

Microstructure of CuInSe₂ Thin Film Solar Cells

Takahiro WADA

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

Interface between Cu(In,Ga)Se₂ (CIGS) absorber and Mo back contact in the CIGS solar cells were investigated by secondary ion mass spectroscopy (SIMS) and analytical transmission electron microscopy (TEM). The solar cell with MgF₂/ITO/ZnO/CdS/CIGS/Mo/glass structure showed an efficiency of over 15 %. In the SIMS depth profile, intensity of Se had a peak at the CIGS/Mo interface. Cross-sectional TEM observation showed that there were two layers at the CIGS/Mo interface. One was MoSe₂ layer with a thickness of 0.15 μm and the other was amorphous layer with a thickness = 0.02 μm. The thickness of the interface layers depend on the deposition conditions of Mo layers.

1. INTRODUCTION

Cu(In,Ga)Se₂ (CIGS) is the most promising material for thin film photovoltaic device because of its desirable bandgap and high absorption coefficient for solar radiation [1]. Some research groups demonstrated CIGS solar cells with efficiencies of over 17 % [2, 3]. A wide variety of techniques have been used to fabricate CIGS thin films. Of these deposition techniques, the films produced by a physical vapor deposition have yielded an CIGS solar cell with the highest efficiency.

Most of the CIGS absorber layers for high performance solar cells were formed by "bi-layer" process in the physical vapor deposition [1]. The first Cu-rich layer was capped by a (In,Ga)-rich CIGS layer. Diffusion during growth of the film mixed the two layers completely, forming a slightly (In,Ga)-rich CIGS film. Recently, NREL group [4] proposed so called "3-stage" process as a deposition of a high quality CIGS film. In the 3-stage process, the first stage formed (In,Ga)₂Se₃ precursor layer. In the second stage, the (In,Ga)₂Se₃ precursor layer was subjected to Cu and Se fluxes to form the Cu-rich CIGS film. In the third stage, a small amount of In, Ga and Se were added to the Cu-rich CIGS film to obtain slightly (In,Ga)-rich CIGS film. The resulting CIGS films had larger grains than a "single-layer" film with comparable composition and the larger grains might be necessary for a good device performance.

The microstructure such as the grain size, twins and the stacking faults in the CIGS absorber layer plays highly important roles in the CIGS solar cells [5]. Recently, some researchers observed the microstructures of the polycrystalline CIS films by a transmission electron microscope (TEM) [6, 7]. We also studied the microstructure of CIS and CIGS thin films by cross-sectional high-resolution transmission electron microscopy [8-11]. The observations were summarized as follows.

- (1) In the CIS layer, many twins as well as overlaps of twinned grains and a fivefold multiply twinned crystallites were observed [8, 9].
- (2) In the CIGS layer, a void, twin band or stacking fault were scarcely observed. The quality of the CIGS absorber is better than that of the CIS absorber from microstructural point of view [10].
- (3) In the CIGS thin film deposited by the 3-stage process, the size of the grains is larger than that in the CIGS layer deposited by the bi-layer process. The surface of the CIGS layer is flatter than that of CIGS layer deposited by the bi-layer process [11].

In this paper, I report on microchemical and microstructural characterization of the CIGS/Mo interface in the high efficiency CIGS solar cells. The characteristics of CIGS/Mo interface are discussed on the basis of deposition condition of Mo layer.

2. EXPERIMENTAL

The Mo back contact with a thickness of 0.8 μm was deposited on soda-lime glass substrate by rf-magnetron sputtering. The condition was controlled at 8×10^{-3} mmHg in Ar gas atmosphere. The sodalime glass substrate was not heated during the deposition. The characteristics of the Mo thin films such as microstructure and resistivity were dependent on the deposition condition [12].

The CIGS absorber layer were deposited by "3-stage" process with composition monitoring system [13]. In the first stage, In, Ga and Se were coevaporated at about 350°C. Next, the heating power was increased to reach the substrate temperature at about 550°C, and then Cu and Se were coevaporated on the (In,Ga)₂Se₃ precursor layer. In the final stage, the rest of In, Ga and Se was added keeping the heater power constant. The composition of the obtained CIGS film was determined by using energy dispersive x-ray spectrometer (EDX).

The solar cells with a structure of MgF₂/ITO/ZnO/CdS/CIGS/Mo/glass were fabricated. The CdS buffer layer with a thickness of 0.05 μm was deposited by a chemical bath deposition. The window layers composed of the ZnO layer with a thickness of 0.3 μm and the ITO [In₂O₃:Sn] layer with a thickness of 0.5 μm were deposited by rf-magnetron sputtering. The MgF₂ anti-reflection layer was deposited by electron beam evaporation. The obtained solar cells were characterized under standard AM 1.5 illumination.

The depth profile of Cu, In, Ga, Se and Mo in the CIGS and Mo layers was examined by using secondary ion mass spectroscopy (SIMS). To realize the high sensitive measurement, ¹³³Cs⁺ was used as primary ion and secondary positive cluster ions such as ¹⁹⁸(Cu+Cs), ²⁴⁶(In+Cs), ²⁰⁴(Ga+Cs), ²¹¹(Se+Cs) and ²³³(Mo+Cs) were used for detecting Cu, In, Ga, Se and Mo, respectively.

The specimen for the cross-sectional high resolution transmission electron microscopy (HRTEM) was prepared by gluing the film to a silicon wafer. It was mechanically thinned and carefully milled by an ion-beam avoiding excessive heating and radiation damage induced by the ion-beam. The HRTEM analyses were performed by a EB-002B

electron microscope operated at 200 keV. The microchemical analyses were conducted by using an energy dispersive X-ray spectrometer (EDX) combined with TEM.

3. RESULTS AND DISCUSSION

Figure 1 shows SIMS depth profile of CIGS and Mo layers. The Mo film was deposited at P(Ar gas)= 8×10^{-3} mmHg. The composition of the CIGS layer was Cu:In:Ga:Se = 23.78:19.24:5.26:51.72 (Cu/[In+Ga]=0.97, Ga/[In+Ga]=0.21). The conversion efficiency of the solar cell by using the CIGS/Mo layers was 15.4 % (V_{oc} = 0.621 V, J_{sc} = 3.5 mA/cm², FF= 0.741). In Fig.1, the intensity of Se is about 6×10^4 counts in the CIGS layer and is background level in the Mo layer. At the CIGS/Mo interface, the intensity of Se has a clear peak. The intensity at the peak is over 10^5 counts, which is considerably larger than that in the CIGS layer containing Se at 50 atomic %. The result indicates that a Se-rich compound containing Se more than 50 atomic % exists at the CIGS/Mo interface.

Dark-field cross-sectional TEM micrograph of the CIGS/Mo interface are shown in Fig. 2. The two layers are observed in the interface. Typical points in the layers, a, b, c and d, were analyzed by micro EDX. Figure 3 shows micro EDX-spectra of the points, a, b, c and d. At the point d, only Mo is detected. Therefore, we can concluded that the bottom layer is Mo. At the point c, Mo and Se are detected. In Mo-Se system, Mo₃Se₄ (Se/[Mo+Se]=0.57) and MoSe₂ (Se/[Mo+Se]=0.67) are known [13]. The compound detected at point c was determined to be MoSe₂ with a hexagonal unit cell and lattice constants of $a=3.2870 \text{ \AA}$ and $c=12.925 \text{ \AA}$ because the electron diffraction spots at points c were understood on the basis of the crystal structure of MoSe₂ [14]. The thickness of MoSe₂ layer is 0.15 μm .

MoSe₂ has layer structure. The spacing between the layers is 12.9 \AA . It was known that MoSe₂ was easily cleaved between the layers. Therefore, the orientation of MoSe₂ grains is very important for the fabrication of the solar cells. Figure 4 shows HRTEM micrograph of MoSe₂ layer near Mo back

contact. In the figure, we can observe polycrystalline MoSe₂ grains with columnar structure in which the lattice with $d \sim 13 \text{ \AA}$ is oriented perpendicular to the Mo layer. The c-axes of the MoSe₂ grains are perpendicular to the Mo layer. It is very important for fabrication of CIGS solar cells. If c-axes of MoSe₂ grains were parallel to the Mo layer, the CIGS film was easily peeled from the Mo layer because MoSe₂ at the interface is easily cleaved between their layers.

Figure 3 (b) shows micro EDX-spectra of the point b. At the point b, Cu, Cr, Fe, Na, O and Si are detected. In these elements, Cr and Fe are considered to be contaminated at TEM sample preparation. The Intensity of Cu and Si is background level. Therefore, it is concluded that the layer at point b mainly contains Na and O. Electron diffraction pattern at point d did not show any clear ring or spots. The result indicates that the layer is amorphous. The thickness of the amorphous layer is $0.02 \mu\text{m}$. Na and O come from the soda-lime glass substrate through the Mo layer when the CIGS film was deposited.

CIGS/Mo interface in the CIGS solar cell whose Mo layer was deposited in $P(\text{Ar gas}) = 2 \times 10^{-3} \text{ mmHg}$ was also investigated. The composition of the CIGS film was Cu:In:Ga:Se = 22.92:17.15:7.61:52.32 (Cu/[In+Ga]=0.93, Ga/[In+Ga]=0.31). The conversion efficiency of the solar cell was 15.0% ($V_{oc} = 0.625 \text{ V}$, $J_{sc} = 33.3 \text{ mA/cm}^2$, $FF = 0.721$). In the SIMS depth profile of CIGS and Mo layers, the intensity of Se is about 6×10^4 counts in the CIGS layer and is background level in the Mo layer. The intensity of Se has a peak at the CIGS/Mo interface but the peak is smaller than that in Fig. 1. HRTEM also showed that the present CIGS/Mo had thinner interface layer than the CIGS/Mo layers whose Mo layer was deposited in $P(\text{Ar gas}) = 8 \text{ mmHg}$ did. MoSe₂ layer was observed at the interface by HRTEM but the amorphous layer could not be observed by HRTEM and electron diffraction.

Interface layers, MoSe₂ and amorphous layers, were produced by the reaction between Cu-In-Ga-Se and Mo during the deposition of the CIGS films on the Mo back contact. The reactivity of Mo is dependent on the microstructure, grain size or density. Sputtering conditions of Mo layer have a large

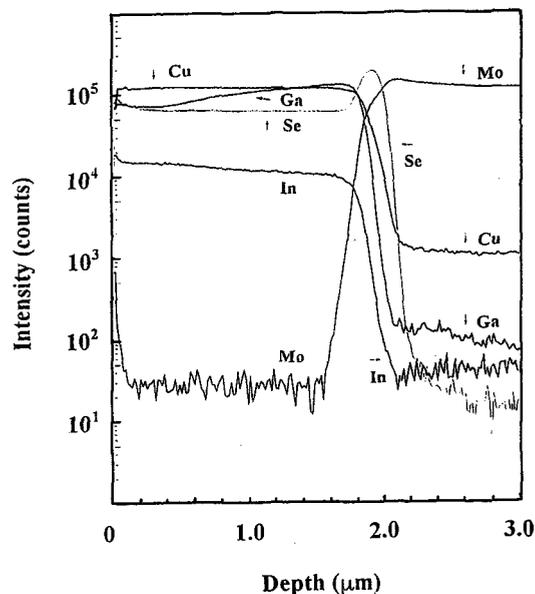


Fig.1 SIMS depth profile of CIGS and Mo layers. The Mo film was deposited at $P = 8 \times 10^{-3} \text{ mmHg}$.

influence on the microstructure [15]. Therefore, sputtering conditions of Mo layers have a large influence on the structure of CIGS/Mo interface. When Mo layer was deposited in low atmospheric pressure, the dense Mo film was obtained [15]. It is understood that the polycrystalline Mo film with dense grain structure had lower reactivity with Se. Therefore, the CIGS/Mo interface whose Mo layer was deposited at lower atmospheric pressure had thinner thickness of the interface layer (reaction layer). As for the characteristics of the solar cells, there was not a significant difference for Mo sputtering atmosphere between $2 \times 10^{-3} \text{ mmHg}$ and $8 \times 10^{-3} \text{ mmHg}$.

4. ACKNOWLEDGMENTS

This work was supported by the NEDO as a part of the Newsunshine Program conducted under the MITI. The author would like to express his sincere appreciation to T. Kozaki for his help in TEM and to Drs. T. Nitta, T. Hirao and H. Ogawa for their encouragement throughout this work.

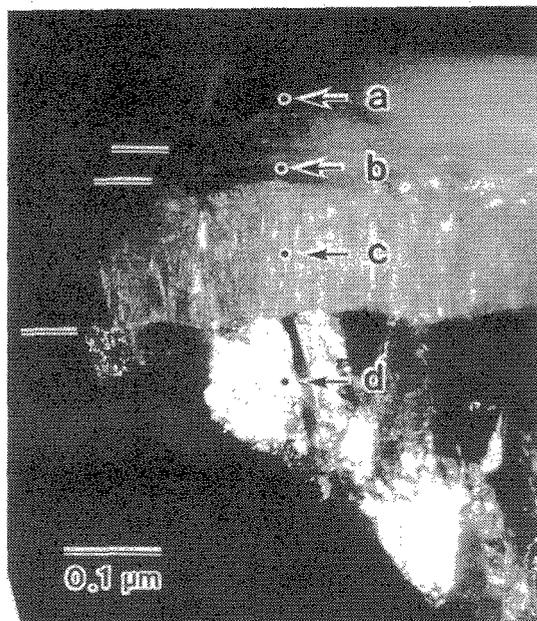


Fig.2 Dark-field cross-sectional TEM micrograph of the CIGS/Mo interface.

REFERENCES

- [1] A. Rockett and R. M. Birkmire, *J. Appl. Phys.* **70**, R81 (1991).
- [2] M. Contreras *et al.*, *Prog. in Photovol.* **2**, 287 (1994).
- [3] T. Negami, *Mat. Res. Soc. Symp. Proc.* **426**, in press (1992).
- [4] A. M. Gabor *et al.*, *Appl. Phys. Lett.* **65**, 198 (1994).
- [5] L. Stolt *et al.*, *Appl. Phys. Lett.* **612**, 597 (1993).
- [6] C. J. Kiely *et al.*, *Philos. Mag. A* **63**, 1249 (1991).
- [7] J. S. Chen *et al.*, *Thin Solid Films* **219**, 183 (1992)
- [8] T. Wada *et al.*, *J. Mater. Res.* **9**, 658 (1994).
- [9] T. Wada *et al.*, *Appl. Phys. Lett.* **64**, 333 (1994).
- [10] T. Wada *et al.*, *Proc. of 12nd ECPVSEC* (held at Amsterdam) 1542 (1994).
- [11] T. Wada, *J. Cryst. Res. Tech.*, in press.
- [12] N. Kohara *et al.*, *Jpn. J. Appl. Phys.* **34**, L1141(1995).
- [13] M. Spiesser *et al.*, *Bull Soc. Chim No.5*, 1427 (1969)
- [14] JCPDS No.29-0914.
- [15] J. H. Scofield *et al.*, *Thin Solid Films* (1995).

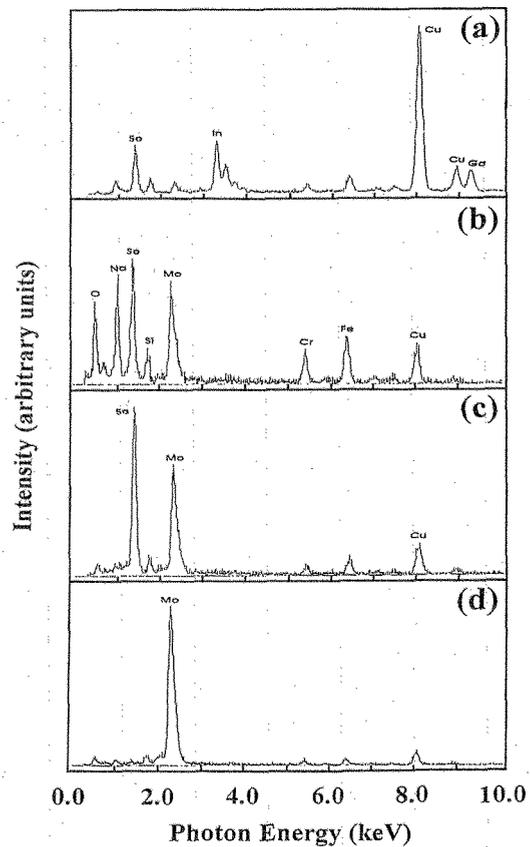


Fig 3 Micro EDX-spectra of points shown in Fig.2.

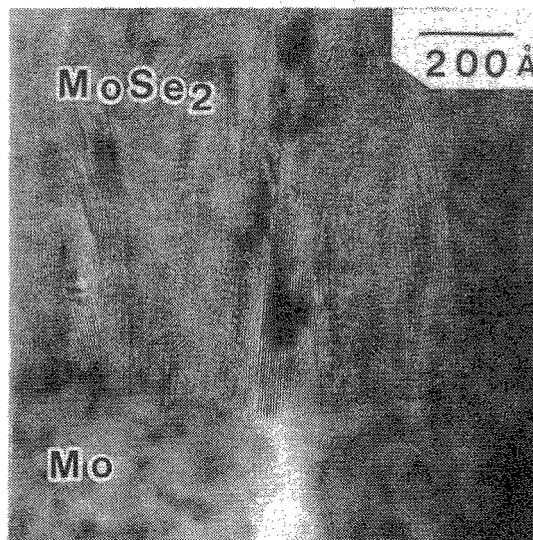


Fig. 4 HRTEM micrograph of MoSe₂ layer near Mo