Electrochemical Deposition of Cu-In-Se Thin Films*

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Abstract: Cu-Se, In-Se and Cu-In-Se thin films have been prepared by electrodepositing method on molybdenum substrates. This paper measures parameter of the electrodeposition process, and discovers the Cu-In-Se thin films are induced codeposition. The Cu-In-Se is not stoichiometric ratio, but is provided with photoelectricity property.

Key words: electrodeposition; $CuInSe_2$; induced codeposition
CLC number: TK513 **Document code**: A **Article ID**: 0529-6579(2003)S1-0045-02

1 Introduction

$CuInSe_2$ (CIS) is a semiconductor with band-gap of 1.04 eV, high absorption coefficient ($> 10^5\ cm^{-1}$), and excellent match with the solar spectrum, so, it is a promising thin-film material for solar cells. The hetero-junction devices made up of $CuInSe_2$ and CdS have many advantages such as: low cost, high efficiency, long term stability, etc. This semiconductor can be prepared by different techniques like: evaporation, sputtering, selenization and electrodeposition etc. The efficiency of modules made up of $CuInSe_2$ has reached 17.7%, and Cu (In, Ga) Se_2 (CIGS) thin-film solar cells have demonstrated 18.8% of efficiency, large scale produced CIS solar cells have reached 13% of efficiency. In china, the efficiency of CIS and CIGS solar cells area of 1 cm^2 made by vapor-selenization have respectively reached 8.83% and 9.13%. For its advantages of low cost, low temperature, no pollution, minimum material waste, and large area uniform film. Electrodeposition (ED) is one of the suitable techniques to prepare solar cells. The efficiency of CIS (made by ED) solar cells has reached 13.5%, and $CuIn_xGa_xSe_2$ solar cells have reached 15.4% of efficiency. So, ED has bright prospect.

The authors explored technology of ED Cu-Se, In-Se and Cu-In-Se thin-film in sulphate system. The solar cell was made up of CIS (produced by ED) and CdS (prepared by chemical bath deposition (CBD)) has V_{oc} of 169 mV and I_{sc} of 2.5 μA.

2 Experimental details

The ED solutions used for proparing Cu-Se, In-Se and Cu-In-Se respectively consist of 0.025 mol/L H_2SO_4, 0.025 mol/L H_2SeO_3: 0.025 mol/L $In(SO_4)_3$, 0.025 mol/L H_2SeO_3 and 0.025 mol/L H_2SO_4, 0.025 mol/L H_2SeO_3, 0.025 mol/L $In(SO_4)_3$. By adding 10% sulphuric acid, the above solutions with pH 1.4 ~ 2.0. A standard three-electrode cell with auxiliary electrode of pt layer, reference electrode of 0.05 mol/L Hg_2SO_4, working electrode of Mo foil. The substrut treatments were curried out as follows.

Flint paper sanding → fint paper sanding → rainsed by water → cleaned by distilled water.

We have measured the polarization curves. A solution containing 3 ~ 5 mmol/L H_2SO_4, 100 ~ 120 mmol/L thiourea solution, 1.34 ~ 2 mmol/L NH_4OH, with pH 11 ~ 12, temperature 70 ℃, time 20 min, was used to deposited CdS on Cu-In-Se thin-film.

3 Result and discussion

Fig.1 shows the polarization curve of Cu-Se deposited on Mo foil, form it we can see that deposition potential is high, thus explains that Cu-Se is easy to be deposited. When deposited under the circumstance of 0.4 V for 5 mins, the film exhibits bronze-like redness, brightness and sood adhesion.

Fig. 2 shows the polarization curve of In-Se deposited on Mo foil, the deposition potential is lower than that of Cu-Se, the current is limited from 1.6 to 2.2 mA/cm^2, changing of deposition potential is slow. When deposited under circumstance of 2.0 mA/cm^2 for 5 mins, the film is uniform, bright, deep blue and adhesion is good.

According to Bhattacharya's researches, ratio of Cu/Se is less than 1 when deposition potential of Cu-Se is high; increasing of pH can make the ratio high. When pH 2.4, the ratio is 2, decreasing of pH can restrain

* Received 10 December 2002; Accepted 18 April 2003
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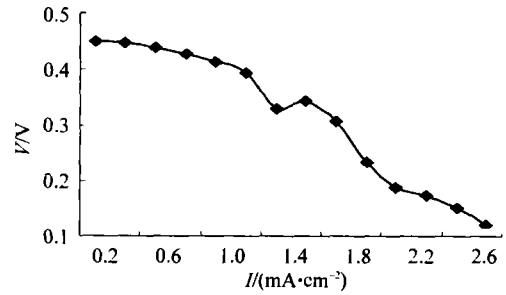

Fig.1 Curve of potential(*vs*. SHE) and current density electrodeposited Cu-Se film in 0.025 mol/L $CuSO_4$ and 0.025 mol/L H_2SeO_3 solution

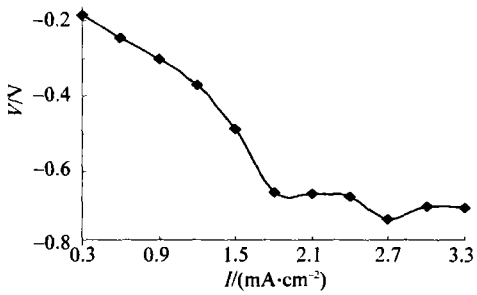

Fig.2 Curve of potential(*vs*. SHE) and current density electrodeposited In-Se film in 0.025 mol/L $In(SO_4)_3$ and 0.025 mol/L H_2SeO_3 solution

deposition of Cu. During the process of In-Se deposition, the ratio of In/Se is about 2/3, changing of potential has little influence on the ratio.

Fig. 3 shows the polarization curve of Cu-In-Se deposited on Mo foil, from it we can see the deposition potential is equal to that of Cu-Se. Then we used chemical bath to deposit CdS on it, the experimental parameters were: applied current density: 2.0 mA/cm^2, temperature: 20 ℃. The film is green-blue, bright, well-distributed, cohesive. When irradiated with sun shine, its V_{oc} is 140 ~ 170 mV, I_{sc} is 1.3 ~ 2.3 mA/cm^2, this shows that the film has photoelectric effect. From reference[7], the film prepared under this circumstance is $CuIn_xGa_xSe_2$, $x = 1.1 \sim 1.2$, $y = 0.7 \sim 0.95$, $z = 2$, so the film is rich in Cu, the deposition potential of In of In-Se is less than that of Cu-In-Se, shows that Cu can induce the deposition of In, thus decreasing the codeposition over potential of In.

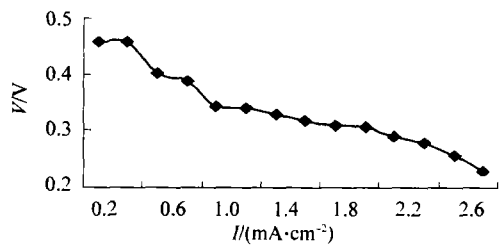

Fig.3 Curve of potential(*vs*. SHE) and current density electrodeposited Cu-In-Se film in 0.025 mol/L $CuSO_4$, 0.025 mol/L $In(SO_4)_3$ and 0.025 mol/L H_2SeO_3 solution

4 Conclusion

Electrodeposition of Cu-In-Se is a kind of induced codeposition, because of the induction of Cu, over potential is more less than that of In-Se, In the solution of $CuSO_4$, $In(SO_4)_3$ and H_2SeO_3, controlling the pH between 1.4 and 2.0, I between 1.6 and 2.2 mA/cm^2, can electrodeposite good quality film of Cu-In-Se. Though the film is not stichiometric, it has photoelectric effect.

Acknowledgment: This project is supported by JiangXi Provincial Natural Science Foundation of China.

References:

[1] Contreras M A, Egass B, Ramanathan K, et al. *Prog Photovolt Res Appl*, 1999, 7: 311.

[2] Powallaa M, Dimmlerb B. Development of large-aera CIGS modules[J]. *Solar Energy Materials & Solar Cells*, 2003, 75: 27 - 34.

[3] SUN Y, ZHANG L Z. Rearsh of CIS and CIGS thin-film solar cells[J]. *J Solar Energy*, 2002, 22(2): 192 - 195.

[4] Ramanathan K, Bhattacharya R N, Granata J, et al. *Proceeding of 26th IEEE Photovoltaic Specialists Conference*, 1997.

[5] Bhattacharya R N, Hiltner J F, Batchelor W, et al. 15.4% $CuIn_{1-x}Ga_xSe_2$-based photovoltaic cells feom solution-based precursor film[J]. *Thin Films*, 2000, 396: 361 - 362.

[6] Guillen C, Fernadez M A, Herrero J. Accurate control of thin film CdS growth process by adjusting the chemical bath deposition parameters[J]. *Thin Films*, 1998, 335: 37 - 42.

[7] Bhattacharya R N, Fernadez A M, Contreras M A, et al. Electrodeposition of In-Se, Cu-Se and Cu-In-Se thin films[J]. *J Electrochem Soc*, 1996, 143: 854 - 858.

电化学沉积 Cu-In-Se 薄膜

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摘 要：采用电化学沉积方法在钼箔上制备 Cu-Se、In-Se 和 Cu-In-Se 薄膜，对电沉积的工艺参数进行了测试，发现 Cu-In-Se 是一种诱导共沉积，虽然沉积膜不具备化学计量比，但具有一定的光电性能。

关键词：电沉积；$CuInSe_2$；诱导共沉积

中图分类号：TK513 **文献标识码**：A