

## SURFACE TREATMENT EFFECT ON $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ SOLAR CELLS

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### 1. Introduction

$\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$  absorber material based on earth abundant elements has shown great potential as an alternative to industrial-proven  $\text{Cu}(\text{In,Ga})\text{Se}_2$  solar cells. Nanoparticle coating is an optimum approach to fabricating CZTSSe thin films with low manufacturing cost because of its high material utilization and high throughput potential by roll-to-roll processing. Although the nanoparticle coating technique has attracted large attention, the conversion efficiency of the CZTSSe solar cells fabricated by this method is lower than that of the cells prepared by the hydrazine-based approach.<sup>[1]</sup> Furuta et al. reported that HCl etching and thiourea aqueous solution treatment before CdS buffer layer deposition improves the conversion efficiency of CZTSSe solar cells.<sup>[2]</sup> In this work, the effect of thioacetamide aqueous solution treatment on photovoltaic properties of CZTSSe solar cells was investigated.

### 2. Experimental methods

$\text{Cu}_2\text{ZnSnSe}_4$  (CZTSe) nanoparticles were fabricated by dissolving CuI,  $\text{ZnI}_2$ , and  $\text{SnI}_4$  in pyridine as metal sources until a clear solution was obtained. Subsequently,  $\text{Na}_2\text{Se}$ , 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 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 sulfur, selenium, and tin powder, and then sintered at 590 °C for 10 min in nitrogen at atmospheric pressure. Next, the samples were subject to three different surface treatments: immersion in HCl, thioacetamide, or sequential treatments of both. The treatment using HCl was conducted for 30 seconds at 50 °C. HCl concentration was fixed at 0.5 mol/L. The treatment using 1 mol/L thioacetamide was carried out for an hour at 65 °C. Finally, solar cells with Al grid/B-doped ZnO/i-ZnO/CdS/CZTSSe/Mo/soda-lime glass structure were fabricated. Then CdS buffer layers were deposited by chemical bath deposition. 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

$J$ - $V$  characteristics for each surface treatment are shown in Fig. 1. The efficiency increased from 5.87 to 7.05% by HCl etching and thioacetamide treatment. Diode quality factor  $n$ , extracted using the method described by Sites et al., decreased from 2.12 to 1.80, suggesting that the surface treatment improves the CdS/CZTSSe interfacial properties.<sup>[3]</sup> External quantum efficiency in the middle and long wavelength regions is slightly increased by surface treatment. This implies that thioacetamide penetrates into the CZTSSe thin films and passivates the interfaces between grain boundaries, leading to the improvement of the film quality.

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#### References

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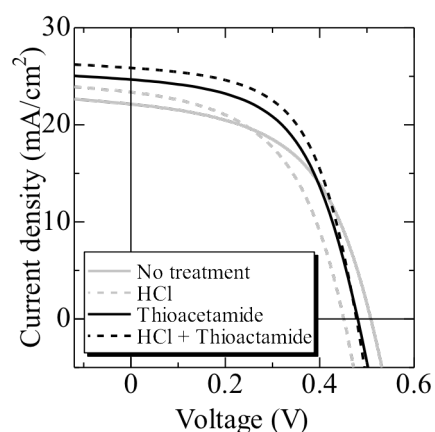


Figure 1:  $J$ - $V$  characteristics of CZTSSe solar cells with different surface treatments.