

Developments of High-Efficiency Flexible Cu(In,Ga)Se₂ Thin Film Solar Cells on a Polyimide Sheet by Sodium Incorporation *

ZHANG Li(张力)^{1**}, LIU Fang-Fang(刘芳芳)¹, LI Feng-Yan(李凤岩)¹, HE Qing(何青)¹,
LI Chang-Jian(李长健)¹, LI Bao-Zhang(李宝璋)¹, ZHU Hong-Bing(朱红兵)²

¹Tianjin Key Laboratory for Photoelectronic Thin Film Devices and Technology, Nankai University, Tianjin 300071

²College of Physics Science and Technology, Hebei University, Baoding 071002

(Received 16 December 2013)

We present the fabrication of flexible Cu(In,Ga)Se₂ (CIGS) solar cells on a polyimide (PI) sheet with and without Na incorporation. A sodium element is incorporated into the CIGS absorber by using a NaF precursor after Mo back contact deposition. X-ray diffraction patterns show that the (112) preferred orientation of the as-grown CIGS films is decreased by Na incorporation. The secondary phase of (In_xGa_{1-x})₂Se₃ is observed for the CIGS films with Na. There is no significant difference in the grain size with and without Na incorporation from surface and cross-sectional SEM images. Additionally, the increase of carrier concentration and decrease of resistivity of CIGS absorber are induced by Na doping. Finally, the flexible CIGS solar cells on PI sheets with efficiency close to 11%, containing Na, are achieved. The improvement of cell efficiency can be attributed to the modified electrical properties of the CIGS film by Na incorporation.

PACS: 84.60.Jt, 81.05.Hd, 81.15.Ef, 81.05.Cy

DOI: 10.1088/0256-307X/31/6/068402

Flexible Cu(In,Ga)Se₂ (CIGS) thin film solar cells on polyimide (PI) sheets have become attractive candidates related to their higher specific power (W/kg),^[1,2] tolerance against high energy radiation,^[3] long-term stability^[4] and compatibility with roll-to-roll process.^[5] This motivated the rapid progress of flexible CIGS solar cells on PI sheets. In contrast to rigid soda-lime glass substrates, Na incorporation is the key issue for further improvements of device performance.^[6] Influences of Na on structural properties of CIGS films are controversial: enhanced and hindered grain growth,^[7,8] improved and reduced texture.^[9,10] The dependence of Na on electrical properties has been recognized for enhancement of net carrier concentration and in-plane conductivity.^[11] The benefits of Na incorporation in CIGS solar cells were observed for the enhancement of open circuit voltage (V_{oc}) and fill factors (FFs) have been reported by several groups.^[12] The effects of Na on the structural and electrical properties of CIGS films by using a low-temperature process on a PI sheet have not yet been reported.

Previously, we have grown CIGS films on the PI and glass substrates using one-stage and three-stage co-evaporation processes.^[13,14] Higher device performance has been demonstrated by using the three-stage process when the substrate temperature is about 400°C.^[15] In this Letter, the CIGS films were grown on a PI sheet by using the three-stage process at low temperature. The influence of Na incorporation on the structural and electrical properties of CIGS films

on the PI sheet is investigated contrastively.

The PI sheet used in this study is a Kapton-E film of thickness of 25 μm . The Mo back contact layer was deposited onto the PI sheet by the dc sputtering process and the typical thickness is around 0.8–1 μm . A NaF precursor was evaporated on the Mo layer prior to the CIGS film deposition. The thickness of the 30 nm NaF layer was controlled with an *in situ* quartz crystal monitor. Polycrystalline CIGS thin films were deposited onto the Mo coated PI sheet by using the three-stage process from the independently controlled Cu, In, Ga and Se sources.^[15] In the first stage, an In-Ga-Se precursor was deposited on the substrate temperature of 380°C. In the second stage, the precursor was exposed to the Cu and Se fluxes to form Cu-rich CIGS films. In the third stage, a small amount of In-Ga-Se was evaporated to form a slightly Cu-poor CIGS film. During the second and third stages, the substrate temperature was kept at 450°C. The substrate temperature was determined by the thermocouple contacting on the back of substrates directly. Compositional control was realized by detecting the initial evaporation rates of Cu, In, Ga, Se sources. The typical thickness of the CIGS films is 1.5–2.5 μm . CIGS solar cells were completed by the chemical bath deposition (CBD) of 50 nm CdS and were followed by MOCVD boron-doped and intrinsic ZnO layer with the thickness of 50 nm and 500 nm. The role of CdS buffer layer can be concluded as follows: protect the junction region from damage during subsequent ZnO deposition, modify the surface of

*Supported by the Fundamental Research Funds for the Central Universities under Grant No 65011991, and the Specialized Research Fund for the Doctoral Program of Higher Education under Grant No BE033511.

**Corresponding author. Email: lzhang@nankai.edu.cn

© 2014 Chinese Physical Society and IOP Publishing Ltd

CIGS absorber by Cd^{2+} , replace Cu to form n-type CIGS, moderate the band gap 2.4 eV between CIGS (1.13 eV) and ZnO (3.3 eV) to reduce the conduction band gap offset. The role of i-ZnO can be explained by improving the locally non-uniform electronic quality of the CIGS layer that can be modeled by a parallel diode with higher recombination current. As a result, the influence of these non-uniform regions on the device performance is reduced by the series resistance of the high resistance i-ZnO. This series resistance has a negligible effect on the performance of the dominant parts of the device area.^[16] The Al grid was evaporated and the cell area was delineated by mechanical scribing to give an area of 0.24 cm^2 . The thickness of the CIGS films was determined by a stylus profiler. Structural properties were determined by a Philips Xpert diffraction with Cu K_α radiation. Surface and cross-sectional images were observed by a Hitachi 800 scanning electron microscope (SEM). The chemical composition of the films was determined by an energy-dispersive x-ray spectroscopy (EDX) measurement. Electrical characterizations of the films were measured by Hall effect measurement at room temperature. For the Hall measurements, the CIGS films on the PI sheets without the Mo back contact layer are used. We have evaporated an Al electrode onto the surface as ohmic contact. The current density-voltage (J - V) measurements were performed under the standard AM1.5 spectrum with 100 mW/cm^2 at 25°C . The light source of solar simulator is calibrated by a standard single crystal Si solar cell.

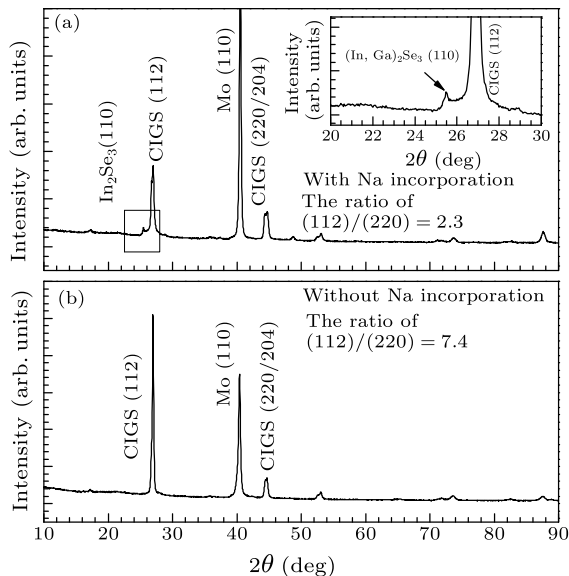


Fig. 1. XRD patterns of CIGS films on the PI sheet with and without Na incorporation.

Figure 1 shows the XRD patterns of CIGS films on the PI sheet with and without Na incorporation. The inset is a magnificent pattern from 2θ of 20–30. The two CIGS films show strong x-ray diffrac-

tion peaks of (112) to (220/204) for chalcopyrite compounds. However, additional reflections of secondary phase $(\text{In}_{0.62}\text{Ga}_{0.38})_2\text{Se}_3$ (110) (JCPDS 87-1482) has been detected when the CIGS films contain Na. Previously, the existence of $(\text{In}_{0.68}\text{Ga}_{0.32})_2\text{Se}_3$ phase was explained by the incomplete diffusion reaction of the In-Ga-Se precursor with the Cu-Se compound in the three-stage process at low substrate temperature compared to the high temperature deposition process. However, it seems that the existence of this secondary phase is related to the Na incorporation in this study. The ratio of peak height intensities of (112) to (220/204) can be utilized as a measure of the preferred orientation. The CIGS films with and without Na have a (112) to (220/204) ratios of 2.3 and 7.4, respectively. This means that CIGS films with Na contain randomly oriented grains since the value of (112) to (220/204) is below 3. It is very different from the previous results that the Na incorporation in CIGS films can lead to preferred (112) orientation.^[12] According to the previous results, the preferred orientation of CIGS films by co-evaporation process originated from the texture of the precursor $(\text{In,Ga})_2\text{Se}_3$. The (006) and (300) oriented- $(\text{In,Ga})_2\text{Se}_3$ films tend to form the (112) and (220/204) oriented-CIGS films.^[17] For our study, the Na incorporation hinders the diffusion of the In and Ga atoms, which has been detected previously.^[18] The formation of $(\text{In,Ga})_2\text{Se}_3$ with small grain size and random orientation with Na incorporation leads to the decrease of the (112) preferred orientation.

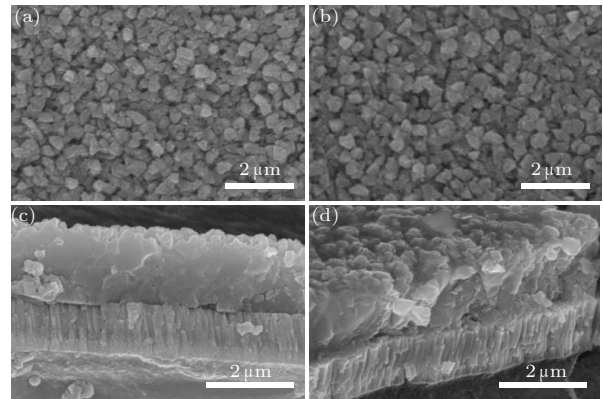


Fig. 2. SEM images of surface and cross section of CIGS films on the PI sheet: (a) and (c) without Na; (b) and (d) with Na.

Figure 2 shows the SEM images of the surface and cross sections of CIGS films on the PI sheet with and without Na incorporation. The two CIGS samples with the same chemical composition were fabricated in the one deposition run. Figures 2(a) and 2(c) show the CIGS films without Na, and Figs. 2(b) and 2(d) show the CIGS film without Na. No obvious difference can be observed for CIGS films with and without Na incorporation. It is found that from Figs. 2(b) and

2(d) that the grain size in the lower is smaller than that in the upper. The reduced grain size towards the back contact can be explained that the inter-diffusion and out-diffusion of In and Ga atoms are hindered at low temperature. Thus the films close to the Mo layer consist of $(\text{In,Ga})_2\text{Se}_3$ and high Ga-content CIGS films which have the smaller grain size. These results are consistent with our XRD results.

The measurements of resistivity (R_S) and carrier concentration (N_P) were performed by the Van Der Pauw technique.^[19] Table 1 lists the Hall effect results of CIGS films on the PI sheet with and without Na. The CIGS films on the PI sheet always show p-type conductivity with and without Na. The Na-free CIGS films on PI show a very high resistivity, inversely R_S can be decreased by 2–3 orders of magnitude by Na incorporation. When the additional Na is supplied, the N_P can be increased from 10^{14} cm^{-3} to 10^{16} cm^{-3} . Similarly, the enhancement of the net carrier concentration and improved in-plane conductivity by Na incorporation has been reported by many groups.^[12] The values of mobility do not seem to be significantly affected by the Na incorporation and are usually in the range of 1–10 ($\text{cm}^2/\text{V}\cdot\text{s}$).

Table 1. The resistivity R_S and carrier concentration N_P for CIGS films on PI with and without Na by Hall effect measurements.

Resistivity R_S	Mobility ($\text{cm}^2/\text{V}\cdot\text{s}$)	Carrier N_P concentration	Na
692	1.93	5.47×10^{14}	without
5.07	0.633	9.21×10^{16}	with

We made the flexible CIGS solar cells with a structure of $\text{Al/B:ZnO/i-ZnO/CdS/CIGS/Mo/PI}$. The J – V curve is shown in Fig. 3. The two CIGS films were obtained under the same deposition conditions. From Fig. 3(b), a conversion efficiency of 10.98% for the CIGS solar cell with Na is demonstrated and the J – V parameters are as follows: short current density $J_{sc} = 32.6 \text{ mA/cm}^2$, open circuit voltage $V_{oc} = 510.9 \text{ mV}$ and fill factor $\text{FF} = 65.9\%$. Compared with the device with Na, the Na-free solar cell shows the lower efficiency of 6.68% ($J_{sc} = 30.4 \text{ mA/cm}^2$, $V_{oc} = 421.2 \text{ mV}$, $\text{FF} = 52.1\%$). The photovoltaic performance of CIGS solar cells without Na is limited by its relatively lower V_{oc} and FF. The enhanced performance by using Na incorporation can be explained by the improvement of electrical properties of CIGS films, as measured by Hall measurements. If we ignore the influence of tunneling mechanisms and surface recombination, the increased V_{oc} corresponding to the N_P in the absorber layer can be expressed as^[20]

$$\Delta V_{oc} = (2kT/q) \ln(N_P/N_{PO}).$$

An increased N_P of one order of magnitude relative to a basic concentration of N_{PO} leads to an increased V_{oc} of about 60 mV by using a diode factor $A = 2$. How-

ever, the increased V_{oc} of 90 mV in this study does not match with the increased N_P by 3–4 orders of magnitude. This is due to the fact that improved V_{oc} by increasing N_P has its limitation by the increased Auger recombination in the neutral region and by the enhancement of tunneling recombination. In the CIGS device, the value of FF is dominated by the series resistance (bulk resistance, electrode and contact resistance) and shunt resistance (leakage current, defect recombination). In this case, the CIGS cell with Na incorporation has very low bulk resistance from Table 1, which improves the value of FF by decreasing the series resistance.

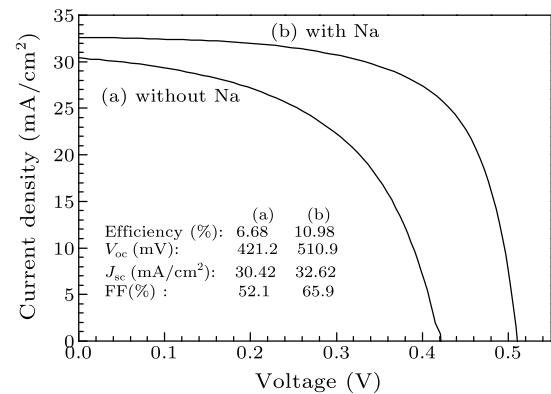


Fig. 3. The J – V curve of CIGS solar cells on the PI sheet with and without Na incorporation.

In summary, high quality $\text{Cu}(\text{In,Ga})\text{Se}_2$ thin films have been successfully fabricated by three-stage process with and without sodium incorporation on the PI sheet. The decreased (112) preferred orientation and an existence of secondary phase $(\text{In}_{0.68}\text{Ga}_{0.32})_2\text{Se}_3$ are observed for Na-containing CIGS films. The enhancement of the net carrier concentration and improved in-plane conductivity by Na incorporation are observed. The benefits of Na incorporation in flexible CIGS solar cells are observed for the enhancement of open circuit voltage and fill factor. A maximum efficiency of 11% has been achieved for a flexible CIGS solar cell on the PI sheet with Na incorporation.

References

- [1] Green M, Emery K, Hishikawa Y, Warta W and Dunlop E D 2013 *Prog. Photovolt.: Res. Appl.* **21** 1
- [2] Zhang L, He Q, Jiang W L, Li C J and Sun Y 2009 *Chin. Phys. Lett.* **26** 026801
- [3] Yamaguchi M 1995 *J. Appl. Phys.* **78** 1476
- [4] Gay R R 1997 *Prog. Photovolt.: Res. Appl.* **5** 337
- [5] Birkmire R, Eser E, Fields S and Shafarman W 2005 *Prog. Photovolt.: Res. Appl.* **13** 141
- [6] Kessler F and Rudmann D 2004 *Sol. Energy* **77** 685
- [7] Shafarman W N and Zhu J 2000 *Thin Solid Films* **361** 473
- [8] Ård M B, Granath K and Stolt L 2000 *Thin Solid Films* **361** 9
- [9] Kessler J, Chityuttakan C, Schödlström J and Stolt L 2003 *Thin Solid Films* **431** 1

-
- [10] Lammer M, Klemm U and Powalla M 2001 *Thin Solid Films* **387** 33
- [11] Wei S H, Zhang S B and Zunger A 1999 *J. Appl. Phys.* **85** 7214
- [12] Kessler F and Rudmann D 2004 *Sol. Energy* **77** 685
- [13] Zhang L, He Q, Jiang W L, Li C J and Sun Y 2008 *Chin. Phys. Lett.* **25** 734
- [14] Zhang L, He Q, Jiang W L, Liu F F, Li C J and Sun Y 2009 *Sol. Energy Mater. Sol. Cells* **93** 114
- [15] Zhang L, Liu, F F, Li, F Y, He Q, Li, B Z and Li C J 2012 *Sol. Energy Mater. Sol. Cells* **99** 356
- [16] Marion S and Uwe R 2001 *Thin Solid Films* **387** 141
- [17] Chaisitsak S, Yamada A and Konagai M 2002 *Jpn. J. Appl. Phys.* **41** 507
- [18] Jiang W L, Zhang L, He Q, Li F Y, Zhou Z Q, Liu W, Li B Z, Li C J and Sun Y 2008 *Proc. 33rd Photovoltaic Specialists Conf.* (San Diego, USA 11–16 May 2008) p 978
- [19] Pauw L J 1958 *Philips Res. Rep.* **13** 1
- [20] Ruckh M, Schmid D, Kaiser M, Schäffler R, Walter T and Schock H W 1994 *Proc. 1st World Conf. on Photovoltaic Energy Conversion* (New York, USA 5–9 December 1994) p 156