

Composition and Morphology of Cu(In,Ga)Se₂ Thin Films Treated by Various Solutions

Y. Hashimoto, N. Kohara, T. Negami, N. Nishitani and T. Wada

Central Research Laboratories, Matsushita Electric Ind. Co., Ltd.,
3-4 Hikaridai, Seika-cho, Soraku-gun, Kyoto 619-02

The surfaces of stoichiometric (slightly [In,Ga]-rich) Cu(In,Ga)Se₂ (CIGS) thin films were investigated by x-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). We observed that Cu(In,Ga)₃Se₅ exists at the surface of the CIGS film. The films were treated by KCN and NH₃ aqueous solutions. The NH₃-treatment removed Cu(In,Ga)₃Se₅ from the surface of the CIGS film. The photoluminescence results show that the recombination of the carriers occurs more in the heterojunction of CdS/NH₃-treated CIGS system than in that of CdS/as-deposited CIGS system.

1. INTRODUCTION

CuInSe₂ (CIS) or Cu(In,Ga)Se₂ (CIGS) is a potential absorber material for high efficiency thin film solar cells because of its desirable bandgap and high absorption coefficient for solar radiation [1]. Several processes have been proposed for the deposition of CIGS films. Composition control is very important in the deposition of CIGS films because the properties of CIGS films depend on the chemical composition, such as Cu/[In+Ga] and Ga/[In+Ga] ratios [2]. We have fabricated a CIGS solar cell with an efficiency of 17.0% by a physical vapor deposition using a composition monitoring system [3,4].

Recently, the Euro-CIS group measured the surface composition of coevaporated CIS films by x-ray photoelectron spectroscopy (XPS). They proposed that the surface of the In-rich CIS film was stabilized by the presence of the CuIn₃Se₅ phase which possesses an ordered vacancy chalcopyrite structure (OVC), whereas on the Cu-rich side, the segregation of increasing amount of Cu_{2-x}Se was observed. Cu-rich CIS films have high hole concentrations, (10^{19} - 10^{20} cm⁻³), due to the coexistence of a semimetallic Cu_{2-x}Se phase. In CIGS solar cells, the introduction of a minute amount of semimetallic impurity such as Cu_{2-x}Se is essential. A KCN solution is known as an

effective medium to remove Cu chalcogenides. This technique has been used to eliminate Cu_{2-x}Se and Cu_{2-x}S impurities on the surface of Cu-rich CIS and CuInS₂ films, respectively [5,6].

A CdS film is commonly used as a buffer layer in high efficiency CIGS solar cells. Chemical bath deposition (CBD) is usually used in the preparation of the CdS layer because the CBD process can produce CdS films at low temperatures (~50°C) and the obtained thin CdS film (~500 Å) completely covers the rough surface of the CIGS film [7]. In the CBD process, the CdS layer is deposited in a NH₃ solution. Treatment of the CIGS film in a NH₃ solution was suggested to have an effect on the modification of the CIGS surface [8].

In this work, almost stoichiometric CIGS films were investigated. The effects of KCN and NH₃ solution treatments were studied in detail. The surface morphologies were observed in a scanning electron microscope (SEM). The bulk and surface composition were measured by an EDX and XPS, respectively.

2. EXPERIMENTAL

Stoichiometric CIGS thin films were deposited on Mo coated soda-lime glass substrates at about

500°C by physical vapor deposition (PVD). The thickness of the films was about 2 μm.

The obtained CIGS films were chemically treated by a KCN or NH₃ solution. The KCN treatment was performed by dipping the CIGS film in a 10 wt% KCN aqueous solution at room temperature for 3 min. Treatment in the NH₃ solution was performed by dipping the CIGS film in a NH₃ aqueous solution controlled at pH 10.5 at 60°C for 3 min, which is close to the condition of the CBD process in CdS buffer layer deposition.

The surface morphologies of the as-deposited, KCN-treated and NH₃-treated CIGS films were observed in a Hitachi S800 high-resolution-type SEM.

The chemical compositions of the films were determined using a Shimadzu EPMA C-1 EDX system with an electron beam energy of 16 keV. The depth profiles of the composition near the surface were analyzed by a VG SCIENTIFIC ESCA SCOPE with Mg Kα radiation. The films were etched by an Ar ion-beam. The peak areas of the Cu 2p_{3/2}, In 3d_{5/2} and Se 3d signals were used for compositional quantification. The quantification for Ga was not carried out because Ga did not have any proper peak in the energy region of Mg Kα radiation. Therefore, the Ga content of the film was fixed to be the bulk value determined by the EDX. The XPS signals were normalized by using the data of CIS and CIGS single crystals grown by the traveling heater method [9]. The Cu/[In+Ga] ratio were calculated by the quantified composition.

Photoluminescence (PL) measurements of the CdS/CIGS heterojunction were carried out at room temperature by using Ar ion laser (λ=5145 Å and 500 W).

3. RESULTS AND DISCUSSION

As-deposited CIGS film with nearly stoichiometric composition has a bulk composition of Cu : In : Ga : Se = 23.7 : 19.5 : 6.2 : 50.6 (Cu/[In+Ga]=0.92 and Ga/[In+Ga]=0.24). Figure 1 (a) shows the depth profile of the Cu/[In+Ga] ratio of the as-deposited film. The Cu/[In+Ga] ratio at

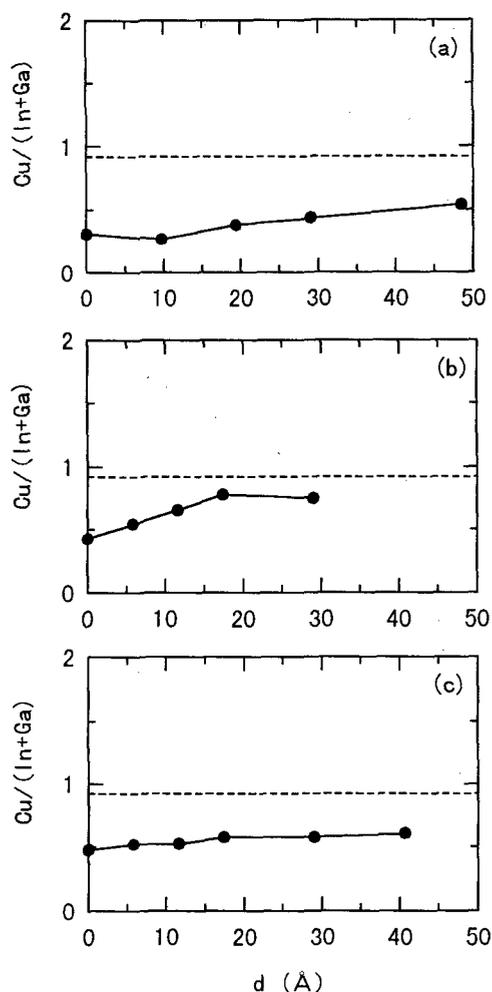


Fig. 1. Depth profiles of the Cu/[In+Ga] ratio of stoichiometric CIGS. (a) as-deposited, (b) KCN-treated and (c) NH₃-treated films. The ratio calculated from the as-deposited bulk composition is shown by a dotted line.

the front surface is about 0.3 which is less than the bulk value of 0.92. The Cu/[In+Ga] ratio increases with increasing the depth of the film. The Euro-CIS group previously reported that the surface of the In-rich CIS film was stabilized by the presence of the CuIn₃Se₅ phase. Therefore, it is

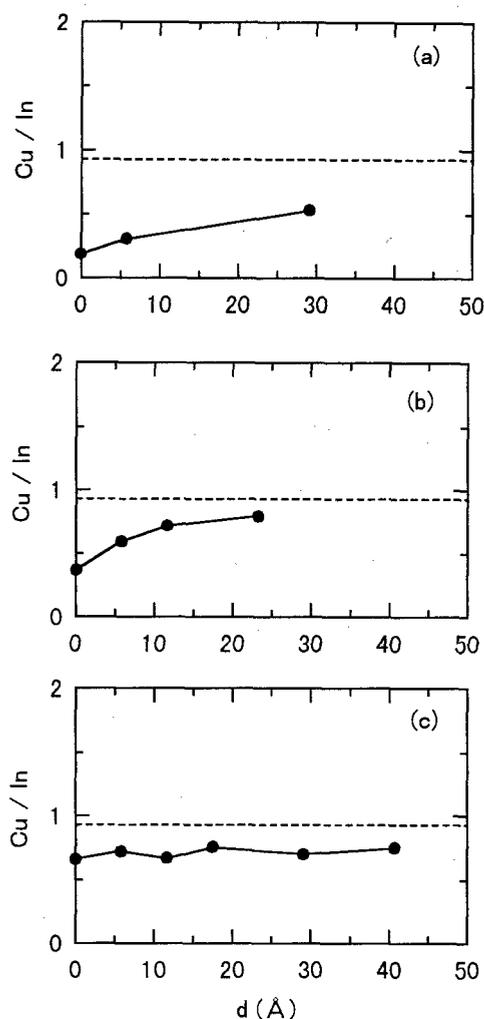


Fig. 2. Depth profiles of the Cu/In ratio of stoichiometric CIS. (a) as-deposited, (b) KCN-treated and (c) NH_3 -treated films. The ratio calculated from the as-deposited bulk composition is shown by a dotted line.

suspected that $\text{Cu}(\text{In,Ga})_3\text{Se}_5$ phase exists at the surface of the stoichiometric (slightly [In,Ga]-rich) CIS film [10,11].

The bulk composition and the surface morphologies of the CIS film were scarcely changed by the KCN and NH_3 -treatments. Figure 1 (b) shows the depth profile of the

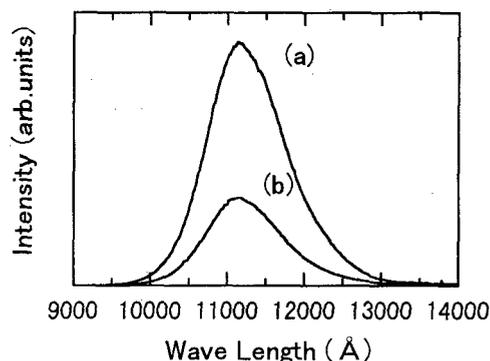


Fig. 3. Photoluminescence spectra of CdS/CIGS heterojunction. (a) CdS/as-deposited CIGS and (b) CdS/ NH_3 -treated CIGS.

Cu/[In+Ga] ratio of the KCN-treated CIS film. The Cu/[In+Ga] ratio at the front surface is about 0.4 which is slightly larger than that of the as-deposited film. The Cu/[In+Ga] ratio rapidly increases with increasing the depth of the film. The Cu/[In+Ga] ratio at $d=20$ Å is 0.8 which is close to the bulk value. In the XPS spectrum of the KCN-treated film, O 1s signal was observed and it disappeared more rapidly than in that of the as-deposited film along the depth. The results indicate that the oxidation layer on the surface of the as-deposited CIS film were removed by the KCN-treatment.

Figure 1 (c) shows the depth profile of the Cu/[In+Ga] ratio of the NH_3 -treated CIS film. Comparison between Figs. 1 (a) and (c) shows that the Cu/[In+Ga] ratio on the front surface was increased by NH_3 -treatment. It is thought that $\text{Cu}(\text{In,Ga})_3\text{Se}_5$ dissolved in the NH_3 solution. The Cu/In ratio in the vicinity of the surface of the NH_3 -treated CIS film also increased compared that of the as-deposited CIS film [12]. The Euro-CIS group previously reported the preferential etching of In on the surface of CIS film in the NH_3 aqueous solution [8]. In the present work, the depth profiles of the CIS films showed the similar tendency as shown in Fig. 2. The O 1s signals in the NH_3 -treated CIS film disappeared more rapidly than those in the as-

deposited film along the depth. The result indicates that NH_3 -treatment also removes the oxidation layer on the surface of the CIGS film. The removal effect of the surface oxidation layer of KCN-treatment is stronger than that of NH_3 -treatment, estimated from the XPS depth profiles.

Heterojunctions of CdS/CIGS system were fabricated by using the as-deposited and NH_3 -treated CIGS films. NH_3 -treatment was done for 20 min at about 60°C . The CdS layers with a thickness of 500 \AA were deposited by CBD.

Figure 3 shows the photoluminescence spectra of CdS/CIGS heterojunction. The significant decrease of PL intensity is observed in the heterojunction of CdS/ NH_3 -treated CIGS system. This indicates that the non-radiative recombination of the carriers occurs more in the heterojunction of the CdS/ NH_3 -treated CIGS system than in that of the CdS/as-deposited CIGS system. The results of photoluminescence study show that $\text{Cu}(\text{In,Ga})_3\text{Se}_5$ phase between CdS and $\text{Cu}(\text{In,Ga})\text{Se}_2$ prevents the carrier recombination in the interface.

4. SUMMARY

The surfaces of the as-deposited and KCN or NH_3 -treated CIGS thin films were investigated by XPS and SEM. The surface of the as-deposited CIGS film with near stoichiometric (slightly In rich) composition is covered by $\text{Cu}(\text{In,Ga})_3\text{Se}_5$. The $\text{Cu}(\text{In,Ga})_3\text{Se}_5$ is removed by NH_3 -treatment. The non-radiative recombination of the carriers occurs more in the heterojunction of CdS/ NH_3 -treated CIGS system than in that of CdS/as-deposited CIGS system because $\text{Cu}(\text{In,Ga})_3\text{Se}_5$ phase was removed by NH_3 -treatment.

ACKNOWLEDGMENTS

This work was supported by the NEDO as a part of the new sunshine program under the MITI. The authors would like to thank Prof. K. Sugiyama and Dr. H. Miyake of Mie University for supplying CIS and CIGS single crystals. We would also like to thank Dr. Paul J. Fons of Electrotechnical

laboratory for a critical reading of the manuscript and to thank Drs. T. Nitta, H. Ogawa and T. Toda for their encouragement throughout this work.

REFERENCES

1. A. Rocket and R. W. Birkmire: *J. Appl. Phys.* 70, R80 (1991).
2. M. Contreras, A. M. Gabor, A. L. Tennant, S. Asher, J. Tuttle and R. Noufi: *Progress in Photovoltaics* 2 (1994) 287.
3. N. Kohara, T. Negami, M. Nishitani and T. Wada: *Jpn. J. Appl. Phys.* 34 (1995) L1141.
4. T. Negami, M. Nishitani, N. Kohara, Y. Hashimoto and T. Wada: submitted to *Proc. MRS Spring Meeting, 1996 San Francisco, CA*.
5. S. Menezes, H. J. Lewerenz and K. J. Bachmann: *Nature* 305 (1983) 615.
6. K. J. Bachmann, S. Menezes, R. Kötz, M. L. Fearheiley and H. J. Lewerenz: *Surf. Sci.* 138 (1984) 475.
7. T. Wada, T. Negami, N. Kohara, M. Ikeda and M. Nishitani: *Proc. 12th European Photovoltaic Solar Energy Conference, Amsterdam, 1992*, p.1542.
8. J. Kessler, K. O. Velthaus, M. Ruckh, R. Laichinger, H. W. Schock, D. Lincot, R. Ortega and J. Vedel: *Proc. 6th International Photovoltaic Science and Engineering Conference (PVSEC-6), India, 1992*, p.1005.
9. H. Miyake and K. Sugiyama: *J. Cryst. Growth* 125 (1992) 548.
10. T. Negami, N. Kohara, M. Nishitani and T. Wada, *Jpn. J. Appl. Phys.* 33 (1994) L1251.
11. T. Negami, N. Kohara, M. Nishitani, T. Wada and T. Hirao, *Appl. Phys. Lett.* 67 (1995) 825.
12. T. Nakada, H. Fukuda, A. Kunioka and S. Niki: *Proc. 13th European Photovoltaic Solar Energy Conference, Nice, 1995 (H.S.Stephens & Associates, Bedford)* p. 1597.