

1-2010

A non-vacuum process for preparing nanocrystalline $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ materials involving an open-air solvothermal reaction

J. Olejníček

University of Nebraska at Kearney,

Chad A. Kamler

University of Nebraska - Lincoln

A. Mirasano

University of Nebraska at Kearney,

A. L. Martinez-Skinner

University of Nebraska at Kearney,

M. A. Ingersoll

University of Nebraska at Kearney,

See next page for additional authors

Follow this and additional works at: <http://digitalcommons.unl.edu/electricalengineeringfacpub>



Part of the [Electrical and Computer Engineering Commons](#)

Olejníček, J.; Kamler, Chad A.; Mirasano, A.; Martinez-Skinner, A. L.; Ingersoll, M. A.; Exstrom, C. L.; Darveau, S. A.; Huguenin-Love, J. L.; Diaz, M.; Ianno, Natale J.; and Soukup, Rodney J., "A non-vacuum process for preparing nanocrystalline $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ materials involving an open-air solvothermal reaction" (2010). *Faculty Publications from the Department of Electrical and Computer Engineering*. 109.

<http://digitalcommons.unl.edu/electricalengineeringfacpub/109>

This Article is brought to you for free and open access by the Electrical & Computer Engineering, Department of at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Faculty Publications from the Department of Electrical and Computer Engineering by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

Authors

J. Olejníček, Chad A. Kamler, A. Mirasano, A. L. Martinez-Skinner, M. A. Ingersoll, C. L. Exstrom, S. A. Darveau, J. L. Huguenin-Love, M. Diaz, Natale J. Ianno, and Rodney J. Soukup

A non-vacuum process for preparing nanocrystalline $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ materials involving an open-air solvothermal reaction

J. Olejníček,¹ C. A. Kamler,² A. Mirasano,¹ A. L. Martinez-Skinner,¹ M. A. Ingersoll,¹ C. L. Exstrom,¹ S. A. Darveau,¹ J. L. Huguenin-Love,² M. Diaz,² N. J. Ianno,² and R. J. Soukup²

¹Department of Chemistry, University of Nebraska at Kearney, 905 W. 25th St., Kearney, NE 68849-1150, USA

²Department of Electrical Engineering, University of Nebraska–Lincoln, 209N WSEC, Lincoln, NE 68588-0511, USA

Corresponding author – C. L. Exstrom, tel 308 865-8565, fax 308 865-8399, email exstromc@unk.edu

Abstract

A non-vacuum, two-step process has been used to prepare a series of nanocrystalline $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ ($x = 0, 0.25, 0.5, 0.75, 1$) materials. An open-air solvothermal preparation in triethylenetetramine solvent was followed by annealing at 500 °C in a nitrogen atmosphere for 20 min. All materials have mixed clustered plate, spherical particle, and nanorod morphologies with the smallest particle diameters ranging between 20 and 40 nm. Raman spectroscopy and X-ray diffraction (XRD) confirm that indium/gallium ratio control is possible over a wide range. The solvothermal reaction step yields a mixture of chalcopyrite and Cu_{2-x}Se . This is converted to pure chalcopyrite product by annealing at 500 °C.

Keywords: chalcopyrites, nanocrystalline, CIGS, solvothermal, processing

1. Introduction

For some time, the chalcopyrite semiconductors CuInSe_2 and $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ have been leading thin-film material candidates for incorporation in high-efficiency photovoltaic devices [1–4]. Interest in the development of more cost-effective, non-vacuum film production techniques has stimulated research in the solution-based preparation of nanocrystalline CuInSe_2 and $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$. Many reported solvothermal preparations involve the reaction of constituent elements or their salts in heated solution for several hours or days [5–12]. The solvent ethylenediamine ($\text{C}_2\text{H}_8\text{N}_2$) has often been employed in the preparation of binary selenides [5–7], CuInSe_2 [8–11], and $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ [10, 12]. A strongly coordinating solvent, $\text{C}_2\text{H}_8\text{N}_2$ has been proposed to solubilize reactant materials through the formation of solvent complexes such as $[\text{Cu}(\text{C}_2\text{H}_8\text{N}_2)_2]^+$ [11, 12] and $[\text{Se}(\text{C}_2\text{H}_8\text{N}_2)_x]$ [13]. Reported CuInSe_2 nanorod morphologies have been attributed to the square-planar geometry of $[\text{Cu}(\text{C}_2\text{H}_8\text{N}_2)_2]^+$ serving as a template for one-dimensional growth [11].

While solvothermal reactions in $\text{C}_2\text{H}_8\text{N}_2$ may be conducted in air, required temperature conditions vary depending on the complexity of the material prepared. Binary selenides may be prepared without solvent heating [5, 6], however, chalcopyrite crystalline structure formation requires elevated temperatures. CuInSe_2 nanorods have been prepared from refluxing $\text{C}_2\text{H}_8\text{N}_2$ (120 °C) [11] and several CuInSe_2 and $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ nanocrystalline samples have been prepared by superheating reaction

mixtures in sealed containers at temperatures ranging from 140 to 280 °C [8–10, 12]. Reaction temperatures in excess of 230 °C were required to form $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ nanoparticles of diameters less than 100 nm [10, 12]. More recently, monodisperse $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ nanoparticles of 15 nm in diameter have been prepared from CuI , InI_3 , GaI_3 , and Na_2Se in pyridine under a nitrogen atmosphere at 0 °C [14].

A two-step process consisting of a solvothermal reaction followed by heat treatment of the isolated solid product has been reported in two cases. Carmalt et al. [15] solvothermally prepared CuInSe_2 from CuBr , InCl_3 , and Na_2Se in toluene, resulting in amorphous CuInSe_2 that converted to crystalline form after annealing at 500 °C for 24 h. Li et al. [5] reported unknown “molecular precursors” following room-temperature reactions of several metals or their salts with Se in $\text{C}_2\text{H}_8\text{N}_2$ solvent. Heat treatments at 250 °C resulted in crystalline Ag_2Se , CuSe , PbSe , SnSe , MnSe , Bi_2Se_3 , and Sb_2Se_3 .

Given that the low boiling point of $\text{C}_2\text{H}_8\text{N}_2$ is a drawback in potential solvothermal preparations of quaternary chalcopyrites, the use of a chemically similar solvent with a higher boiling point may show greater promise. In this paper, we report the preparation of a series of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ ($x = 0, 0.25, 0.5, 0.75, 1$) nanocrystalline materials of varying indium–gallium ratios via a two-step process that features an open-air solvothermal reaction in refluxing triethylenetetramine ($\text{C}_6\text{H}_{18}\text{N}_4$) followed by annealing of the resulting solid-state product. With a molecular structure and coordinating ability similar to $\text{C}_2\text{H}_8\text{N}_2$, $\text{C}_6\text{H}_{18}\text{N}_4$ greatly

increases the utility of chelating amine solvent use in this preparation as well as its scaleup potential. Without the need of an inert atmosphere, expensive commercial selenium source, or necessity to exceed the normal boiling point of the solvent (267 °C), this reaction followed by annealing in a nitrogen atmosphere at 500 °C yields $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ nanocrystalline materials of varying indium-gallium ratios. The reaction system shows potential for generating a variety of ternary and quaternary chalcopyrite materials in the CuInSe_2 family. To the best of our knowledge, we are the first to report solvothermally prepared $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ ($x > 0$) via open-air means.

2. Experimental

$\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ product samples are labeled as follows: CIS ($x = 0$), CIGS-1 ($x = 0.25$), CIGS-2 ($x = 0.5$), CIGS-3 ($x = 0.75$), and CGS ($x = 1$). Desired stoichiometric quantities of Se (1.00 mmol), CuCl_2 (0.50 mmol), InCl_3 (0–1.00 mmol), and GaCl_3 (0–1.00 mmol) were refluxed in $\text{C}_6\text{H}_{18}\text{N}_4$ at 267 °C for 24 h (CIS) or 48 h (CIGS-1, CIGS-2, CIGS-3, and CGS). After isolation by centrifugation, rough films of the products were cast on borosilicate glass substrates from methanol and acetone suspensions. The samples were placed in an enclosed graphite chamber [16]. This was inserted into a quartz tube surrounded by an 8000 W Quad Ellipse Chamber Heater that was connected to a Model 915 power supply/temperature controller from Research, Inc. The tube was evacuated, filled with nitrogen (99.99% purity), and heated to a set point that was varied between 200 and 500 °C in different experiments with a ramp rate of 8 °C/s. After annealing for 20 min at the set point, the sample was cooled under flowing N_2 . The product materials were characterized by micro-Raman spectroscopy (Horiba/Jon Yvon LabRAM HR800), AES (Physical Electronics 560 AES/XPS), XRD (Bruker-AXS D8 Discover), and SEM (Hitachi S4700).

3. Results and discussion

Upon refluxing the starting materials in $\text{C}_6\text{H}_{18}\text{N}_4$, a fine black precipitate forms within 5 min. This has been isolated and identified by micro-Raman spectroscopy and XRD as Cu_{2-x}Se [17]. Over 24–48 h of continued refluxing, conversion to a mixture of solid-state $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$, Cu_{2-x}Se , and uncharacterized In- and Ga-containing species takes place. Formation of the final nanocrystalline $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ ($0 \leq x \leq 1$) products is complete after annealing at 500 °C.

SEM images of post-annealed CIGS-1 and CGS products are shown in Figure 1. These and the CIS, CIGS-2, and CIGS-3 samples show similar morphologies consisting of mixtures of plate-like particles or large nodules (100–400 nm in diameter), nanorods (50–100 nm diameter), and clusters of spherical nanoparticles in the diameter range of 20–40 nm each. Under the annealing conditions studied, no thin-film formation was observed.

XRD data (Figure 2) are consistent with standard values reported for $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ crystalline materials [18]. Each product shows seven orientations in expected 2θ positions for the (1 1 2), (2 0 4/2 2 0), (1 1 6/3 1 2), (4 0 0), (3 1 6/3 3 2), (4 4 2/2 2 8), and (5 1 2) crystal planes. The CIGS-3 (2 0 4/2 2 0) and (1 1 6/3 1 2) peaks exhibit broadening due to the separation of the (2 0 4), (2 2 0), (1 1 6), and (3 1 2) plane diffractions. In CGS, these four signals are completely resolved. As gallium concentration increases, all signals shift toward larger diffraction angles. Figure 3 shows this effect on the $d(1 1 2)$ signal. The (1 1 2) lattice plane spacing correlates linearly with $\text{Ga}/(\text{Ga}+\text{In})$. Lattice parameters a and c decrease with increase in gallium concentration, ranging be-

tween those for the CIS ($a = 5.779 \text{ \AA}$, $c = 11.569 \text{ \AA}$) and CGS ($a = 5.617 \text{ \AA}$, $c = 11.051 \text{ \AA}$) samples.

All post-annealed products exhibit Raman spectra (Figure 4) with single, intense scattering peaks between 172 and 185 cm^{-1} corresponding to the A_1 optical phonon mode that is characteristic of the chalcopyrite crystal structure [19]. With increase in Ga content, the peak position shifts to higher frequency and correlates linearly to $\text{Ga}/(\text{Ga}+\text{In})$ as has been reported for thin-film $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ [20]. In the CIGS-3 and CGS Raman spectra, intense broad peaks are also observed in the 260–275 cm^{-1} range. Based on literature reports [21] and matching with authentic

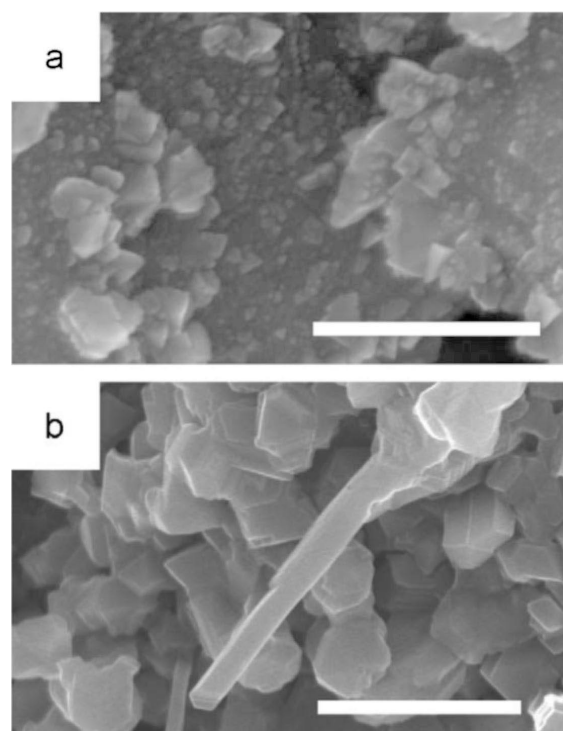


Figure 1. SEM images of post-annealed (a) $\text{CuIn}_{0.75}\text{Ga}_{0.25}\text{Se}_2$ (CIGS-1 sample) and (b) CuGaSe_2 (CGS sample). The white bar lengths equal (a) 300 and (b) 1000 nm.

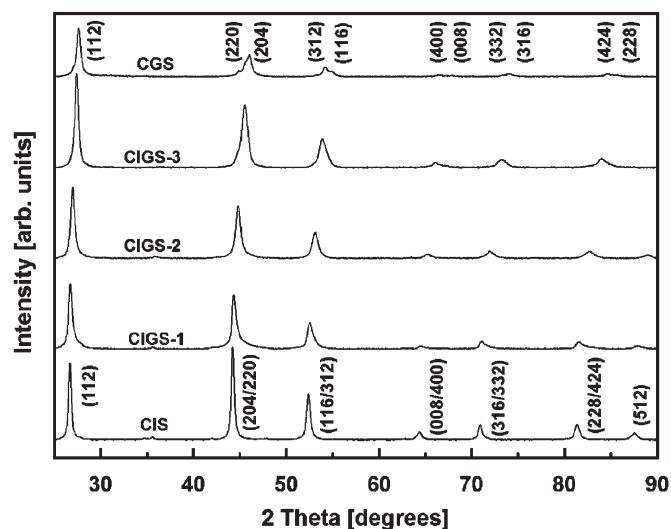


Figure 2. XRD patterns for CIS, CIGS-1, CIGS-2, CIGS-3, and CGS nanocrystalline samples. Intensity signals are offset for clarity.

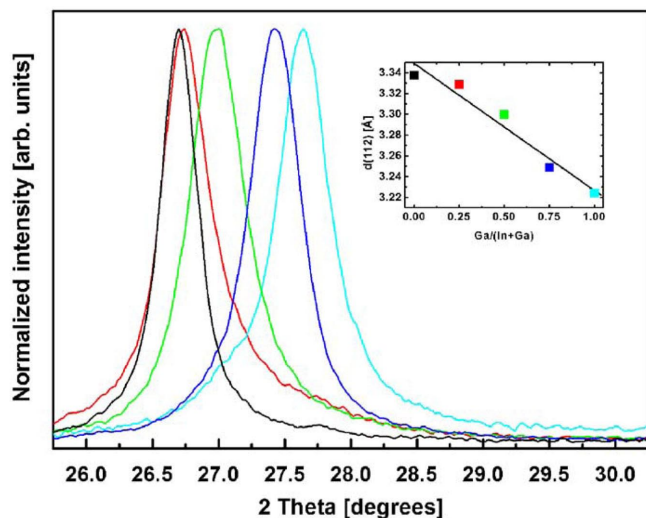


Figure 3. Overlaid XRD patterns ($d(1\ 1\ 2)$ region) of post-annealed (left-to-right) CIS, CIGS-1, CIGS-2, CIGS-3, and CGS samples. Inset is a plot of $(1\ 1\ 2)$ plane spacing as a function of Ga/(Ga+In) ratio.

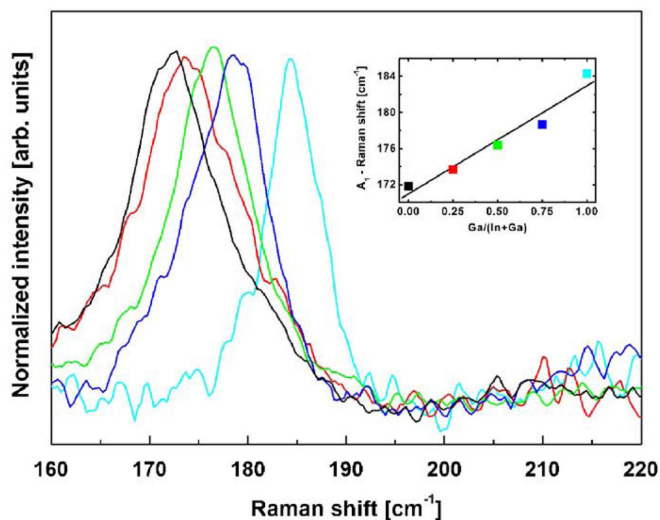


Figure 4. Overlaid Raman spectra (A_1 phonon region) of post-annealed (left-to-right) CIS, CIGS-1, CIGS-2, CIGS-3, and CGS samples. Inset is a plot of A_1 phonon frequency as a function of Ga/(Ga+In) ratio.

samples, this peak has been assigned to one or more Cu_{2-x}Se -phase impurities. Close examination of the XRD patterns of these products reveal small impurity signals at $2\theta = 44.9^\circ$ consistent with Cu_{2-x}Se phases. Depth-profile Auger analyses indicate that the impurities reside on the particle surfaces. In the CGS sample, a separate Raman peak at 274 cm^{-1} corresponding to the CuGaSe_2 B_2 phonon [22] can be discerned.

Employing only the solvothermal reaction step can yield nanocrystalline CuInSe_2 of reasonable quality but in $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ ($x > 0$) preparation, there is often significant Cu_{2-x}Se contamination. The latter annealing step in our two-step process serves to convert this to the final $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ product. To determine the effects of annealing temperature on this process, the solid $\text{CuGaSe}_2/\text{Cu}_{2-x}\text{Se}$ mixture from a CGS solvothermal preparation reaction was isolated. Portions of this sample were annealed at 200, 300, 400, and 500 °C for 20 min each. Raman spectra (Figure 5) reveal that the portion of Cu_{2-x}Se converted to CuGaSe_2 increases with temperature, with complete

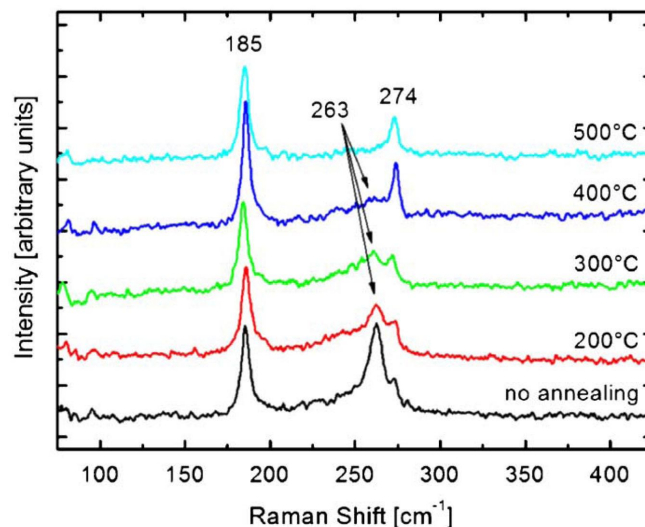


Figure 5. Raman spectra of solvothermally prepared CGS after annealing for 20 min at 200, 300, 400, and 500 °C.

conversion occurring at 500 °C or higher. The Raman intensities at 185 cm^{-1} (CuGaSe_2 A_1 phonon) and 274 cm^{-1} (CuGaSe_2 B_2 phonon) [22] slightly increase with increase in annealing temperature while the 263 cm^{-1} peak connected with several phases of Cu_{2-x}Se rapidly disappears. This effect was also observed for the CIS, CIGS-1, CIGS-2, and CIGS-3 samples, but the B_2 phonons are much less prominent due to less tetragonal distortion in the crystal lattices [22].

If the Cu_{2-x}Se -to- $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ conversion mechanisms are consistent with what has been previously reported for solid-state $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ formation [23], direct reactions of $\text{Cu}_2\text{Se} + \text{In}_2\text{Se}_3$ (in CuInSe_2 formation), $\text{CuInSe}_2 + \text{Ga}_2\text{Se}_3$ (in $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ formation), and $\text{Cu}_2\text{Se} + \text{Ga}_2\text{Se}_3$ (in CuGaSe_2 formation) may be responsible. While no In_2Se_3 or Ga_2Se_3 species were observed by XRD or Raman in the pre-annealed samples, it must be concluded that in addition to Cu_{2-x}Se , one or more In- and/or Ga-containing species are present. At this point, the nature of these species is unknown. They must be amorphous, as no XRD signals from materials other than CuInSe_2 , $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$, CuGaSe_2 , and Cu_{2-x}Se were observed. Although Raman-active phonon frequencies for amorphous In_{1-x}Se alloys [24] and GaSe [25] have been reported, none of these were exhibited by our samples. Studies of the solvothermal reaction pathways and the nature of the pre-annealed material products are in progress.

4. Conclusion

We have developed a two-step, non-vacuum process for the preparation of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ nanocrystalline materials of varying In/Ga composition ratios ($0 \leq x \leq 1$). An open-air solvothermal reaction of CuCl_2 , InCl_3 (for $x < 1$), GaCl_3 (for $x > 0$), and Se in refluxing $\text{C}_6\text{H}_{18}\text{N}_4$ was followed by the annealing of the isolated solid product in a nitrogen atmosphere at temperatures between 200 and 500 °C. To the best of our knowledge, this is the first reported open-air solvothermal procedure employed in the preparation of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ ($x > 0$) materials. The high boiling point ($267\text{ }^\circ\text{C}$) of $\text{C}_6\text{H}_{18}\text{N}_4$ appears to facilitate gallium incorporation into the nanocrystalline product structures. Annealing at 500 °C serves to convert precursor solids to the chalcopyrite product and improve the crystallinity of any pre-existing chalcopyrite.

Acknowledgments

Work supported by the US Department of Energy (Grant nos. DE-FG02-06ER64235 and DE-FG36-08GO88007) and the Nebraska Research Initiative Program.

References

- [1] A. Rockett and R. W. Birkmire, Copper indium selenide (CuInSe_2) for photovoltaic applications, *J. Appl. Phys.* **70** (1991), pp. R81–R97.
- [2] C. Guillen and J. Herrero, Optical properties of electrochemically deposited copper indium selenide (CuInSe_2) thin films, *Sol. Energy Mater.* **23** (1991), pp. 31–45.
- [3] U. Rau and H. W. Schock, Electronic properties of Cu(In,Ga)Se_2 heterojunction solar cells. Recent achievements, current understanding, and future challenges, *Appl. Phys. A: Mat. Sci. Process.* **69** (1999), pp. 131–147.
- [4] A. Miguel, K. Contreras, J. Ramanathan, F. AbuShama, D. L. Haskoon, B. Young, B. Egass, and R. Noufi, Diode characteristics in state-of-the-art $\text{ZnO/CdS/Cu(In}_{1-x}\text{Ga}_x\text{)Se}_2$ solar cells, *Prog. Photovolt.: Res. Appl.* **13** (2005), pp. 209–216.
- [5] Y. Li, Z. Wang, and Y. Ding, Room temperature synthesis of metal chalcogenides in ethylenediamine, *Inorg. Chem.* **38** (1999), pp. 4737–4740.
- [6] W. Wang, Y. Geng, P. Yan, F. Liu, Y. Xie, and Y. Qian, A novel mild route to nanocrystalline selenides at room temperature, *J. Am. Chem. Soc.* **121** (1999), pp. 4062–4063.
- [7] Z.-H. Han, S.-H. Yu, Y.-P. Li, H.-Q. Zhao, F.-Q. Li, Y. Xie, and Y.-T. Qian, Convenient solvothermal synthesis and phase control of nickel selenides with different morphologies, *Chem. Mater.* **11** (1999), pp. 2302–2304.
- [8] B. Li, Y. Xie, J. Huang, and Y. Qian, Synthesis by a solvothermal route and characterization of CuInSe_2 nanowhiskers and nanoparticles, *Adv. Mater.* **11** (1999), pp. 1456–1459.
- [9] Y. Jiang, Y. Wu, X. Mo, W. Yu, Y. Xie, and Y. Qian, Elemental solvothermal reaction to produce ternary semiconductor CuInE_2 ($E = \text{S, Se}$) nanorods, *Inorg. Chem.* **39** (2000), pp. 2964–2965.
- [10] K.-H. Kim, Y.-G. Chun, B.-O. Park, and K.-H. Yoon, Synthesis of CuInSe_2 and CuInGaSe_2 nanoparticles by solvothermal route, *Mater. Sci. Forum* **449–452** (2004), pp. 273–276.
- [11] Y.-H. Yang and Y.-T. Chen, Solvothermal preparation and spectroscopic characterization of copper indium diselenide nanorods, *J. Phys. Chem. B* **110** (2006), pp. 17370–17374.
- [12] Y.-G. Chun, K.-H. Kim, and K.-H. Yoon, Synthesis of CuInGaSe_2 nanoparticles by solvothermal route, *Thin Solid Films* **480–481** (2005), pp. 46–49.
- [13] J. Lu, Y. Xie, F. Xu, and L. Zhu, Study of the dissolution behavior of selenium and tellurium in different solvents—a novel route to Se, Te tubular bulk single crystals, *J. Mater. Chem.* **12** (2002), pp. 2755–2761.
- [14] S. J. Ahn, K. H. Kim, Y. G. Chun, and K. H. Yoon, Nucleation and growth of Cu(In,Ga)Se_2 nanoparticles in low temperature colloidal process, *Thin Solid Films* **515** (2007), pp. 4036–4040.
- [15] C. J. Carmalt, D. E. Morrison, and I. P. Parkin, Solid-state and solution phase metathetical synthesis of copper indium chalcogenides, *J. Mater. Chem.* **8** (1998), pp. 2209–2211.
- [16] F. A. Durodli, J. Song, S. K. Kim, K. H. Kang, K. H. Yoon, S. H. Kwon, B. T. Ahn, and S. D. Kim, CuInSe_2 thin films prepared from high-vapor selenization of co-sputtered Cu-In precursor layers, *J. Kor. Phys. Soc.* **32** (1998), pp. 87–92.
- [17] C. L. Exstrom, S. A. Darveau, A. L. Martinez-Skinner, M. A. Ingersoll, J. Olejniczek, A. Mirasano, A. T. Haussler, J. L. Huguenin-Love, C. A. Kamler, M. Diaz, N. J. Ianno, and R. J. Soukup, Reaction pathway insights into the solvothermal preparation of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ nanocrystalline materials, in: *Proceedings of the 33rd IEEE Photovoltaic Specialist Conference, 12–16 May 2008, San Diego, CA, USA*.
- [18] International Centre for Diffraction Data nos. 40-1487, 40-1488, 79-1809.
- [19] C. Rincon and F. J. Ramirez, Lattice vibrations of CuInSe_2 and CuGaSe_2 by Raman microspectrometry, *J. Appl. Phys.* **72** (1992), pp. 4321–4324.
- [20] S. Theodoropoulou, D. Papadimitriou, N. Rega, S. Siebentritt, and M. Ch. Lux-Steiner, Raman and photoreflectance study of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ epitaxial layers, *Thin Solid Films* **511–512** (2006), pp. 690–694.
- [21] V. Izquierdo-Roca, A. Perez-Rodriguez, A. Romano-Rodriguez, J. R. Morante, J. Alvarez-Garcia, and L. Calvo-Barrio, Raman microprobe characterization of electrodeposited S-rich CuIn(S,Se)_2 for photovoltaic applications, microstructural analysis, *J. Appl. Phys.* **101** (2007), pp. 103517-1–103517-8.
- [22] C. Xue, D. Papadimitriou, and Y.S. Raptis, Micro-Raman study of orientation effect of Cu_xSe -Crystallinities on Cu-rich CuGaSe_2 thin films, *J. Appl. Phys.* **96** (2004), pp. 1963–1966.
- [23] F. Hergert, R. Hock, A. Weber, M. Purwins, J. Palm, and V. Probst, In situ investigation of the formation Cu(In,Ga)Se_2 from selenized metallic precursors by X-ray diffraction—the impact of Gallium, Sodium and Selenium excess, *J. Phys. Chem. Solids* **66** (2005), pp. 1903–1907.
- [24] J. Weszka, P. Daniel, A. M. Burian, A. Burian, M. Elechower, and A. T. Nguyen, Raman scattering in amorphous films of $\text{In}_{1-x}\text{Se}_x$ alloys, *J. Non-Cryst. Solids* **315** (2003), pp. 219–222.
- [25] C. E. M. Campos, J. C. de Lima, T. A. Grandi, M. S. Souza, and P. S. Pizani, Age-induced phase transitions on mechanically alloyed amorphous GaSe , *Solid State Commun.* **142** (2007), pp. 270–275.