Room Temperature Processed Transparent Cu-Zn-S Nanocomposites as Hole Transport Materials in CdTe Photovoltaics

Ebin Bastola, Kamala Khanal Subedi, Fadhil K. Alfadhili, Adam B. Phillips, Michael J. Heben and Randy J. Ellingson

Wright Center for Photovoltaics Innovation and Commercialization (PVIC), Department of Physics and Astronomy, University of Toledo, Toledo, Ohio, 43606, USA

Abstract — Here, we report room temperature processed Cu-Zn-S ternary thin films fabricated using SILAR method as a back-contact hole transport layer in cadmium telluride (CdTe) solar cells. These Cu-Zn-S films are transparent to visible region with compact grains, and high conductivity. X-ray diffraction (XRD) measurements shows the crystalline nature of the as-deposited Cu-Zn-S films. The Cu-Zn-S nanocomposite as a back contact buffer layer in CdTe devices improves the device performance to 12.7% (average 12.4%) from 10.4% (average 9.8%) compared to a Au only back contact and is comparable to Cu/Au back contact (thermally evaporated). The temperature dependence current voltage characteristics shows the reduced back barrier height compared to Au only and Cu/Au back contact.

Index Terms- SILAR, Cu-Zn-S, hole transport layer (HTL), back contact, solar cells.

I. INTRODUCTION

Cu-Zn-S (CZS) nanocomposite thin films are p-type materials possessing very high carrier concentration ($\sim 10^{21}$ cm^{-3}), high transparency (>70% for 50 nm film) in visible region, and high conductivity.[1, 2] The optical band gap of these materials can be tuned by changing the material composition which makes these materials promising for opto-electronics.[2, 3] Additionally, the band edges of these materials change with the material composition, strengthening the applicability of these materials in various opto-electronic applications including photovoltaics.[1]

Cadmium telluride (CdTe) solar cells comprise a renowned thin film technology for harvesting solar energy with a suitable band gap of 1.5 eV. For the fabrication of CdTe solar cells, wem have used copper/gold (Cu/Au) as a standard laboratory-scale back contact.[4, 5] However, the Cu/Au contact does not facilitate the low-barrier transport of photo generated holes due to the deep valence band edge (VBE) of CdTe ($\sim$-5.9 eV wrt vacuum)[6]. Since the work function of Au is low ($\sim$5.0 eV)[7] compared with the VBE of CdTe, a Schottky barrier forms. To reduce this potential barrier, a material with suitable band edge location is applied for the smooth extraction of holes and repel of electrons at the back contact of the CdS/CdTe devices. Materials such as carbon nanotubes, CuSCN, FeS_2, ZnTe, Sb_2Te_3 and Cu_2Te have been tested as the back-contact buffer layer in CdS/CdTe solar cells.[8-10] Other solution-processed back contact buffer layers include $Ni_xFe_{1-x}S_2$, $CuFeS_2$ and perovskite.[11-13] These interface layers facilitatehole transport to the metal contact and/or repel electrons to reduce recombination and enhancing the device performance.

These Cu-Zn-S nanocomposite materials are p-type with high hole concentration ($\sim 10^{21}$cm^{-3})[2] and conductivity (438-2964 Scm^{-1})[1] indicating the possible application of these materials as low barrier contact materials for CdTe devices.[3] These materials can be prepared by solution-based techniques including chemical bath deposition (CBD) and successive ionic layer adsorption and reaction (SILAR) methods.[1, 2] In SILAR, the thin film is deposited by reaction of cations and anions forming an atomic layer, improving the quality of the films fabricated. Here, we have prepared Cu-Zn-S nanocomposite thin films with various compositions and applied them as a back-contact buffer layer in CdTe photovoltaics. Our results indicate the photoconversion efficiency of CdTe can be significantly enhanced compared to Au only back contact on using Cu-Zn-S as hole transport materials and is comparable to standard Cu (3 nm) (thermally evaporated) and Au (40 nm) back contact.

II. EXPERIMENTAL

The Cu-Zn-S nanocomposite films were deposited using a SILAR method at room temperature adapting a procedure from literature.[1] First, Cu-Zn-S thin films were deposited onto a sodalime glass substrate. For this, glass superstrates were cleaned using Micro-90 detergent by sonication for 30 mins at 150 °C and rinsed several times with deionized water (DIW) followed by cleaning with acetone, methanol and 2-propanol for 5 mins each by sonication.

To deposit the "CZS-50" film, the cationic precursor was prepared by dissolving 0.05 M $CuCl_2$, 0.05 M zinc acetate, with a total of 0.1 M, and 5 mL triethanolamine (TEA) (in a total volume of 25 mL), and the anionic precursor was made using 0.05 M Na_2S in DIW. The glass substrate was first submerged in cationic precursor for 15 S, then in DIW for 5 S, in anionic precursor for 15 S, and finally rinsed in DIW for 5 S which completes one cycle for SILAR deposition. A dip-coater was employed to complete all SILAR cycles and repeated for 40 complete cycles to make a Cu-Zn-S film of thickness around 250 nm. The same procedure was followed to deposit Cu-Zn-S film on CdTe surface.

The CdS/CdTe device stacks were obtained from Willard and Kelsey solar group. To fabricate standard CdTe device, 3 nm Cu and 40 nm Au were thermally deposited to complete the back contact after $CdCl_2$ treatment followed by thermal annealing at 150 °C for 35 mins. For Cu-Zn-S as HTMs, first CdTe devices were treated for $CdCl_2$ at 390 °C for 30 mins in dry air environment and rinsed with methanol to remove excel $CdCl_2$. Then, Cu-Zn-S films were deposited on CdTe using SILAR method as described above. Then, 40 nm Au was thermally evaporated to complete a metal contact.

The fabricated CZS thin films were characterized using an Hitachi S-4800 scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and optical properties using PerkinElmer Lambda 1050 UV-Vis-NIR spectrophotometer. The XRD pattern was obtained from a Rigaku Ultima III X-ray diffractometer operated at 40 KV and 44 mA. The sheet resistance was measured using 4-point probe, and thickness was measured using a Dektak profilometer. The completed devices were laser scribed[14] and measured under simulated AM1.5G solar irradiance to find the photoconversion efficiency and external quantum efficiency measurements were performed using a PV Instruments (model IVQE8-C) system.

III. RESULTS AND DISCUSSION

The Cu-Zn-S thin films were deposited at room temperature using SILAR method in which first cations get adsorbed on the surface, and while rinsing, weakly bound cations are washed away. When the substrate is immersed in anion solution, reaction takes place, and loosely bound S ions are rinsed again. This process is continued several times to make a thin film of desired thickness.

The optical properties of Cu-Zn-S films were measured using Lambda PerkinElmer 1050 spectrophotometer. Typical transmission and reflection spectra are shown in Fig. 1 for CZS-50. Here, CZS-50 denotes thin films prepared using Zn precursor 50 percent (0.05 M zinc acetate) of the total cations (0.1 M) used. As represented by the transmission spectra, these films have more than 50% transmission in visible region. Also, band gaps of these films were found using transmission and reflection spectra. For this, absorption coefficients of these films were obtained using equation below with transmission (T) and reflection (R) spectra and thickness (t) of the film.

$$\alpha = -\ln(\ T/(1-R))/t$$

Further, the band gap was estimated by plotting $(\alpha h\nu)^2$ vs $(h\nu)$ for Cu-Zn-S thin films. The estimated band gap values for CZS-50 film is ~ 2.5 eV for CZS-50 film. The inset in Fig. 1 shows the band gap for CZS-50 film.

Fig. 1 (b) shows the XRD pattern for a CZS-50 film deposited on sodalime glass. Based on XRD, as deposited Cu-Zn-S thin films have crystalline properties. The diffraction patterns are similar to the standard diffraction patterns of CuS as shown in the reference lines. The standard powder diffraction patterns for

CuS and ZnS were obtained from MDI ZADE software. In a previous report, Jose and Kumar have reported the crystalline properties of Cu-Zn-S thin films prepared by SILAR deposition method.[1] Fig. 2 (a, b) displays the plano-SEM micrograph for Cu-Zn-S thin films deposited on sodalime glass for CZS-50. The surface appears compact, and grains have size of around 200 nm in length.
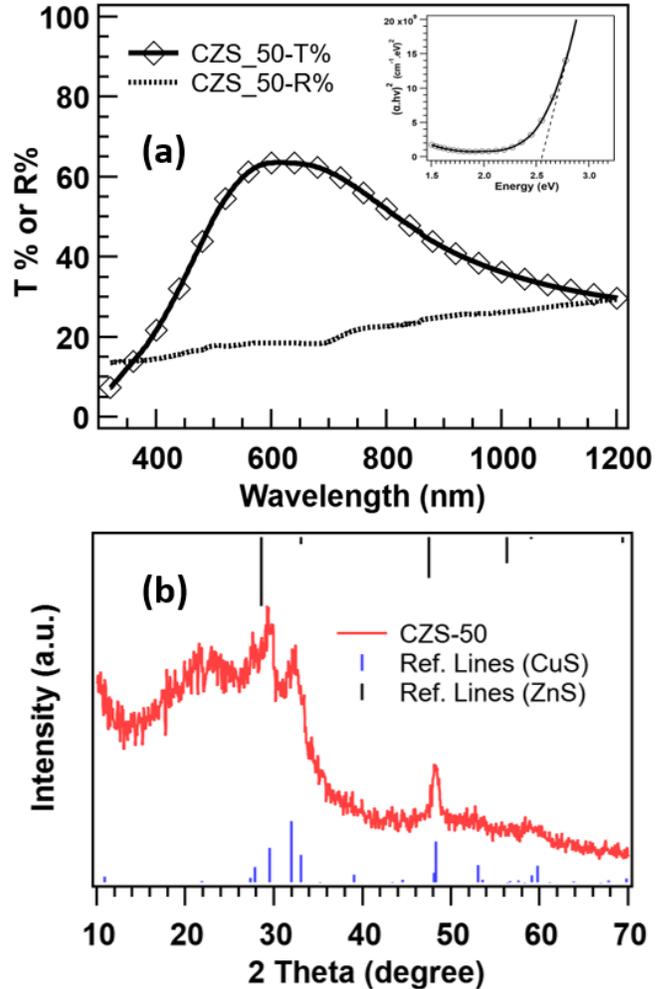

Fig. 1. (a) Transmission and reflection (dotted lines) spectra of a Cu-Zn-S ternary thin film prepared by SILAR deposition technique and (b) XRD pattern of a Cu-Zn-S film. The references lines (along top and bottom axes) include the standard diffraction patterns for CuS (PDF # 98-001-3414) and ZnS (PDF#98-000-0405).
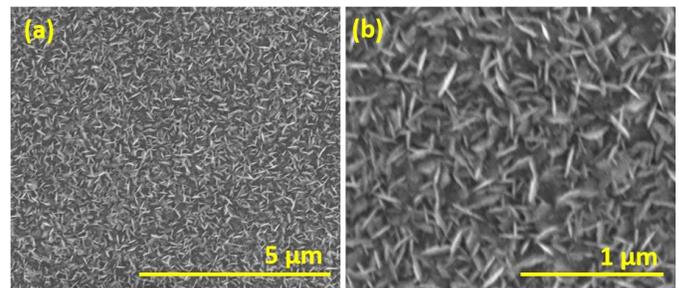
Fig. 2. Plano-SEM micrographs of Cu-Zn-S thin films prepared at room temperature using SILAR deposition technique on soda lime glass.

Fig. 3 shows the plano-SEM micrograph of CdTe films after CdCl$_2$ treatment (Fig. 3 (a)), with CZS-50 on deposited on CdTe (Fig. 3 (b)), and a schematic diagram for the complete device (Fig. 3 (c)) and cross-sectional SEM image of CdTe device with CZS-50 as the back interface layer. The EDS analysis of these films revealed chemical composition consisting of Cu, Zn and S atoms. The average atomic percentage revealed the chemical composition for Cu, Zn and S to be 32.0±1.4, 35.4±1.7, and 32.9±0.6 respectively. The sheet resistance measurement using 4-point probe for a CZS-50 film of thickness around 250 nm was 609 Ω/□ indicating these films have a resistivity of 0.015 Ω cm. P-type conductivity, low resistivity (ie, high conductivity) and high hole concentration make CZS films appropriate as hole transport materials in photovoltaic devices. Further, to study the hole transport properties, Cu-Zn-S thin films were deposited on the top of CdTe device, and 40 nm Au was thermally evaporated to complete the back-contact. The current-voltage characteristics of these completed devices with and without CZS films were measured under simulated AM1.5G spectrum.
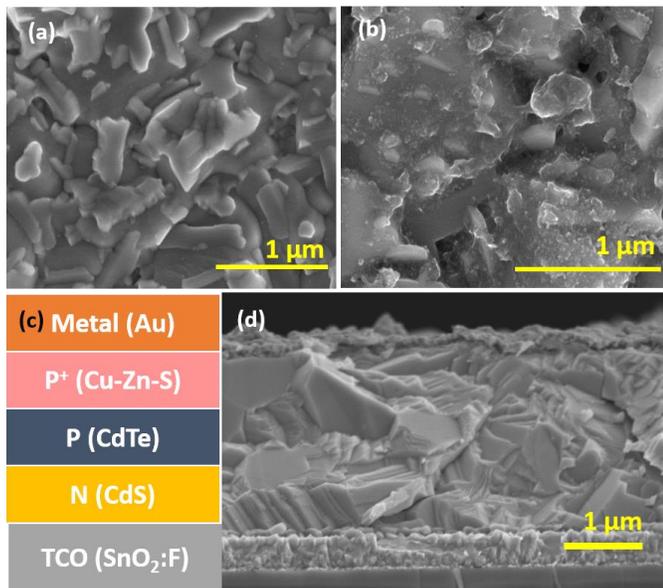

Fig. 3. SEM images of (a) standard CdTe after CdCl$_2$ treatment (b) CdTe with CZS-50 thin films (c) schematic device diagram and (d) cross-sectional SEM image of CdTe with CZS-50 as hole transport materials (CZS-50 represent a Cu-Zn-S film prepared using 0.05 M zinc acetate and 0.05 M CuCl$_2$ as cationic precursor).

Current-voltage (J-V) characteristics for the best cell with and without Cu-Zn-S as HTMs under light and dark measurement conditions are shown in Fig. 4 (a). For Au only back contact, the best cell has an efficiency of 10.4% with short

circuit current density 20.8 mA cm^{-2}, open-circuit voltage (V$_{OC}$) 746 mV, and fill factor (FF) 67.3%. Including the CZS-50 hole transport layer, the device efficiency was 12.6% with V$_{OC}$ = 800 mV, and FF = 73.7%. The average device parameters are presented in Table I. The average device efficiency for the Au only back contact devices is 9.8% and with CZS-50 as interface layer is 12.4%. In case of standard Cu/Au back contact, the average device parameters are similar to CZS-50/Au back contact presented in Table I with the best cell reaching the efficiency of 12.7%. Note that, for devices with CZS films, no additional Cu layer was deposited, and no any thermal annealing was performed. Previously, CZS deposited by chemical bath deposition (CBD) at 80 °C was demonstrated as an HTM in CdTe devices and the highest efficiency reported was 13.0% with CZS layer and Cu/Au (3/40 nm) back contact.[3] Here, we are also investigating devices with CZS layer and additional Cu layer with varying thickness.
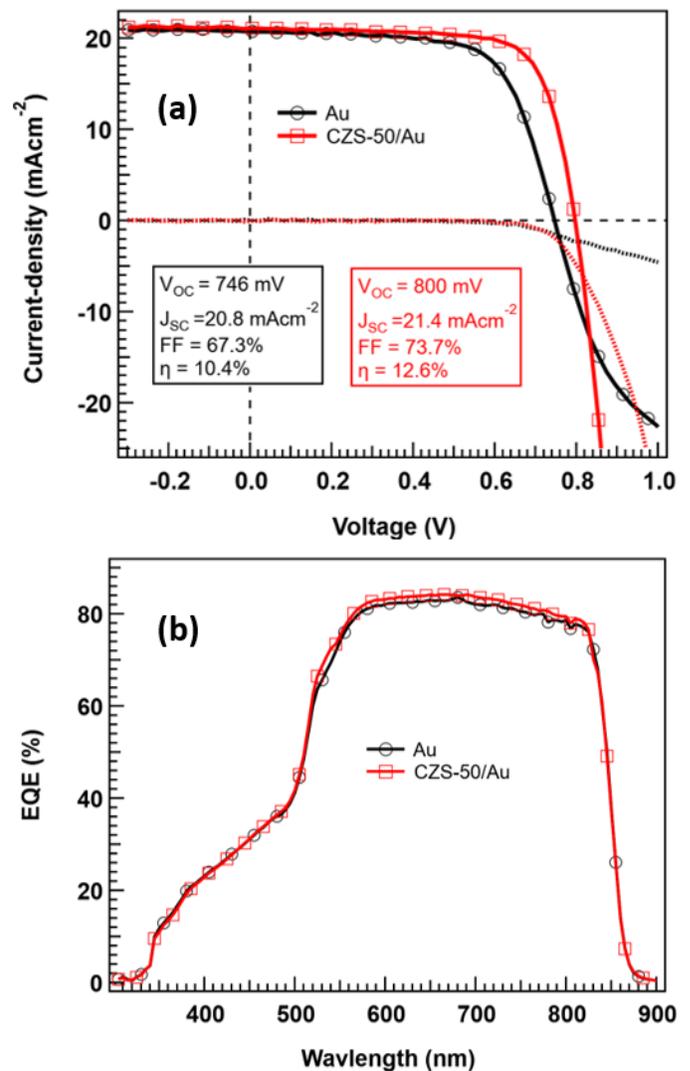

Fig. 4. Current-voltage characteristics (a) and external quantum efficiencies (b) of CdTe photovoltaics with Cu-Zn-S nanocomposites as hole transport material (HTM).

TABLE I
SUMMARY OF J-V CHARACTERISTICS OF CDTE SOLAR CELLS WITH AU AND CZS-50 AS
BACK CONTACTS

Device	V_{OC} (mV)	J_{SC} (mAcm^{-2})	FF (%)	Eff. (%)	R_s ($\Omega.cm^2$)	R_{sh} ($\Omega.cm^2$)
Au	733±6	20.8±0.2	64.5±3.4	9.8±1.1	6.9±0.7	970±33
CZS-50/Au	798±2	21.0±0.4	73.7±2.2	12.4±0.3	3.8±1.2	1700±470
Cu/Au	806±6	21.1±0.3	72.8±1.2	12.4±0.2	3.3±0.7	6560±980

Further, we measured and analyzed the devices with CZS-50 as the interface layer with temperature dependence current-voltage (J-V-T) characteristics in the temperature range of

180 K to 300K to study the effect of interface layer on back barrier height. The back-barrier height (ϕ_b) was obtained assuming thermionic emission model as given by equation below.

$$J_0 \; \alpha \; T^2 . \exp\left[\frac{-q.\phi_b}{k_B T}\right]$$

Here J_0 is the saturation current, q electronic charge, and k_B is the Boltzmann constant. The back-barrier heights were obtained by Arrhenius plots of ln (J_0/T^2) versus $1/k_B T$. Fig. 5 (a) shows the J-V-T characteristics of CdTe device with CZS-50 as the interface layer and Fig. 5(b) shows the graph for ln(J_0/T^2) versus $1/k_B T$ to extract back barrier height of the device. Based on the analysis and fitting of the graphics, the back-barrier height is found to be 0.238 eV for CdTe device with CZS-50 as the interface layer. Based on the literature, for Au only back contact the back barrier height is 0.395 eV and for Cu/Au back contact is about 0.331 eV.[15] Thus, due to the CZS-50 interrace layer in CdTe device, the back barrier height is reduced.

IV. CONCLUSION

Here, we have successfully fabricated the Cu-Zn-S nanocomposites thin films at room temperature using SILAR method. The Cu-Zn-S thin films are transparent to light in visible region and highly conductive materials with suitable properties as hole transport materials. The application of room-temperature processed CZS films as the back-contact hole transport layers in CdS/CdTe solar cells have been demonstrated. The devices completed using CZS-50 as HTM and Au as the back metal electrode show the highest efficiency of 12.6% with average 12.4% (comparable to standard Cu/Au back contact) while for Au only back contact 10.4% with average 9.8%. The temperature dependence current-voltage characteristics shows the reduced back barrier height.
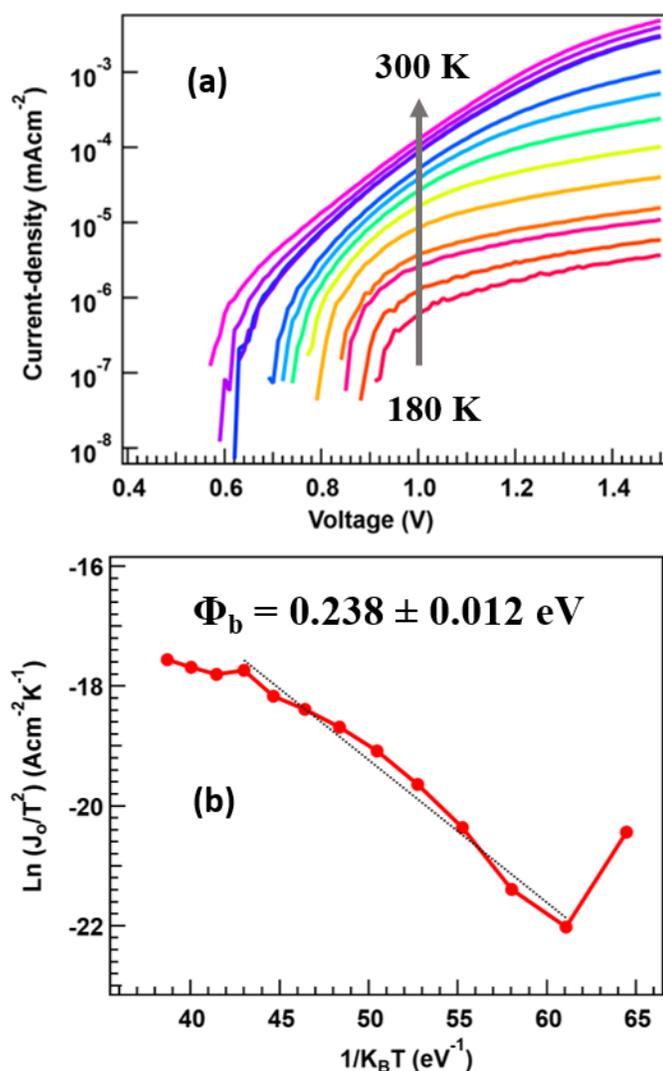
Fig. 5. (a) Temperature dependent current-voltage (J-V-T) characteristics and (b) plots of ln (J_o/T^2) versus $1/k_B T$ to extract back barrier height for CdTe solar cells with CZS-50/Au back contact.

V. ACKNOWLEDGEMENT

REFERENCE

[1] E. Jose and M. C. Santhosh Kumar, "Room temperature deposition of highly crystalline Cu-Zn-S thin films for solar cell applications using SILAR method," *Journal of Alloys and Compounds,* vol. 712, pp. 649-656, 2017/07/25/ 2017.

[2] X. Xu *et al.*, "Chemical Bath Deposition of p-Type Transparent, Highly Conducting $(CuS)_x:(ZnS)_{1-x}$ Nanocomposite Thin Films and Fabrication of Si Heterojunction Solar Cells," *Nano Lett.,* vol. 16, no. 3, pp. 1925-1932, 2016.

[3] K. K. Subedi *et al.*, "Nanocomposite $(CuS)_x(ZnS)_{1-x}$ thin film back contact for CdTe solar cells: Toward a bifacial device," *Solar Energy Materials and Solar Cells,* vol. 186, pp. 227-235, 2018.

[4] E. Janik and R. Triboulet, "Ohmic contacts to p-type cadmium telluride and cadmium mercury telluride," *Journal of Physics D: Applied Physics,* vol. 16, no. 12, p. 2333, 1983.

[5] C. R. Corwine, A. O. Pudov, M. Gloeckler, S. H. Demtsu, and J. R. Sites, "Copper inclusion and migration from the back contact in CdTe solar cells," *Solar Energy Materials and Solar Cells,* vol. 82, no. 4, pp. 481-489, 5/30/ 2004.

[6] J. L. Freeouf and J. M. Woodall, "Schottky barriers: An effective work function model," *Applied Physics Letters,* vol. 39, no. 9, pp. 727-729, 1981.

[7] B. de Boer, A. Hadipour, M. M. Mandoc, T. van Woudenbergh, and P. W. M. Blom, "Tuning of Metal Work Functions with Self-Assembled Monolayers," *Advanced Materials,* vol. 17, no. 5, pp. 621-625, 2005.

[8] N. R. Paudel and Y. Yan, "Application of copper thiocyanate for high open-circuit voltages of CdTe solar cells," *Progress in Photovoltaics: Research and Applications,* vol. 24, no. 1, pp. 94-101, 2016.

[9] A. B. Phillips *et al.*, "Wiring-up carbon single wall nanotubes to polycrystalline inorganic semiconductor thin films: low-barrier, copper-free back contact to CdTe solar cells," *Nano letters,* vol. 13, no. 11, pp. 5224-5232, 2013.

[10] J. Li *et al.*, "Controlled activation of ZnTe:Cu contacted CdTe solar cells using rapid thermal processing," *Solar Energy Materials and Solar Cells,* vol. 133, pp. 208-215, 2// 2015.

[11] E. Bastola, K. P. Bhandari, and R. J. Ellingson, "Application of composition controlled nickel-alloyed iron sulfide pyrite nanocrystal thin films as the hole transport layer in cadmium telluride solar cells," *J. Mater. Chem. C,* vol. 5, no. 20, pp. 4996-5004, 2017.

[12] E. Bastola, K. K. Subedi, K. P. Bhandari, and R. J. Ellingson, "Solution-processed Nanocrystal Based Thin Films as Hole Transport Materials in Cadmium Telluride Photovoltaics," *MRS Advances,* vol. 3, no. 41, pp. 2441-2447, 2018.

[13] E. Bastola, K. P. Bhandari, I. Subedi, N. J. Podraza, and R. J. Ellingson, "Structural, optical, and hole transport properties of earth-abundant chalcopyrite $(CuFeS_2)$ nanocrystals," (in English), *MRS Communications,* vol. 8, no. 3, pp. 970-978, Sep 2018.

[14] A. B. Phillips *et al.*, "High speed, intermediate resolution, large area laser beam induced current imaging and laser scribing system for photovoltaic devices and modules," *Review of Scientific Instruments,* vol. 87, no. 9, p. 093708, 2016.

[15] F. K. Alfadhili, A. B. Phillips, G. K. Liyanage, J. M. Gibbs, M. K. Jamarkattel, and M. J. Heben, "Controlling Band Alignment at the Back Interface of Cadmium Telluride Solar Cells using ZnTe and Te Buffer Layers," *MRS Advances,* vol. 4, no. 16, pp. 913-919, 2019.