Solar Energy Materials & Solar Cells 94 (2010) 1880–1883

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Tandem solar cells with Cu(In,Ga)S_2 top cells on ZnO coated substrates

R. Kaigawa [a,*], K. Funahashi [a], R. Fujie [a], T. Wada [b], S. Merdes [c], R. Caballero [d], R. Klenk [c]

[a] Department of Electronics and Informatics, Ryukoku University, Seta, Otsu 520-2194, Japan
[b] Department of Materials Chemistry, Ryukoku University, Seta, Otsu 520-2194, Japan
[c] Helmholtz-Zentrum Berlin für Materialien und Energie, Institute for Heterogeneous Material Systems, Glienickerstr.100, D14109 Berlin, Germany
[d] Helmholtz-Zentrum Berlin für Materialien und Energie, Institute for Technology , Glienickerstr.100, D14109 Berlin, Germany

ARTICLE INFO

Available online 17 July 2010

Keywords:
Tandem solar cells
Cu(In,Ga)S2
ZnO back contact
Wide gap
Transmission

ABSTRACT

We have prepared transparent top cells for stacked tandems with wide gap Cu(In,Ga)S_2 absorbers on ZnO:Al/soda-lime-glass (SLG) and Mo/ZnO:Al/SLG substrates. Their overall transmission increases with the absorber band gap. The band gaps were 1.63, 1.72, and 1.79 eV. We investigated the properties of mechanically stacked tandem solar cells using these top cells and a $CuInSe_2$ bottom cell. The short circuit current density of the tandem cells is typically limited by that of the bottom cell illuminated through the top cells. Our best tandem efficiency was estimated to be 4.4% with an open circuit voltage of 1.08 V.

1. Introduction

The tandem configuration solar cell is highly desirable in order to realize solar cells with higher efficiency. Several groups reported studies on chalcopyrite-based thin film tandem solar cells. Top cell absorbers such as $CuGaSe_2$ [1] or $AgGaSe_2$ [2] on tin-doped indium oxide or tin oxide back contacts were investigated. However, a tandem cell with a Cu(In,Ga)S_2 top cell has not been reported so far.

Cu(In,Ga)S_2 solid solutions can have band gaps ranging from 1.5 to 2.43 eV depending on the ratio of Ga/In. We have previously studied the deposition of Cu-rich Cu(In,Ga)S_2 films for thin film solar cells by two stage sequential multi-source evaporation [3,4]. An inherent grading of the Ga/(In+Ga) ratio could be almost avoided by including a certain amount of Cu in the precursor [5,6]. A homogeneous Ga depth distribution has made control of the absorber band gap possible. An efficiency of more than 10% (on a non-transparent Mo back contact) had been demonstrated for the first time with wide gap chalcopyrite absorbers as required for tandem configurations [7]. Solar cells based on $CuGaSe_2$ [8,9] and $AgGaSe_2$ [10] absorbers have been reported to have lower efficiency. Our initial efforts concerning transparent Cu(In,Ga)S_2 cells are described in [11–13].

Here, we have prepared transparent top cells with wide gap Cu(In,Ga)S_2 (nominal band gaps 1.64, 1.73 and 1.81 eV) on ZnO:Al/SLG and Mo/ZnO:Al/SLG, and have investigated the properties of mechanically stacked tandem solar cells by combining these with a $CuInSe_2$ bottom cell.

2. Experimental

Cu(In,Ga)S_2 absorbers prepared by multi-source evaporation have been employed using an EL10 evaporator manufactured by Eiko engineering. The evaporation chamber was evacuated by a diffusion pump (500 l/s) to a base pressure of about 1×10^{-3} Pa. Molecular beams of In, Ga, Cu, and S were obtained by means of four Knudsen cells. ZnO:Al (500 nm) back contact was deposited on an SLG by sputtering . In addition, semi-transparent thin Mo films have been deposited on the top of ZnO:Al/SLG in some cases. In the first evaporation stage, In–Ga–Cu–S precursor layers (Cu/(Ga+In) ratio ≈ 0.9) were deposited at 250 °C. In the next stage, the substrate was heated to growth temperatures of 450 °C, and Cu and S were deposited onto the precursor layer in order to shift to Cu-rich condition. The conversion from Cu-deficiency to Cu-excess is accompanied by a change in the film's emissivity. We have used this effect for *in-situ* monitoring by observing the substrate and heater temperature with separate thermocouples. The nominal Cu-excess in the film has been adjusted to 10% by continuing the second stage evaporation for a certain time after detection of the stoichiometry transition. Film thicknesses were in the range from 1.5 to 1.8 μm after a total evaporation period close to 1 h. The thickness of the films was estimated from SEM cross-section images and stylus profiling.

Hall measurements of the back contacts were performed at an AC magnetic field of 0.45 T in van der Pauw geometry using a high-impedance Hall multiplexer setup by TOYO Corporation. The

* Corresponding Author. Tel.: +81 77 543 7402; fax: +81 77 543 7428.
E-mail address: kaigawa@rins.ryukoku.ac.jp (R. Kaigawa).

0927-0248/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.solmat.2010.06.029

sample size was 10×10 mm^2, and indium–alloy contacts applied by ultrasonic soldering showed Ohmic behavior. The free carrier concentration and Hall mobilities were calculated from Hall voltages and van der Pauw resistivity measurements. Optical film transmission was recorded using a spectrophotometer (Shimazu UV-310PC) with a deuterium lamp (wavelength below 340 nm) and a halogen lamp (above 340 nm). The Ga/(In+Ga) and Cu/(In+Ga) ratios of the absorbers were measured using the wavelength dispersive X-ray spectrometry (WDS).

Solar cells have been fabricated by depositing our standard window layer, which consists of CdS deposited from the chemical bath and sputtered *i*-ZnO/ZnO:Al or *i*-(Zn,Mg)O/ZnO:Al. The absorbers were etched in KCN solution prior to CdS deposition. Ni/Al has been evaporated through a shadow mask to obtain a front contact grid. Solar cells were characterised by measuring the wavelength-dependent quantum efficiency and the current-density–voltage (*j*–*V*) curve under simulated AM 1.5 illumination at 25 °C. We measured top and filtered (illuminated through the top cell) bottom cells separately and then calculated the resulting IV assuming series connection. This procedure simulates a two-terminal, mechanically stacked tandem cell.

3. Results

The stability of the back contacts in the absorber process was estimated by sulfurizing back contacts. Fig. 1 shows optical transmission spectra of ZnO:Al and Mo/ZnO:Al coated SLG substrates before and after sulfurization for 30 min at 450 °C. After sulfurization, the transmission of both substrates increased in the higher wavelength region above 800 nm. The overall transmission of the substrate with the Mo film is quite poor even after sulfurization, indicating that a conversion to Mo_xS was not achieved (at least not completely).

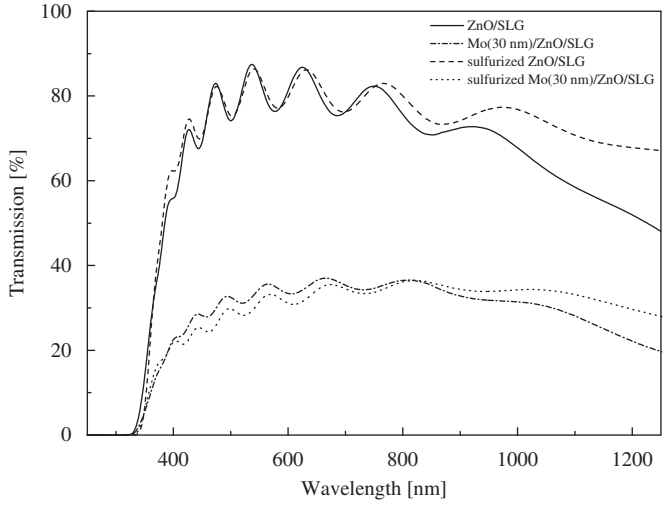

Fig. 1. Optical transmission spectra of ZnO:Al and Mo/ZnO:Al coated SLG substrates before and after sulfurization for 30 min at 450 °C.

Fig. 2 shows carrier density (a), mobility (b), and sheet resistance (c) of ZnO:Al and Mo/ZnO:Al coated SLG substrates as a function of annealing temperature. Carrier density of films annealed over 350 °C decreases with increase in the annealing temperature. It can be considered that oxygen vacancies in ZnO (presumably donors) are passivated by sulfurization. The increased infrared transmission shown in Fig.1 is therefore likely due to a decrease in the carrier density after sulfurization. The electron mobilities of Mo/ZnO:Al were almost constant; however, those of ZnO:Al coated SLG substrates decreased over 350 °C. The decrease in mobility suggests an increase in damage, such as defects, by annealing. The Mo film appears to protect the ZnO from sulfurization damage but the interpretation of the electrical properties of the ZnO film is ambiguous in the presence of a thin metal film on top of it. The significant increase in the resistance of substrates without Mo at 450 °C and above is problematic in terms of cell performance (series resistance).

The typical Ga/(Ga+In) ratios of grown Cu(In,Ga)S_2 films were 0.151, 0.245, and 0.334 from WDS analysis. The typical band gaps are therefore estimated to about 1.64, 1.73 and 1.81 eV ($CuInS_2$=1.5 eV, $CuGaS_2$=2.43 eV), assuming Ga and In to be distributed homogeneously.

Parameters of the best cells prepared from these absorbers on two different types of substrates are shown in Fig. 3. The current density decreases with increase in absorber band gap. This is caused not only by the shift in band gap but also by an overall decrease in the quantum efficiency (Fig. 4). Band gaps deduced from the long wavelength cutoff of the quantum efficiency were about 0.1–0.2 eV, smaller than those calculated from the Ga/(In+Ga) ratio measured by WDS. This may indicate a remaining depth gradient of the Gallium content. The open circuit voltage hardly increases with the band gap and is generally much lower than that of our best cells on non-transparent contacts [7]. Fig.4 also shows the transparency of the cells. The transparency is limited, in particular of the cells with thin Mo layer (note the different Mo thicknesses of the cell with the lowest band gap). The Mo layer is, however, beneficial in terms of electrical cell parameters (except V_{oc}).

Stacked tandems with the same $CuInSe_2$ bottom cell have been evaluated for the best of each of the six types of top cells. The current density of the filtered bottom cell increased with top cell band gap and was slightly higher in the absence of the thin Mo

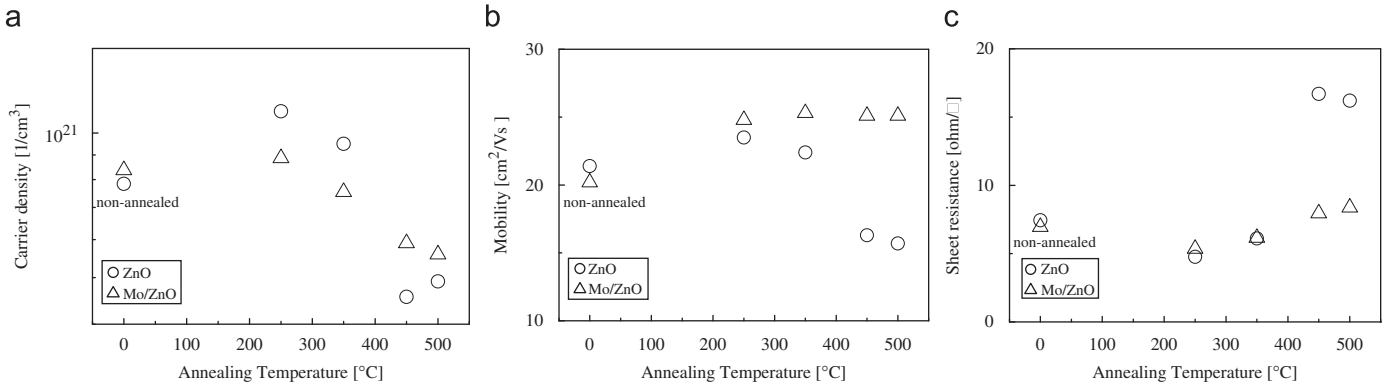

Fig. 2. Carrier density (a), mobility (b), and sheet resistance (c) of ZnO:Al and Mo/ZnO:Al coated SLG substrates as a function of annealing temperature.

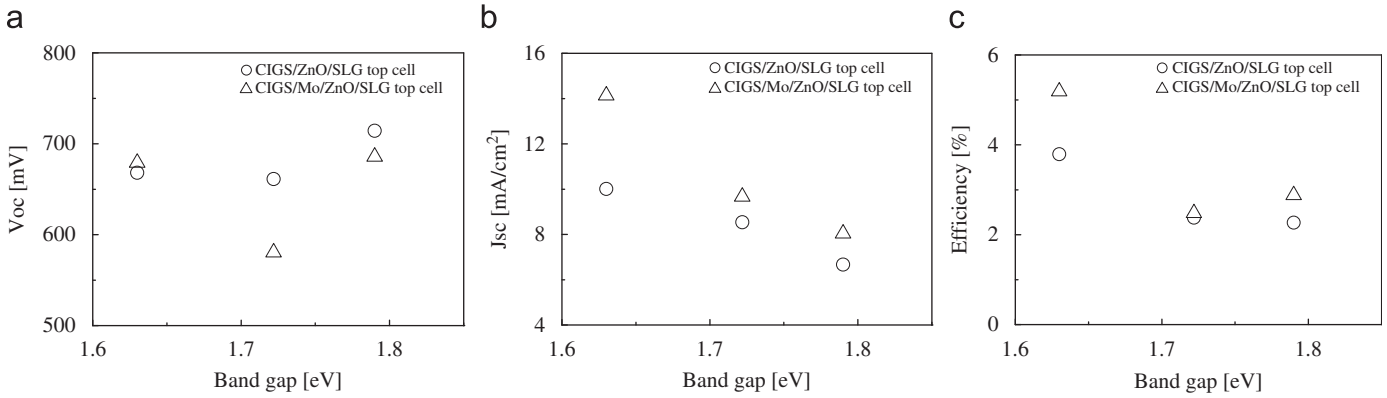

Fig. 3. *J–V* characteristic of a tandem cell, comprised of a $Cu(In,Ga)S_2$ (1.63 eV)/ZnO:Al top cell and the $CuInSe_2$ bottom cell under AM 1.5 illumination at 25 °C.

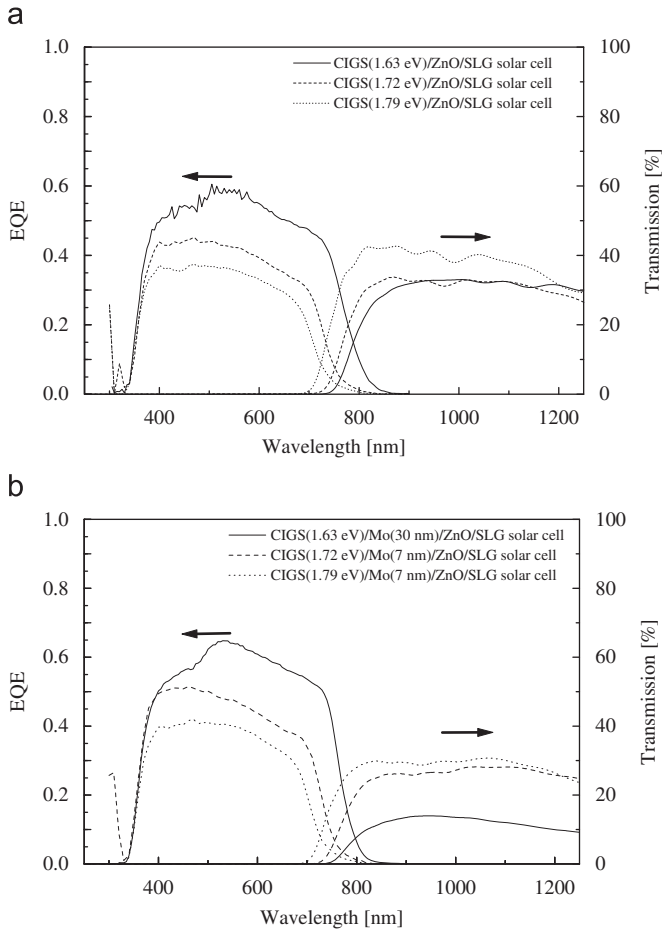

Fig. 4. Wavelength-dependent external quantum efficiency (EQE) and optical transmission spectra of ZnO/CdS/$Cu(In,Ga)S_2$/ZnO:Al/SLG (a) and ZnO/CdS/$Cu(In,Ga)S_2$/Mo/ZnO:Al/SLG (b) solar cells.

Table 1
Solar cell performances of top cell, bottom cell and estimated tandem cell.

	V_{oc} [mV]	J_{sc} [mA/cm^2]	FF [%]	Efficiency [%]
Two-terminal tandem	1079	5.5	74.4	4.4
Top	668	10.0	56.7	3.8
Filtered bottom	411	5.4	72.0	1.6
Bottom	465	37.2	73.3	12.7

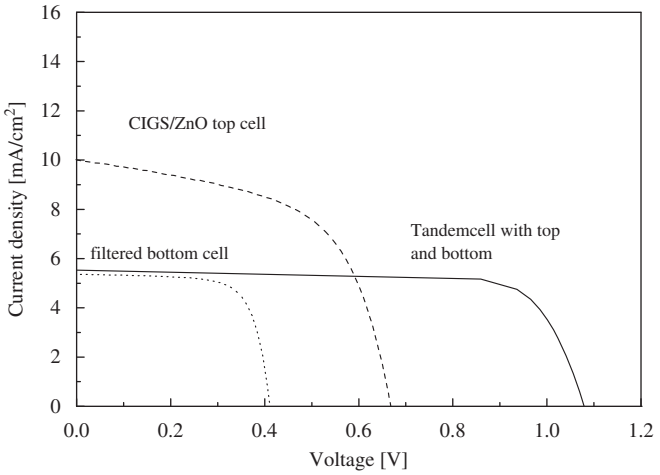

Fig. 5. V_{oc} (a), J_{sc} (b), and efficiency (c) of $Cu(In,Ga)S_2$ top cells with best efficiency as a function of band gap.

layer. The highest tandem efficiency was obtained for the 1.63 eV top cell without the Mo film (Table 1, Fig. 5).

4. Discussion and conclusions

We have prepared transparent top cells with wide gap $Cu(In,Ga)S_2$ absorbers. The performance of the transparent top cells is inferior to that of cells on non-transparent Mo back contacts. Likely causes are the substrate temperature, which had to be reduced to avoid excessive degradation of the transparent contact, a somewhat more problematic contact (semiconductor/semiconductor instead of semiconductor/metal), limited back contact conductivity, and poisoning of the absorber by out-diffusion from the substrate [11,12,14]. A thin intermediate Mo film is beneficial in terms of these problems but significantly reduces the transparency. Even without the Mo film the transparency is not high enough to result in sufficient illumination of the bottom cell in a mechanically stacked tandem. This results in a poor current match of top and bottom cells. The bottom cell current increases with top cell band gap, and a maximum current of 8.1 mA/cm^2 was observed when filtering with the 1.79 eV top cell without Mo. However, this positive trend is counteracted by the decreasing top cell performance. In analogy to our earlier results on non-transparent cells, the open circuit voltage hardly increases with the band gap above 1.6 eV and the

overall quantum efficiency is reduced [7]. Another possibility to improve the current match would be a reduction in the top cell absorber thickness, which has not been examined here. The current match in related chalcopyrite tandems has been discussed and calculated in [15]. The best result was achieved here with the 1.63 eV top cell without the thin intermediate Mo layer. The calculated efficiency of the stacked tandem was 4.4% with an open circuit voltage of 1.08 V.

Acknowledgments

This work was partially supported by New Energy and Industrial Technology Development Organization (NEDO) under Ministry of Economy, Trade and Industry (METI). This work was also partially supported by a grant from the High-Tech Research Center Program for private Universities from the Japan Ministry of Education, Culture, Sports, Science and Technology. Preparation of window layers by C. Kelch and M. Kirsch in Helmholtz-Zentrum für Materialien und Energie, Institute for Heterogeneous Material Systems.

References

[1] S. Nishiwaki, S. Siebentritt, P. Walk, M.C.h Lux-Steiner, A stacked chalcopyrite thin-film tandem solar cell with 1.2 V open-circuit voltage. Prog. Photovolt. Res. Appl. 11 (2003) 243–248.
[2] T. Nakada, S. Kijima, Y. Kuromiya, R. Arai, Y. Ishii, N. Kawamura, H. Ishizaki, and N. Yamada, in: Proceedings of the fouth World Conference on Photovoltaic Energy Conversion, 2006,pp. 400–403.
[3] R. Kaigawa, T. Wada, S. Bakehe, R. Klenk, The effect of sulphur pressure on the depth distribution of elements in $Cu(In,Ga)S_2$ films. Thin Solid Films 480–481 (2005) 71–75.
[4] R. Kaigawa, T. Wada, S. Bakehe, R. Klenk, Three-stage evaporation of $Cu(In,Ga)S_2$ solar cell absorber films without KCN treatment and Na control. Thin Solid Films 511–512 (2006) 430–433.
[5] S. Bakehe, A. Karen, R. Kaigawa, R. Klenk, and M.C.h Lux-Steiner, in: 20th European Photovoltaic Solar Energy Conference: Proceedings of the International Conference, Barcelona, 2005, pp. 1767–1770.
[6] R. Kaigawa, A. Ohyama, T. Wada, R. Klenk, Electrical properties of homogeneous $Cu(In,Ga)S_2$ films with varied gallium content. Thin Solid Films 515 (2007) 6260–6264.
[7] R. Kaigawa, A. Neisser, R. Klenk, M.C.h Lux-Steiner, Improved performance of thin film solar cells based on $Cu(In,Ga)S_2$. Thin Solid Films 415 (2002) 266–271.
[8] V. Nadenau, D. Hariskos, and H.W. Schock, in: H.A. Ossenbrink, P. Helm, H. Ehmann (Eds.), Proceedings of the 14th European Photovoltaic Solar Energy Conference, Barcelona, Spain, June 30–July 4, 1997, H.S. Stephens and Associates, Bedford, UK, 1997, pp. 1250–1253.
[9] J. AbuShama, R. Noufi, S. Johnston, S. Ward, X. Wu, in: Proceedings of the 31st IEEE Photovoltaic Specialists Conference, Lake Buena Vista, USA, January 3–7, 2005, IEEE New York, 2005, pp. 299–302.
[10] T. Nakada, K. Yamada, R. Arai, H. Ishizaki, N. Yamada, Novel Wide-Band-Gap $Ag(In_{1-x}Ga_x)Se_2$ Thin Film Solar Cells. Mater. Res. Soc. Symp. Proc. 865 (2005) 327–334.
[11] R. Kaigawa, A. Morimoto, K. Funahashi, R. Fujie, T. Wada, S. Merdes, R. Klenk, Preparation of wide gap $Cu(In,Ga)S_2$ films on ZnO coated substrates. Thin Solid Films 517 (2009) 2395–2398.
[12] R. Kaigawa, A. Morimoto, K. Funahashi, R. Fujie, T. Wada, M. Sasaki, S. Merdes, R. Klenk, $Cu(In,Ga)S_2$ films prepared by two-stage evaporation on ZnO coated substrates. Phys. Status Solidi (c) 5 (2009) 1051–1054.
[13] S. Bakehe, R. Klenk, M.Ch. Lux-Steiner, in: Proceedings of the 19th European Photovoltaic Solar Energy Conference, 7–11 June 2004, Paris, France.
[14] D. Braunger, Th. Dürr, D. Hariskos, Ch. Köble, Th. Walter, N. Wieser, and H.W. Schock, in: Proceedings of the 25th IEEE PVSC, 13–17 May 1996, Washington, DC, p. 1001.
[15] M. Schmid, J. Krč, R. Klenk, M. Topič, M.C.h Lux-Steiner, Optical modeling of chalcopyrite-based tandems considering realistic layer properties. Appl. Phys. Lett. 94 (2009) 053507.