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Effects of alkali treatments and thermal annealing on the property of CIGS solar cell

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Abstract

In this work, a secondary effect of alkali-metal post deposition treatment (PDT), an annealing effect, on the CIGS solar cell was studied separately from a main effect of alkali-metals addition. Alkali metals (K, Na) were found to thermally diffuse from soda lime glass substrate into CIGS absorber during the annealing process which resulted in improved minority carrier lifetime (τ). The annealing was also found to enhance In and Ga inter-diffusion modulating Ga grading in CIGS absorber. However, the open circuit voltage (V_{OC}) was not always improved with the annealing due to negative effects of the thermal annealing such as decreased carrier density (N_{CV}) estimated by capacitance voltage measurement. The KF irradiation together with the annealing resulted in improved efficiency mainly due to increased V_{OC} due to increased τ and N_{CV}.

1. Introduction

The chalcopyrite $Cu(In,Ga)Se_2$ (CIGS), an absorber for thin-film solar cells, has been widely studied. Its efficiency for laboratory level solar cells have already reached 22.3%[1]. It has been widely reported that incorporation of alkali-metals improve property of CIGS solar cell. In recent years, post deposition treatment of potassium compound (KF-PDT) have been attracting much attention which have reported to be effective to improve photovoltaic property of CIGS solar cell[2]. The effectiveness of the KF-PDT was highlighted by Chirilá *et. al.* A high efficiency (20.4%) was achieved with the KF-PDT[2]. KF-PDT is basically a process of irradiation of KF and Se flux on the surface of CIGS absorber with substrate heating. In our previous work, the promotion of alkali metal diffusion from soda lime glass (SLG) substrate was observed during the KF-PDT due to its secondary effect, an annealing effect [3].

In this work, a secondary effect of the alkali-metal PDT, an annealing effect, on the CIGS solar cell was studied separately from a main effect of K addition. An annealing was performed for 0 ~ 60 min under Se flux in vacuum chamber immediately after CIGS crystal growth. For some samples, the KF was evaporated during the annealing process.

2. Experimental

Fig. 1 shows the schematic structure of CIGS solar cell fabricated in this work. SLG was used as a substrate for the CIGS solar cells. A 1 µm -thick Mo back contact was deposited by in-line type direct current (DC) sputtering on the SLG substrate. The argon backpressure was set at 0.5 Pa. The CIGS absorber was grown through three-stage process. Growth temperature for the first stage was 350 °C, and that for the second and third stages was 550 °C. The beam equivalent pressure (BEP) ratio of Se (P_{Se}) to group III metals ($P_{III} = P_{Ga} + P_{In}$), P_{Se}/P_{III}, was ~7. The BEP ratio and growth durations were set to obtain a Ga/III and Cu/III target ratio of 0.37~0.4 and ~0.93, respectively. Immediately after the CIGS crystal growth, an annealing was performed for 0 ~ 60 min under Se flux in vacuum chamber immediately at 550 °C. For a sample, the KF was evaporated during the annealing process for 10 min. A CdS buffer layer with ~50 nm thickness was fabricated by chemical bath deposition. Intrinsic ZnO (~60 nm) and n-type ZnO:Al (~350 nm) were then deposited by radio frequency and direct current sputtering. An Al electrode was deposited on the ZnO:Al layer. Some of the solar cells were with anti-reflection coating (ARC) of acrylic film.

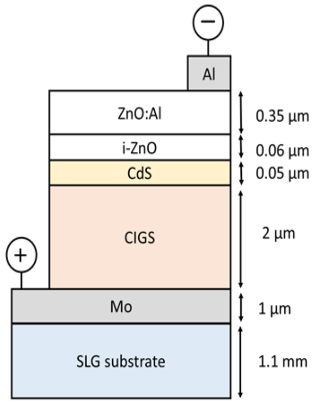

Fig. 1 Schematic structure of CIGS solar cell fabricated in this work. The substrate was soda lime glass (SLG). The total area of a cell was 0.519 cm^2.

The space charge density (N_{CV}) was evaluated at room temperature by capacitance vs. voltage (*C-V*) measurement on an LCR meter (Agilent E4980A) at an alternative voltage of 10 kHz. Current density vs. voltage curves (*J-V*) under white light (~100 mW/cm^2) or in the dark were obtained with a total area of 0.519 cm^2. Depth profiles of Secondary Ion Mass Spectrometry (SIMS) for constituent elements and alkali metals were studied by using Cs^+ as a primary ion.

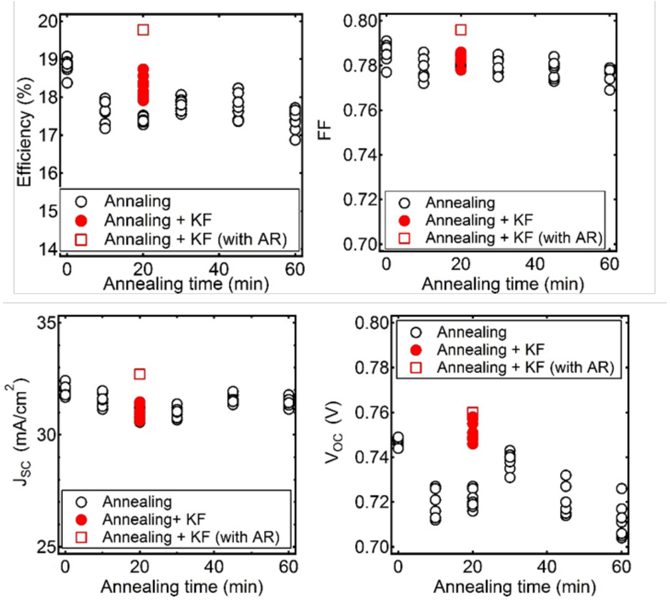

Fig. 2 Photovoltaic properties for CIGS solar cells which underwent annealing (open circles) and KF-PDT, i.e. annealing with KF flux (closed circles). A solar cell had an anti-reflection (AR) coating (open squares).

3. Results and discussion

Fig. 2 shows photovoltaic properties for CIGS solar cells which underwent annealing (open circles) and KF-PDT, i.e. annealing with KF flux (closed circles). A solar cell had an ARC (open squares). The total areas used for the measurement were 0.519 cm^2 (without ARC) or 0.5 cm^2 (with ARC). The highest efficiency was obtained when no annealing was introduced. The J_{SC} gradually decreased with annealing. The decrease in J_{SC} is mainly due to reduced Ga grading in the absorber as a result of thermally enhanced diffusion of Ga and In during the annealing process. Reduction in V_{OC} by introducing annealing was observed. The space charge densities (N_{CV}) as a function of annealing time were shown in Fig. 4 for the CIGS solar cell fabricated without (open circles) and with

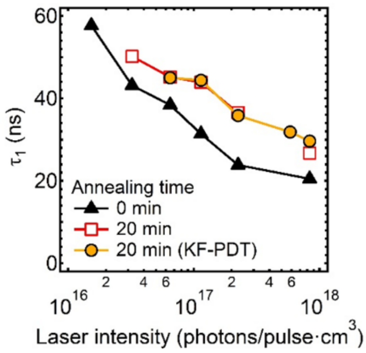

Fig.3 Estimated minority carrier lifetimes for the CIGS thin films covered with CdS buffer layer as a function of laser intensity. The lifetimes were estimated by fitting TRPL decay curves by double exponential model. The shorter (τ_1) lifetime components were shown.

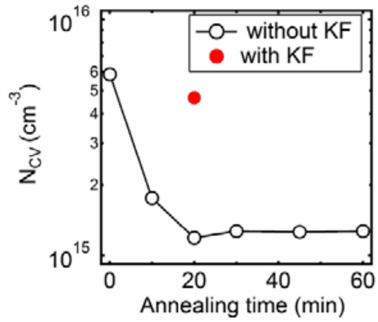

Fig. 4 The N_{CV} as a function of annealing time for the CIGS solar cell fabricated without (open circles) and with KF-PDT process.

KF-PDT (closed circle) processes. The reduction in V_{OC} by introducing annealing time should mainly due to the reduced carrier concentration. The varied density and depth profile of vacancies in the CIGS absorber with increasing post-growth annealing have been reported by Uedono *et. al.*[4] and agreed well with this work.

SIMS measurements revealed that thermal diffusion of alkali metals (K, Na) from soda lime glass substrate into CIGS absorber during the annealing process was enhanced with increasing annealing time. However, the open circuit voltage (V_{OC}) was not always improved with the annealing due to negative effects of the thermal annealing such as decreased carrier density (N_{CV}) as mentioned before. The KF irradiation together with the annealing resulted in improved efficiency mainly due to increased V_{OC} due to increased minority life time τ and N_{CV}.

4. Conclusions

The side-effect of post deposition treatment, annealing effect was studied. Reduction in the space charge density was observed by *C-V* measurement. The reduction in the N_{CV} with introducing annealing process agreed well with the reduction in V_{OC}. The KF irradiation together with the annealing resulted in improved efficiency mainly due to increased V_{OC} due to increased minority life time τ and N_{CV}.

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