The Research Reports of the Faculty of Engineering, Kagoshima University, No.47 (2005)

Doctoral Dissertation, Graduate School of Science and Engineering, Kagoshima University, Doctorate No.208

Characterization of Electronic Structure of Functional Thin Films by Photoemission Spectroscopy and Inverse Photoemission Spectroscopy

Rusminto Tjatur Widodo*

1. Introduction

It is commonly recognized that performances of multi-layered electronic devices are dominated by natures of interfaces in them. There are, however, few reports about the details of the electronic structures around Fermi level (E_F) of interfaces in those devices, because of the technological difficulties of direct determination of them. The main purposes of this research are to establish a novel technique for characterizing both occupied and non-occupied electronic structure of the interfaces in multi-layered devices based on functional thin films, and to clarify correlation between interface nature and device properties. The developed technique includes a novel damage-less etching for expose intrinsic natures of buried interfaces and *in-situ* photoemission spectroscopy (PES), inverse photoemission spectroscopy (IPES). By utilizing them, interface natures of solar cell structure based on $Cu(In_{1-x}Ga_x)Se_2$ [CIGS] compound semiconductor have been investigated.

2. Results and Discussions

In this study, a low-energy Ar ion etching has been developed for exposing intrinsic nature of the interior regions of the devices initially located at an arbitrary depth of those specimens. Contaminations and degraded regions of surfaces of the CIGS base solar cells were successfully removed by using this technique. The subsequent *in-situ* PES/IPES measurements of the $CuInSe_2$ showed that valence band maximum and conduction band minimum CBM located at 0.54 eV below and 0.56 eV above E_F, respectively. After the identical etching procedure, $CuGaSe_2$ and $CuIn_{0.72}Ga_{0.28}Se_2$ showed a band gap of 1.7 eV and 1.27 eV, respectively. These agree well with the corresponding reported data. A low kinetic energy below 400 eV of the irradiating ions in the etching process was a key to develop the intrinsic features.

For the bi-layer structure consist of chemical bath deposited CdS top layer and CIGS substrate with various Ga substitution ratio (x), the dependence of the valence and conduction band alignment over the CdS/CIGS interfaces on x has been determined. A band gap energy of the cleaned CdS was about 2.5 eV, in good agreement with standard data. The present study has also revealed continuous decrease of conduction band offset CBO at the interfaces with an increase of Ga concentration. For the specimens with x of 0.24, the CBO and valence band offset (VBO) were 0.2 eV ~ 0.3 eV ($CBM_{CdS} > CBM_{CIGS}$) and 0.6 eV ~ 0.7 eV ($VBM_{CdS} < VBM_{CIGS}$), respectively. When the x increased to 0.45, the VBO was expanded to 0.9 eV ~ 1.0 eV, whereas CBO was reduced below 0.1 eV. So, almost flat conduction band alignment was realized in the specimens with $x \sim 0.45$. Further increase of x resulted in a sign change of CBO and continuous extension of VBO. For the samples with $x > 0.6$, negative CBO was observed. These results indicate that the most suitable band alignment for photovoltaic conversion should be realized between x of 0.24 and 0.45, which is consistent with the performances of solar cell structure fabricated over these interfaces. They and also suggest that there may be some rooms to improve the efficiency of the cells based on the wider band gap CIGS with high x.

3. Conclusions

The strong correlation between interface electronic structure and device properties revealed in this research, indicates the usefulness of the direct determination of the interface nature using PES/IPES developed in this study. They also reveal that the precise control of the electronic structure is one of the keys to pursue further improvements of device performances.

* Electronic Engineering Polytechnic Institute of Surabaya, Institute of Technology Sepuluh Nopember, Srabaya, Indonesia