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Characterization of interface nature and band alignment in CBD-CdS/Cu(In,Ga)Se_2 bi-layer structure by photoemission and inverse photoemission spectroscopy

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Abstract

Depth profiles of electronic structure at the interface between Cu($In_{1-x}Ga_x$)Se_2 (CIGSe) grown by three-stage process and CdS through chemical bath deposition have been studied by ultraviolet X-ray photoelectron spectroscopy (UPS, XPS) and inverse photoemission spectroscopy (IPES). Especially, a dependence of band alignment on Ga content in the CIGSe was investigated. An intrinsic feature at an arbitrary depth was successfully exposed by etching with an Ar ion beam with a low ion energy of 330 eV. After the removal of surface contamination, the CdS layer exhibited a band gap of 2.4 eV. The band gap started to shrink when XPS core signals of CIGSe became detectable. For the interface over the CIGSe with a Ga substitution ratio x of 0.20%, valence band offset (VBO) was about 0.7 eV, and conduction band offset (CBO) looked finite. An increase of the Ga substitution ratio to 0.40 resulted in an increase of the VBO and a reduction of the CBO. An almost flat conduction band alignment was observed at the interface of CdS/$Cu_{0.93}(In_{0.60}Ga_{0.40})Se_2$.

Keywords: Photoemission spectroscopy; Chemical bath deposition; Conduction band

1. Introduction

Intensive studies and developments about the optimization of process parameters of thin-film solar cell based on Cu(Ga_xIn_{1-x})Se_2 (CIGSe) with CdS buffer layer have resulted in high conversion efficiency both on small and practically large area modules [1–3]. Band gap energy of the CIGSe layer in such high-performance cells was around 1.1 to 1.2 eV, which corresponded to the Ga substitution ratio x about 0.3. For the cells with a wider band gap energy of CIGSe around 1.4–1.5 eV, a higher efficiency has been theoretically estimated. However, a degradation of the efficiency in the cells based on such wide-gap CIGSe has been reported. [4]. For further improvement of the cell performance, it is desired to clarify the detailed electronic structure, especially band alignment of the CIS/CIGSe hetero-interface as a function of the band gap of the CIGSe and their effects on the conversion efficiency.

Because of the difficulty of a direct characterization of unoccupied electronic states, in most of the previous reports, the conduction band alignment over the interface has been deduced from the valence band data obtained by photoemission spectroscopy (PES) and reported band gap values. Since band gap energy of CIGSe absorber and CdS buffer can be modified by several factors, including compositional deviation and interface diffusion, the possible variation of the band gap might cause a spread of the conduction band offset (CBO) deduced by the valence band offset (VBO) [5–10]. For determining the CBO without assumption, novel techniques, such as Kelvin probe method [11] and inverse photoemission spectroscopy [12], have been adopted. The direct determination of the CBO by inverse photoemission spectroscopy for the direct determination of the conduction

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band alignment at the interface has firstly been done by Morkel et al. [12]. They have reported an almost flat conduction band alignment, which has been consistent with the high efficiency of the measured cells, at the interface between $CuInSe_2$ layer prepared by rapid thermal annealing of elemental layers and CdS by chemical bath deposition (CBD). Since nature of the CdS/CIGSe interfaces would change with preparation methods and the composition of the CIGSe layer, an accumulation of intrinsic information of electronic structure of the various CdS/CIGSe interfaces should be important to reach a systematic understanding of the electronic properties of the CIGSe-based cells. In the present study, by utilizing the combination of PES and IPES, we have attempted a characterization of valence and conduction band alignment at the interfaces between CBD-CdS and $Cu(Ga_xIn_{1-x})Se_2$ prepared by three-stage process. The change of the band connection with the Ga concentration in the CIGSe layer is also discussed.

2. Experimental procedure

CIGSe layers were prepared on Mo-coated soda–lime glass by evaporation using a molecular beam epitaxy system in the so-called three-stage process [13,14]. CdS buffer layer was subsequently deposited by CBD process [15]. Two kinds of absorber layers of $Cu_{0.93}(In_{0.80}Ga_{0.20})Se_2$ and $Cu_{0.93}(In_{0.60}Ga_{0.40})Se_2$ were examined. In ultraviolet photoemission spectroscopy (UPS) and X-ray photoemission spectroscopy (XPS), He I irradiation and monochromatized Al $K\alpha$ radiation were used for excitation, respectively. The IPES measurements were done in Bremsstrahlung Isochromat mode using an Erdman-Zipf type electron source and a photon detector with SrF_2 window and photoelectron multiplier with a Cu–Be first dynode [16]. The detector has an energy resolution of 0.47 eV at a photon energy of 9.4 eV. Electron energy of obtained spectra was calibrated using the Fermi edge of a gold plate commonly grounded with the specimen. Conduction band minimum (CBM), valence band maximum (VBM) and band gaps were determined by a linear extrapolation of the leading edges in IPES and UPS spectra. Accuracies of band gap and the band offset in the present experiment were ± 0.15 and ± 0.20 eV, respectively. As-received surfaces of the specimen were covered with contaminations because of the CBD process and transport procedure through ambient atmosphere. Ar ion etching by using a low-energy electron–cyclotron–resonance type Ar ion beam source was adopted for cleaning and exposure of the buried interface region. Since a thickness of damaged layer by the ion irradiation should mainly depend on kinetic energy of the ions, an effect of acceleration voltage V_{acc} of the Ar ion on the PES and IPES spectra was examined. On the condition of V_{acc} above 500 V, broadening of XPS core signals and a development of Fermi edge in UPS spectra were observed after a long-time etching. By limiting V_{acc} no higher than 400 V and an inclined incidence onto the sample surface, surface contaminations were successfully removed without any broadening of the XPS signals. The 400-V etching, however, induced a finite slope within the band gap. Further lowering the acceleration voltage was effective to suppress the spectral weight within the band gap. Fig. 1 shows a photoelectron take-off angle (TOA) dependence of UPS spectra of the surface of the CdS layer of the CdS/$Cu_{0.93}(In_{0.80}Ga_{0.20})Se_2$ sample etched at the condition of V_{acc}=330 V for 600 s. For the CdS layer, an etching rate at V_{acc}=330 V was estimated about 2.5 nm/min. In this experiment, TOA was defined with respect to surface normal, and a resolution of the photoelectron acceptance angle of the detector was $\pm 2^\circ$. There was no apparent shift of the VBM in spite of the wide variation of TOA. For ideally flat surface, a probing depth on the condition of TOA=85° was estimated much smaller than 1 nm. Although this surface sensitivity would be weakened by a roughness of the surfaces, the identical VBM and absence of Fermi edge indicate that the thickness of the damaged layers should be thin enough to investigate their electronic structure. The UPS measurements shown below were therefore performed under the condition of the TOA=0°.

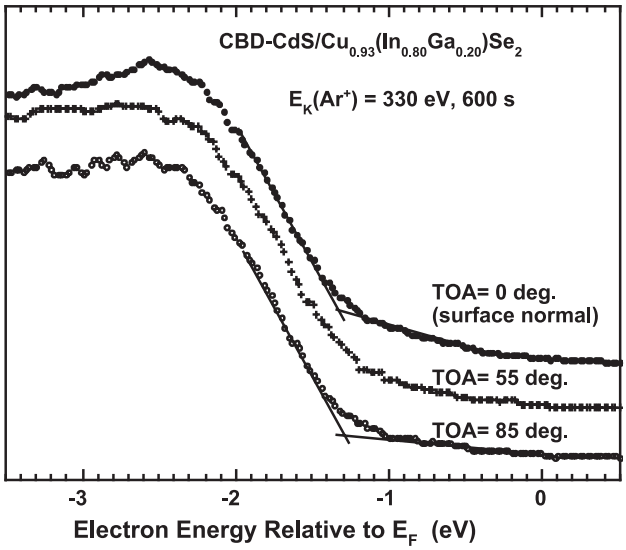

Fig. 1. Photoelectron take-off angle (TOA) dependence of ultraviolet photoemission spectra of surface of CdS surface of the chemical bath deposition (CBD)-CdS/$Cu_{0.93}(In_{0.80}Ga_{0.20})Se_2$ sample after the etching with the Ar ion beam with kinetic energy E_K of 330 eV for 600 s. TOA was defined with respect to surface normal direction.

3. Results and discussion

Most of the as-received surfaces exhibited a wide band gap above 2.7 eV, which should be attributed to the degraded surface layer. In the early stage of the Ar ion etching, the band gap was rapidly reduced. For the CBD-CdS/$Cu_{0.93}(In_{0.80}Ga_{0.20})Se_2$, the CdS surface etched at V_{acc}=330 V for 400 s showed a clean feature without carbon- and oxygen-related contamination. In this stage of