface of the Cu-In alloy deposited with a low 0.001M concentration of saccharin under various current densities as shown in Fig. 8(a), (b), and (c). However, for Cu-In film deposited in a high 0.082M concentration of saccharin, a larger grain size and better crystallized surface occurred at the current density of 1.5 mAcm^{-2}, as shown in Fig. 9(a), (b), and (c). As the current increased to 2.0 mAcm^{-2}, the grain size became smaller and the poorly crystallized phase reoccurred. The AFM measurements were consistent 4 with previous XRD analyses, indicating that a proper saccharin addition and a moderate current density can form a Cu-In film of better quality.

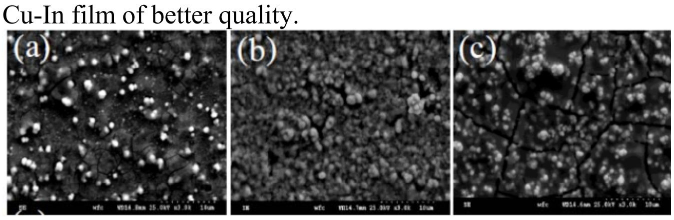

Fig. 7. SEM images of surface morphology with different current densities without saccharin (a) 1.0 mAcm^{-2} (b) 1.5 mAcm^{-2} (c) 2.0 mAcm^{-2}

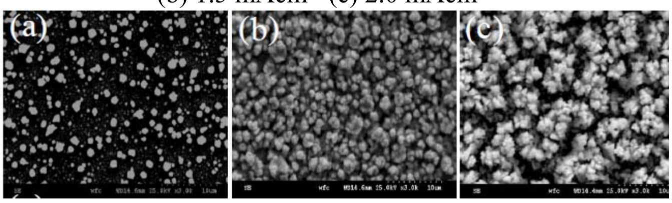

Fig. 8. SEM images of surface morphology with different current densities and addition of 0.001M saccharin (a) 1.0 mAcm^{-2} (b) 1.5 mAcm^{-2} (c) 2.0 mAcm^{-2}

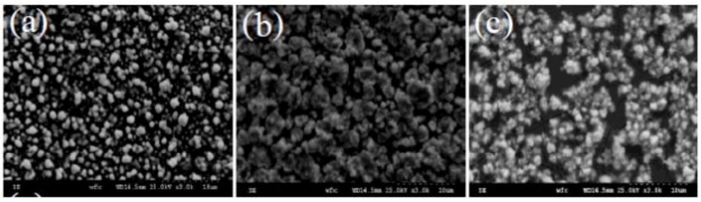

Fig. 9. SEM images of surface morphology with different current densities and addition of 0.082M saccharin (a) 1.0 mAcm^{-2} (b) 1.5 mAcm^{-2} (c) 2.0 mAcm^{-2}

IV. Conclusion

In this research, electrodeposition of Cu-In film with various concentrations of saccharin additive under different bias currents has been investigated. Findings indicate that addition of an appropriate amount of saccharin in the plating solution can reduce Cu precipitate and form well-crystallized $Cu_{16}In_9$. Furthermore, higher current densities for electrodeposition in a plating solution with a low saccharin concentration can result in Cu-In film of improved material quality and crystalline phase. Nevertheless, a high current density of 2.0 mAcm^{-2} with a high concentration of saccharin additive can degrade the Cu-In film quality and worsen the crystalline phase. Cu-In film with a proper amount of saccharin additive is promising for future applications of CuInS or CuInSe solar cells.

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