ANNEALING EFFECT AFTER CdS LAYER DEPOSITION
ON Cu$_2$ZnSn(S,Se)$_4$ SOLAR CELLS

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1. Introduction
Cu$_2$ZnSn(S,Se)$_4$ (CZTSSe) is a promising alternative material to Cu(In,Ga)Se$_2$ in thin-film solar cells because all the constituent elements are earth abundant. Nanoparticle coating is an optimum approach to fabricating CZTSSe films with low manufacturing cost because of its high material utilization ratio and high throughput potential by roll-to-roll processing. Although the nanoparticle coating technique has attracted large attention, the efficiency of the CZTSSe solar cells fabricated by this approach is still lower than that of the cells prepared by the hydrazine-based approach.[1] Tajima et al. reported that post-annealing at 330 °C after CdS buffer layer deposition improves the efficiency of CZTS solar cells.[2] In this study, we investigated the effect of the post-annealing following CdS deposition on the photovoltaic properties of CZTSSe solar cells fabricated from nanoparticles.

2. Experimental methods
Cu$_2$ZnSnSe$_4$(CZTSe) nanoparticles were fabricated by dissolving CuI, ZnI$_2$, and SnI$_2$ in pyridine as metal sources until a clear solution was obtained. Subsequently, Na$_2$Se, used as the chalcogenide source, was added to methanol and transferred into the metal source solution to synthesize CZTSe nanoparticles. Thiourea was then added into the CZTSe nanoparticle solution as a binder, followed by spraying using an ultrasonic spray system onto Mo-coated substrates heated at 250 °C. After spraying, sintering treatments were carried out under nitrogen atmosphere in a tube furnace. The precursors consisting of CZTSe nanoparticles were sealed in a graphite box together with 24 mg of S, 40 mg of Se, and 10 mg of Sn powder, and then sintered at 600 °C for 20 min in nitrogen at atmospheric pressure. The CdS buffer layers were grown on the CZTSSe thin films by a chemical bath deposition. After the CdS buffer layer deposition, the specimens were annealed at 330 °C for 30min. Finally, solar cells with Al grid/B-doped ZnO/CdS/CZTSSe/Mo/soda-lime glass structure were fabricated. Intrinsic ZnO and B-doped ZnO layers were deposited by metal organic chemical vapor deposition, and the Al grid fabricated by evaporation.

3. Results and discussion
Fig. 1 shows the current-voltage characteristics of CZTSSe solar cells with and without post-annealing after CdS deposition. The efficiency greatly increased from 1.52 to 5.32 % by performing the post-annealing. Diode quality factor $n$, extracted using the method described by Sites et al., decreased from 2.67 to 1.67, suggesting that post-annealing improves the CdS/CZTSSe interfacial properties.[3] EBIC images show that the pn-junction shifts to the CZTSSe absorber after post-annealing. This implies that the Cd atoms diffuse from the CdS buffer to the CZTSSe absorber, inducing the improvement of CdS/CZTSSe interfacial properties.

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References