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Effect of the concentration of Cu^{2+} in the electrolytes on $CuInS_2$ thin films

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Abstract: $CuInS_2$ thin film, $CuIn_{11}S_{17}$ thin film and a mixture of both were formed on ITO glass substrates by sulfurizing Cu-In-S precursors which were electrodeposited in the electrolytes solutions with different Cu^{2+} concentrations. The properties of the thin films were characterized by X-ray diffraction (XRD), scanning electron micrographs (SEM) and energy dispersive spectroscopy (EDS). The experiment results indicate that while keeping the In^{3+} and S_2O_{32-} concentrations fixed, the concentration of Cu^{2+} has significant influence on the chemical composition, morphology and crystal structure of the resulting thin films. With a proper Cu^{2+} concentration, a single-phase polycrystalline $CuInS_2$ thin film can be achieved with ideal stoichiometry and a suitable band gap of 1.5 eV, which will be used as the absorber layer of a thin film solar cell in further work.

Key words: $CuInS_2$ thin films; electrodeposition; sulfurization; thin film solar cell
PACS: 68.55.-a, 81.15.Pq, 84.60.Jt

电解液中 Cu^{2+} 浓度对 $CuInS_2$ 薄膜的影响

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摘要:采用硫化 Cu-In-S 预制层方法制备出 $CuInS_2$、$CuIn_{11}S_{17}$ 及两相混合共存的薄膜,其中 Cu-In-S 预制层通过在含有不同 Cu^{2+} 浓度的电解液中电化学沉积制得.通过对薄膜的 XRD、SEM 及 EDS 的表征,发现当 In^{3+} 和 S_2O_{32-} 浓度不变时,Cu^{2+} 浓度的改变对薄膜的性质有很大的影响.在最优的 Cu^{2+} 浓度下,制备出了单一的、具有理想化学计量比的、禁带宽度为 1.5eV 的 $CuInS_2$ 薄膜.这种薄膜在后续工作中有望被用作太阳能电池的吸收层.

关 键 词:$CuInS_2$ 薄膜;电化学沉积;硫化;薄膜太阳能电池
中图分类号:TM914.4 **文献标识码**:A

Introduction

Chalcopyrite compound Copper indium disulfide ($CuInS_2$) is a promising material as a photo-absorbing layer for high-efficiency, low-cost thin film solar cells, since this semiconductor has an ideal direct band gap (1.5 ~ 1.55eV) and a large absorption coefficient in visible spectrum range[1-4]. Various techniques have been used to prepare $CuInS_2$ thin films, such as sputtering[5], spray pyrolysis[6], electrodeposition[7], molecular beam epitaxy[8] etc. Among them, electrodeposition is of interest due to its simplicity, low energy, cheap requirements and further it is an easily scalable technique for mass manufacture.

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In this paper, we prepared the $CuInS_2$ thin films through one-step electrodeposition of Cu-In-S precursors followed by sulfurization at 550℃ in the atmosphere of $N_2 + H_2S(5\%)$. The effect of Cu^{2+} concentration on the properties of $CuInS_2$ thin films was investigated.

1 Experiment

The Cu-In-S precursor films were electrodeposited onto indium tin oxide (ITO) glasses with dimensions of 1 × 1 cm^2. Prior to the film deposition the ITO glasses were cleaned with detergent and rinsed with acetone, ethanol and distilled water sequentially. The electrodeposition procedure was carried out with a CHI 1140A electrochemical workstation (CH Instrument, USA) and a standard 3-electrode system consisted of an ITO glass working cathode, a platinum sheet as the anode and a Saturated Calomel Electrode (SCE) as the reference electrode. The electrolyte bath used in this work contained 9.6 mM $InCl_3 \cdot H_2O$, 25mM $Na_2S_2O_3 \cdot 5H_2O$, 240mM $LiCl \cdot 4H_2O$ and $CuCl_2 \cdot 2H_2O$ with varied concentrations in the range of 2.6 ~ 9.1mM. All chemicals are analytical reagent grade (from Sinopharm Chemical Reagent Co. Ltd. China) and were used without further purification. The Cu-In-S precursor films were deposited at −1.0v vs. SCE in potentiostatic mode for 30 minutes without stirring at 25℃. In this study four thin film samples were prepared with Cu^{2+} concentrations of 2.6 mM, 3.9 mM, 7.8mM and 9.1mM, respectively. After electrodeposition, the samples were rinsed in deionized water and dried under flowing nitrogen. The sulfurization procedure was performed in the atmosphere of $Ar + H_2S$ (5%). The precursor films were first treated at 100℃ for 30 minutes to ensure sufficient reaction. Then the temperature was increased to 550℃ quickly and held for 60 minutes. Finally, the samples were cooled down without control to room temperature.

The structure properties of the resulting $CuInS_2$ thin films were characterized by X-ray diffraction (XRD) using BrukerD8 diffractometer with CuK_α radiation. The surface morphology was measured by a PhilipsS360 scanning electron microscope (SEM). Microanalysis was obtained using the energy dispersive X-ray spectroscopy (EDS). Optical properties of the films were recorded in the wavelength range 300 ~ 1500 nm by a Cary-5000 UV-Vis-NIR double-beam spectrophotometer at room temperature. The thickness of the sample was monitored by a DEKTAK profilometer.

2 Results and discussion

Fig. 1 depicts the XRD patterns of the four sulfurized $CuInS_2$ samples electrodeposited with different Cu^{2+} concentrations The main peaks in the XRD patterns can be assigned to $CuInS_2$ (marked by asterisk (*)) or $CuIn_{11}S_{17}$ (marked by pound sign (#)). As shown in Fig. 1(a) the film exhibits XRD peaks related to the (311), (400), (511), (440) and (220) planes of $CuIn_{11}S_{17}$, which can be confirmed by PDF # 34 − 0797. Therefore, it can be concluded that single-phase polycrystalline $CuIn_{11}S_{17}$ exists in the film when 2.6 mM Cu^{2+} is used in the electrolyte bath. Comparatively, when increasing the Cu^{2+} concentration to 3.9 mM the formed film exhibits some other peaks corresponding to the (112), (220), (312) and (200) planes of $CuInS_2$ (Fig. 1(b)), which can be confirmed by PDF #27 − 0159. Obviously, $CuIn_{11}S_{17}$ and $CuInS_2$ mixed crystals coexist in this sample. The other two samples were prepared with higher Cu^{2+} concentrations of 7.8 mM (c) and 9.3 mM (d), both of which showed XRD peaks corresponding to chalcopyrite structure of polycrystalline $CuInS_2$, as shown in Fig. 1(c) and Fig. 1(d).

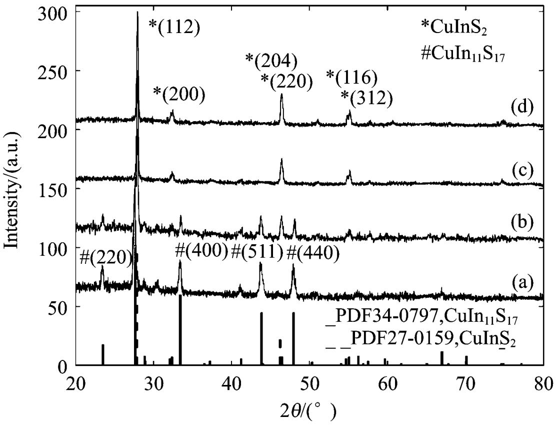

Fig. 1　XRD patterns of sulfurized $CuInS_2$ thin films with different Cu^{2+} concentrations

图 1　不同 Cu^{2+} 浓度下沉积的 $CuInS_2$ 薄膜的 XRD 图

The XRD results suggest that Cu^{2+} concentrations play a crucial role in determining the final phase of the $CuInS_2$ thin films. Similar result has been obtained by R. P. Wijesundera et al[9]. In their work Cu-In precursors were prepared by sequentially electrodeposited Cu and In layers, and final phase of $CuInS_2$ thin films could be determined by Cu/In atomic ratio of the Cu-In precursors. In our work, Cu, In and S were co-electrodeposited to form the precursor films, and the Cu/In atomic ratios were controlled by Cu^{2+} concentrations while keeping In^{3+} concentration fixed. Additionally, it should be noted that no obvious diffraction peaks are observed from the XRD patterns (unpublished data) of the non-sulfurized films, which suggests that the crystallites of the electrodeposited precursor films are very small or the formed compound are of amorphous nature. Therefore, sulfurization procedure is necessary to obtain well-crystalized films.

Typical surface morphologies of sulfurized $CuInS_2$ thin films with different Cu^{2+} concentrations are shown in Fig. 2. It is seen that some microparticles are distributed on the surface of the thin film and no defined boundaries of grains are observed for the sample with Cu^{2+} concentration of 2.6 mM (Fig. 2(a)). When Cu^{2+} concentration is increased to 3.9 mM, the film crystallinity is improved and grains appear (Fig. 2(b)). The sizes of some grains are up to 2 μm while some small particles with different sizes still exist on the surface. Fig. 2(c) and Fig. 2(d) show distinct, uniform and densely packed grains with well defined grain boundaries and the grain sizes are about 1 ~ 2 μm. Hence, Cu^{2+} concentrations of 7.8 mM and 9.1mM in the solution are optimum conditions and the prepared $CuInS_2$ thin films may be suitable for the application in thin film solar cells.

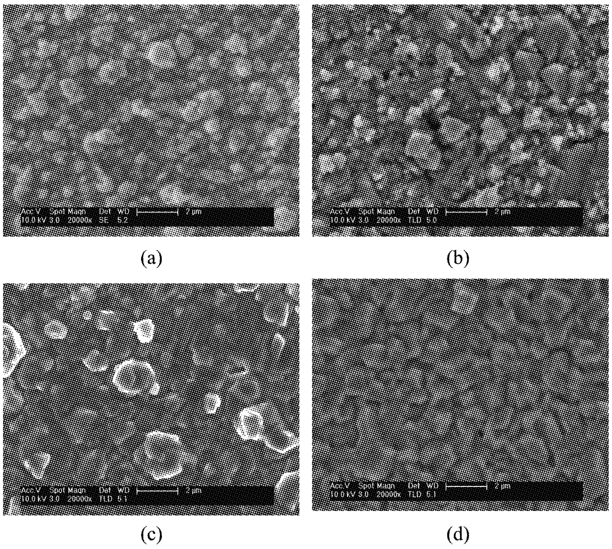
(a) (b) (c) (d)

Fig. 2 SEM surface micrographs of sulfurized $CuInS_2$ thin film with different Cu^{2+} concentrations (a)2.6 mM,(b)3.9 mM,(c)7.8 mM,(d)9.1 mM

图2 不同 Cu^{2+} 浓度下沉积的 $CuInS_2$ 薄膜的表面形貌图 (a)2.6 mM,(b)3.9 mM,(c)7.8 mM,(d)9.1 mM

Table 1 The atomic percentages of Cu, In and S for the sulfurized $CuInS_2$ thin films electrodeposited with different Cu^{2+} concentrations

表1 不同 Cu^{2+} 浓度下沉积的 $CuInS_2$ 薄膜的原子百分比

Cu^{2+}	Cu/(%)	In/(%)	S/(%)	Cu/In	S/Metal
2.6mM	4.7	41.8	53.5	0.11	1.15
3.9mM	15.8	31.8	52.4	0.50	1.10
7.8mM	22.1	23.5	54.5	0.94	1.20
9.1mM	24.9	21.2	53.8	1.17	1.17

Table 1 summarizes the atomic percentages of Cu, In and S for the sulfurized $CuInS_2$ thin films electrodeposited with different Cu^{2+} concentrations in the solution. It is noted that as Cu^{2+} concentration in the solution increases the copper atomic percent of the sulfurized $CuInS_2$ thin films increases as expected while the indium atomic percent decreases. The sulfur atomic percent has a little change and is more than 50%. When Cu^{2+} concentration is 2.6mM the relative ratio between components of Cu∶In∶S = 1∶9∶11, which is near the composition ratio of $CuIn_{11}S_{17}$ thin film although the sulfur content is deficient. When Cu^{2+} concentration is increased to 3.9mM the relative ratio of Cu∶In∶S = 1∶2∶3. Based on the XRD results, $CuIn_{11}S_{17}$ and $CuInS_2$ may coexist in this sample. For the two samples which Cu^{2+} concentrations are 7.8 mM and 9.1mM in the solution, stoichiometric chemical compositions are obtained (Cu∶In∶S = 1∶1∶2). The EDS results are in accordance with that of XRD. So the concentrations of Cu^{2+} in the solution significantly affect the chemical composition of the sulfurized $CuInS_2$ thin films.

The absorption coefficient (α) can be determined from the transmission spectra using the following formula

$$\alpha = \frac{1}{d}\ln\left[\frac{(1-R)^2}{T}\right] \quad , \tag{1}$$

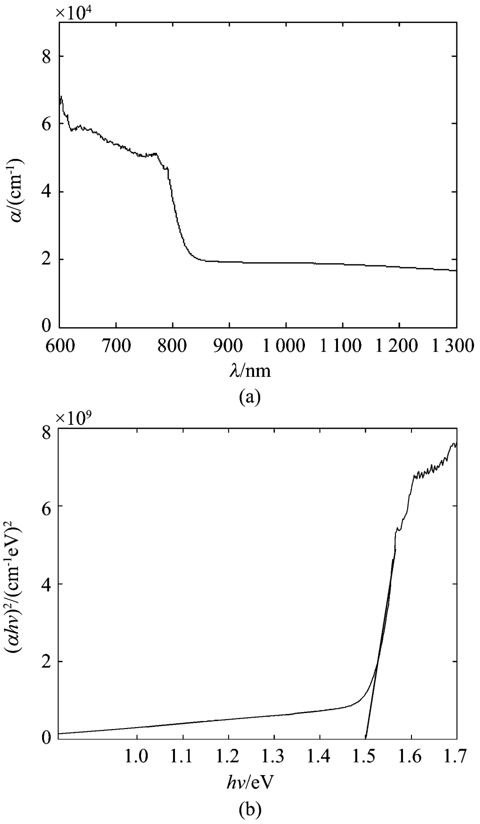

Fig. 3 Plots of (a) Absorption coefficient versus wavelength and, (b) $(\alpha h\nu)^2$ versus photon energy ($h\nu$) for the sulfurized $CuInS_2$ thin film electrodeposited with Cu^{2+} concentration of 7.8 mM

图3 Cu^{2+}浓度为7.8 mM的$CuInS_2$薄膜的(a)吸收系数与波长关系图,(b)$(\alpha h\nu)^2$与($h\nu$)关系图

where d is the thickness of the film, R and T are the reflectance and transmittance, respectively. The optical band gap (E_g) can be obtained by the equation

$$\alpha h\nu = A(h\nu - E_g)^n \quad , \qquad (2)$$

where A is a constant, $h\nu$ is the photon energy. The exponent n takes the value of 1/2 for a direct transition in present case. Fig. 3 (a) presents the optical absorption coefficient versus wavelength plot for the sulfurized $CuInS_2$ thin film electrodeposited with Cu^{2+} concentration of 7.8 mM. The thickness of the sample is 1.95 μm determined by the profilometer. The value of the absorption coefficient is approximate 6×10^4 cm^{-1} in visible spectrum range, which is in agreement with reports of other literaters [6, 10]. It is noted that the film shows an abrupt absorbance edge around 820 nm, which means a good optical property. Fig. 3 (b) shows the plot of $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$). The band gap E_g is determined by extrapolating the linear region of the curve $(\alpha h\nu)^2$ versus $h\nu$ to zero. Thus the optical band gap value is estimated to be 1.5 eV, which is in good agreement with the other literatures [11-12]. The value is close to the optimum band gap energy and the $CuInS_2$ thin film is appropriate for the application of thin film solar cells.

3 Conclusions

$CuInS_2$ thin film, $CuIn_{11}S_{17}$ thin film and a mixture of both have been successfully prepared on ITO substrates by sulfurizing the Cu-In-S precursors which are electrodeposited in the electrolyte bath containing different Cu^{2+} concentrations. It is found that Cu^{2+} concentration in the electrolytic bath has a significant effect on the microstructure, morphology, composition and optical properties of $CuInS_2$ thin films. The results indicate that when Cu^{2+} concentrations are 7.8 mM and 9.1 mM $CuInS_2$ thin films have single phase, stoichiometric chemical compositions and good surface morphologies. The direct band gap energy of the $CuInS_2$ thin film is about 1.5 eV.

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REFERENCES

[1] Gheluwe J V, Versluys J, Poelman D, *et al.* A photoluminescence and structural analysis of $CuInS_2$-on-Cu-tape solar cells (CISCuT) [J]. *Thin Solid Films*, 2006, **511-512**: 304 - 308.

[2] Garuthara R, Wijesundara R, Siripala W. Characterization of $CuInS_2$ thin films prepared by electrodeposition and sulfurization with photoluminescence spectroscopy [J]. *Solar Energy Materials & Solar Cells*, 2003, **79**(3): 331 - 338.

[3] Xu X H, Wang F, Liu J J, *et al.* Effect of potassium hydrogen phthalate (C8H5KO4) on the one-step electrodeposition of single-phase CuInS2 thin films from acidic solution [J]. *Electrochimica Acta*, 2010, **55**(15): 4428 - 4435.

[4] Braunger D, Hariskos D, Walter T, *et al.* An 11.4% efficient polycrystalline thin film solar cell based on $CuInS_2$ with a Cd-free buffer layer [J]. *Solar Energy Materials and Solar Cells*, 1996, **40**(2): 97 - 102.

[5] Cayzac R, Boulc'h F, Bendahan M, *et al.* Direct preparation of crystalline $CuInS_2$ thin films by radiofrequency sputtering [J]. *Materials Science and Engineering B*, 2009, **157** (1 - 3): 66 - 71.

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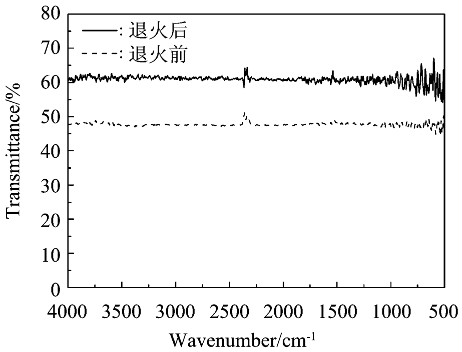

图 6　退火前后 Cd$_{1-x}$Mn$_x$Te 晶片典型的中红外透过光谱
Fig. 6　Typical mid-infrared transmission spectra of Cd$_{1-x}$Mn$_x$Te wafers in as-grown and annealed states

长 700 ~ 800 nm 的近红外光范围，吸收边的截止波长反映生长态晶片（30 mm × 40 mm ）的 Mn 含量范围为 $0.1887 \leqslant x \leqslant 0.2039$，晶片中轴向成分波动差值约为 0.0152，径向成分波动差值约为 0.0013. $x = 0.2$ 的 Cd$_{1-x}$Mn$_x$Te 晶体吸收边的吸收系数 α 变化范围为 2.5 ~ 55 cm^{-1}，其与入射光能量的关系符合 Urbach 方程；在波数 4000 ~ 500 cm^{-1}（2.5 ~ 20 μm）中红外入射光波段，生长态晶体的红外透过率在 45% ~ 55% 范围内，且不随波数的变化而改变. 晶体对该波长范围红外光的吸收表现为晶格吸收和自由载流子吸收；Cd 气氛退火后，Cd$_{1-x}$Mn$_x$Te 晶片的吸收边位置基本没有变化，晶片中 Mn 的成分含量未受到退火的影响. 退火后，晶片在 4000 ~ 500 cm^{-1}波数范围内的红外透过率提高到 61% 以上，接近理论值 65%.

REFERENCES

[1] CHU Jun-Hao. *Physics and properties of narrow gap semiconductors*[M]. Beijing: Science and Technology Press(褚君浩. **窄禁带半导体物理学**. 北京：科学技术出版社)，2005：6 − 100.

[2] Donald A R, Stuart H, James C, *et al.* Third generation imaging sensor system concepts[J]. *SPIE*, 1999, **3701**: 108 − 117.

[3] YANG Jian-Rong, ZHANG Chuan-Jie, FANG Wei-Zheng, *et al.* Te-rich dipping technique of HgCdTe liquid phase epitaxy[J]. *Journal of Infrared and Millimeter Waves*(杨建荣，张传杰，方维政，等. 碲镉汞富碲垂直液相外延技术. **红外与毫米波学报**)，2009, **28**(5): 325 − 309.

[4] Triboulet R, Heurtel A. and Rioux J. Twin-free (Cd, Mn)Te substrates[J]. *Journal of Crystal Growth*, 1990, **101**: 131 − 134.

[5] Zhang J J, Jie W Q, Wang L J, *et al.* Twins in CdMnTe single crystals grown by Bridgman method[J]. *Crystal Research and Technology*, 2010, **45**: 7 − 12.

[6] Belas E, Bugar M, Grill R, *et al.* Reduction of inclusions in (CdZn)Te and CdTe: In single crystals by post-growth annealing[J]. *Journal of Electronic Materials*, 2008, **37**(9): 1212 − 1218.

[7] LI Guo-Qiang, JIE Wan-Qi, HUA Hui. Deducing the properties of CdZnTe wafers by IR transmission[J]. *Journal of Infrared and Millimeter Waves*(李国强，介万奇，华慧. 根据红外透过率推断 CdZnTe 晶片的性能. **红外与毫米波学报**)，2003, **22**(6): 469 − 472.

[8] Nakagawa K, Maeda K, Takeuchi S. Observation of dislocations in cadmium telluride by cathodoluminescence microscopy[J]. *Applied Physics Letters*, 1979, **34**: 574 − 575.

[9] Zhang J J, Jie W Q, Luan L J, *et al.* Evaluation of Mn uniformity in CdMnTe crystal grown by the vertical Bridgman method[J]. *Journal of Electronic Materials*, 2008, **37**(8): 1158 − 1162.

[10] Zaets W, Watanabe K, Ando K. Cd$_{1-x}$Mn$_x$Te magneto-optical waveguide integrated on GaAs substrate[J]. *Applied Physics Letters*, 1997, **70**: 2508 − 2510.

[11] Urbach F. The long-wavelength edge of photographic sensitivity and of the electronic absorption of solids[J]. *Physics Review*, 1953, **92**: 1324.

[12] Andr R, Dang L S. Low-temperature Refractive Indices of Cd$_{1-x}$Mn$_x$Te and Cd$_{1-x}$Mg$_x$Te [J]. *Journal of Applied Physics*, 1997, **82**(10): 5086 − 5089.

[13] HUANG Kun, HAN Ru-Qi. *Solid-state physics*[M]. Beijing: Higher Education Press(黄昆，韩汝琦. **固体物理学**. 北京：高等教育出版社)，1988: 437 − 463.

[14] SUN Yi-Cai. *Semiconductor measurement technology*[M]. Beijing: Metallurgy Industry Press(孙以材. **半导体测试技术**. 北京：冶金工业出版社)，1984: 225 − 260.

（上接 105 页）

[6] Sahal M, Mar B, Mollar M. CuInS$_2$ thin films obtained by spray pyrolysis for photovoltaic applications[J]. *Thin Solid Films*, 2009, **517**(7): 2202 − 2204.

[7] Martineza A M, Arriagab L G, Fern andeza A M, *et al.* Band edges determination of CuInS2 thin films prepared by electrodeposition [J]. *Materials Chemistry and Physics*, 2004, **88**(2 − 3): 417 − 420.

[8] Gosslam, Hahn T H, Metezner H, *et al.* Thin CuInS$_2$ films by three-source molecular beam deposition[J]. *Thin Solid Films*, 1995, **268**(1 − 2): 39 − 44.

[9] Wijesundera R P, Siripala W. Preparation of CuInS$_2$ thin films by electrodeposition and sulphurisation for applications in solar cells[J]. *Solar Energy Materials & Solar Cells*, 2004, **81**(2): 147 − 154.

[10] Hou X H, Choy K L. Synthesis and characteristics of CuInS$_2$ films for photovoltaic application[J]. *Thin Solid Films*, 2005, **480** − **481**: 13 − 18.

[11] Sharma A K, Rajaram P. Nanocrystalline thin films of CuInS$_2$ grown by spray pyrolysis[J]. *Materials Science and Engineering B*, 2010, **172**(1): 37 − 42.

[12] Peng S J, Cheng F Y, Liang J, *et al.* Facile solution-controlled growth of CuInS$_2$ thin films on FTO and TiO$_2$/FTO glass substrates for photovoltaic application[J]. *Journal of Alloys and Compounds*, 2009, **481**(1 − 2): 786 − 791.