



Recovery of rectifying behavior in $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4/\text{Zn}(\text{O,S})$ thin-film solar cells by *in-situ* nitrogen doping of buffer layers



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ABSTRACT

The possibility of using N-doping to reduce the carrier concentration of zinc oxysulfide ($\text{Zn}(\text{O,S})$) thin films grown by atomic layer deposition (ALD) was investigated. The effect of N-doping on the structural, chemical, and electrical properties of the $\text{Zn}(\text{O,S})$ films was investigated using X-ray diffraction, X-ray photoelectron spectroscopy, and Hall measurements. The $\text{Zn}(\text{O,S})$ films were applied as alternative *n*-type buffers replacing conventional CdS for earth-abundant $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ thin-film solar cells. With increased O/(O + S) ratio up to ~ 0.87 – 0.90 , the fabricated cells suffered severe drops in efficiency, mainly due to the increased shunt conductance coming from excessive carrier concentration of ZnO-like $\text{Zn}(\text{O,S})$. Recovery of the rectifying diode behavior and cell efficiency was demonstrated by applying N-doping to the conductive $\text{Zn}(\text{O,S})$ buffer layer, further supported by current–voltage and external quantum efficiency measurements.

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1. Introduction

$\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ (CZTSSe) thin-film solar cells (TFSCs) have emerged as a potential alternative to the existing $\text{Cu}(\text{In,Ga})\text{Se}_2$ and CdTe solar cells for terawatt-scale PV generation (Wang et al., 2014; Walsh et al., 2012). The abundance of raw materials and the lack of toxicity triggered intense research into the development of highly efficient CZTSSe-based cells. CdS layers grown by chemical bath deposition (CBD) have conventionally been used for *n*-type buffer layers for CZTSSe and other TFSCs, achieving record efficiencies. To achieve eco-friendly CZTSSe TFSCs, however, CdS should be replaced with alternative buffer materials composed of earth-abundant and non-toxic elements (Hariskos et al., 2005; Bhattacharya and Ramanathan, 2004; Siebentritt, 2004).

For buffer layers, it is beneficial to have a wide bandgap of more than 3.0 eV, proper conduction band offset with an absorber, sufficiently high doping density exceeding that of the absorber, and a good interface with the absorber (Roedern and Bauer, 1999; Scheer and Schock, 2011). Precise control over the conduction band offset with an absorber layer ($0 < \Delta E_c < 0.4$ eV) is a crucial factor to obtain high open-circuit voltage (V_{oc}) and fill factor (FF), leading to better cell efficiency (Minemoto et al., 2001). In this regard, CdS is not a suitable buffer, especially for S-containing CZTSSe solar cells

(Bär et al., 2011; Siebentritt, 2013), because ΔE_c at the CZTSSe/Cd interface is negative (cliff-type).

To meet the requirements of a buffer layer, ternary buffer layers are preferred for alternative buffer materials because the properties of their deposited films can be tuned by changing either the anion (e.g., $\text{Zn}(\text{O,S})$ (Ericson et al., 2014; Persson et al., 2006; Sun et al., 2015) or $\text{Sn}(\text{O,S})$ (Kim et al., 2014)) or cation (e.g., $(\text{Zn,Mg})\text{O}$ (Hironiwa et al., 2014; Ikuno et al., 2013) or $(\text{Zn,Sn})\text{O}$ (Lindahl et al., 2013; Lee et al., 2013)) ratios. $\text{Zn}(\text{O,S})$ buffer layers have been considered good candidates for CZTSSe solar cells due to the large bandgap (~ 3.0 – 3.6 eV) and tunability of the films' properties by optimizing the O/(O + S) ratio (Ericson et al., 2014; Persson et al., 2006; Hiroi et al., 2012; Steirer et al., 2014; Merdes et al., 2014). Moreover, varying the O/(O + S) ratio for $\text{Zn}(\text{O,S})$ films can change the conduction band offset by ~ 1.3 eV experimentally at 300 K (Persson et al., 2006). These $\text{Zn}(\text{O,S})$ buffer layers have been deposited by atomic layer deposition (ALD) due to the excellent conformality, thickness-control down to the atomic scale, and controllability over complex composition (Niu et al., 2015).

Meanwhile, from the perspective of carrier concentrations, it is reported that $\sim 10^{18} \text{ cm}^{-3}$ is the optimized electron concentration for *n*-type buffer layers (Scheer and Schock, 2011). If the concentration is too low, the depletion width within the absorber layer is decreased, which adversely limits the short-circuit current density (J_{sc}). If the carrier concentration is too high, there is a strong possibility of forming a shunting path and increased recombination at the buffer/absorber interface. Similar issue was also reported for

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SnS/Zn(O,S) TFSCs (Sinsermuksamakul et al., 2014). In the case of ALD-Zn(O,S), the carrier concentrations increase significantly to mid- 10^{19} cm^{-3} as the O/(O + S) ratio approaches ~ 1 , resembling that of the conductive ZnO films (Yamada et al., 1997; Janotti and Van de Walle, 2009). In this case, there is a high chance of shunting the solar cells, leading to low conversion efficiency. This fact led us to conclude that it is crucial to control both the carrier concentration and the conduction band position of the buffer layers simultaneously.

In this study, we explored the potential of N-doping to reduce the excessive carrier concentration of the O-rich Zn(O,S) buffer layers for CZTSSe TFSCs. Instead of using deionized water, a conventional oxygen source for ALD, NH_4OH was used for both the O and N sources during ALD growth. ALD-ZnO:N growth using NH_4OH was reported by Lim et al., demonstrating the successful operation of ZnO:N-based thin-film transistors (Lim et al., 2010). Adopting this scheme, we confirmed that N is incorporated into the Zn(O,S) films by X-ray photoelectron spectroscopy (XPS), lowering its carrier concentration by 40-times. In addition, we fabricated CZTSSe TFSCs and confirmed successful recovery of the rectifying diode behavior and improved junction interface (reduced recombination) by using NH_4OH especially for O-rich Zn(O,S) composition. This strategy can be applied to other buffer layers, such as ALD-(Zn,Mg)O, (Zn,Sn)O, or In(O,S), for which the anion or cation ratios are optimized for the conduction band offset with excessive high carrier concentrations.

2. Experimental

A thermal ALD reactor (NCD, Lucida D100, Korea) was used for the growth of the Zn(O,S) thin films. The growth temperature was 120 °C. Diethylzinc (DEZ, EGChem., Korea), deionized water (H_2O), and 10% hydrogen sulfide (mixed with N_2 , Gaschem., Korea) were used as the Zn, O, and S sources, respectively. The growth of Zn(O,S) thin films was conducted using a supercycle scheme (Heo et al., 2012, 2011), which combined ZnO and ZnS binary ALD growth. One ALD cycle consisted of source pulse (t_1) – purge (t_2) – reactant pulse (t_3) – purge (t_4). The ZnO and ZnS ALD cycles used 0.2 s – 10 s – 0.2 s – 20 s and 0.2 s – 10 s – 5 s – 20 s, respectively. The actual O/(O + S) ratio was controlled by changing the subcycle numbers of ZnO (m) and ZnS (n). For N-doping, NH_4OH solution (27%, Sigma Aldrich) was used instead of H_2O with the same pulse time (t_3) of 0.2 s. In this study, two different cycle ratios were tested: $m:n = 9:1$ and 32:1. The 9:1 ratio was the optimized condition from our preliminary study (Hong et al., 2016). $m:n = 9:1$ means that one ZnS cycle was conducted after nine consecutive ZnO cycles. By XPS analysis, a more precise O/(O + S) ratio was calculated (Table 1). N-doping was applied for $m:n = 32:1$, and the sample is noted as Zn(O,S):N hereafter.

Fabrication of CZTSSe TFSCs was initiated from the pure metal deposition of Zn, Sn, and Cu on Mo/glass substrates. The samples were placed in a graphite box with S (0.003 g)/Se (0.077 g) powder, and soft annealing at 300 °C for 1 h and rapid thermal annealing at 520 °C for 10 min were sequentially performed in a box chamber furnace (VTS, Korea). Finally, Cu-poor and Zn-rich CZTSSe absorber layers ($\text{Cu}_{1.8}\text{Zn}_{2.0}\text{Sn}_{1.4}\text{S}_{1.4}\text{Se}_{3.4}$) were formed, as estimated from the

X-ray fluorescence. KCN etching for 5 min in 0.1 M aqueous solution was performed prior to the formation of the buffer layers. Intrinsic ZnO/Al-doped ZnO layers were sputter-deposited, and an Al grid was formed using a shadow mask. Six cells were made from one sample, and the cell size was 0.31 cm^2 . More details on the formation of the CdS and solar cells can be found elsewhere (Gang et al., 2015). The thickness of the absorbers, Zn(O,S), and CdS layers were $\sim 1.5 \mu\text{m}$, $\sim 50 \text{ nm}$, $\sim 60\text{--}70 \text{ nm}$, respectively. The carrier concentration of the fabricated absorbers was estimated as $\sim 7 \times 10^{15}\text{--}1 \times 10^{16} \text{ cm}^{-3}$ by capacitance–voltage analysis at 100 kHz.

The thickness of the Zn(O,S) films was monitored using an ellipsometer (Gaertner, Stokes Ellipsometer LSE). The crystallinity of the Zn(O,S) buffer layers were determined by glancing angle X-ray diffraction (GAXRD, PANalytical, X'Pert Pro MPD) at $\omega = 1^\circ$. X-ray photoelectron spectroscopy (XPS, VG, Multilab 2000) analysis was performed to identify the incorporation of nitrogen in the Zn(O,S) films. The electrical properties of the grown Zn(O,S) films were obtained by Hall measurements (Ecopia, HMS-3000) using a Van der Pauw configuration and a four-point probe (Changmin Tech., CMT-SR2000).

The current–voltage characteristics (I – V) of the fabricated solar cells were acquired under AM 1.5G illumination (100 mW cm^{-2}) using a Keithley 2400 and a solar simulator (San-ei Electric, XES-301S). The I – V characteristics under dark conditions were measured using a Keithley 236 SourceMeter to assess the quality of the fabricated diode. The shunt components of the fabricated cells were removed using the procedure reported by Dongaonkar et al. (2010) to estimate more reliable diode parameters. The spectral response was monitored using a quantum efficiency (QE) system (PV Measurements, Inc., QEXL).

3. Results and discussion

The crystallinity of the grown Zn(O,S) thin films was investigated using GAXRD, and the recorded spectra are shown in Fig. 1. The Zn(O,S) and Zn(O,S):N films exist in a crystalline phase. The observed peaks roughly correspond to those of ZnO peaks (JCPDS 00-036-1451). For the Zn(O,S) film with $m:n = 9:1$, the peaks are shifted toward slightly to lower angles than those of the standard ZnO. Zn(O,S) with $m:n = 9:1$ has more S atoms than that with $m:n = 32:1$, which leads to the increase of the d spacing and the corresponding decrease of the Bragg angle. Moreover, the peak intensities are much lower for the film with $m:n = 9:1$ than that with $m:n = 32:1$. The growth of ZnO film is more frequently disturbed by one ZnS cycle for the film with $m:n = 9:1$ than that with $m:n = 32:1$, which explains why the degree of crystallinity for the Zn(O,S) film with $m:n = 9:1$ is lower than that with $m:n = 32:1$.

When NH_4OH is pulsed instead of H_2O for $m:n = 32:1$ (Zn(O,S):N), peaks at similar positions but with slightly smaller intensities are observed compared with the Zn(O,S) $m:n = 32:1$. The change in the intensities of the peaks suggests the successful incorporation of nitrogen into the film, as further proved by the XPS analysis. Nitrogen atoms incorporated during the ZnO:N subcycles are believed to suppress the crystallinity of the Zn(O,S) film. Similar suppression of the crystallinity of the ZnO film growth during the

Table 1
Chemical composition of the Zn(O,S) and Zn(O,S):N films estimated from the XPS analysis.

Sample	Composition (at.%)				Ratio O/(O + S)
	Zn	O	S	N	
Zn(O,S) $m:n = 9:1$	43.9	42.8	13.3	–	0.76
Zn(O,S) $m:n = 32:1$	44.3	50.3	5.4	–	0.90
Zn(O,S):N $m:n = 32:1$	42.7	48.6	7.0	1.7	0.87

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