Toward Understanding Chalcopyrite Solar Cells via Advanced Characterization Techniques

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In response to global environmental concerns, the importance of renewable energy, especially photovoltaic technology, is widely emphasized. As such, various efforts are made to improve the efficiency of solar cells, leading to significant technological advances supported by effective analysis and characterization techniques. Understanding these characterization techniques is important when looking to overcome technological limits and set the direction of technological development. Because the electrical properties of device, such as the carrier lifetime, doping density, energy levels, and surface potential, are generally determined based on the crystallographic phase, morphology, and compositional distribution, characterization techniques are developed to provide quantitative information on the absorber, surface, and interfaces of solar cells in order to improve their overall performance. In this review, basic to advanced characterization techniques for chalcopyrite solar cells are introduced. Because chalcopyrite solar cells exhibit high efficiency and are already commercialized, this can be a good lesson for studying the technological development history regarding efficiency improvement with characterization of thin-film solar cells. Based on the various characterization techniques reviewed in this paper, structure–property relationships are established, thus providing a foundation for the development of strategies to improve processing conditions and thus increase the efficiency of solar cells.

1. Introduction

The development and use of solar cells has been a major strategy for resolving issues associated with global energy and environmental crises.[1] While silicon solar cells are current market leaders in this respect, thin-film solar cells based on chalcopyrite, perovskite, and organic materials can be used to produce portable, flexible, wearable, and building-integrated devices for the generation of electricity.[2-4] Chalcopyrite solar cells are particularly promising because they offer long-term durability and a high efficiency of over 20%,[5,6] both of which are comparable to the performance of silicon solar cells.[8] In general, chalcopyrite solar cells are fabricated by employing either vacuum or solution processes.[9] Although vacuum-processed chalcopyrite solar cells have been reported to deliver a record efficiency of 23.4%,[4] processing for large-area applications with price competitiveness is difficult.[9] In contrast, solution-based processes have the potential to manufacture solar cells on a large scale while also offering a low-cost and customized option for a variety of applications. More recent solution processes have replaced toxic hydrazine as a solvent[11,12] with benign solvents such as an amine–thiol mixture,[13-15] alcohol,[16-19] dimethyl sulfoxide (DMSO),[20] dimethylformamide (DMF),[21-23] and N-methyl-pyrrolidine (NMP).[24] An efficiency of over 15% for solution-processed Cu(In,Ga)1−x,AgxS1−yS1+y (CIGS) solar cells has also been reached.[11,15] However, a performance gap still exists between vacuum- and solution-processed CIGS solar cells, and device efficiency requires further improvement.[25] For this reason, extensive research has been dedicated to tuning the morphology and composition of chalcopyrite.

Recently, foreign elements such as alkali metals (AMs) and Ag have been incorporated into devices to produce multifunctional effects, thus increasing their overall efficiency. While light AMs can diffuse into the grain interior and affect the hole concentration via p-doping,[26,27] heavy AMs form a segregated AM-In-Se secondary phase at the grain boundaries and CdS/CIGS interface, which passivates defects at the grain boundaries and surface.[28,29] Both vacuum and solution processing often employs two separate steps of coevaporation of elements and precursor coating with postchalcogenization, respectively. While, in vacuum process chalcogenization develops...
CIGS thickness of ~4 µm from Se penetration, solution process provides CIGS thickness of ~1 µm and bilayered morphology, with a large-grained upper layer and a fine-grained bottom layer since Se penetration is hampered from organic residues, resulting in a decrease in efficiency of solution processed devices.[17,18] In addition, the chemical affinity of K and Se increases Se penetration into the film, which accelerates selenization and increases Se levels at the bottom, leading to a desirable band gap grading structure. Surface AM treatment, called post deposition treatment (PDT), also reduces parasitic absorption, increasing light absorption,[30] widening the surface band gap,[31,32] and facilitating defect passivation,[33] thus leading to an increase in charge selectivity and reduced carrier recombination. Various researches on introducing and understanding of PDT to achieve high-efficiency CIGS solar cells have been reported. It has been known that the effect of PDT is affected by the Cu concentration near the CIGS surface.[34–36] In addition, the properties of the CIGS surface are changed by PDT.[30,36,37] In particular, since the Cu concentration on the CIGS surface is known to affect the growth of the buffer layer and ion exchange with the CIGS during chemical bath deposition (CBD) process,[30,37,38] elucidating the crucial effect of surface chemical and electrical properties of CIGS before and after PDT on the CIGS properties. In addition, different chalcogenization processing temperatures,[39] and high Se partial pressures[40] have been tested during selenization, while Ar pressure is used to improve the quality of Cu-rich chalcopyrite films.[23] In addition to modifying the morphology of the absorber layer, various Cd-free interlayers such as ZnS, InP3S5, Zn1−xMgxO, and Zn(O,S,OH)2 have been utilized for the highest efficiency.[4] This variety of approaches to tuning the morphology, band gap grading structure, and interlayers have contributed to a significant improvement in the efficiency of solar cells. Based on the better analysis techniques, a deeper understanding was possible, thus those improved results could be finally obtained.

Analysis techniques for the characterization of the composition, morphology, and energy levels of solar cells provide qualitative and quantitative information that can be employed to understand light absorption and charge carrier separation, transport, and collection in bulk CIGS and at the CIGS/CdS interface. Previous research aiming to improve the efficiency of solar cells has thus employed various characterization techniques. In this review, we summarize recent developments in various characterization techniques, as shown in Figure 1. Chalcopyrite crystal ordering and grain size are quantified using synchrotron-based hard X-ray grazing-incidence wide-angle X-ray scattering (GI-WAXS) and soft X-ray small-angle X-ray scattering (SAXS), respectively,[17,18] while crystallographic chalcopyrite phases, including secondary phases and ordered vacancy compounds, are analyzed using Raman spectroscopy.[14,41] The band gap grading structure is investigated by quantifying the composition using Auger electron spectroscopy (AES)[18,70] and dynamic secondary-ion mass spectroscopy (D-SIMS).[16,17] The electronic structure and energy levels of CIGS films are assessed using ultraviolet photoelectron spectroscopy (UPS), hard X-ray photoelectron spectroscopy (HAXPES), and inverse photoelectron spectroscopy (IPES) in order to appraise the charge carrier selectivity of a device.[31,32,42]

The electrical properties of a device, such as its surface potential, electron diffusion length, space charge region width, recombination properties, and defect energy levels, are also determined; these are affected by the composition, morphology, and band grading of the CIGS absorber layer. Variation in the surface potential in the grain interior and at the grain boundaries are analyzed using Kelvin probe force microscopy (KPFM), which enables the effect of the electronic grain boundary properties on grain boundary band bending and charge transport to be determined.[43–45] The electron diffusion length and space charge region, which are associated with charge photogeneration, are monitored using electron beam induced current (EBIC).[46,47] While the carrier lifetime, which is inversely correlated with the recombination rate, is calculated based on time-resolved photoluminescence (TRPL) measurements.[48,49] In addition, the change in the defect distribution and carrier concentration due to doping is estimated using capacitance-voltage (CV) and deep-level capacitance profiling (DLCP).[17]
while the defect energy level is determined using admittance spectroscopy (AS), deep level transient spectroscopy (DLTS), and photoluminescence (PL). In this manuscript, we have reviewed various characterization techniques related to morphology, crystallography, composition, energy level, and device electrical properties. A comprehensive understanding of the multifunctional and complex effects of their composition and morphology can be used to understand the device physics of chalcopyrite solar cells. Based on quantitative information, correlations between the morphology, structure, and electrical properties of a device can be determined, thus providing references to further improve the efficiency of solar cells and design criteria for the chalcopyrite absorber layer and solar-cell processing.

2. Characterization of Crystal Ordering, Morphology, and Composition

The morphology and bandgap grading structure of the absorber layer strongly affect the charge photogeneration of CIGS solar cells. Bandgap grading structure with a wide minimum notch region and mitigated notch depth lead to increasing light absorption efficiency and crystal ordering and large crystal grains are required to facilitate the movement of photogenerated electrons and holes within the chalcopyrite absorber layer. Therefore, precise characterizations of crystal ordering, morphology, composition, energy levels, grain boundaries, secondary phase and ordered vacancy compounds are important to understand CIGS devices. Those relevant technologies are reviewed in the next following sections.

2.1. Quantification of Crystal Ordering

Crystal ordering significantly affects charge carrier transport within thin-film solar cells. X-ray diffraction is generally used to observe the crystal structure. It is also possible to identify and image the plane direction of the grains in a polycrystalline material based on the diffraction patterns of backscattered electrons from an electron beam using electron backscatter diffraction (EBSD). GI-WAXS is a common technique used to explore the crystal ordering of samples in reciprocal space (i.e., Fourier space), providing information about the amount, size, and orientation of the crystals. The high flux of synchrotron radiation provides sufficient scattering to enable sophisticated experimental setups with complicated optical geometries. In general, the grazing angle (α) is larger than the critical angle so that the X-rays can penetrate the entire film to increase the scattering volume, with the scattering profile representing the crystal structure of the entire film. When incident X-ray waves (q_i) propagate through a film, a proportion is diffracted by the periodic planes of the species, and the wave vector of the scattered beam (q_f) is determined. The scattering q vector, representing the momentum transfer, is estimated using $q = q_f - q_i$. $q$ is orthogonal to the lattice plane, which is separated by distance $d = \frac{2\pi}{q}$. Scattering profiles normal and perpendicular to the sample plane are denoted as $q_z$ and $q_{xy}$, respectively, representing the crystal ordering in the out-of-plane and in-plane directions along the substrate plane, respectively.

When a specular pattern is obtained from a chalcopyrite thin film (Figure 2a), this represents a random crystal orientation. From the 2D patterns, a 1D profile can be derived (Figure 2b).

![Figure 2.](image-url) a) Schematic of a GI-WAXS experimental geometry. $q_i$ and $q_f$ denote the incident beam and scattered beam wave vector, respectively, while $\alpha$ is the grazing angle. b) Chalcopyrite (220) peak for centrally localized Ag-incorporated CIGS (C-ACIGS 0.05) and quenched Ag-incorporated CIGS (q-CA) samples. The dashed line indicates the shift in the peak. Reproduced with permission.© Copyright 2020, American Chemical Society. c) Degree of ordering variation in U-CIGS, BK-CIGS, and SK-CIGS films during chalcogenization with an increase in processing temperature. The inset presents a schematic of U-CIGS, BK-CIGS, and SK-CIGS films, indicating the position of the K-layer. Reproduced with permission.© Copyright 2020, Wiley-VCH.
By comparing the integrated peak area estimated by fitting the peak with a Lorentzian function, the degree of ordering can be derived,[57] as shown in Figure 2c.[57] Note that the coherence length \( L_{\text{CL}} \) can be estimated as \( L_{\text{CL}} = \frac{2\pi}{q_{\text{FWHM}}} \), and this is correlated with the crystal size.[57] The chalcopyrite (220) peak for centrally localized Ag-incorporated CIGS (C-ACIGS 0.05) and quenched Ag-incorporated CIGS (q-CA) films contains multiple subpeaks, indicating that the films contain crystals of various sizes from multiple chalcopyrite phases, which are changed during the phase transformation process (Figure 2b). The low and high \( q \) peaks represent In/Se- and Ga/S-rich phases, respectively. The incorporation of Ag leads to high \( q \) peaks, indicating a composition rich in Se. As another example, when a BK-CIGS film in which a K-doped layer has been incorporated into the bulk CIGS is compared with an unmodified U-CIGS and an SK-CIGS film in which the K-doped layer is positioned at the surface of the CIGS film (inset of Figure 2c), the BK-CIGS film has a larger degree of ordering than other two films, arising from the greater Se uptake and chalcogenization due to the K–Se affinity (Figure 2c). In addition, the increase in crystal ordering is due to the introduction of the foreign element, which enables early crystallization as a result of the lower melting temperature because K and Ag act as a fluxing agent.[57] Cu, In, and Ga diffuse through the fluxing agent to form nuclei, initiating early crystal growth. Also, the chalcogenization temperature and S/Se supply is adjusted to maximize the crystal ordering.[16]

2.2. Quantification of Domain Spacing

Because charge carrier recombination mainly occurs at the grain boundaries, the precise estimation of the grain size is important for assessing the percolation paths within a thin film. While hard X-ray SAXS employs the measurement geometry of a small angle at a distance from the incident X-ray,[54,55,57] soft X-ray SAXS utilizes low energies (~250 eV) with long wavelengths.[58–60] Given the definition of scattering vector \( q \), a small scattering vector is achieved using long wavelengths, enabling the use of a transmission geometry rather than the small-angle geometry of conventional SAXS (Figure 3a).[58–60] SAXS requires a high angular resolution, which can only be achieved using complicated optics and high collimation, leading to a significant loss of intensity, whereas soft X-ray SAXS can obtain a high contrast and scattering intensity from the transmission geometry. In addition, while scanning electron microscope (SEM) and scanning transmission electron microscopy (STEM) produce real-space images based on differences in the electron density (Figure 3b),[57] soft X-ray SAXS profiles are generated from the scattering contrast between the crystalline grains and air. The soft X-ray scattering profiles provide information about the spatial distribution of the correlated length scale (Figure 3c). Using the peak position \( q \), the domain spacing (i.e., the domain size) is estimated as \( 2\pi q \).[58–60] Because CIGS films have a multilength scale morphology consisting of an upper layer and bottom grains, the domain spacing is determined by comparing the quantified values for the reciprocal and real spaces. Similar to the crystal ordering in K-doped BK-CIGS films, incorporating an AM or foreign element is effective in facilitating chalcopyrite grain growth in CIGS films from an initial period of chalcogenization.[57] As such, BK-CIGS films show higher grain growth compared to U-CIGS and SK-CIGS films, as illustrated by real space SEM and STEM images (Figure 3b), which is also consistent with the quantified domain spacing in reciprocal space (Figure 3c). Synchrotron-based soft X-ray SAXS is thus a useful technique for quantifying domain spacing in reciprocal space.

2.3. Composition Distribution and Bandgap Estimation

In compound semiconductors, the bandgap and energy level vary depending on the element combination when forming the crystal phase, unlike the wafer-based silicon in which doping concentration is determined. Therefore, to check the elements distribution in the film is important because it determines the energy band structure. The composition ratio of elements in the thin-film is evaluated with inductively coupled plasma-atomic emission spectrometry (ICP-AES), X-ray fluorescence (XRF), and electron probe microanalysis (EPMA).[64] While the concentration distributions of the components according to the depth of the thin film is estimated using D-SIMS and AES profiles (Figure 4a–c).[39,13] Nondestructive methods such as Elastic recoil detection analysis (ERDA)[62,63] using elastic scattering of the incident ion beam or grazing-incidence X-ray fluorescence (GIXRF)[64] have also been employed to characterize elemental depth profiles. Although examples are not presented in this paper, glow discharge optical emission spectroscopy (GD-OES) is also widely used to obtain the depth profile of constituent elements due to its rapid measurement, low-vacuum conditions, and sufficiently high depth resolution with thick films. In addition, as another rapid depth profile analysis technique, laser-induced breakdown spectroscopy (LIBS), which separates a sample with a laser and analyzes elements through spectroscopy, has been reported.[64,65] For D-SIMS measurements, an ion beam is used to etch the film surface, and the ions that are produced are passed through a mass spectrometer to determine the concentration of the components. In AES, the atomic composition is estimated based on the orbital energy of the atoms originating from Auger electron emissions generated by the inter- and intrastate electron transitions from higher energy levels. As shown in Figure 4b,c,[33] atomic composition profiles are produced by dividing the D-SIMS or AES profiles by the relative sensitivity factor (RSF).[66] The RSF is determined by integrating the total ion intensity of the profile and dividing this by the atomic concentration obtained using atomic absorption spectrometry (AAS) and inductively coupled plasma-optical emission spectroscopy (ICP-OES). Ga/(Ga + In) and S/(S + Se) depth profiles are produced from the atomic concentrations and bandgap \( (E_g) \) depth profiles are calculated from the atomic ratio using Equation (1) (Figure 4d).[62]

\[
E_{\text{CuInGaSe}}^{\text{CuInGaSe}}(X,Y) = (1-Y)[(1-X)E_{\text{CuInGaSe}}^{\text{CuInGaSe}}(Y) + XE_{\text{CuInGaSe}}^{\text{GaS}}(Y)] - Y[XE_{\text{CuInGaSe}}^{\text{GaS}}(X) + XE_{\text{CuInGaSe}}^{\text{GaS}}(Y)] \tag{1}
\]

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where $X = \text{Ga/(Ga + In)}$, $Y = \text{S/(S + Se)}$, and $b$ is the optical bowing constant for the corrections. For CuInGaSe and CuInGaS, $b$ is 0.13 and 0.21, respectively.

In general, highly performing CIGS solar cells adopt a bandgap grading structure with the minimum bandgap region near the surface and an increasing bandgap toward both the top and bottom to maximize the open-circuit voltage ($V_{oc}$) and short-circuit current density ($J_{sc}$), respectively.\[67,68\] Recently, the bandgap grading structure has been further optimized with the use of a wide minimum bandgap region (notch region)\[63\] and a moderately steep gradient to the bottom (notch depth) to maximize light absorption and reduce the accumulation of charge carriers, respectively, thus increasing $J_{sc}$ without reducing $V_{oc}$. Variation in bandgap within a CIGS film is primarily governed by the atomic distribution, which is affected by the inclusion of AMs or other foreign elements,\[4,17,18,69\] the chalcogenization process,\[16,39\] and the applied Se pressure\[40\] or Ar pressure during chalcogenization.\[23,70\] In particular, in the solution process, the incorporation of AMs or Ag into the CIGS film allows Se to penetrate the film deeply during selenization, leading to a low $S/(S + Se)$ ratio, a wide notch region, and a modestly steep notch depth.\[17,18\] In addition, a CIGS film with a wide notch region and high Cu content can be achieved by adjusting the evaporation rate of Ga and In during Cu-rich phase formation.\[69\]
2.4. Atomic Concentrations at Grain Boundaries

The atomic concentration needs to be assessed to describe the mechanisms responsible for the morphology of chalcopyrite films. Atomic probe tomography (APT) can be used for 3D atomic scale compositional mapping. To disentangle the grain boundary effect, Colombara et al. reported an epitaxial CIGS film on a GaAs substrate followed by annealing with elemental Se and Na₂Se vapor (Se + Na₂Se), which was compared to an untreated CIGS/GaAs film. The region, close to the supply of Na and Se during PDT exhibited a higher Ga concentration, indicating that Na is diffused and accumulated in the Ga-rich area of the film due to the high affinity between Ga and Na. Magnified APT images show the atomic concentration near defects, spanning 10 nm (Figure 5a,b). The untreated film was enriched in In and Se and had lower levels of Cu near the defect, while the Na/Se-treated film had a higher Na concentration at the defect, while the Ga concentration may also be high (Figure 5a). When Na is introduced after the film growth, In, Na, and Ga, which takes the place of Cu, form a defect supercomplex and are stabilized enthalpically via electrostatic attraction. Therefore, Na facilitates In/Ga interdiffusion when the film is free from grain boundaries (Figure 5b,c). However, in a polycrystalline CIGS film, the high concentration of Na hampers the interdiffusion of In/Ga because Na occupies V_Cu defects. In addition, when either component is enriched beyond its solubility limit, clusters form, hindering In/Ga interdiffusion at the grain boundaries (Figure 5d). In addition to Na, AMs such as K, Rb, and Cs form the segregated secondary phase AM-In-Se at the grain boundaries, which passivates defects and reduces charge carrier recombination, thus enhancing charge carrier transport. Grain boundaries may function as barriers that impede the interdiffusion of elements but this may have a beneficial effect on the properties of the device.

2.5. Secondary Phase and Ordered Vacancy Compounds

It has been reported that the performance of CIGS solar cells is determined by the variation in the elemental composition for different chalcopyrite phases. When the CIGS phase is formed, Cu depletion layer is thermodynamically introduced on the surface. Cu-deficient CIGS forms an ordered vacancy compound (OVC) or ordered defect compound (ODC) phase, and has properties that can play positive effects in solar cell characteristics such as forming wider bandgap, hole blocking barrier, and buried p–n junction. Therefore, many studies have been reported on the formation of OVC near the surface of CIGS through process optimization and Cu concentration control. Furthermore, device efficiency is higher in Cu-poor conditions, under which a Cu-deficient OVC phase forms while the Cu₂₋ₓSe and Cu₂₋ₓS secondary phases are suppressed. Because Cu-rich secondary phases are highly conductive, shunt paths are established, reducing solar cell performance. However, when an OVC with a large bandgap forms on the CIGS surface, it functions as a buried homojunction and suppresses the recombination of holes. Although it is difficult to observe the positions of phases due to limitations of depth resolution.
of spectroscopy, these OVC and CIGS phases are effectively distinguished using Raman spectroscopy. A dominant CIGS A1 mode appears at around 170 cm$^{-1}$ and various compositional phases can be identified using other peak positions and Raman shifts.

Figure 6a presents the Raman spectra of CIGS solar cells measured at an excitation wavelength of 785 nm, which allows the highly sensitive detection of OVC secondary phases in the CIGS surface region in the absence of interference spectra from other layers, such as CdS. The peaks at 174 and 152 cm$^{-1}$ correspond to the A1 Raman peak of CIGS and the Cu-poor OVC phase, respectively. The spectral regions at 212–228 cm$^{-1}$ represent different ordering of the OVC phases. In particular, the peak at 228 cm$^{-1}$ is associated with the OVC secondary phase in the surface region of the CIGS absorber layer, and this increases with a decrease in the Cu/(Ga + In) ratio.

To investigate the effect of the presence of the OVC phase on solar cell performance, the relative intensity of the OVC peak (228 cm$^{-1}$) to the main CIGS peak (174 cm$^{-1}$) is calculated and compared with the $V_{oc}$ and efficiency. As shown in Figure 6b, the optimal range of the relative OVC spectral contribution in the CIGS surface region is observed because the downshift of the valence band maximum due to the optimal OVC functions as a hole barrier. A further increase in the OVC leads to a Cu deficiency and resulting Ga$_2$Cu$_2$O$_4$ defects, which function as an electron trap, thus lowering $V_{oc}$. Raman spectroscopy analysis provides a qualitative or quantitative analysis of crystal phases. These results are associated with the properties of solar cells.

### 2.6. Surface Chemistry and Energy Band Bending

Because the CIGS and CdS layers form a heterogeneous p–n junction, the composition distribution and energy band structure near the interface significantly affect the photovoltaic properties of solar cells. In particular, the composition distribution at the CIGS surface is an important factor that determines the surface recombination properties of CIGS solar cells. As previously discussed, the surface properties of CIGS solar cells can be tuned by introducing an alkali element to the CIGS surface, and it is important to evaluate the surface composition and energy band structure of the CIGS surface and the resulting effects on the electrical properties.

The change of the CIGS surface by PDT can be intuitively evaluated by observing the annular dark-field (ADF) image of STEM and comparing with energy dispersive spectroscopy (EDS) result. Furthermore, X-ray photoelectron spectroscopy (XPS) is employed to identify the chemical and electronic structure of both the surface and depth profiles of CIGS films, which is made possible by etching the film in a vertical direction. The escape depth of the electrons generated by the photoelectric effect is relatively small, contributing to an increase in the surface sensitivity of this measurement approach. Chirila et al. observed variation in the surface and bulk composition using XPS when NaF and KF were added via PDT to CIGS films. When Na and K were introduced to the surface of the CIGS film, Cu depletion occurred at the surface to a greater extent for KF-PDT than for NaF-PDT. This Cu deficiency via KF-PDT alters the p–n junction characteristics on the surface.
and facilitates ion exchange with Cd during the CdS deposition process, leading to the formation of a thin CdS buffer layer. Therefore, the current generation increases due to the higher light absorption arising from the reduced parasitic absorption. In addition, secondary phase formation on the CIGS surface via alkali-PDT, which modifies the interface by functioning as a passivation layer, was identified using XPS measurements.[32,82]

The energy band of the CIGS surface is assessed by evaluating the photoelectronic kinetic energy.[31,32,42,45] Figure 7a,b display the valence band maximum (VBM) and conduction band minimum (CBM) of NaF-PDT and NaF/KF-PDT CIGS films, respectively.[31] The VBM is estimated via synchrotron-based HAXPES and UPS by analyzing the kinetic energy of photoelectrons emitted from samples during X-ray and ultraviolet irradiation, respectively. The CBM is estimated using IPES, in which injected low-energy electrons couple with high-lying unoccupied energy levels and decay to low-lying unoccupied energy levels, emitting photons (Figure 7b). By injecting high energy, the inelastic mean free path (IMFP) of the emitted electrons increases, and it is possible to monitor the electrical information for the near-surface bulk state. The valence band spectra feature delocalized bands arising from the strong hybridization of electrons in the NaF and NaF/KF-PDT samples. A lower incident photon energy (a lower IMFP) leads to a lower VBM from the Fermi level, which indicates that VBM shifts down towards the surface. Introducing K also alters the chemical and electronic structure. In particular, when NaF/KF-PDT is employed, the VBM is lower than the position of the NaF-PDT CIGS film (Figure 7c). On the other hand, the CBM of NaF/KF-PDT CIGS films slightly increases compared to the energy band of NaF-PDT CIGS films. These changes are caused by Cu and Ga depletion in the surface region of the NaF/KF PDT CIGS films. This wider bandgap at the surface of the NaF/KF-PDT CIGS films acts as a passivation layer, blocking hole injection into the n-type CdS layer, reducing interface recombination.

3. Characterization of the Electrical Properties of A Device

Tuning morphology and bandgap primarily determine the CIGS solar cell performances. Also, the doping concentration affects the junction depletion width and bulk saturation current, while the bulk lifetime determines the carrier diffusion length, which affects $J_{sc}$ and $V_{oc}$. In addition, surface, interface, and bulk recombination increase the leakage current of the device, thus reducing $V_{oc}$. Therefore, a precise understanding of the electrical characteristics of a device is crucial to completely understand CIGS solar cell and boost solar cell performances. In this section, we review characterization techniques for the electrical properties of a device, such as charge carrier collection, carrier lifetime, surface potential, defect distribution and energy level, and device recombination pathways.

3.1. Estimation of the Charge Carrier Collection Efficiency

In solar cell devices, photogenerated carriers in the absorber need to be efficiently collected by the electric field of the space charge region (SCR), contributing to $J_{sc}$. The collection probability is limited by the diffusion length and surface recombination, which is reflected in the quantum efficiency (QE). By measuring the voltage-bias-dependent QE, the bulk recombination properties can also be evaluated for various depletion widths.[83] In addition, 2D maps of the spatial charge carrier collection efficiency can be produced using EBIC measurements,[17,18,46,47,84,85] in which the electron beam from SEM

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**Figure 6.** a) Raman spectra of CIGS films with different Cu/(Ga + In) ratios (0.86, 0.94, and 0.97). b) $V_{oc}$ and efficiency in accordance with the relative intensity of the OVC Raman peak compared to the main CIGS Raman peak, measured at an excitation wavelength of 785 nm. Reproduced with permission.[41] Copyright 2014, AIP Publishing.
generates excited charge carriers, contributing to the measured current. Meanwhile, through cathodoluminescence (CL), to analyze the recombination kinetics by collecting the emission image from the CIGS using the electron beam of the SEM is also possible.[85]

In a previous study, Cd-free and Cs-treated CIGS solar cells were prepared and aged for 1 week, 2 months, and 10 months.[47] The EBIC image contrast was used to represent the level of current generation, and EBIC profiles for the measured current were derived from line scans. The 10 month CIGS solar cells exhibited improved photocurrent generation because the greater surface oxidation led to the formation of $\text{In}_x(\text{O},\text{S})_y$ near the surface, which functioned as a hole barrier and pushed the electrical junction away from the defective CIGS/interlayer interface (Figure 8).[47] A high EBIC was observed in the upper region of the CIGS layer, where the charge collection function ($f_c$) was derived by deconvoluting the lateral generation function of the electrons using the following equation[86]

$$f_c(x) = \frac{1}{L_e} \cosh \left( \frac{x - x_c}{L_e} \right) - \frac{S_c}{D_e} \sinh \left( \frac{x - x_c}{L_e} \right)$$

where $S_c$ is the recombination velocity at the back contact, $D_e$ is the electron diffusion coefficient, and $x_{\text{SCR}}$ and $x_c$ are the positions of the edge of the SCR and semiconductor-metal contact, respectively. In the SCR, the charge collection probability approached 1 because the charge carriers were swept by the electrical field. The width of the SCR ($W_{\text{SCR}}$) and the electron diffusion length ($L_e$) were estimated by fitting Equation (2). The
charge collection length was obtained by adding $W_{\text{SCR}}$ and $L_e$. In the CIGS absorber layer, minority charge carriers were generated and these were either recombined or collected. $W_{\text{SCR}}$ and $L_e$ offer a quantitative measure of the photocurrent-generating region in p–n junctions.

### 3.2. Carrier Lifetime

To achieve a high-efficiency solar cell, it is crucial to employ a high-quality absorber material with a long carrier lifetime. The photocurrent decreases due to the recombination of charge carriers, and photovoltage decreases due to a reduction in Fermi-level splitting due to leakage current.[87,88] Through PL measurement, evaluating the recombination characteristics by calculating the quantum yield in the high energy spectrum and deriving the quasi-Fermi level splitting (QFLS) value which corresponds to the upper limit of the device $V_{\text{oc}}$ has also been reported.[89,90] Photogenerated carriers should not be recombined until they are collected at the electrode. Because their lifetime is inversely proportional to the charge carrier recombination rate,[91] accurately estimating the lifetime is important in understanding device physics and in the design of solar cell devices with reduced charge carrier recombination. The lifetime of the carriers in a semiconductor device can be evaluated by measuring the time-dependent variation in electrical (e.g., photocurrent or $V_{\text{oc}}$) and optical (e.g., PL or absorption) signals. Similarly, recombination kinetics has been observed using transient $V_{\text{oc}}$ under different wavelength light irradiation conditions.[92,93] Because silicon solar cells have a relatively long bulk lifetime, the effective lifetime is determined by directly measuring the excess minority carrier density in accordance with the light intensity, which is estimated by measuring the change in photoconductance using quasi-steady-state photoconductance (QSSPC) and microwave photoconductivity decay ($\mu$-PCD).[94–96]

In contrast, for thin-film devices, including CIGS solar cells, that have a relatively short lifetime, TRPL is a widespread technique used to measure the carrier lifetime.[29,48,49,80,97] After switching the incident light off, the effective carrier lifetime is established by tracking the time-dependent transient decay of PL. In many cases, time-dependent PL decay is determined based on time-correlated single-photon counting (TCSPC). When pulsed laser light is incident to a light-absorbing material, the time between irradiation and detection is measured and the luminescent photons emitted by the recombination of photogenerated carriers are counted. Decay curves are derived by tracking the number of single photons according to the time difference between the incident light and the measured luminescence signal. If band-to-tail recombination originating from local deviations in the distribution of donor and acceptor states or other forms of nonradiative recombination mediated by deep-trap states dominates band-to-band recombination,[98] the measured photon signal will exist for a time that is shorter than the ideal case. The PL intensity is related to the number of remaining excess carriers ($\Delta n$), which is based on the diffusion equation for minority carriers, a time-dependent parameter mediated by the carrier lifetime.[91] A solution for $\Delta n$ can be simplified into an exponential decay form based on the minority carrier diffusion equation and the carrier lifetime is calculated via curve fitting with a double exponential function.[48]

Using TRPL measurements, various electrical properties related to the carrier lifetime, such as the bulk lifetime of the absorber material, surface passivation properties, and the selective carrier-collection ability of the carrier-transporting layer, are evaluated based on the incident laser wavelength and the device structure. Figure 9a shows an example of minority carrier lifetime measurements using TRPL with a pulsed laser at a wavelength of 638 nm.[99] TRPL signals for postselemination-treated CIGS films at different temperatures are measured. The decay characteristics for the PL intensity are presented in Figure 9a, and the minority carrier lifetime for each sample.

![Figure 8. Cross-sectional EBIC images and EBIC profiles (inset) of CIGS solar cells with Cs-treated CIGS absorber layers aged for a) 1 week, b) 2 months, or c) 10 months. The dashed white lines show the Mo/CIGS interface and CIGS surface and the red lines indicate the scanning area. Reproduced with permission.[47] Copyright 2019, Wiley-VCH.](image-url)
is derived from the curves. The results indicate that postsele-
nization treatment at higher temperatures produces a longer
lifetime. Steady-state PL measurements also show that the PL
intensity is higher for CIGS films fabricated at higher seleni-
zation temperatures (Figure 9b). A short lifetime and low car-
rier density arise from the continuous photoactive transition
band and the band-to-band transition generated by the defect
energy states of the CIGS components within the bandgap
and resulting nonradiative recombination. The lifetime and
PL intensity are improved by passivating the defects through
the supply of additional Se during 400 °C postselenization

Other distinctive techniques for monitoring carrier dynamics
are terahertz probe spectroscopy (TPS)\([100\text{--}103]\) and transient
absorption spectroscopy (TAS).\([104]\) Both techniques detect
changes in the optical properties due to photoexcited carriers.
Chang et al. recently used TAS to elucidate the carrier dynamics
in CIGS solar cells with a graded bandgap using varying exci-
tation energies.\([104]\) They found that the region near the back
contact, which has a high gallium ratio, is a major recombina-
tion region, thus restricting carrier diffusion from the bulk to
the junction. As with TRPL, TPS utilizes a pulsed laser that is
injected into the sample, with photogenerated carriers detected
using a terahertz probe beam. The carriers are generated by
the incident light, and the terahertz probe beam is transmitted
through the sample, leading to changes in absorption according
to the photoexcited carrier density. Changes in the photocon-
ductivity due to additional carriers in the film lead to changes
in the refractive index of the sample, which influences the elec-
tromagnetic field of the terahertz beam. Therefore, the change
in the transmittance of the terahertz probe beam can be used
to indicate the photoconductivity and excess carrier density.\([103]\)

The carrier dynamics of the absorber layer are examined by
tracing the difference in the transmittance compared to the
ground state (\(-\Delta T/T\)) according to the time delay between exci-
tation via the optical pump and the transferred terahertz pulse
(i.e., the pump–probe delay). The carrier lifetime is evaluated
by observing the change in the transmittance of the terahertz
beam, reflecting the decay curve of photogenerated carrier
relaxation over time. The carrier dynamics near the surface and
in the bulk can be analyzed by employing different wavelengths
for the pump beam, which leads to different penetration depths
in the absorber layer.\([101,102]\)

Ballabio et al. recently demonstrated differences in surface
passivation according to the Ga composition at the CdS/CIGS
interface using an optical pump–TPS.\([103]\) Figure 9c–e presents
the normalized differential transmittance of the terahertz probe
for CIGS films with different levels of Ga as a function of the
delay time. All of the graphs exhibit a biexponential decay curve,
with decay time constants obtained from exponential curve fit-
ting. A laser with a wavelength of 800 nm was employed for
excitation, and the penetration depth was adjusted to observe
the dynamics of the photogenerated carriers at the absorber
layer. The results for the air/CIGS interface revealed that the
recombination kinetics were faster as the Ga content increased.
This indicates that bulk recombination in CIGS films is
enhanced when the Ga content is increased. In addition, unlike
the decay curve for the low-Ga film, the recombination kinetics
were only slightly affected by the presence of ZnO and CdS
layers at high Ga levels above a 1.2 eV bandgap. Therefore, the
surface passivation effect of the CdS buffer layer appears to
be negligible in high-Ga CIGS films. TPS is a useful analysis

**Figure 9.** a) TRPL signals for CIGS films with different forms of postselenization treatment. b) Steady-state PL spectra of pristine and postselenization
CIGS films at 300 and 400 °C. Reproduced with permission.\([99]\) Copyright 2016, Elsevier. Normalized optical pump–TPS dynamics with a pump–probe
delay time for CuIn\(_1\)–\(x\)Ga\(_x\)Se\(_2\) samples with a relative Ga content of c) \(x = 0.3\), d) \(x = 0.5\), and e) \(x = 0.7\). Adapted with permission.\([103]\) Copyright 2019,
Wiley-VCH.

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and carrier lifetime using high-frequency and long-wavelength beams.

### 3.3. Bulk Doping and Defect Concentration

The doping concentration (i.e., the carrier concentration) of the absorber layer in a semiconductor junction is important because it affects the built-in potential, space charge region width, and recombination rate. In the case of silicon, because the dopants are specified and most are already activated, the doping concentration is estimated based on the atomic concentration derived from SIMS measurements. However, due to the presence of various shallow charged energy states in the compound semiconductor, measuring the atomic concentration cannot precisely represent the doping density. A typical method for evaluating the doping density in a compound semiconductor is CV measurement.\[^{[4,42,46,105,106]}\] The charge density at the edge of the depletion region is expressed as\[^{[105]}\]

$$N(W) = \frac{2}{q\varepsilon A^2} \left[ \frac{d(1/C^2)}{dV} \right]^{-1}$$

where $W$ is the depletion region width, $A$ is the area of the device, and $\varepsilon$ is the permittivity. By monitoring the charge density in accordance with the depletion width at a given DC bias, a depth profile for the charge density can be obtained. In addition to the use of CV, the carrier density can be acquired using DLCP.\[^{[33,46,73,106,107]}\] Unlike CV measurements, changes in the amplitude of AC voltage are used.\[^{[105]}\] The deep charged defect states above or below the Fermi level respond differently at different AC biases depending on the type of the semiconductor, and the measured capacitance has nonlinear dependence on the change in voltage.\[^{[102]}\]

$$C = C_0 + C_1dV + C_2(dV)^2 + \cdots$$

where $C_0$ is determined by the polynomial fitting of $C$ and $dV$. The maximum applied voltage, $V = V_{xc} + V_{dc}$, remains constant by adjusting the DC bias in accordance with the variation in the AC bias, thus the depletion edge ($x_e$) is fixed. The drive-level charge density for a p-type semiconductor ($N_{DL}$), which includes both the carrier density and the defect density, is obtained from

$$N_{DL} = -\frac{C_0}{2q\varepsilon A^2 C_1} = p + \int_{E_0}^{E_F} g(E, x_e) dE$$

where, $E_F$ is the Fermi energy in the bulk, $E_e$ is the emission energy from the defect state, and $g(E, x_e)$ is the density of states near location $x_e$. By applying the estimated $C_0$, the defect density can be derived and, by changing the DC bias, a depth profile for the charge density can be obtained. The response of the defect states is controlled by adjusting the temperature and frequency. Because the CV reflects the response of both free carriers and charged trap states, it is less accurate for materials with a high density of defects. The charge density derived from DLCP is less affected by the interface states in comparison to CV characterization using the dynamic AC response. Indeed, the CV method produces a larger charge density than does DLCP at both high and low frequencies (Figure 10). From the results shown in Figure 10a,\[^{[107]}\] the contribution of the density of interface states (5.6E14 cm$^{-3}$) is derived by subtracting the DLCP defect density from the CV defect density. In addition, the free carrier concentration (3.2E14 cm$^{-3}$) can be obtained from the DLCP defect density at a high frequency. Similar result is shown in Figure 10b.\[^{[106]}\] Charge carrier density from C–V method provides two times larger in the absorber layer than DLCP at both high and low-frequency sides. Also, low-frequency side measurement exhibits larger charge carrier density since it is lower than the emission rate, where the traps respond to the ac bias. The CV and DLCP measurements are suitable for defect analysis, enabling the in-depth investigation of defect distributions in solar cells.

### 3.4. Defect Distribution and Defect Energy Level

To improve the carrier lifetime and increase the diffusion length, the precise evaluation of defects, which act as the recombination center in the absorbing material, is important. CIGS film consists of inorganic crystal phases that vary in their composition. When element vacancies (e.g., Cu and Se) form due to a lack of these elements and substitution with other
elements, defects with different energy levels are generated and carrier recombination occurs. Aggregated secondary phases which are out of the stoichiometry also function as defects. Because recombination occurs at the grain boundaries due to unbounded dangling bonds, it is important to (1) evaluate the energy level of the defects and (2) provide a quantitative estimation of the defects density. First, PL is used to observe the defect energy level within the forbidden bandgap of the absorbing material. The energy level associated with deep traps can be distinguished from the main PL peak, which represents the bandgap of the CIGS film.[29,33,49,99,108,109]

Figure 11 shows PL spectra of CIGS films under various PDT conditions.[29] P1 and P2 indicate near band edge emissions and shallow defect transitions, respectively. When the sample is annealed in a vacuum without PDT, a change in the PL peak is not observed. However, after NaF or KF-PDT, two additional PL peaks are observed at a lower photon energy position. By comparing this with the defect energy states reported in literature,[110–112] it can be concluded that the EP1 transition may be related to the oxidation of the CIGS film, which is promoted more by the addition of K than of Na, while the EP2 transition is caused by K-induced deep defects. In Figure 11b, when only NaF-PDT is employed, the EP1 and EP2 transition peaks are not clearly observed. It can be assumed that there is an increase in the number of oxidation-mediated and K-induced defects with higher levels of K. K significantly reduces the number of V_{Se} donor defects but, because K atoms are larger than Na atoms, K is less likely to occupy Cu sites, thus In_{Cu} donor defects are not eliminated. In addition, the main P1 peak decreases and the EP2 peak increases as the PDT temperature increases, indicating that solar cell performance is weakened by deep defects. This compositional analysis suggests that Na and K have a complementary relationship, while the optimal solar cell characteristics were obtained using PDT at 250 °C, where passivation is appropriately tuned. Based on this analysis, PL represents the defect level of CIGS thin films.

Defect distributions within the bandgap can also be analyzed using electrical measurements such as AS and DLTS.[86,113–115] Both techniques detect the change in capacitance due to the trapping (i.e., capture) or de-trapping (i.e., emission) of carriers at different trap-energy levels. AS measures capacitance as a function of frequency and temperature, while DLTS measures the transient change in the capacitance induced by a pulsed voltage signal. By employing AS or DLTS, electrical parameters such as the activation energy, defect energy level, capture cross-section, and defect density can be evaluated. In AS, a step-like change in capacitance is observed when measuring the capacitance frequency from low to high capacitance. Generally, measurements are performed at zero DC bias but, to analyze recombination at the near interface, bias-dependent AS measurements are also taken by adjusting the junction depth.[116,117] At a low AC frequency, the measurement process can contribute to the capacitance, with the additional capacitance from the carriers added to the device capacitance from the depletion region, while at high frequencies, the measurement process does not contribute to the change in capacitance due to limitations of dielectric relaxation, in which the carriers are trapped in deep level energy states. Based on the relationship between capacitance and frequency, the defect distribution according to the energy level at a given temperature can be derived. The defect distribution function is expressed as follows[113]

\[
N_i(E_a) = \frac{U_d}{q \omega} \frac{dC}{d\omega} kT
\]

(6)

where \(U_d\) and \(\omega\) are the built-in potential and the depletion width, respectively. In addition, because the capture and emission rates are temperature-dependent, the measured capacitance increases with higher temperatures. The frequency at which the maximum rate of change in capacitance is observed is defined as the inflection angular frequency (\(\omega_0\)), which is related to the emission rate as follows[114]

\[
\omega_0 = 2\xi_0 T^{-1} \exp\left(\frac{E_a}{kT}\right)
\]

(7)

where \(\xi_0\) is a constant related to emissions, \(k\) is the Boltzmann constant, and \(E_a\) is the activation energy related to the deviation of the trap energy level from the conduction or valence band. Using an Arrhenius relation between \(\omega_0\) and \(T\), \(E_a\), \(\xi_0\), and the capture cross-section can be extracted.

Figure 12 presents the use of AS measurements to analyze flexible CIGS solar cells fabricated under different deposition conditions.[119] Flexible CIGS solar cells on a polyimide substrate
were prepared using different duration times and temperatures in a three-state coevaporation process. Briefly, the deposition temperature increased from WC492 to WC497, where the evaporated elements, duration time, and substrate temperature for each stage were finely tuned. Based on these results, inflection points were obtained. The defect levels were calculated from the Arrhenius plot of the inflection frequency, and the defect density was derived from the AS spectra. As shown in Figure 12a, two types of defect level, referred to as shallow (N1) and deep defects (N2), were observed for all samples. As the process temperature increased (WC497, Figure 12b, both defect levels moved to shallower energy level and the density of the defects, especially the deep defects, decreased, which may increase $V_{oc}$. The defect levels for WC497 were comparable with those for previously reported high-efficiency flexible solar cells, which is consistent with the increasing efficiency. In summary, AS measurements are useful for characterizing defects in solar cells.

DLTS measures the transient change in capacitance over time by applying a pulsed bias over a range of temperatures. Depending on the measurement purpose, an optical source can be employed instead of bias. Nanoscale defect level mapping has also been reported in combination with a scanning probe microscope (SPM) based on the transient emission characteristics of traps. As with AS, this is based on the capture and emission of carriers by trap states; however, the measurements for detecting trapped carriers differ. At the beginning of the DLTS process, a reverse DC bias is applied to the device to create a fully depleted capacitive region where only the junction capacitance is measured. A pulsed bias is then applied to measure the change in capacitance over time. When the pulsed bias is applied, the width of the depletion region is reduced and then recovers due to the rapid relaxation time of the free carriers, but the carriers in the trap energy state remained trapped. Transient changes in capacitance occur due to the relaxation of trapped carriers, and thermal emission occurs over time, leading to a return to the original capacitance. As previously discussed, the emission rate is a temperature-dependent function, and defect energy levels can be derived by evaluating the change in capacitance over a range of temperatures. In addition, DLTS can distinguish between majority and minority carrier traps by observing whether the change in capacitance is negative or positive when tuning the initial DC bias. The analysis process for DLTS has been summarized in past studies. The DLTS signal is derived from the change in capacitance at times $t_1$ and $t_2$ in the transient capacitance curve for each temperature: $S(T) = [C(t_1) - C(t_2)]/\Delta C(0)$. Because charge relaxation in trap states occurs with exponential decay after the bias is removed, the maximum time constant is calculated from $t_1$ and $t_2$

$$\tau_{max} = (t_1 - t_2) \frac{\ln(t_1/t_2)}{\ln(t_1/t_2)}$$

$$\tau_{max} = \frac{\epsilon}{K_{th}} \frac{n_{e} N_{a} e}{kT} \exp\left(\frac{E_a}{kT}\right)$$

Figure 12. Admittance spectroscopy results for CIGS solar cells produced under different processing conditions of a) WC492 and b) WC497. Reproduced with permission. Copyright 2018, Wiley-VCH. The left, middle, and right columns show capacitance–frequency–temperature curves, the Arrhenius plots for calculating the defect levels, and the defect density of states for four different deposition conditions, respectively.
where $\sigma$ is the capture cross-section, $v_{th}$ is the thermal velocity, $E_a$ is the activation energy, and $C$ is a constant. $E_a$ is calculated using the Arrhenius plot of $\tau_{max} \cdot T^2$ or $e/\tau T$ over $1/T$ for various $t_1$ and $t_2$. The trap density is calculated from the change in capacitance ($\Delta C$) compared to the initial capacitance ($C_0$)

$$N = 2 \frac{\Delta C}{C_0} N_a$$

where $N_a$ is the net acceptor concentration.

Figure 13 presents an application of DLTS to analyze the defect level in a CIGS absorber and device,[125] Figure 13a,b shows the DLTS spectra for CIGS/Al Schottky junctions and CIGS/CdS/ZnO:B heterojunctions, respectively. DLTS spectra were obtained from the difference in capacitance over time for different temperatures. Defects in the bulk and interface were distinguished using DLTS analysis of the Schottky junction and heterojunction structures according to the absence and presence of a buffer, respectively. The positive (peaks A and C) and negative (peaks B, D, and E) peaks represent minority-carrier electron traps and majority-carrier hole traps, respectively. Using the DLTS signal, the activation energy for each defect state was derived (Figure 13c). A similar deep majority carrier trap level (peaks B and D) of 440 meV was observed regardless of the presence of the buffer layer, which originated from the CIGS bulk. The shallow donor levels of about 70 meV at the Schottky junction and 8.4 meV at the heterojunction were suspected to be caused by InCu and CdCu, respectively.

In addition to the deep trap states, it is also important to take into account the effect of band tail states to reduce $V_{oc}$ loss in the energy band. Because many thin films, including CIGS films, do not have perfect crystal ordering and have nonuniform fluctuations in the energy band, a broad absorption tail below the band edge is present. If the number of tail states or the energy level of the tail states from the band edge increase, band-to-tail recombination occurs and the $V_{oc}$ of the device decreases. The band tails are characterized by the Urbach energy ($E_U$) which indicates the level of sharpness of the absorption near the band edge. $E_U$ can be derived from various optical measurements, including the external or internal QE (EQE or IQE, respectively), absorption spectra, absorption coefficient, transient photocapacitance, and PL.[17,69,126–129] Figure 14 shows the $E_U$ calculated from the EQE spectra of CIGS samples for different substrate growth temperatures.[129] $E_U$ was calculated from the slope of $\ln(\text{EQE})$ as a function of the photon energy along the long-wavelength edge (Figure 14a). Various CIGS samples with different substrates, gallium ratios, and substrate temperatures were analyzed, and the correlation between $E_U$ and the $V_{oc,def}$ (Voc,def) was derived (Figure 14b). As $E_U$ decreased, $V_{oc,def}$ also fell regardless of the processing conditions. This suggests that $V_{oc}$ is related to the band tail states and that $E_U$ is an indicator of the photovoltaic performance of solar cells.

3.5. Surface Electrical Properties in the Grain Interior and at the Grain Boundaries

Because CIGS is polycrystalline material, it contains grain boundaries, with the surface electrical properties differing between grains. In addition, as mentioned above, the electrical properties at the surface, especially near the grain boundaries, affect the performance of solar cells; therefore, various surface treatments such as postsulfurization or PDT are employed. To observe the electrical properties of the CIGS surface, SPM is
utilized to determine a localized nanometer scales image of the surface. First, KPFM can be used to measure differences in the surface contact potential via atomic force microscopy (AFM). If the sample and the conductive tip are in electrical contact, the Fermi levels of the two materials align and KPFM detect the difference in potential. Surface electrical properties such as potential barriers at the grain boundaries or the work function can be evaluated using KPFM.\cite{43–45,52} \textbf{Figure 15a,b} presents an example of KPFM being used to evaluate the effect of PDT on the grain boundaries at the CIGS surface.\cite{45} The surface topography acquired from AFM, including the grain boundaries, is presented in Figure 15a. Based on the image of the contact potential difference shown in Figure 15b, the potential variation at the grain boundaries was analyzed (Figure 15c). The topography and difference in the contact potential were used to distinguish the grain interior from the grain boundaries, and it was found that a potential difference exists at the grain boundaries. Statistically evaluated data from different alkali-treated samples are plotted in Figure 15d. Positive potential variation at the grain boundaries was observed for the RbF- and CsF-treated samples but, for the KF-PDT samples, negative potential variation was observed. Positive or negative potential variation at the grain boundaries indicates a barrier for minority (i.e., electrons) or majority (i.e., holes) carriers, respectively. Downward band bending with KF-PDT promoted carrier recombination at the grain boundaries, which reduced AM accumulation at the grain boundaries, forming alkali-In-Se compounds and reducing the charged defects at the grain boundaries, thus improving solar cell performance, which is supported by other research.\cite{44} KPFM is a useful technique for the direct observation of potential variation at the surface or for the cross-section of devices with various polycrystalline materials, including CIGS.

Next, current imaging tunneling spectroscopy (CITS) can be used to evaluate the local surface defect density by measuring the tunneling current (\(I(U)\)) as a function of the applied bias (\(U\)) between a metallic tip and the CIGS surface via scanning tunneling microscopy (STM). Since the differential conductivity (\(dI/dU\)) is approximately proportional to the local density of states, it is possible to relatively compare the

device performance, especially \(V_{oc}\). Heavy alkali PDT led to carrier recombination at the grain boundaries, which reduced AM accumulation at the grain boundaries, forming alkali-In-Se compounds and reducing the charged defects at the grain boundaries, thus improving solar cell performance, which is supported by other research.\cite{44} KPFM is a useful technique for the direct observation of potential variation at the surface or for the cross-section of devices with various polycrystalline materials, including CIGS.

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local defect density on the sample surface, based on the \(dI/dU\) mapping obtained by converting the image of CITS at a given applied potential within the bandgap. In other words, the higher the tunneling current at a given voltage, the more energy states associated with the defect in the forbidden energy bandgap.\cite{110,111} \textbf{Figure 15e} shows the SEM image of the CIGS surface, STM topography, and corresponding \(dI/dU\)-CITS mapping image.\cite{112} The CITS image was extracted at a bias voltage of 0V. The CITS map shows that the basalt-like long columns are brighter compared to the nanofacets, which means that the basalt-like columns exhibit higher differential conductance and are more defective. The surfaces of Cu-poor CIGS are constructed with polar planes which are defective and prone to oxidation and nonpolar planes which have passivated surfaces without surface dipoles. Therefore, by comparing the crystallography analysis with the CITS result, it was confirmed that polar planes correspond to basalt-like columns and nonpolar planes correspond to nanofacets, respectively.

### 3.6. Dominant Device Recombination Pathway Analysis

Understanding charge carrier recombination pathways is important when interpreting the physics of solar cells. The charge carrier recombination properties of solar cells are obtained by measuring current–voltage characteristics and calculating the saturation current and the ideality factor. However, these are not effective for identifying the spatial distribution of recombination in solar cells. In addition, temperature-dependent current–voltage (IVT) measurements are widely used to evaluate the recombination properties of a device.\cite{111,15,16,18,19,39,42,132,133}

The standard diode equation is expressed as

\[
J = J_0 \left[ \exp \left( \frac{qV}{AKT} \right) - 1 \right] \tag{11}
\]

In a heterojunction device, the saturation current \(J_0\) for the various recombination pathways is defined as

\[
J_0 = J_0 \exp \left( \frac{-E_x}{AKT} \right) \tag{12}
\]
where $J_0$ is a weakly temperature-dependent prefactor, $E_a$ is the activation energy for the recombination, and $A$ is the ideality factor. $E_a$ is determined by an Arrhenius plot of $A \ln(J_0)$ or $A \ln(J_0/J_0)$ and $1/T$. In addition, under solar cell operating conditions, $V_{oc}$ is expressed as

$$
V_{oc} = \frac{E_a}{q} \ln \left( \frac{J_0}{J_{sc}} \right)
$$

Figure 16 presents the experimental determination of $E_a$ based on temperature-dependent current–voltage measurements. $E_a$ was derived from the activation energy of $J_0$ and $A$ for different PDT and CdS layer thicknesses, with the bandgap of the absorber about 1.2 eV (Figure 16a). $E_a$ was similar to the bandgap for the other samples; however, the $E_a$ of the NaF-PDT and thin CdS samples was lower than the bandgap because interface recombination was dominant. Based on these results, interface recombination can be reduced in thin CdS films using KF-PDT by reducing the hole concentration of CIGS near the interface. $V_{oc}$ at 0 K was then obtained by extrapolating the $V_{oc}$–temperature data for samples with or without KF-PDT, with the bandgap of the absorber being about 1.15 eV (Figure 16b). The $V_{oc}$ at 0 K was estimated to be 1.09 and 1.14 eV for the samples without and with KF-PDT, respectively. Similar to the previous results, the $V_{oc}$ (0 K) without KF-PDT was lower than the bandgap, which can be explained by dominant interface recombination. It is suspected that the diffusion of Cd into the absorber, enhanced by K, improves the quality of the p–n junction.
measurements are thus an effective approach to determine the dominant recombination pathway. In addition, abnormal charge transport can be explored using this method. A rollover in the current–voltage curve can be observed with a decrease in temperature due to restricted carrier injection at the front or rear side arising from interface recombination, an energy band offset, or carrier injection Schottky energy barriers.\[134,135\]

By measuring the dependence of $V_{oc}$ on light intensity and temperature ($V_{oc}$–GT), the spatial distribution of recombination at the interface, in the SCR, and in the quasineutral region (QNR) can also be derived.\[78,87,136,137\] Shockley–Read–Hall (SRH) recombination depends on the local charge carrier concentration and defect characteristics. SRH recombination occurs at the interface and in the SCR (i.e., the depletion region) and the QNR (i.e., the bulk), and the recombination rates are represented as $R_i$, $R_d$, and $R_b$, respectively (Figure 17a,b). Because recombination rates are exponentially dependent on the voltage ($V$) and the total recombination generation rate in the absorber layer thickness ($W$) at $V_{oc}$ is affected by $R_i$, $R_d$, and $R_b$, $V_{oc}$ as a function of light intensity ($G$) can be derived as\[78,136,137\]

$$V_{oc} = \frac{2kT}{q} \ln \left[ \frac{1}{2} \frac{R_i}{R_d + R_b} \left( \frac{4GW R_i^d + R_b^d}{R_b} \right)^{1/2} + 1 \right]$$

(14)

where $R_i^d$, $R_b^d$, and $R_d^d$ are the voltage-independent recombination coefficients in the interface, bulk, and depletion regions, respectively.

Due to the dependence of $V_{oc}$ on $G$ (Suns–$V_{oc}$), the recombination coefficients at the interface and in the QNR ($R_i^d + R_b^d$) and SCR ($R_d^d$) can be extracted using Equation (14). Temperature-dependent current–voltage measurements are also used to interpret defect-mediated recombination in solar cells.\[132\] Under high illumination, the SCR recombination term in Equation (14) is removed and the dependence of QNR recombination on $V_{oc}$ can be derived. The activation energy

Figure 16. a) Arrhenius plot of $J_0$ derived from illumination-dependent $J_{sc}$–$V_{oc}$ measurements at different temperatures for different PDT and CdS layer thicknesses. Adapted with permission.\[37\] Copyright 2014, Royal Society of Chemistry. b) Temperature-dependent $V_{oc}$ for samples without PDT and with KF-PDT at 300 °C for 20 min. Adapted with permission.\[133\] Copyright 2018, Elsevier.

Figure 17. a) Schematic band diagram of a CIGS solar cell under short-circuit conditions. Charge carrier recombination occurs at the interface and in the SCR and QNR. Adapted with permission.\[136\] Copyright 2018, Elsevier. $W$ and $W_d$ are the width of the absorber and the depletion region, respectively. $E_C$, $E_V$, and $E_F$ are the conduction band, valance band, and Fermi energy level, respectively. $\zeta_i$ and $\zeta_b$ are the separation of $E_F$ from $E_C$ and $E_V$, respectively. $\phi_{bi,CIGS}$ is the built-in potential and $\phi_{b0}$ is the hole potential barrier at the interface. $S_w$ is the surface recombination velocity for holes and $\tau_e$ is the electron lifetime. b) Normalized carrier recombination rates as a function of $V_{oc,def}$ for solar cells with different interlayers. Reproduced with permission.\[138\] Copyright 2008, AIP Publishing. Recombination rates of $R_i$ (at the buffer/absorber interface), $R_d$ (in the SCR), and $R_b$ (in the QNR) are normalized using $R_b$.\[138\]
of recombination \( (E_a) \), which is associated with the effective energy gap for charge carrier recombination, is obtained by extrapolating \( V_{oc} \) \( (T) \) to 0 K\(^{[78,87,136,137]} \)

\[
E_a = \frac{R^i_0 \phi_{b0} + R^i_b E_g}{R^i_0 + R^i_b}
\]

where \( \phi_{b0} \) and \( E_g \) are the potential barriers at the buffer/absorber interface and bandgap, respectively. By determining all of the relevant parameters, \( R^i_0 \) and \( R^i_b \) can be calculated separately. In addition, based on the recombination coefficients, the effective carrier lifetime and surface recombination velocities of the charge carriers can be estimated.\(^{[136]} \)

The recombination rates of CIGS solar cells with different buffer layers, such as CdS, Cd\(_{0.75}\)Zn\(_{0.25}\)S, Zn\(_2\)(O,OH), and Zn\(_{1-x}\)Mg\(_x\)O, which produce a device efficiency of over 17% have been examined. \( R^i_0, R^i_b, R^i_l, R^i_l, \) and \( R^d \) were extracted from Equation (15), and \( R^i, R^0, \) and \( R^d \) were normalized with \( R^b \) and presented as a function of the \( V_{oc} \) deficit (\( V_{oc,\text{def}} \); Figure 17b ).\(^{[138]} \)

At a high \( V_{oc,\text{def}} \) recombination in the SCR and at the interface was higher than that in the QNR. In contrast, at a low \( V_{oc,\text{def}} \) recombination in the SCR and at the interface was lower than in the QNR. When \( V_{oc,\text{def}} \) was reduced to its lowest point (0.373 V), the normalized recombination rate at the interface was far lower than that in the SCR or QNR. This indicates that interface recombination is significantly affected by the device structure even when the same absorber material is used. Detailed analysis of recombination in a device is important because it strongly affects the device parameters of solar cells. By quantitatively defining the recombination rates for different locations in a solar cell, the strategies for improving targeted areas of the device can be devised.\(^{[78,138]} \)

4. Imaging Characterization Techniques

In addition to the factors associated with device physics that affect device performances, the performance of a solar cell can also be limited by nonuniformity within the constructed layers.\(^{[139,140]} \)

Therefore, detecting the location of degradation using imaging analysis techniques on a 2D scale is necessary. In particular, imaging analysis can be used to resolve current inhomogeneity in films and to obtain large-scale devices. Several characterization techniques, such as electroluminescence (EL), PL, light-beam induced current (LBIC), and lock-in thermography (LIT), have been used for solar cells.\(^{[141–148]} \) Local electrical properties such as the series resistance, shunt resistance, and various types of recombination have been evaluated using these analysis techniques, which allow to investigate local current–voltage characteristics and local efficiency properties.\(^{[149,150]} \) Luminescence imaging using EL and PL detect radiative recombination, with dark points in images indicating less recombination of excess carriers either due to nonradiative recombination or leakages through weak diodes or shunts. As with the aforementioned EBIC, LBIC measures the local short-circuit current under illumination, and useful information regarding the quantum efficiency can be determined in this way. LIT detects a local heat source under illumination or bias to observe local current–voltage characteristics. In silicon solar cells, local loss analysis and efficiency prediction using combinations of imaging techniques have also been employed.\(^{[149,150]} \) The resolution of imaging characterization techniques depends on the degree of focusing of the source and the performance of the detector. In general, those techniques show a resolution of micrometer to several tens of micrometers; however, sub-micrometer scale analysis is also possible using the designed equipment.\(^{[151,152]} \) As shown in Figure 18a, dark spots are observed in PL and EL images of

![Figure 18](https://example.com/figure18.png)

**Figure 18.** a) Images produced using PL, ILIT, EL, and DLIT at forward bias (DLIT\(_{\text{fwd}}\)), and reverse bias (DLIT\(_{\text{rev}}\)) for two different CIGS solar cells fabricated by the same institute. Adapted with permission.\(^{[144]} \) Copyright 2012, American Vacuum Society. b) XRF mapping of the Cu, Ga, In, GGI, and CGI and XBIC mapping image. Adapted with permission.\(^{[152]} \) Copyright 2017, Elsevier.
sample 1 which correspond to the bright spots in illuminated LIT (ILIT) and dark LIT (DLIT) images. Only a reverse-bias shunt is observed in the DLIT_{rev} image. In sample 2, weak diode defects are observed for all imaging measurements, except in the DLIT_{rev} image. Based on cross-sectional SEM analysis, a direct short path is observed, which does not contribute to heat generation.

Next, to evaluate the cause of the nonuniform characteristics of the device, comparing the compositional nonuniformity with the electrical characteristics is essential. As described above, the elemental composition, including a localized elemental image, can be analyzed through XRF. Meanwhile, like LBIC, X-ray beam-induced current (XBIC) enables electrical performance mapping using an X-ray beam. When XRF and XBIC are combined, it is possible to compare the electrical properties with the distribution of elements at the same location within a sample.\(^{[152,153]}\) Figure 18b shows the Cu, In, Ga, and Ga ratio (GGI = Ga/(Ga + In)) and Cu ratio (CGI = Cu/(Ga + In)) mapping results of the CIGS solar cell measured by XRF and XBIC at the same location.\(^{[152]}\) Three large grains were seen, and a difference in composition inside each grain was observed. The composition of Cu and Ga was high in the position where indium content was relatively low. Moreover, the X-ray induced current had a tendency to be increased near regions with higher CGI and GGI. Furthermore, by comparing compositions of the grain cores and grain boundaries with the XBIC results, it was confirmed that the collection efficiency was independent of the grain boundary composition in the high gallium (GGI) CIGS, and electrical properties were improved when the CGI within the grain was higher. In summary, the location and type of deterioration points can be determined by comparing various imaging techniques. Furthermore, these imaging techniques are a useful option for sorting failure and evaluating the nonuniformity of large-area devices.

Figure 19. Shockley–Queisser limit-normalized \(V_{oc}\) and \(J_{sc}\) reported by past research. The black point represents the record efficiency for a vacuum-processed CIGS solar cell. The other colors represent solution-processed CIGS solar cells with an efficiency over 15% (red, blue, green, purple, brown, cyan, orange, and pink). Figure 20. Correlation between morphological and electrical properties: a) \(L_e\) and b) carrier lifetime in accordance with the average domain spacing and c) \(J_{sc}\) in accordance with \(L_e\). Reproduced with permission. Copyright 2020, Wiley-VCH. Correlation between average grain size and solar cell parameters: d) \(J_{sc}\), e) \(V_{oc}\), and f) PCE. Reproduced with permission. Copyright 2020, American Chemical Society.
5. Outlook: Lesson from Correlations Between Materials and Electrical Properties

The performance of chalcopyrite solar cells can be assessed using electrical properties such as $L_e$, $W_{SCR}$, the carrier lifetime, surface potential, and defect characteristics, and these properties are governed by the morphology, crystal ordering, grain size, bandgap grading structure, and atomic concentration of the constituent elements. The precise quantification of a target morphology using synchrotron-based techniques, composition analysis using SIMS, AES, and ICP-OES, and electrical property analysis using EBIC, TRPL, KPFM, AS, DLTS, and CV are possible. Chalcopyrite morphology has been quantified using the average domain spacing acquired from soft X-ray SAXS, while the electrical properties of chalcopyrite solar cells, represented by $L_e$ and the carrier lifetime, can be estimated using EBIC, TRPL, TPS, and TAS.

Considering the parameters that determine the characteristics of solar cells, a high efficiency of over 20% has been reported for vacuum-processed CIGS solar cells.\cite{4,45,69} For example, large-grained CIGS with optimal composition has been fabricated using three-stage evaporation or sulfurization-after-selenization methods. Carrier collection has been improved by creating a graded energy band through compositional control and surface...
sulfurization. Junction properties have been improved using alkali PDT, and interfacial recombination has been controlled by tuning the buffer layer. On the other hand, solution-processed CIGS has been reported to have a lower efficiency compared to CIGS fabricated using a vacuum process. Figure 19 presents the Shockley–Queisser limit-normalized \( V_{oc} \) and \( J_{sc} \) for various CIGS solar cells. The black point represents the record efficiency reported for vacuum-processed CIGS as a comparison, and the other colors represent solution-processed CIGS with an efficiency of over 15%. Although the bandgap is different for each solar cell, the deviation of the voltage from the ideal value is larger than that of the current. Therefore, solution-processed CIGS solar cells require more effort to suppress recombination in the bulk and at the interface to improve \( V_{oc} \). We previously demonstrated that \( J_{sc} \) increases and \( V_{oc,def} \) decreases as the grain size increases in solution-processed CIGS solar cells by analyzing previously reported results.\(^{25}\) This indicates that it is important to fabricate high-quality large-grained CIGS thin films with few crystal defects prior to controlling the other electrical properties. Because Se vapor is primarily used for selenization in solution-processed CIGS, processes that produce large grains are required. Because morphological, crystallographic, and electrical properties are mutually dependent, it is important to determine the governing correlations between interacting parameters, which can lead to an improvement in efficiency.

Based on quantified morphological and electrical properties, correlations between the two parameters have been derived (Figure 20).\(^{25}\) Increasing the average domain spacing by incorporating K into bulk CIGS creates charge carrier percolation paths, which improves charge carrier transport and suppresses charge carrier recombination, as indicated by the increase in \( L_e \) obtained from EBIC and in the carrier lifetime obtained from TRPL, respectively (Figure 20a,b). Indeed, \( L_e \) and the carrier lifetime have been proven to increase with an increase in the average domain spacing, which contributes to photocurrent generation as shown by the linear increase in \( J_{sc} \) with \( L_e \) (Figure 20c). A greater domain spacing leads to stronger charge carrier transport because the gaps between the grains act as carrier recombination centers. Based on the published papers, the correlation between the average grain size of solution-processed CIGS solar cells and photovoltaic characteristics was obtained.\(^{25}\) From the results, \( J_{sc} \) increased with average grain size and saturated with further increase in the grain size (Figure 20d). \( V_{oc,def} \) decreased with increasing average grain size and power conversion efficiency (PCE) increased with the grain size (Figure 20e,f).

As in these examples, the characteristics of the elements constructing the solar cell and of the device are correlated. Therefore, to understand how to accurately evaluate each characteristic, and to explain and understand them in relation to each other is important. Useful information for improving solar cell can be obtained. Finally, the measurement techniques introduced in this review paper are summarized in Table 1.

### 6. Conclusions

Although recently developed chalcopyrite solar cells exhibit remarkably higher device efficiency using either vacuum or solution processing, this efficiency needs to be increased further and commercially viable manufacturing processes need to be developed. Particularly, solution-processed chalcopyrite solar cells need to overcome the low device efficiency and improve to be similar to their vacuum-processed counterparts. A deeper understanding of the morphological and electrical properties of these devices allows correlations to be determined, which will suggest design criteria for the absorber layer and chalcopyrite solar cells. This leads to further increases in device efficiency and to the development of commercial manufacturing processes. The advanced characterization techniques summarized in this review will be helpful for further understanding the thin-film solar cells to improve their efficiency based on their working principles, morphology, electrical properties, and developments in research trends.

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### Conflict of Interest

The authors declare no conflict of interest.

### Keywords

chalcopyrite, characterization of thin-film solar cells, CIGS solar cells

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