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Improvement in Performance of CIGS Solar Cells by Surface Modification

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Abstract

In order to enhance solar cell performances, the importance of a valence band offset (ΔEv) at the CdS/Cu(InGa)Se_2 interface is theoretically and experimentally shown in the paper. The ΔEv acts as a hole barrier, and it repels holes from the hetero-interface into bulk region, resulting in the reduction of the surface recombination. One candidate to produce the ΔEv at the interface is a formation of a Cu-deficient layer on the CIGS surface, and a Se-interval method to grow the layer has been proposed. Finally, a cell efficiency of 19.8% was achieved by applying the technique.

1. Introduction

There are several kinds of materials for high-efficiency thin-film solar cells, and Cu(In,Ga)Se_2 (CIGS) is a promising candidate due to tunability of bandgap. The highest efficiency of 22.6% has been achieved [1, 2], and recently potassium-induced surface modification of CIGS has attracted a great attention for new technique to obtain high-efficiency solar cells [3]. On the contrary, we have proposed a formation of ΔEv (a valence band offset) at the CdS/CIGS interface in order to enhance the cell performance [4]. In the article, we show the concept of ΔEv effect on the solar cell performance, and a formation of the uniform Cu-deficient layer on top of the CIGS surface.

2. Numerical Analysis of ΔEv Effect on Cell Performance

Calculation Procedure

The theoretical evaluation of solar cell performance was carried out using wxAMPS [5]. The solar cell structure investigated was a ZnO:B/i-ZnO/CdS/CIGS/Mo, and a defective layer (DL) was introduced into the CdS/CIGS interface to reproduce the effect of the carrier recombination at the interface. The effects of the ΔEv at the CdS/CIGS interface were evaluated by incorporating a surface layer (SL) at the DL/CIGS interface. In order to clarify the effect of ΔEv, we didn't introduce a double-grading band profile which is usually used to boost the cell efficiency, therefore, the bandgap of CIGS was a flat conduction band profile. The band gap energy varied from 1.1 to 1.6 eV, corresponding to the Ga content from 0 to 1. Each bandgap of the DL and SL was varied, maintaining the same electron affinity as the CIGS and the same bandgap as CIGS plus ΔEv. In this calculation, ΔEv was changed from 0 to 0.3 eV. In the device simulation, we assumed the donor- and acceptor-like defects existed in the DL with a density of 10^{17} cm^{-3}, and a density of the donor-like defect in the CIGS layer was fixed at 10^{14} cm^{-3}.

Calculation Results and Discussions

Figure 1 shows the relationship between the bandgap of the CIGS layer and the cell efficiency, and the efficiencies of solar cell with a different ΔEv are also summarized. When ΔEv is small, the efficiency increases with increasing the band gap, however, it turns to decrease when the band gap energy is larger than 1.2 eV. This tendency is consistent with the experimental results reported by the NREL group [6] shown as black dots in Fig. 1. As a result, the highest efficiency is realized with a band gap energy around 1.15 eV. On the other hand, the efficiency of wide-bandgap CIGS increases monotonically when ΔEv increases, and then the highest efficiency was obtained at approximately 1.35 eV with a ΔEv = 0.3 eV, which is close to the estimated bandgap for obtaining the highest efficiency due to the matching of the sunlight spectrum. The calculation clearly showed the ΔEv is quite useful to enhance the solar efficiency. The mechanism of efficiency improvement is a hole barrier at the hetero-interface.

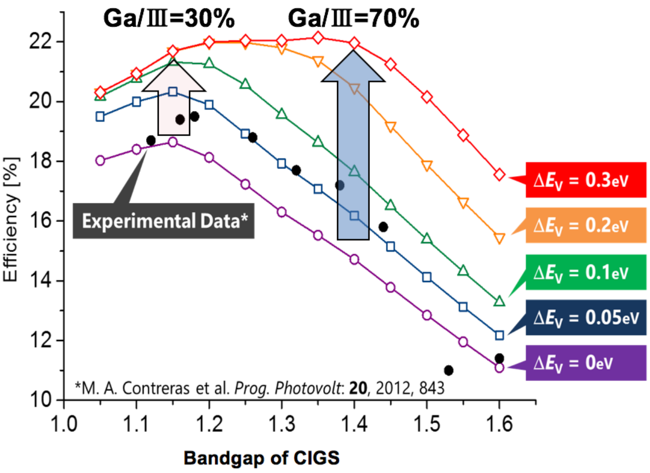

Fig. 1 Relationship between the bandgap of the CIGS layer and the cell efficiency.

3. Creation of ΔEv Layer on the CIGS Surface

It is found from the calculation that ΔEv formation at the CdS/CIGS interface leads to a boost in cell performance. There is no report on intentional insertion of ΔEv layer at the interface. It is widely known that the valence band maximum decreases when the Cu content in CIGS is decreased [7-9]. Therefore, a candidate material to form ΔEv is a Cu-deficient CIGS. Although a Cu-deficient condition was incidentally formed at the surface [10, 11], the ΔEv formation mechanism and its controlling techniques have not yet been reported. Recently, we have reported on the relationship between the existence of Cu_2Se during the second stage and the formation of Cu-deficient layer [12].

Formation of Cu-deficient Layer on the CIGS Surface

CIGS thin films were deposited on a Mo-coated soda-lime glass substrate by a three-stage method. In order to modify the surface of CIGS, Se irradiation time (t_{Se}) of 0, 2.5, 5, 7.5, and 10min was introduced after the second stage. In the conventional three-stage method, $Cu_{2-x}Se$ layer with a variable x is randomly segregated after the second stage. Then if we supply Cu-Se in the third stage, non-uniform Cu-deficient layer is grown on the CIGS layer. In the case, we can partially use the ΔEv effect. In our new modified three-stage process, called as a Se-interval method, we introduced t_{Se}, and the CIGS surface was changed into $Cu_{2-x}Se$ solid phase with a fixed x and $Cu_{2-x}Se$ liquid phase during the t_{Se}. Thus, the uniform and compositionally fixed Cu-deficient layer was formed on the surface by supplying Cu-Se in the third stage.

Cell Performances

Figure 2 shows the cell parameters of CIGS solar cells subjected to Se-irradiation as a function of t_{Se}. Voc and FF were improved from 0.666 to 0.678 V and from 0.716 to 0.764, respectively, by introducing Se irradiation (t_{Se} = 5 min). The highest efficiency of 19.8% (Voc: 0.672 V, Jsc: 38.6 mA/cm^2, FF: 0.762) was achieved. We also measured a quantum efficiency (QE) of solar cells, and QEs of a Se irradiation time of 0 min and 5 min were compared, respectively, by applying a forward bias. The former showed a significant decrease in the QE in the wavelength region from 500 to 1000 nm by applying a forward bias of 0.6 V. On the contrary, the degradation of QE by applying bias was remarkably suppressed for the sample fabricated by the Se-interval technique. The results indicated that the Cu-deficient layer leads to suppression of minority carrier recombination at the CdS/CIGS interface, resulting both in improvement of Voc and FF and in the high quality pn interface compared to the solar cells without the Cu-deficient layer.

4. Conclusions

In the article, the importance of a valence band offset (ΔEv) was shown. The main effect of the ΔEv is a hole barrier, and the holes are repelled from the CdS/Cu(InGa)Se_2 interface by the barrier, resulting both in the suppression of the surface recombination and in the enhancement of cell performances. The insertion of a Cu-deficient layer at the interface is promising for the formation of the ΔEv, and a Se-interval method has been newly proposed to grow the uniform Cu-deficient layer on top of the CIGS layer. Finally, an efficiency of 19.8% was realized for a sample with the Cu-deficient layer.

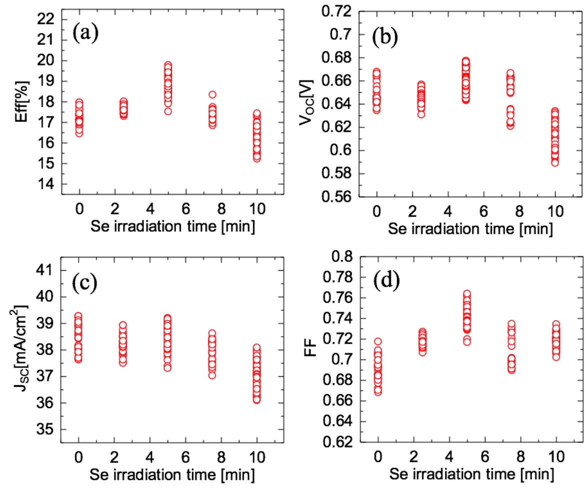

Fig. 2 Dependence of CIGS solar cell parameters (a) conversion efficiency, (b) Voc (c) Jsc, and (d) FF on t_{Se}.

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