

# Effects of Cu Doping on CdTe Thin-Film Solar Cells in Substrate Configuration

Tamotsu Okamoto, Ayuki Murata, Yusuke Hayashi and Daichi Watanabe

National Institute of Technology, Kisarazu College, Kisarazu  
2-12-1, Kisarazu  
Chiba 292-0041, Japan  
Phone: +81-438-30-4100 E-mail: okamoto@e.kisarazu.ac.jp

## Abstract

**Substrate-type CdTe thin-film solar cells with a Ag / ZnO:Al / CdS / CdTe / carbon structure were fabricated. For promoting the formation of the  $\text{CdS}_x\text{Te}_{1-x}$  mixed crystal layer in the CdS/CdTe interface, the heat treatment of the CdS/CdTe:Cu structure was performed. The cell performance was slightly improved due to the heat treatment after the CdS deposition, but conversion efficiency remained low (less than 2%). In order to improve cell performance, Cu doping was performed after the heat treatment (second Cu doping), in addition to the Cu doping before CdS deposition (first Cu doping). Conversion efficiency increased with increasing Cu concentration in the second Cu doping, and approximately 10% efficiency was achieved.**

## 1. Introduction

CdTe solar cells are conventionally fabricated in a superstrate configuration. On the other hand, the research on substrate-type CdTe solar cells has been limited [1]. The substrate-type CdTe solar cells offer the possibility of choosing a variety of substrate materials, but the conversion efficiencies of the substrate-type CdTe solar cells are lower than those in the superstrate configuration [1].

In the conventional superstrate configuration, a  $\text{CdS}_x\text{Te}_{1-x}$  mixed crystal layer is formed in the CdS/CdTe interface due to the intermixing of CdS and CdTe. The formation of  $\text{CdS}_x\text{Te}_{1-x}$  mixed crystal layer is very important for reducing the interface states at the CdS/CdTe interface. However, it is difficult to form the  $\text{CdS}_x\text{Te}_{1-x}$  mixed crystal layer in substrate configuration, because the deposition temperature of CdS layer is lower than that of CdTe layer.

Furthermore, Cu doping of the CdTe layer is very important in the conventional superstrate configuration for increasing acceptor concentration. It was reported that the cell performance was markedly improved by the Cu doping.

In this work, we attempted to fabricate the substrate-type CdTe solar cells by close-spaced sublimation (CSS) method. For promoting the formation of the  $\text{CdS}_x\text{Te}_{1-x}$  mixed crystal layer, the heat treatment of the CdS/CdTe:Cu structure was performed. Furthermore, in addition to the Cu doping before CdS deposition (first Cu doping), we attempted the Cu doping of the CdTe layer after the heat treatment of the CdS/CdTe:Cu structure (second Cu doping).

## 2. Experimental Procedure

Polycrystalline substrate-type CdTe thin-film solar cells

with a Ag / ZnO:Al / CdS / CdTe / carbon structure were fabricated. The carbon substrates were used as back contacts for p-CdTe layer. The CdTe films were deposited by the CSS method at 595°C. The thickness of the CdTe films was approximately 10  $\mu\text{m}$ .

$\text{CdCl}_2$  treatment was performed (first  $\text{CdCl}_2$  treatment) for improving solar cell performance. The CdTe films were coated with 0.3 M  $\text{CdCl}_2$  aqueous solution and then annealed at 415°C for 15 min.

After the first  $\text{CdCl}_2$  treatment, Cu doping of the CdTe layer was performed (first Cu doping). The CdTe layer was coated with Cu-doped diethylene glycol monobutyl ether (DEGBE) and then heat-treated to induce Cu diffusion to the CdTe layer. The heat treatment for Cu diffusion was performed at 325°C for 15 min. The Cu concentration in DEGBE was 50 ppm.

Following the first Cu doping, the CdS layer was deposited on the CdTe layer by chemical vapor deposition (CVD) at 420°C. We used cadmium diethyldithiocarbamate as a source material of CdS. The thickness of the CdS layers was approximately 80 nm.

The heat treatment of the CdS/CdTe:Cu structure was performed for promoting the formation of the  $\text{CdS}_x\text{Te}_{1-x}$  mixed crystal layer. First, a face-to-face annealing was performed at 600°C for 60 min. In the face-to-face annealing method, the surface of the CdS/CdTe film was covered with that of another CdS/CdTe film for avoiding the re-evaporation of the CdS and/or the CdTe. After that,  $\text{CdCl}_2$  treatment was performed (second  $\text{CdCl}_2$  treatment) by the same method as the first  $\text{CdCl}_2$  treatment.

Next, we performed the Cu doping of the CdTe layer (second Cu doping) by the same method as the first Cu doping. The Cu concentration in DEGBE was varied in the range of 200 to 1600 ppm.

ZnO:Al was prepared by rf-sputtering. The thickness of ZnO:Al layer was approximately 300 nm. Finally, a Ag electrode was prepared by screen printing. The area of the CdTe solar cells was approximately 0.6  $\text{cm}^2$ .

## 3. Results and Discussion

First of all, we fabricated the substrate-type CdTe solar cells without the heat treatment after the CdS deposition, and without the second Cu doping, but low conversion efficiency less than 1% was obtained. Next, we fabricated the substrate-type CdTe solar cells with the heat treatment after the CdS deposition and without the second Cu doping. We confirmed the formation of the  $\text{CdS}_x\text{Te}_{1-x}$  mixed crystal lay-

er due to the heat treatment by means of junction photoluminescence (PL) measurements. The heat treatment slightly improved cell performance, but conversion efficiency remained low (less than 2%). C-V measurements revealed that the heat treatment after the CdS deposition caused the decrease in the acceptor concentration in CdTe layer probably because of the re-diffusion of Cu atoms and/or the passivation of Cu acceptors.

For improving cell performance, we attempted the Cu doping after the heat treatment of the CdS/ CdTe:Cu structure (second Cu doping) in addition to the Cu doping before CdS deposition (first Cu doping). Figure 1 shows the cell parameters of the substrate-type CdTe solar cells as a function of the Cu concentration in DEGBE in the second Cu doping. The cell parameters of (a) the cells without the heat treatment after CdS deposition and without the second Cu doping, and (b) the cells with the heat treatment and without the second Cu doping were also shown for comparison. It was found that the second

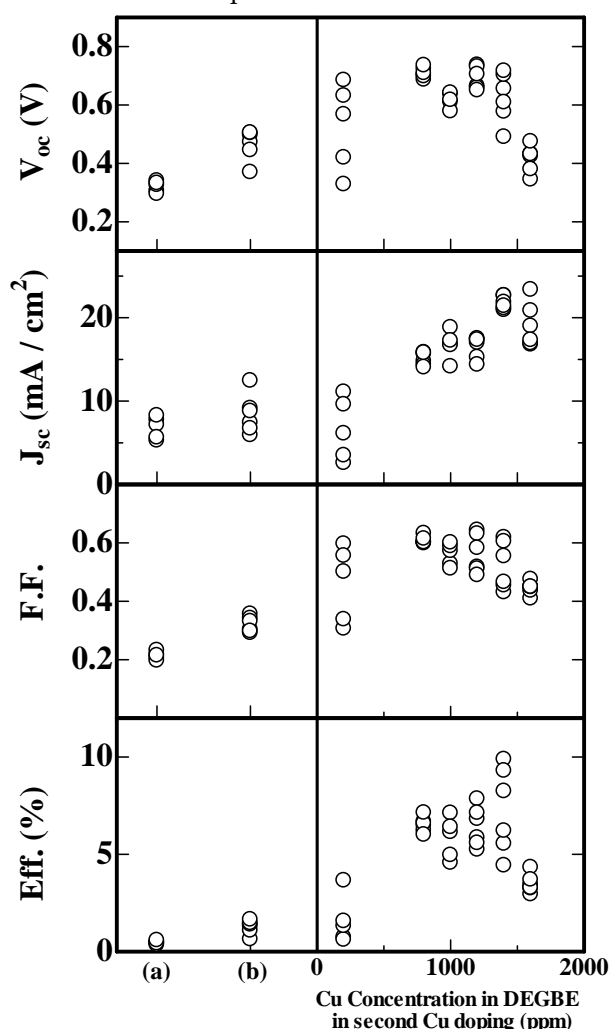


Fig. 1 Cell parameters of the substrate-type CdTe solar cells as a function of the Cu concentration in DEGBE in the second Cu doping. The cell parameters of (a) the cells without the heat treatment after CdS deposition and without the second Cu doping, and (b) the cells with heat treatment and without the second Cu doping were also shown for comparison.

Cu doping caused the improvement of  $J_{sc}$ ,  $V_{oc}$ , and fill factor at the Cu concentrations below 1400 ppm. The performance improvement was probably due to the increase in acceptor concentration in the CdTe layer by the second Cu doping. However, the decrease in the efficiency was observed at 1600 ppm owing to the decrease in  $V_{oc}$  and fill factor, probably because of the excess Cu doping. We achieved 9.9% efficiency ( $J_{sc}$ : 22.6 mA/cm<sup>2</sup>,  $V_{oc}$ : 0.704 V, FF: 0.619) at the Cu concentration of 1400 ppm.

In order to evaluate acceptor concentration in CdTe layer, we measured depletion layer width at zero bias by capacitance measurements. Figure 2 shows dependence of depletion layer width at zero bias on the Cu concentration in DEGBE in the second Cu doping. Depletion layer widths of (a) the cells without the heat treatment after CdS deposition and without the second Cu doping, and (b) the cells with the heat treatment and without the second Cu doping were also shown for comparison. The depletion layer widths in the case of (b) is much larger than that of (a). On the other hand, the second Cu doping caused decrease in the depletion layer width. These results indicate that acceptor concentration decreased due to the heat treatment after CdS deposition, and increased due to the second Cu doping. C-V measurements revealed that the acceptor concentration increased with increasing the Cu concentration in DEGBE in the second Cu doping. Therefore, we concluded that the cell performance improved due to the increase in acceptor concentration by the second Cu doping.

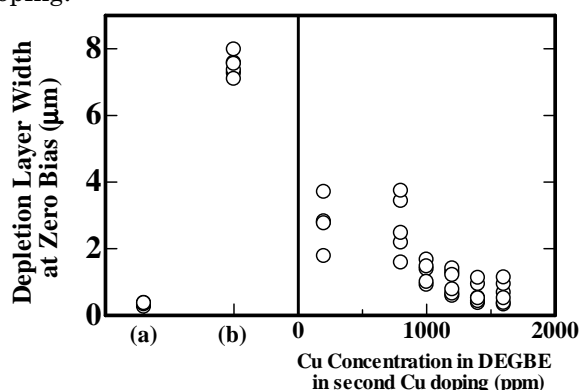


Fig. 2 Dependence of depletion layer width at zero bias on the Cu concentration in DEGBE in the second Cu doping. Depletion layer widths of (a) the cells without the heat treatment after CdS deposition and without the second Cu doping, and (b) the cells with the heat treatment and without the second Cu doping were also shown for comparison.

## Acknowledgements

This work was supported in part by a grant from the Futaba Electronics Memorial Foundation, Chiba, Japan.

## References

- [1] L. Kranz, *et al.*, Nat. Commun., 4, 2306, DOI:10.1038/ncomms3306 (2013).