DOI: 10.1002/cey2.336



Identifying the relationships between subsurface absorber defects and the characteristics of kesterite solar cells

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Abstract

Understanding the defect characteristics that occur near the space-charge regions (SCRs) of kesterite (CZTSSe) solar cells is important because the recombination loss at the CZTSSe/CdS interface is considered the main cause of their low efficiency. CZTSSe surfaces with different elemental compositions were formed without polishing (C00) and with polishing for 20 s (C20) and 60 s (C60). For C60, a specific region near the SCR was excessively Cu-rich and Zn-poor compared to C00 and C20. Various charged defects formed where the elemental variation was large. As the main deep acceptor defect energy level (E_{a2}) near the SCR increased, the efficiency, open-circuit voltage deficit, and current density degraded, and this phenomenon was especially rapid for large E_{a2} values. As the E_{a2} near the SCR became deep, the carrier diffusion length decreased more for the CZTSSe solar cells with a low carrier mobility than for the CuInGaSe₂ (CIGSe) solar cells. The large amplitude of the electrostatic potential fluctuation in the CZTSSe solar cells induced a high carrier recombination and a short carrier lifetime. Consequently, the properties of the CZTSSe solar cells were more strongly degraded by defects with deep energy levels near the SCR than those of the CIGSe solar cells.

K E Y W O R D S

defect density, defect energy level, elemental variation, kesterite, space charge region

1 | INTRODUCTION

Supply instability and a sharp rise in raw material prices caused by the COVID-19 pandemic, resource constraints, and social instability are severely impacting the global economy.^{1–4} To replace existing energy sources with

energy sources from solar photovoltaic (PV) technology, an abundant and stable supply of raw materials is necessary. Kesterite ($Cu_2ZnSn(S,Se)_4$, CZTSSe) thin-film solar cells are composed of Earth-abundant materials, but their low efficiency is a weakness that must be overcome to build an industrial ecosystem and expand

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the market. The theoretical Shockley-Queisser (SQ) efficiency limits of Cu(In,Ga)Se2 (CIGSe) and Cu2ZnSnS4 (CZTS) solar cells are 32.0% and 32.4%, respectively.^{5,6} However, the trap-limit (TL) efficiency limits of CZTS and CZTSe solar cells are 20.9% and 20.3%, respectively,⁷ and the best research-cell efficiencies of CIGSe, CZTS, and CZTSSe solar cells are 23.35%, 11%, and 13.6%, respectively.^{8,9} The TL efficiency limit is considered to be a maximum value based on the absorber characteristics when losses through other degradation factors are minimal.⁷ Therefore, for kesterite solar cells, the characteristic losses of the absorber are the main cause of their low efficiency. The main factors for the characteristic losses of the CZTSSe absorber are the secondary phase and defects.^{10,11} Understanding the defect and phase properties near the absorber surface is because the CZTSSe/CdS important interface recombination loss is considered to be the main cause of the low efficiency.^{5,12} In the absorber layer, various defects, such as vacancies (V_A), interstitials (A_i), antisites (A_B) , and defect clusters, can form.^{13,14} Drive-level capacitance profiling (DLCP) and admittance spectroscopy (AS) techniques can be used to investigate the defect characteristics of the absorber. DLCP can be used to measure the bulk defect density (N_{DL}) and the depletion width (x_d) of the absorber.^{15–28} AS measurements can be used to analyze the acceptor defect energy levels within the band gaps (E_g) of the space-charge region (SCR).^{15,29,30} Moreover, the main acceptor defect energy level (E_a) relative to the valence band maximum $(E_{\rm v})$ and the acceptor defect density $(N_{\rm AS})$ can be measured.³¹⁻³⁵ Defects in the absorber layer act as electron-hole recombination centers.¹⁰ Poor opencircuit voltage (V_{OC}) deficit ($E_g/q - V_{OC}$, where q is the elementary charge) values have been observed due to the band edge shifts caused by defect clusters and electron-hole recombination by various defects.¹⁰ The correlation between the $V_{\rm OC}$ deficit and the density of recombination centers (N) in bulk CZTSSe can be expressed as $E_g/q - V_{OC} \propto A \ln N$, where A is the diode ideality factor.³⁶ Therefore, the relationship between the properties of kesterite solar cells and absorber defects must be identified.

In this study, we investigated the relationship between the properties of kesterite solar cells and the characteristics of the defect energy levels and densities in the subsurface absorber. We identified the bulk defect densities using DLCP and the acceptor defect energy levels and the defect densities near the SCR using AS measurements. In particular, for kesterite solar cells, defects near the SCR must be identified. In this regard, CZTSSe/CdS interfaces were formed using absorbers with different elemental conditions near the SCR, and the defect characteristics were confirmed. Consequently, the correlations between the properties of the kesterite solar cells and the defect characteristics were identified. Additionally, we confirmed the differences in the correlations by studying CIGSe and CZTSSe solar cells and the cause of the low efficiency of CZTSSe solar cells, in contrast to CIGSe solar cells. As a result, we developed a method for improving the efficiency of kesterite solar cells.

2 | EXPERIMENTAL SECTION

2.1 | Solar cell fabrication

The structure of the CZTSSe solar cell was composed of a soda-lime glass (SLG) substrate, a Mo back contact, a CZTSSe absorber, a CdS buffer layer, a ZnO layer, an Al-doped ZnO (AZO) layer, and an Al collection grid. The Mo layer was deposited on the SLG substrate via DC magnetron sputtering using a Mo target with a purity of 99.99%. The metal precursor was deposited onto the Mo layer using 99.99% pure Cu, Sn, and Zn sputtering targets with a stacking order of Sn (274 nm)/Cu (164 nm)/Zn (217 nm)/Mo/SLG. For the sulfo-selenization process, H₂S gas diluted with 90 vol% Ar was used as the sulfur source, and Se pellets were used as the Se source. The annealing processes were conducted in a rapid thermal processing (RTP) chamber at slightly above 1 atm. The samples were heated from room temperature to 300°C at a 0.5°C/s ramping rate and then maintained for 900 s. Subsequently, they were heated from 300°C to 510°C at a 0.1°C/s ramping rate and then maintained at 510°C for 600 s. After the sulfo-selenization process, the sample prepared without a polishing process was denoted C00, and the absorber surfaces of the other two samples were polished at 50 RPM for 20 s (C20) and 60 s (C60) using a Multiprep Polishing System (ALLIED High Tech Products Inc.), respectively. In detail, the sample was attached in parallel on the upper side of the polishing equipment with the absorber surface facing down using adhesive wax. On the lower part of the equipment, sandpaper coated with diamond particles 0.25 µm in size was placed. The lower side to which the sandpaper was attached was rotated clockwise and the upper side to which the sample was attached was rotated counterclockwise. To minimize damage to the sample, the equipment was set to polish only through gravity without applying a force in the vertical direction. In addition, to minimize the heat generated in the polishing process and lubricate the sample and sandpaper, polishing was performed while applying DI water. After the polishing process, a CdS buffer layer (50 nm) was deposited via

chemical bath deposition (CBD) using a bath containing CdSO₄, NH₄OH, NH₂CSNH₂, and DI H₂O. An intrinsic ZnO layer (50 nm) was deposited with radio-frequency (RF) sputtering. A 300-nm-thick AZO layer was deposited with RF sputtering. Finally, an Al collection grid (500 nm) was deposited on the tops of the devices using thermal evaporation. The total cell area was ~0.185 cm².

2.2 | Device characterization

Cross-sectional images of the absorber layers were acquired using a scanning electron microscopy (SEM) apparatus (model S-4800; Hitachi Co.). Scanning transmission electron microscopy-energy-dispersive spectrometry (STEM-EDS; QUANTAX-200, Bruker Co.) measurements were performed to analyze the elemental compositions and distributions near the absorber surfaces. The current-voltage characteristics were determined under a simulated air mass with a 1.5 global (AM 1.5 G) densities, spectrum and 100 mW cm^{-2} (1 sun) illumination at 25°C using a 94022A solar simulator (Newport Co.). The EQE values were obtained using an SR 830 digital signal processor (DSP) lock-in amplifier system (McScience Co.). To analyze the carrier lifetime, time-resolved photoluminescence (TRPL) measurements were performed at room temperature using a compact near-infrared fluorescence lifetime spectrometer (C12132; Hamamatsu). For the excitation laser line, the second harmonic of a YAG laser (532 nm) was used with a repetition frequency of 15 kHz. DLCP measurements were carried out with an inductance-capacitance-resistance (LCR) meter (E4980A; Agilent) to estimate the depletion width and the carrier density. DLCP was performed with DC bias ranging from 0 to -4.5 V at a frequency of 100 kHz and AC amplitude ranging from 20 to 200 mV. To identify the acceptor defect energy levels and densities, AS was performed at 90-300 K using an E4980A LCR meter (Agilent Co.), which utilized probe frequencies between 20 Hz and 2 MHz.

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To confirm the defect energy levels from the valence band maximum within the band gaps of the CZTSSe absorber layers, we obtained Arrhenius plots of the AS curve inflection points.

3 | RESULTS AND DISCUSSION

3.1 | Elemental variations near the absorber surface

In our previous studies, the elemental distributions of Cu. Zn. Sn. S. and Se varied from the absorber surface to the bulk.^{10,32,33} Therefore, CZTSSe surfaces with different elemental compositions can be formed by polishing the absorber surface. Figure 1 shows the corresponding sample preparation procedure. After precursor deposition (Figure 1A) and the sulfo-selenization process of the precursor (Figure 1B), three types of devices with different elemental compositions near the absorber surface without polishing (C00) and with polishing for 20 s (C20) and 60 s (C60) were prepared (Figure 1C). Figure 1D shows the structure of the CZTSSe device with a total cell area of ~0.185 cm². All samples were prepared with the same process that included batch-precursor deposition, sulfo-selenization, and deposition of CdS, intrinsic ZnO, Al-doped ZnO, and an Al collection grid.

Figure 2 shows the cross-sectional images and the elemental distributions near the absorber surfaces of the three types of devices. For the reported kesterite solar cells with over 5% efficiencies, the Cu/(Zn + Sn) ratio is between 0.75 and 1, and the Zn/Sn ratio is between 1 and 1.25.¹³ The average Cu/(Zn + Sn) ratios near the absorber surface were 0.97 for C00 (Figure 2A), 1.03 for C20 (Figure 2B), and 0.80 for C60 (Figure 2C). The absorber surface of C20 was more Cu-rich than that of C00. The average Zn/Sn ratios near the absorber surface were 1.23 for C00, 1.24 for C20, and 1.24 for C60. In a specific region of C60 (dashed line box in Figure 2C), the



FIGURE 1 Schematic diagram of sample preparation. (A) Precursor deposition, (B) sulfo-selenization process, (C) absorber surface polishing for 0, 20, and 60 s, and (D) structure of the CZTSSe device.



FIGURE 2 Cross-sectional SEM and STEM images, and elemental variations in the lateral directions near the absorber surface obtained using energy-dispersive spectrometry (EDS) line scans: (A) C00, (B) C20, and (C) C60. The average elemental ratio of Cu/(Zn + Sn) was 0.97 for C00, 1.03 for C20, and 0.80 for C60; that of Zn/Sn was 1.23 for C00, 1.24 for C20, and 1.24 for C60; and that of S/(S + Se) was 0.08 for C00, 0.11 for C20, and 0.15 for C60. In the dashed line box in (C), Cu/(Zn + Sn) increased to 1.23 and Zn/Sn decreased to 1.06 near the absorber surface of C60.

Cu/(Zn + Sn) ratio increased to 1.23, and the Zn/Sn ratio decreased to 1.06. Compared to C00 and C20, C60 was abundant in Cu and relatively poor in Zn near the absorber surface. Therefore, the absorber surface of C60 was more Cu-poor than those of C00 and C20 on average but more Cu-rich and more Zn-poor than those of C00 and C20 in a specific region. As a result, C60 showed a large variation in the elemental ratio near the absorber surface. The average S/(S + Se) ratios near the absorber surface were 0.08 for C00, 0.11 for C20, and 0.15 for C60.

Therefore, the CZTS/CZTSe phase ratio near the absorber surface can be assumed to increase in the order of C00 < C20 < C60.

3.2 | Solar cell device properties with the elemental variations near the absorber surface

The effects of the difference in the elemental variation near the absorber surface on the characteristics of the device were investigated. Figure 3 and Table 1 show the solar cell properties with the elemental variations near the absorber surface. Figure 3A,B shows the current-voltage curve, external quantum efficiency (EQE), and band gap energy (E_g) for the best cell of each type. The boxplots show the efficiencies (Figure 3C), $V_{\rm OC}$ values (Figure 3D), current densities (Figure 3E), fill factors (Figure 3F), and V_{OC} deficits (Figure 3G) of 16 cells of each type. All properties were degraded in the samples with elemental ratios that were more Cu-rich (C20, C60), more Cu-poor (C60), and more S-rich (C20, C60) than those of C00 near the absorber surface. As mentioned above, as the bulk defect density in the absorber increases, the $V_{\rm OC}$ deficit degrades.³⁶ The minority carrier lifetimes measured by time-resolved photoluminescence (TRPL)

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were 3.13 ns for C00, 1.30 ns for C20, and 0.71 ns for C60 (Figure 3H). TRPL measurements were performed on completed devices using a 532 nm laser, so considering the laser penetration depth, the TRPL data can be interpreted as the lifetime near the absorber surface. The carrier lifetime of CZTSSe is related to the electrostatic potential fluctuations induced by charged defects.³³ Therefore, understanding this correlation by separating the effects of charged defects and defect densities from defect characteristics is necessary.

3.3 | Defect characteristics in the absorber bulk

DLCP measurements can be used to obtain the bulk defect density (N_{DL}) and the depletion width (x_d) of the absorber bulk.¹⁵ N_{DL} was 1.35×10^{16} cm⁻³ for C00, 4.92×10^{16} cm⁻³ for C20, and 4.93×10^{16} cm⁻³ for C60. As shown in Figures 3G and 4, as N_{DL} increased, $E_g/q - V_{OC}$ degraded. The secondary phase, nonuniform elemental ratio distribution, and nonstoichiometry of the absorber may be the cause of a high bulk defect density.^{10,13,21,32,33,7,38} From Figure 4, it can be seen that x_d was 0.185 µm for C00, 0.060 µm for C20, and 0.103 µm for C60. Accordingly, the elemental variations



FIGURE 3 Properties of CZTSSe solar cells with elemental variations near the absorber surfaces. Sixteen cells with $\sim 0.185 \text{ cm}^2$ cell areas were included in the SLG substrate, with a size of $\sim 2.5 \text{ cm} \times 2.5 \text{ cm}$. (A) Current density–voltage curves and (B) EQE curves at a bias of 0 V and calculated band gaps of the best cell of each type. Boxplots of the (C) efficiency, (D) open-circuit voltage (V_{OC}), (E) current density (J_{SC}), (F) fill factor (*FF*), and (G) V_{OC} deficit ($E_g/q - V_{OC}$) of 16 cells of each type. The average efficiency, V_{OC} , J_{SC} , *FF*, and $E_g/q - V_{OC}$ values were 8.04%, 0.436 V, 34.21 mA cm⁻², 53.15%, and 0.614 V for C00; 4.28%, 0.369 V, 30.61 mA cm⁻², 37.63%, and 0.681 V for C20; and 0.85%, 0.257 V, 10.97 mA cm⁻², 29.34%, and 0.793 V for C60, respectively. (H) TRPL data using a 532 nm laser at 300 K. The carrier lifetimes were 3.13 ns for C00, 1.30 ns for C20, and 0.71 ns for C60.

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Sample	Efficiency (%)	$V_{\rm OC}$ (V)	$J_{\rm SC}$ (mA cm ⁻²)	FF (%)	$R_{\rm SL}^{\rm a}$ ($\Omega \ {\rm cm}^2$)	$G_{\rm SL}^{\rm b}$ (mS cm ⁻²)	$E_{\rm g}$ (eV)	$E_{\rm g}/q - V_{\rm OC}$ (V)
C00	9.69	0.456	35.01	60.74	1.08	1.73	1.05	0.594
C20	5.07	0.403	32.64	38.59	1.67	12.20	1.05	0.647
C60	1.48	0.263	16.44	34.23	1.12	28.89	1.05	0.787

TABLE 1 Properties of CZTSSe solar cells for the best cell with various elemental ratios near the absorber surface

^aSeries resistance.

^bShunt conductance.



FIGURE 4 Bulk defect density $(N_{\rm DL})$ and depletion width (x_d) measured by DLCP. The $N_{\rm DL}$ value in the absorber bulk was 1.35×10^{16} cm⁻³ for C00, 4.92×10^{16} cm⁻³ for C20, and 4.93×10^{16} cm⁻³ for C60. The x_d value at $V_{\rm bias} = 0$ was 0.185 m for C00, 0.060 µm for C20, and 0.103 µm for C60.

and ratios shown in Figure 2 may represent the region near the edge of the SCR.

3.4 | Defect characteristics with elemental variations near the SCR

As mentioned above, AS provides information about the energy levels and densities of the acceptor defects near the SCR.^{15,29,30} Therefore, the elemental variation characteristics near the SCR are important for investigating these defects. Using AS, we characterized the charged defects near the SCR (Figure 5). From the AS curves (Figure 5A-1,B-1,C-1), the E_a relative to E_v was determined (Figure 5A-2,B-2,C-2) by Arrhenius plots. Each Arrhenius plot was constructed via $\omega_0 = 2\pi v_0 T^2 \exp(-E_a/kT)$, where ω_0 is the inflection point of the capacitance function, v_0 is the pre-exponential factor, T is the Kelvin temperature, and k is the Boltzmann constant.^{31,32} The defect properties are summarized in Table 2. For C00 (Figure 5A-2), the main shallow

acceptor defect energy level (E_{a1}) was 79 meV $(E_{a1 C00})$, and the main deep acceptor defect energy level (E_{a2}) was 93 meV ($E_{a2,C00}$). As shown in Figure 5A-3, shallow acceptor defects existed in the energy-level range below 93 meV, with a density of 1.07×10^{16} cm⁻³ (N_{1 C00}), and deep acceptor defects existed in the energy-level range below 116 meV, with a density of $1.0 \times 10^{16} \text{ cm}^{-3} (N_{2,C00})$ near the SCR of C00. The elemental ratios (Figure 2A) indicated Cu-poor (Cu/(Zn + Sn) = 0.97) and Zn-rich (Zn/Sn = 1.23) regions and a S/(S + Se) ratio = 0.08 near the SCR of C00. Based on the main acceptor defect energy levels (Figure 5A-2), the energy-level ranges (Figure 5A-3), and the elemental ratios (Figure 2A), various acceptor defects, including V_{Cu}^{-1} and V_{Zn}^{-1} in CZTS and V_{Cu}^{-1} , V_{Zn}^{-1} , Cu_{Zn}^{-1} , and Zn_{Sn}^{-1} in CZTSe, likely formed near the SCR of C00.¹³ Additionally, various donor defects, including Zn_{Cu}^{+1} and Sn_{Zn}^{+1} in CZTSe, likely formed near the SCR of C00.13 The charged defects for C20 and C60 were identified in the same way. For C20 (Figure 5B-2), E_{a1} was 65 meV ($E_{a1,C20}$) and E_{a2} was 107 meV ($E_{a2,C20}$). As shown in Figure 5B-3, the shallow acceptor defects were distributed below the energy level of 82 meV, with a density of 1.99×10^{16} cm⁻³ ($N_{1,C20}$), and the deep acceptor defects were distributed between 87 and 135 meV, with a density of $2.82 \times 10^{16} \text{ cm}^{-3}$ (N_{2,C20}) near the SCR of C20. C20 was more Cu-rich and S-rich than C00, and the Zn ratio near the SCR of C20 was similar to that of C00 (Figure 2B). Under the condition of a Cu-rich elemental ratio, the formation energies of defects such as Cu_{Zn}, Cu_{Sn}, and Sn_{Zn} are lower, indicating the ease of formation.^{13,39} Based on the E_a values (Figure 5B-2), the energy-level range (Figure 5B-3), and the elemental ratio (Figure 2B), in addition to the acceptor defects formed in C00, various acceptor defects, including Cu_{Zn}^{-1} and Zn_{Sn}^{-1} in CZTS, likely formed near the SCR of C20. In addition to the donor defects formed in C00, various donor defects, including Zn_{Cu}^{+1} and Sn_{Zn}^{+1} in CZTS, likely formed near the SCR of C20. For C60 (Figure 5C-2), E_{a2} was 180 meV $(E_{a2,C60})$. As shown in Figure 5C-3, deep acceptor defects formed in the energy-level range below 223 meV, with a density of $4.22 \times 10^{16} \text{ cm}^{-3}$ (N_{2,C60}) near the SCR of C60. The elemental ratios (Figure 2C) indicated a region near the SCR of C60 that was more Cu-poor and more S-rich



FIGURE 5 Charged defect characteristics of CZTSSe with various elemental ratios near the SCR; (A) C00, (B) C20, and (C) C60. (A-1), (B-1), (C-1) AS measurements were performed at 90–300 K. (A-2) For C00, the main shallow acceptor defect energy level ($E_{a1,C00}$) and the main deep acceptor defect energy level ($E_{a2,C00}$) were 79 and 93 meV, respectively. (A-3) For C00, the defect density of shallow acceptor defects ($N_{1,C00}$) and the defect density of deep acceptor defects ($N_{2,C00}$) were 1.07×10^{16} cm⁻³ and 1.0×10^{16} cm⁻³, respectively. (B-2) For C20, $E_{a1,C20}$ and $E_{a2,C20}$ were 65 and 107 meV, respectively. (B-3) For C20, $N_{1,C20}$ and $N_{2,C20}$ were 1.99×10^{16} cm⁻³ and 2.82×10^{16} cm⁻³, respectively. (C-2) For C60, $E_{a2,C60}$ was 180. (C-3) For C60, $N_{2,C60}$ was 4.22×10^{16} cm⁻³.

TABLE 2	Properties of the acceptor defect en	lergy level (E_a) ,	the acceptor d	defect density	$(N_{\rm AS})$, the bulk	defect density	$(N_{\rm DL})$, and the
depletion wid	th (x_d)						

	AS measureme	ent	DLCP measurement			
	Shallow accept the SCR	tor defect near	Deep acceptor the SCR	defect near	In the absorber bulk	
Sample	<i>E</i> _{a1} (meV)	$N_1 ({\rm cm}^{-3})$	$\overline{E_{a2}}$ (meV)	$N_2 ({\rm cm}^{-3})$	$N_{\rm DL}~({\rm cm}^{-3})$	<i>x</i> _d (μm)
C00	79	1.07×10^{16}	93	1.00×10^{16}	1.35×10^{16}	0.185
C20	65	1.99×10^{16}	107	2.82×10^{16}	4.92×10^{16}	0.060
C60	-	-	180	4.22×10^{16}	4.93×10^{16}	0.103

than that of C00 and C20, and the Zn ratio was similar to that of C00 and C20. Under the condition of a Cu-poor elemental ratio, the formation energies of defects such as Cu_{Zn} and Cu_{Sn} are higher, indicating the difficulty of formation.^{13,14} However, the specific region of C60 (dashed line box in Figure 2C) was more Cu-rich and Zn-poor than those of C00 and C20 near the SCR of C60. Under the condition of a Zn-poor elemental ratio, the formation energies of defects such as V_{Zn}, Cu_{Zn}, and Sn_{Zn} are lower, indicating the ease of formation.^{14,39} Therefore, almost all acceptor and donor defects can form near the SCR of C60, which shows Cu-poor/rich and Zn-poor elemental ratios. Based on the E_a values (Figure 5C-2), the energy-level range (Figure 5C-3), and the elemental ratio (Figure 2C) of C60, in addition to the acceptor defects formed in C20, deep acceptor defects, including V_{Zn}^{-2} , V_{Sn}^{-1} , and Cu_{Sn}^{-1} in CZTS and V_{Zn}^{-2} , V_{Sn}^{-1} , V_{Sn}^{-2} , Cu_{Sn}^{-1} , and Zn_{Sn}^{-2} in CZTSe, likely formed near the SCR. Along with the donor defects formed in C20, deep donor defects, including ${\rm Sn_{Cu}}^{+1}$ and ${\rm Sn_{Cu}}^{+3}$ in CZTS and $\text{Sn}_{\text{Cu}}^{+1}$, $\text{Sn}_{\text{Cu}}^{+3}$, and $\text{Sn}_{\text{Zn}}^{+2}$ in CZTSe, formed near the SCR of C60. In the Cu-rich and Znpoor regions (dashed line box in Figure 2C), charged deep defects, including V_{Zn}^{-2} , Cu_{Zn}^{-1} , Cu_{Sn}^{-1} , Sn_{Zn}^{+1} , and Sn_{Zn}^{+2} , formed near the SCR of C60.

From the energy levels (Figure 5B) and the distribution ranges (Figure 5C) of the acceptor defects, charged defects were identified near the SCR (Figure 6A-1,A-2,B-1,B-2,C-1,C-2). From the charged defects, defect clusters near the SCR were deduced, as shown in Figure 6A-3,A-4,B-3,B-4,C-3,C-4. Defect clusters can form by compensating and attracting acceptor and donor defects to each other.¹³ The defect cluster formation energy is smaller than the sum of the formation energies of each defect due to charge-transfer and Coulomb interactions.^{13,39} Similar to the charged defects, as the elemental ratio changes, the defect cluster formation energy changes. As the Cu content increases, the defect cluster density of $2Cu_{Zn} + Sn_{Zn}$ increases.^{13,39} As the Cu content decreases, the formation energies of Zn_{Sn} + $2Zn_{Cu}$ and V_{Cu} + Zn_{Cu} decrease and the defect cluster densities of $Zn_{Sn} + 2Zn_{Cu}$ and $V_{Cu} + Zn_{Cu}$ increase. Additionally, as the Zn content decreases, the formation energies of $V_{Cu} + Zn_{Cu}$ and $Zn_{Sn} + 2Zn_{Cu}$ increase, and those of $V_{Zn} + Sn_{Zn}$ decreases.³⁹ The effects of defect clusters such as $V_{Cu} + Zn_{Cu}$, $Cu_{Zn} + Zn_{Cu}$, and $Zn_{Sn} + 2Zn_{Cu}$ on the band edge shift are negligible. As mentioned above, under the condition of Cu-rich and Zn-poor elemental ratios (dashed line box in Figure 2C), Sn_{Zn}, which is a deep donor defect, forms easily, and Sn_{Zn}-related



FIGURE 6 Charged defects and defect clusters near the SCR with various elemental ratios: (A) C00, (B) C20, and (C) C60. Defect energy levels near the SCRs of (A-1, A-2) C00, (B-1, B-2) C20, and (C-1, C-2) C60. Defect clusters and band edge shifts near the SCRs of C00 (A-3, A-4) C00, (B-3, B-4) C20, and (C-3, C-4) C60. As the elemental variation increased, the band edge shift increased.

defect clusters, including $2V_{Cu} + Sn_{Zn}$, $V_{Zn} + Sn_{Zn}$, $Zn_{Sn} + Sn_{Zn}$, and $2Cu_{Zn} + Sn_{Zn}$, can form. Accordingly, $2Cu_{Zn} + Sn_{Zn}$ can form near the Cu-rich SCR of C20 and $2Cu_{Zn} + Sn_{Zn}$ and $V_{Zn} + Sn_{Zn}$ can form near the Cu-rich and Zn-poor SCR of C60. These defect clusters, such as $2Cu_{Zn} + Sn_{Zn}$ and $V_{Zn} + Sn_{Zn}$, cause shifts in the valence and conduction band edges.^{13,32,39} In our previous studies, various charged defects were assumed to form when the elemental variations caused by the secondary phase or nonstoichiometric phase were large.^{10,32,33,37,38,40} Under the condition of a large elemental variation near the SCR of C60, this previous expectation can be confirmed using AS.

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3.5 | Relationships between the properties of kesterite solar cells and the defects near the SCR and in the absorber bulk

The bulk defect densities were measured using DLCP (Figure 4), and the charged defects and defect clusters were identified from the AS results (Figures 5 and 6). The correlation between the characteristics of the solar cells and the main deep acceptor defect energy level (E_{a2}) near the SCR is shown in Figure 7A. For CZTSSe,^{31–35} CIGSe,^{16,40–46} and the results of this work (Table 1 and Figure 5), as the E_{a2} value near the SCR increased, the



FIGURE 7 Relationships between the main deep defect energy level (E_{a2}) near the SCR and (A-1) the efficiency, $(A-2) E_g/q - V_{OC}$, and (A-3) the current density (J_{SC}) for CZTSSe (13 ea),^{31–35} CIGSe (19 ea),^{16,40–46} and the results of this work (3 ea). For the large main deep acceptor defect energy-level samples of CZTSSe (right side of black dotted lines), the efficiency, $E_g/q - V_{OC}$, and J_{SC} rapidly degraded. Relationships between the acceptor defect density ($\ln (N_{AS})$) near the SCR and (B-1) the efficiency, $(B-2) E_g/q - V_{OC}$, and $(B-3) J_{SC}$ for CZTSSe (13 ea)^{31–35} and the results of this work (3 ea). For the main deep acceptor defect energy-level samples over 150 meV (black dotted lines), the efficiency, $E_g/q - V_{OC}$, and $(B-3) J_{SC}$ for CZTSSe (13 ea)^{31–35} and the results of this work (3 ea). For the main deep acceptor defect energy-level samples over 150 meV (black dotted lines), the efficiency, $E_g/q - V_{OC}$, and J_{SC} showed different trends from those for samples below 150 meV. Relationships between the bulk defect density ($\ln (N_{DL})$) and (C-1) the efficiency, (C-2) $E_g/q - V_{OC}$, and (C-3) J_{SC} for CZTSSe (19 ea),^{16–28} CIGSe (10 ea),^{43,44,47,48} and the result of this work (3 ea). For all samples, as $\ln (N_{DL})$ increased, the efficiency, V_{OC} deficit, and J_{SC} degraded with similar trends.

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efficiency (Figure 7A-1) and $E_g/q - V_{\rm OC}$ (Figure 7A-2) degraded. Moreover, as the E_{a2} value near the SCR increased, the current density (J_{SC}) (Figure 7A-3) degraded for CZTSSe but was constant for CIGSe. For CZTSSe with a large E_{a2} value over 150 meV (dashed lines in Figure 7A), the efficiency, $E_g/q - V_{OC}$, and J_{SC} rapidly degraded. For CZTSSe, as the acceptor defect density (N_{AS}) near the SCR increased, the efficiency (Figure 7B-1) slightly degraded, but $E_g/q - V_{OC}$ (Figure 7B-2) and J_{SC} (Figure 7B-3) were constant. Additionally, these characteristics had different values according to the E_{a2} values near the SCR being above or below 150 meV (dashed lines in Figure 7B). Therefore, the E_{a2} value near the SCR affected the CZTSSe characteristics more than the CIGSe characteristics, especially in the case of deep acceptor defect energy levels of over 150 meV. Figure 7C shows the correlation between the characteristics of the solar cells and the bulk defect densities $(N_{\rm DL})$ from DLCP. For CZTSSe,^{16–28} CIGSe,^{43,44,47,48} and the results of this work (Table 1 and Figure 4), as $\ln (N_{\rm DL})$ increased, the efficiency (Figure 7C-1), $E_g/q - V_{OC}$ (Figure 7C-2), and J_{SC} (Figure 7C-3) degraded, with similar trends. According to the relationship of $E_g/q - V_{OC} \propto A \ln N$,³⁶ the V_{OC} deficit for CZTSSe and CIGSe showed a relationship proportional to $\ln (N_{\rm DL})$.

To explain the effect of E_{a2} near the SCR, the results of the elemental variation (Figure 2), SCR (Figure 4), and defects (Figure 6) are summarized in Figure 8. As the elemental variation and the S/(S + Se) ratio near the SCR (Figure 2) increased, various charged defects and defect clusters formed, and E_{a2} became large (Figures 5 and 6). As Cu/(Zn + Sn) increased and Zn/Sn decreased, deep energy-level defects formed easily (Figure 6). Defects with

deep energy levels act as carrier trap sites, cause electron-hole recombination, and increase nonradiative recombination.⁴⁹ In addition, defect clusters caused by elemental variations increase the shifts of the valence and conduction band edges.^{13,39} Charged defects and defect clusters can form in CZTSSe more easily than in CIGSe because the formation energies in CZTSSe are low.¹³ Additionally, the carrier mobility, carrier lifetime, and diffusion length of CZTSSe are lower than those of CIGSe.^{14,50–52} The carrier mobility determines how fast a carrier can move in a solid material under an applied electric field.⁵³ The diffusion length, which can be defined as the average distance that an excited carrier will move before recombination, is proportional to the square root of the mobility and carrier lifetime.⁵⁴ Therefore, as the E_{a2} value near the SCR increased, the diffusion length decreased more in CZTSSe with a low carrier mobility than in CIGSe. Consequently, as the E_{a2} value near the SCR increased, J_{SC} decreased more rapidly in CZTSSe than in CIGSe (Figure 7A-3). Charged defects cause electron-hole recombination and electrostatic potential fluctuations in the band gap.⁵⁵ The smaller the dielectric constant, the greater the amplitude of the electrostatic potential fluctuation.⁵⁵ The dielectric constant of CIGSe is $\sim 12^{52}$ and that of CZTSSe changes from 6.7 (CZTS) to 8.5 (CZTSe) as the S/(S + Se) ratio changes.⁵⁶ Therefore, the amplitude of the electrostatic potential fluctuation is larger in CZTSSe than in CIGSe.55 As the amplitude of the electrostatic potential fluctuation becomes large, electrons and holes can be separated over a short distance.⁵⁵ Consequently, the electrostatic potential fluctuation due to the deep charged defects and small dielectric constant in CZTSSe causes a high carrier recombination and a short



FIGURE 8 Charged defects and elemental ratios near the SCRs of (A) C00, (B) C20, and (C) C60.

TABLE 3 Summary of the properties of CZTSSe solar cells with varying elemental ratios near the absorber surface

Poor	Cu/(Zn + Sn)	Rich
Forming V_{Cu} , V_{Zn} , V_{Sn} , Zn_{Sn} , Zn_{Cu} , Sn_{Cu}		Forming Cu_{Zn} , Cu_{Sn} , Sn_{Zn} , $2Cu_{Zn} + Sn_{Zn}$
		Increasing band edge shift
		Decreasing carrier lifetime
Poor	Zn/Sn	Rich
Forming V_{Zn} , Cu_{Zn} , Sn_{Zn}		Forming $Zn_{Sn} + 2Zn_{Cu}$
Increasing band edge shift		
Decreasing carrier lifetime		
Poor	S/(S + Se)	Rich
Decreasing CZTS/CZTSe		Increasing CZTS/CZTSe
Increasing conduction band offset (spike-like)		Decreasing conduction band offset (cliff-like)
		Increasing electrostatic potential fluctuation

carrier lifetime. As a result, the E_{a2} value near the SCR was more strongly proportional to $E_g/q - V_{OC}$ and inversely proportional to J_{SC} in CZTSSe than in CIGSe. As mentioned above, as N_{AS} increased, the efficiency, $E_{\rm g}/q - V_{\rm OC}$, and $J_{\rm SC}$ showed different value levels according to the E_{a2} near the SCR being above or below 150 meV (dashed lines in Figure 7B). Under the conditions of Cu/(Zn + Sn)-rich and Zn/Sn-poor elemental ratios, the defect energy levels of Cu_{Zn} , Cu_{Sn} , and V_{Zn} were approximately over 150 meV and showed different trends. Therefore, these defects can be regarded as deep defects. In general, the secondary phase can exist more in the CZTSSe absorber bulk than near the SCR due to large elemental variations.^{10,33,37,57,58} Therefore, defects and defect clusters can form more easily in the CZTSSe absorber bulk than near the SCR. However, it is difficult to investigate the defect energy levels in the absorber bulk due to the limitation of the AS measuring region.

When the S/(S + Se) ratio changes, the conduction and valence bands of CZTSSe change, and E_g fluctuates.^{55,59} Additionally, as the S/(S + Se) ratio increases, the conduction band offset (CBO) decreases at the CZTSSe/CdS interface. When CBO is small and "clifflike," the characteristic losses increase due to electron diffusion, thermionic emission, and trap-assisted recombination at the CZTSSe/CdS interface.⁶⁰ As S/(S + Se) increased, the characteristics of C20 and C60 degraded. However, when S/(S + Se) is lowered to form a "spike-like" CBO, the V_{OC} can also be lowered. Therefore, it is important to induce an appropriate S/(S + Se) ratio for "cliff-like" CBO and the S/(S + Se) ratio grading to minimize characteristic losses.⁶¹ Table 3 summarizes the above results.

4 | CONCLUSIONS

In summary, we investigated the relationships between the properties of kesterite solar cells and the defect characteristics in subsurface absorbers. From the DLCP measurements, it was found that the bulk defect densities in CZTSSe and CIGSe showed a relationship proportional to the $V_{\rm OC}$ deficit and inversely proportional to the efficiency and J_{SC} , with similar trends. The AS results show that various defects and defect clusters easily formed near the SCRs with elemental variations. These defects degraded the properties of the solar cells, especially for CZTSSe, with deep main defect energy levels of over 150 meV. The low formation energy of the charged defects and the defect clusters in CZTSSe may cause these defects to form more easily than in CIGSe. As the main defect energy level near the SCR became deep, the carrier diffusion length decreased more in CZTSSe with low carrier mobility than in CIGSe. Therefore, the $J_{\rm SC}$ decreased more rapidly in CZTSSe than in CIGSe. The charged defects caused electron-hole recombination and electrostatic potential fluctuations in the band gap. The large amplitude of the electrostatic potential fluctuation due to the deep charged defects and the small dielectric constant in CZTSSe induced a high carrier recombination and a short carrier lifetime. Consequently, the defects with deep energy levels near the SCR were proportional to the $V_{\rm OC}$ deficit and inversely proportional to J_{SC} more strongly in CZTSSe than in CIGSe. To improve the efficiency of kesterite solar cells, the formation of defects with deep energy levels near the SCR must be suppressed. Defect passivation with the alkali doping of the absorber surface or the substitution of

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Sn site with Sb is candidate methods to improve the Voc deficit and suppress carrier recombination loss.

ACKNOWLEDGMENTS

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Ministry of Science and ICT (No. 2022M3J1A1085371) and by the DGIST R&D programs of the Ministry of Science and ICT (23-ET-08 and 23-CoE-ET-01). It was also supported by the National Research Foundation of Korea (NRF), funded by the Korean Government (NRF-2021R1A2C1008598).

CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

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How to cite this article: Son D-H, Jeon D-H, Kim D-H, et al. Identifying the relationships between subsurface absorber defects and the characteristics of kesterite solar cells. *Carbon Energy*. 2023;5:e336. doi:10.1002/cey2.336