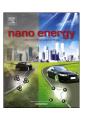


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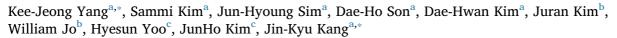
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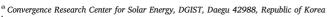
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Full paper

The alterations of carrier separation in kesterite solar cells





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ABSTRACT

Cu₂ZnSn(S,Se)S₄ (CZTSSe) thin films have attracted attention as low-cost absorber materials for solar cells; however, further studies are required to develop flexible solar cells from this material and to achieve a high power conversion efficiency. Toward this objective, this work investigated eight types of precursors applied on flexible Mo foil substrates, some of which also contained a layer of NaF. Secondary phases, defects, and defect clusters were different in the various samples, and the surface electrical characteristics of the CZTSSe absorber layer varied accordingly. In contrast to those in the CIGS-based cells, defects and defect clusters generated in the CZTSSe absorber layer caused an upward band bending-like band structure to form at the grain boundaries (GBs), thereby forming an intra-grain (IG) current path. By improving carrier separation, a flexible CZTSSe thin-film solar cell was developed on a Mo foil substrate with a power conversion efficiency of 7.04%. Thus, the efficiency of CZTSSe thin-film solar cells could be increased through carrier separation measures that enabled the collection of holes toward the GBs and of electrons toward IGs.

1. Introduction

Solar cells formed on wafers or glass substrates are heavy and vulnerable to damage, which impacts the extent to which they can be installed over a large area; therefore, the development of relatively light flexible substrates would expand the practical applicability of solar cells. Moreover, flexible solar cells incur lower manufacturing costs because the top and bottom glass plates of thin-film solar cells constitute most of their cost. In addition to flexible substrates, low-cost absorber materials are also required to reduce manufacturing costs. A lower manufacturing cost would result in a shorter energy payback time, thus expanding the market for renewable energy.

Thin-film solar cells based on Cu_2ZnSnS_4 (CZTS) and related materials (e.g., CZTS, $Cu_2ZnSnSe_4$ (CZTSe), and $Cu_2ZnSn(S,Se)_4$ (CZTSSe)) are more advantageous for their lower cost than that of conventional thin-film solar cells based on CdTe or $Cu(In,Ga)Se_2$ (CIGS) [1]. However, the power conversion efficiencies (PCEs) of CdTe and CIGS are 22.1% and 22.8%, respectively [2,3], whereas CZTS-based thin-film solar cells show a relatively low PCE of 12.6% [4]. Flexible CIGS thin-film solar cells have shown a 20.4% PCE on a polyimide (PI) substrate and a 17.7% PCE on a stainless steel (SS) foil substrate [5,6]. In contrast, flexible CZTS-based thin-film solar cells have shown PCEs of 6.1%

[7], 3.82% [8], 3.08% [9], 1.94% [10], and 0.49% [11] on ferritic SS foil, Mo foil, flexible glass, Al foil, and PI substrates, respectively.

High PCEs are currently unavailable with CZTS-based thin-film solar cells because the narrow phase stability of their quaternary and secondary phases and associated defects can cause electron–hole recombination and reduce both the open circuit voltage (V_{OC}) and current density (J_{SC}) [12–17]. CIGS thin-film solar cells produce fewer secondary phases and defects because of their higher phase stability [16,18], whereas in CZTS-based absorber layers, secondary phases and defects can be generated in a wide variety of forms [12–26]. Thus, the formation of secondary phases and defects must be suppressed to inhibit electron–hole recombination, and this can be accomplished by improving carrier separation.

In CIGS thin-film solar cells, higher current flows are measured in the vicinity of the grain boundaries (GBs) than near the intra-grains (IGs) [27–29]. Thus, the GBs in CIGS behave as benign minority carrier collection regions, where electrons are collected. Similar research results have been reported for CZTS-based thin-film solar cells [13,27]. However, efficiency improvements in carrier separation are limited because the constituent atoms at the GBs in CZTS-based absorber layers create localized defects that promote electron–hole recombination [13,30,31]. Nevertheless, the performance of CZTS-based thin-film

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