Band Alignment at CdS/wide-band-gap Cu(In,Ga)Se_2 Hetero-junction by using PES/IPES

Sok-Hyun Kong
HDD program Team, Material & Devices Research Center,
Samsung Advanced Institute of Technology, Giheung-eup, Yongin-si, Kyunggi 449-712, Korea

Kyung-Hwan Kim[a]
Department of Electrical Information Engineering, KyungWon University,
Bokjeong-dong, Sujeong-gu, Seongnam-si, Kyunggi 461-701, Korea

[a]E-mail : khkim@kyungwon.ac.kr

(Received August 29 2005, Accepted September 30 2005)

Direct characterization of band alignment at chemical bath deposition (CBD)-CdS/$Cu_{0.93}(In_{1-x}Ga_x)Se_2$ has been carried out by photoemission spectroscopy (PES) and inverse photoemission spectroscopy (IPES). Ar ion beam etching at the condition of the low ion kinetic energy of 400 eV yields a removal of surface contamination as well as successful development of intrinsic feature of each layer and the interfaces. Especially interior regions of the wide gap CIGS layers with a band gap of 1.4 ~ 1.6 eV were successfully exposed. IPES spectra revealed that conduction band offset (CBO) at the interface region over the wide gap CIGS of x = 0.60 and 0.75 was negative, where the conduction band minimum of CdS was lower than that of CIGS. It was also observed that an energy spacing between conduction band minimum (CBM) of CdS layer and valance band maximum (VBM) of $Cu_{0.93}(In_{0.25}Ga_{0.75})Se_2$ layer at interface region was no wider than that of the interface over the $Cu_{0.93}(In_{0.60}Ga_{0.40})Se_2$ layer.

Keywords : Conduction band offset, Band alignment, CdS layer, Wide gap CIGS layer

1. INTRODUCTION

$Cu(In_{1-x}Ga_x)Se_2$ (CIGS) thin films have greatly attracted as absorber layer in solar cell with CdS buffer layer owing to tunable band gap by varying the ratio of Ga substitution[1-4]. Several model-calculations have indicated a potential of a high conversion efficiency as high as 25 % in the solar cells based on CIGS with a wide band gap of around 1.4 eV corresponding to Ga/(In+Ga)=0.7 ~ 0.8. In previous reports, the efficiency of the CIGS based cells takes a maximum of 19.2 % at a condition of the band gap around 1.2 eV. A serious degradation of the efficiency has been also observed in the wide gap CIGS based cells. One of the origins of this discrepancy between the expectation and the experiments is a saturation of open circuit voltage (V_{oc}) in the wide-gap region, which is correlated with band alignment at p-n junction in the cell structure[5,6]. Determination of the band alignments has been attempted by various techniques[7-9]. In our previous study about the interfaces over the CIGS with a Ga substitution ratio x up to 40 % fabricated by three stage co-evaporation, a decrease of CBO at the interface as a function of x has been observed. For the samples with a low x of 20 %, conduction band minimum (CBM) of CBD-CdS was higher than that of CIGS by 0.3 eV (positive conduction band offset (CBO)), whereas the CBO fell below 0.1 eV in the sample with x of 40 %[10]. For further improvement of the cell performance, characterization of the band alignment in the wide band gap CIGS based solar cell is desired. In the present study, we have carried out a development of etching technique with low kinetic energy Ar ion beam to develop an intrinsic surface nature and a direct characterization of electronic structure over interfaces between CdS and the wide gap CIGS with the Ga substitution ratio up to 75 % by using combination system of photoemission (PES) and inverse photoemission spectroscopy (IPES).

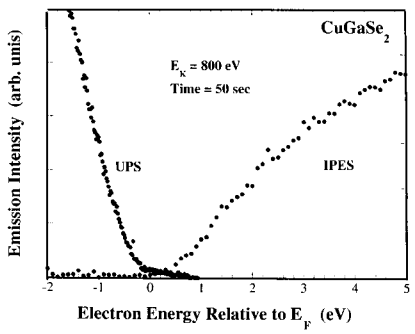
2. EXPERIMENT

$Cu_{0.93}(In_{0.25}Ga_{0.75})Se_2$ absorber layers were prepared

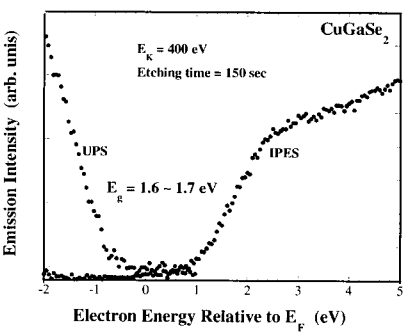
on Mo back contact layer over soda lime glass by means of so-called three step co-evaporation using molecular beam epitaxy system. CdS buffer layers were deposited on the CIGS layers by chemical bath deposition method. X-ray photoemission (XPS) with monochromatized Al K_α radiation was used for investigating chemical state of surface[11]. VBM and CBM alignment were evaluated by using ultraviolet photoemission spectroscopy (UPS) and inverse photoemission spectroscopy (IPES), respectively. He I radiation was used for excitation in UPS. IPES measurement was performed in Bremsstrahlung Isochromat mode using an Erdman-Zipf type electron source and a photon detector with SrF_2 window, which has energy resolution of 0.47 eV. Electron energy of obtained IPES spectra was calibrated using the Fermi edge of in-situ deposited silver thin films. CBM and VBM were determined by a linear extrapolation of the leading edges in IPES and UPS spectra, respectively. The band gap obtained from IPES and UPS spectra had error tolerance of ±0.15 eV in the present experiment. For removing surface contamination caused by transfer in ambient atmosphere and for exposing buried interfaces and interior regions, ion beam etching at room temperature using a low kinetic energy Ar ions generated by electron cyclotron resonance type ion source was adopted.

3. RESULTS

As the first step of characterization of the interior regions and the wide-gap CIGS and the interfaces over it, an optimization of the kinetic energy (E_k) of the Ar ion beam for etching was carried out. Figure 1 shows UPS and IPES spectra of surfaces of $CuGaSe_2$ (CGS) single layers etched at the condition of E_k of (a) 800 eV for 50 sec and (b) 400 eV for 150 sec. The high energy etching caused an apparent reduction of band gap, even if its duration was short. Though a lowering of E_k was effective to reduce the irradiation damages, the narrowing of the band gap of the etched surface still remained in the surfaces etched at the condition of E_k above 550 eV. Present experiments show that, in our system, the E_k below 400 eV should be low enough to develop an intrinsic surface nature of the CGS films. As shown in Fig. 1(b), the intrinsic band gap of CGS around 1.6 ~ 1.7 eV was obtained by setting E_k at 400 eV. XPS measurements revealed that this optimaized etching was also effective in removal of oxygen- and carbon-related surface contaminations. Consequently, in all of the experiment mentioned below, the etching was performed at the condition of E_k of 400 eV.

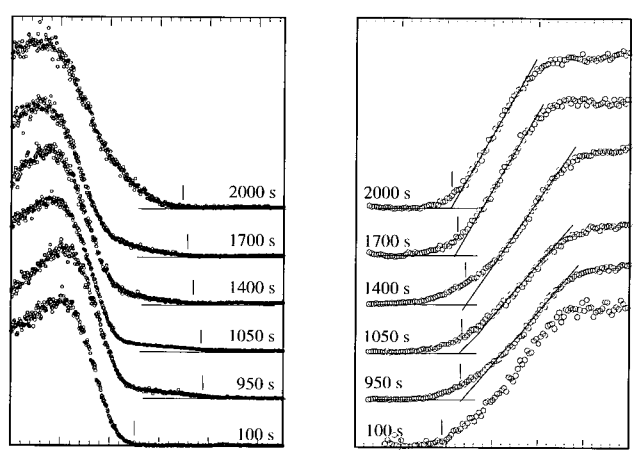


(a)



(b)

Fig. 1. UPS and IPES spectra for (a) $CuGaSe_2$ thin film after etching by Ar ion beam with kinetic energy of 800 eV for 50 sec and (b) $Cu(In_{0.25}Ga_{0.75})Se_2$ thin film after etching by Ar ion beam with kinetic energy of 400 eV for 150 sec.



(a) (b)

Fig. 2. Change of (a) UPS spectra and (b) IPES for $CdS/Cu_{0.93}(In_{0.25}Ga_{0.75})Se_2$ specimen as a function of the etching time.

Figure 2 shows a change of UPS (a) and IPES (b) spectra of the CBD-$CdS/Cu_{0.93}(In_{0.25}\ Ga_{0.75})Se_2$ specimen

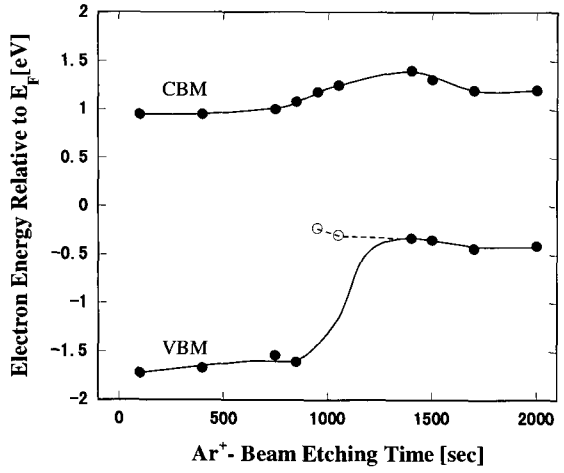


Fig. 3. Change of VBM and CBM for CdS/$Cu_{0.93}$($In_{0.40}Ga_{0.60}$)Se_2 specimen with Ar ion beam etching time. Open circles represent VBMs of the region containing oxygen and carbon.

as a function of etching time. XPS measurements of this sample indicate that the interface should lie around a range of the etching time from 950 to 1400 sec. For the UPS spectra, an elongation of the etching beyond 950 sec resulted in a gradual increase of spectral weight in a region of electron energy between – 0.2 ~ – 1.5 eV. It led a significant rise of VBM in this region. For the IPES spectra, a rise of electron energy of the intersections of baseline and the extrapolation line of the leading edge by about 0.3 eV was detected in the interface region, though the edge structure was broadened in comparison with that of the interior regions of CdS and CIGS. Moreover, CBM of the 2000 sec etched surface was still higher than that of the CdS located apart from the interface. These results indicate that the CBM_{CIGS} of this specimen should be higher than CBM_{CdS}. After this rise, VBM and CBM gradually decreased with etching time. It means that the heavily p-type nature should be locally created around the interface. A similar change of electronic structure was also observed for the CBD-CdS/$Cu_{0.93}$($In_{0.40}Ga_{0.60}$)Se_2.

Figure 3 shows changes of VBM and CBM of the CBD-CdS/$Cu_{0.93}$($In_{0.40}Ga_{0.60}$)Se_2 specimen with etching time. Positive shifts of VBM and CBM were observed. For this interface, CBO = CBM_{CdS} – CBM_{CIGS} was negative. Our previous study about the conduction band alignment at the CdS/CIGS interfaces showed a lowering of CBM_{CIGS} with an increase of the Ga substitution ratio, where CBO of CdS/$Cu_{0.93}$($In_{0.80}Ga_{0.20}$)Se_2 and CdS/$Cu_{0.93}$($In_{0.60}Ga_{0.40}$)Se_2 were about +0.3 and 0~0.1 eV, respectively. Taking these results into account, the sign change of CBO at the CdS/$Cu_{0.93}$($In_{0.25}Ga_{0.75}$)Se_2 interface indicates that the rise of CBM and VBM of CIGS with a increase of Ga substitution ratio should

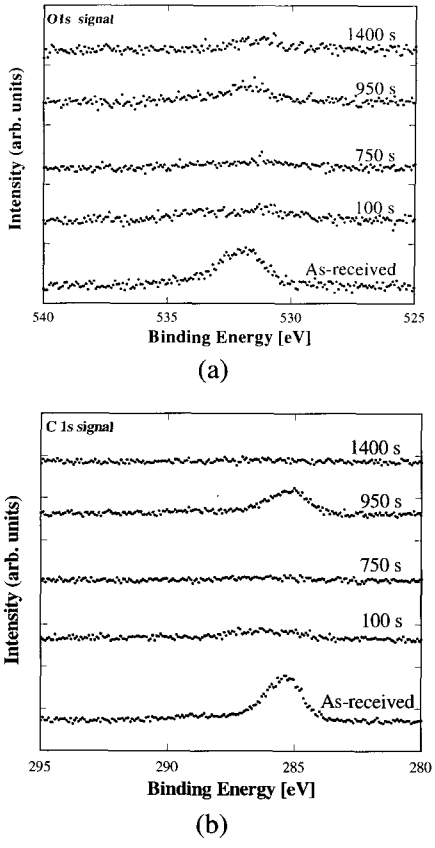


Fig. 4. Change of XPS spectra for (a) O 1 s and (b) C 1 s signal in CdS/$Cu_{0.93}$($In_{0.25}Ga_{0.75}$)Se_2 specimen as a function of the etching time.

systematically continue up to the high Ga concentration region. In spite of the higher Ga substitution ratio, the minimum of energy spacing between CBM_{CdS} and VBM_{CIGS} in the interface-region of the Ga = 75 % specimen was similar to that of the Ga = 40 % sample.

This band alignment at the interface was accompanied with the lowering of the edge-like structure in UPS spectra as mentioned before. In the interior region of CIGS, gradual decreases of VBM and CBM were observed. These results suggest a presence of a local structure at the interface. Figure 4 shows a change of O 1 s (a) and C 1 s (b) core signals with etching time. In the early stage of the etching, these contamination-related signals were remarkably suppressed. They, however, appeared again in the interface region. This phenomenon was also observed for the CdS/$Cu_{0.93}$($In_{0.40}Ga_{0.60}$)Se_2 interface. Taking it into consideration that all of the measurements were performed under identical conditions including base pressure of the analysis chambers and durations of each measurement, this result means that oxygen and carbon should be locally incorporated at the interface over the wide gap CIGS. This depth profile of the contamination should cause the broadening of the

band edge structures. It is reported that oxidization of CIGS surfaces may suppress formations of donors such as anti-site In in Cu sites and Se vacancies[12-14].

Taking it into consideration, this depth profile of the contaminations seems to be consistent with the enhancement of p-type electronic structure around the interface region as shown in Fig. 4. The experimental results obtained in the present study are consistent with the saturation of open circuit voltage and degradation of conversion efficiency of our cells using a wide gap CIGS. It is also suggested that band engineering of the buffer layer and precise control of impurity in the formation process of the interface should be useful for improving performances of a wide gap CIGS based cells.

4. CONCLUSION

A low energy Ar ion beam etching technique has been developed to expose intrinsic features of buried interfaces and interior region for CdS/CIGS structure. Direct characterization of their electronic structure using PES and IPES was carried out by PES/IPES. The Ar ion beam etching with a low kinetic energy of 400 eV was effective in removing surface contamination as well as yielding successful exposure of interior region for $Cu_{0.93}(In_{0.25}Ga_{0.75})Se_2$ with intrinsic band gap about ~ 1.5 eV. The etching time dependence of the IPES spectra revealed that CBM_{CIGS} of this specimen should be higher than CBM_{CdS}. Systematic rises of CBM and VBM of CIGS with respect to those of CdS as a function of Ga substitution ratio up to 75 % have been confirmed.

REFERENCES

[1] G. Voorwinden, R. Kiese, and M. Powalla, "In-line Cu(In,Ga)Se_2 co-evaporation processes with graded band gaps on large substrates", Thin Solid Films, Vol. 431-432, p. 538, 2003.

[2] M. A. Contreras, J. Tuttle, A. Gabor, A. Tennant, K. Ramanathan, S. Asher, A. Franz, J. Keane, L. Wang, and R. Noufi, "High efficiency graded bandgap thin-film polycrystalline Cu(In,Ga) Se_2-based solar cells", Sol. Energy Mater. Sol. Cells, Vol. 41/42, p. 231, 1996.

[3] T. Minemoto, Y. Hashimoto, W. S. Kolahi, T. Satoh, T. Negmi, H. Takakura, and Y. Hamakawa, "Control of conduction band offset in wide-gap Cu(In,Ga)Se_2 solar cells", Sol. Energy Mater. Sol. Cell, Vol. 75, p. 121, 2003.

[4] R. Herberholz, V. Nadenau, U. Ruhle, C. Koble, H. W. Schock, and B. Dimmeler, "Prospects of wide-gap chalcopyrites for thin film photovoltaic modules", Sol. Energy Mater. Sol. Cell, Vol. 49, p. 227, 1997.

[5] T. Minemoto, Y. Hashimoto, T. Satoh, T. Negami, H. Takakura, and Y. Hamakawa, "Cu(In,Ga)Se[sub2] solar cells with controlled conduction band offset of window/Cu(In,Ga)Se[sub2] layers", J. Apply. Phys., Vol. 89, p. 8327, 2001.

[6] D. Schmid, M. Ruckh, and H. W. Schock, "A comprehensive characterization of the interfaces in Mo/CIS/CdS/ZnO solar cell structures", Sol. Energy Mater. Sol. Cell, Vol. 41-42, p. 281, 1996.

[7] T. Schulmeyer, R. Hunger, A. Klein, W. Jaegermann, and S. Niki, "Photoemission study and band alignment of the CuInSe[sub2](001)/CdS heterojunction", Appl. Phys. Lett, Vol. 84, p. 3067, 2004.

[8] L. Kronik, L. Burstein, M. Leibovitch, Y. Shapira, D. Gal, E. Moons, J. Beier, G. Hodes, D. Cahen, D. Hariskos, R. Klenk, and H. W. Schock, "Band diagram of the polycrystalline CdS/Cu(In,Ga) Se[sub2] heterojunction", Appl. Phys. Lett., Vol. 67, p. 1405, 1995.

[9] M. Morkel, L. Weinhardt, R. Lohmuller, C. Heske, E. Umbach, W. Riedl, S. Zweigart, and F. Karg, "Flat conduction-band alignment at the CdS/ CuInSe[sub2] thin-film solar-cell heterojunction", Appl. Phys. Lett., Vol. 79, p. 4482, 2001.

[10] N. Terada, R. T. Widodo, K. Itoh, S. H. Kong, H. Kashiwabara, T. Okuda, K. Obara, S. Niki, K. Sakurai, A. Yamada, and S. Ishizuka, "Characterization of interface nature and band alignment in CBD-CdS/Cu(In,Ga)Se_2 bi-layer structure by photoemission and inverse photoemission spectroscopy", Thin Solid Films, Vol. 480-481, p. 183, 2005.

[11] B. Canava, J. Vigneron, A. Etcheberry, D. Guimard, P. P. Grand, J.-F. Guillemoles, D. Licot, S. Ould Saad Hamatly, Z. Djebbour, and D. Mencaraglia, "Studies of buried interfaces Cu(In,Ga)Se_2/CdS XPS and electrical investigations", Thin Solid Films, Vol.431-432, p. 289, 2003.

[12] G. K. Padam, G. Malhotra, and S. K. Gupta, "Study of intrinsic defects in vacuum/air annealed $CuInSe_2$", Solar Energy Materials, Vol. 22, p. 303, 1991.

[13] D. Cahen and R. Noufi, "Surface passivation of polycrystalline, chalcogenide based photovoltaic cells", Solar Cells, Vol. 30, p. 53, 1991.

[14] I. Dirnstorfer, W. Burkhardt, W. Kriegseis, I. Osterreicher, H. Alves, D. M. Hofmann, O. Ka, A. Polity, B. K. Meyer, and D. Braunger, "Annealing studies on CuIn(Ga)Se_2: the influence of gallium", Thin Solid Films, Vol.361-362, p. 400, 2000.