Positron annihilation spectroscopy on colloidal CuIn$_{1-x}$Ga$_x$Se$_2$ semiconductor nanocrystals

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Abstract. Simple and low-cost hot-injection method was used to synthesize three samples of colloidal nanocrystals with general chemical formula CuIn$_{1-x}$Ga$_x$Se$_2$ (x=0.0, 0.6 and 0.82). X-ray diffraction (XRD) and transmittance electron microscopy (TEM) have been used to investigate the structural properties of the synthesized nanocrystals and proved their high crystallinity. Positron annihilation lifetime (PAL) and Doppler broadening (DB) techniques were used to give more insights on the structural defects of the grown samples. The results of the positron lifetime measurements indicate that the shortest lifetime component ($\tau_1$) with intensity $\gtrsim 97\%$ is greater than the calculated positron bulk lifetime, 235-240 ps. This indicates that the concentrations of the vacancy-type defects for the as-synthesized CuIn$_{1-x}$Ga$_x$Se$_2$ samples are greater than the saturation trapping limit ($10^{18}$ cm$^{-3}$). Moreover, results of the PAL measurements and the theoretically calculated positron lifetimes indicate that Cu-Se, In-Se and/or Ga-Se are the dominant vacancy-type defect for all studied range of Ga. Also, the results show that the vacancy-type defect concentrations of samples with Ga content of 0.6 and 0.82 are reduced compared with that for zero-Ga content sample.

1. Introduction.
Copper indium gallium selenide CuIn$_{1-x}$Ga$_x$Se$_2$ is one of the most investigated semiconductor materials for solar cells with power conversion efficiency exceeding 20% [1]. Indeed, CuIn$_{1-x}$Ga$_x$Se$_2$ has the feature of being bandgap tuneable by exchanging the In atom by Ga atom. The energy conversion efficiency of CuIn$_{1-x}$Ga$_x$Se$_2$ solar cells is expected to increase by increasing CuIn$_{1-x}$Ga$_x$Se$_2$ bandgap up to 1.4 eV, with Ga content $\geq 70\%$, due to their matching with the sunlight spectrum [2]. Yet, the efficiency of CuIn$_{1-x}$Ga$_x$Se$_2$ solar cells is found to be significantly reduced when CuIn$_{1-x}$Ga$_x$Se$_2$ bandgap is above 1.2 eV. The latter is most likely due to the formation of deep defects at CuIn$_{1-x}$Ga$_x$Se$_2$ mid-gap. Traditionally, CuIn$_{1-x}$Ga$_x$Se$_2$ materials are usually grown using Bridgman method (for bulk materials) while in thin film form can be deposited using vacuum-based techniques including for example, multi-stage co-evaporation [3],
molecular beam epitaxy [4] and sputtering [5]. The common factor among all these preparation techniques is the usage of “vacuum” as necessarily condition, which makes the fabrication process very costly and sophisticated. A combination between thin film technology and nanostructures (NCs) technology of CuIn$_{1-x}$Ga$_x$Se$_2$ using chemical solution routes, yielded cheaper solar cells device with interesting physical properties. However, this kind of chemical solution-processed solar cells is still in its early stage of development due to complexity of the synthesis process of CuIn$_{1-x}$Ga$_x$Se$_2$ by chemical routes. In addition, there is no report on the structural defects analysis, using positron annihilation spectroscopy, on such chemically synthesized material particularly for wide bandgap CuIn$_{1-x}$Ga$_x$Se$_2$ (i.e., x is around 0.7).

Many techniques are used to study the defect distribution in semiconductors as some properties of these materials (e.g. optical and electrical) are strongly affected by the presence of low concentrations of defects. Positron annihilation spectroscopy (PAS) as a non-destructive test is widely used to study the structural changes and to probe the defects in a wide variety of materials as well as semiconductors [6-8]. The positrons, emitted from $^{22}$Na source as an example, are implanted in the semiconductors, and then are thermalized and diffused for a few hundred µm depth. These diffused positrons suffer a direct annihilation with the bulk electrons, trapping in defects, or forming a positronium atom (Ps) with singlet state ($p$-Ps) and a triplet state ($o$-Ps). The trapped positrons and the Ps will be annihilated with the electrons. In positron annihilation lifetime technique (PAL), different lifetime components ($\tau$) with their relative intensities ($I_\tau$) can be obtained for each state at the annihilation site. Thus, the lifetime components of the trapped positrons in defects of bulk or thin layers of nanocrystal semiconductors reflect the defect type and concentration. On the other hand, the positron annihilation Doppler broadening (DB) technique gives more information about the electron momenta distribution at the annihilation site through the spectral $S$ and $W$ line-shape parameters. Therefore, many studies were carried out to study defects in semiconductors using the PAS techniques [9-12].

Here, we report on the structural defects of colloidally synthesized CuIn$_{1-x}$Ga$_x$Se$_2$ nanocrystals grown using solution-based hot-injection method. Three samples were synthesized with various compositions of “Ga” (i.e., x=0.0, 0.6 and 0.82) and investigated using X-ray diffraction (XRD), transmission electron microscopy (TEM) and PAS techniques (PAL and DB). The solution-based techniques have advantages, over vacuum-based methods, of being lower cost and more scalable especially for applications like thin film solar cells.

2. Experimental Methods.

2.1. Sample preparation.

For the synthesis of CuIn$_{1-x}$Ga$_x$Se$_2$ nanocrystals, high purity chemicals: copper chloride (CuCl; 99.995%), indium chloride (InCl$_3$; anhydrous 99.999%), gallium chloride (GaCl$_3$; anhydrous 99.999%), selenium (Se; 99.99%), oleylamine (OLA; 70%), ethanol, chloroform (99.99%), anhydrous hexane (95%) and tetrachloroethylene (TCE) were purchased from Sigma Aldrich and used as received. The nanocrystals were synthesized in a three-neck flask mounted on hot-plate magnetic stirrer and under nitrogen gas environment, as shown in figure 1 according to equation 1:

$$\text{CuCl} + \text{InCl} + 2\text{Se} + \text{GaCl}_3 \xrightarrow{11\text{ml oleylamine + heat}} \text{CuIn}_{1-x}\text{Ga}_{x}\text{Se}_2 \text{nanocrystals + by-products} \quad (1)$$

According to the desired Ga content in CuIn$_{1-x}$Ga$_x$Se$_2$, different molarities of CuCl, InCl and GaCl$_3$ were used (e.g., for Ga = 0.6 a 1 mmol of CuCl, 0.25 mmol of InCl and 0.75 mmol of GaCl$_3$ were added to a flask followed by 11 ml of OLA in N$_2$ atmosphere). The contents in the flask were heated to 72 °C for 30 minutes. The solution was subsequently heated to 260°C, and 1 ml of Se in OLA was rapidly injected into the reaction mixture. The contents of the flask were cooled down to 60 °C. Details of collecting the nanocrystals after purification can be found in Ref.13. For PAS measurements, the obtained
CuIn\textsubscript{1-x}Ga\textsubscript{x}Se\textsubscript{2} powders were pressed under hydraulic pressure of 3 ton where 8 mm diameter pellets were formed.

2.2. Measurements
The synthesized CuIn\textsubscript{1-x}Ga\textsubscript{x}Se\textsubscript{2} nanocrystals were characterized using XRD diffractometer (type Bruker D8, at operating conditions of 40 kV, 30 mA, with Cu K\textalpha radiation of $\lambda = 0.15406$ nm and a scanning rate of 4°/m in the 2θ range from 20° to 80°). Also, the shape and size of the nanocrystals were determined using TEM type JOEL 200.

PAL measurements were carried out in the air at room temperature using fast-fast coincidence spectrometer [14] with a time resolution of ~350 ps measured using a $^{60}$Co source at $^{22}$Na energy window setting. About 30 $\mu$Ci $^{22}$Na source was prepared using $^{22}$NaCl solution that was deposited and dried between two thin Kapton foils (7.6 μm thick). The PAL spectra were measured using a 4π configuration for the prepared $^{22}$Na source and two identical samples. Each sample was measured at least two times with total count of each time spectrum of ~ 1.5 million counts. The obtained spectra were analyzed using the LT computer program of Kansy [15], with a suitable correction for the positrons annihilated in the Kapton. Two-lifetime components ($\tau_1$ and $\tau_2$) with relative intensities ($I_1$ and $I_2$), respectively, were obtained from the analysis of the measured spectra. The fit’s variance for determination of these lifetime components is ranged from 1.02 to 1.25.

The DB spectra were measured in air at room temperature using an Ortec p-type HPGe detector with an energy resolution of 1.6 keV for 1.33 MeV gamma line of $^{60}$Co and relative efficiency of 25%. The detector signals were amplified with an Ortec 570 amplifier then recorded with an Ortec 919 multichannel analyzer. Two disk samples were arranged with the 3 $\mu$Ci $^{22}$Na source in a 4π configuration. The energy calibration (~68 eV/channel) was achieved using the $^{133}$Ba source. More than three million counts in the annihilation line were accumulated for each spectrum. The analysis of the obtained DB spectra was done using SP program ver. 1.1 [16]. The centroid channel with maximum counts of the 511 keV peak was carefully defined as it is a base for calculations of $S$ and $W$-parameters. The input data for this program are fixed for all spectra of the studied samples.

3. Results and Discussion
Figure 2 shows the XRD pattern of CuIn\textsubscript{1-x}Ga\textsubscript{x}Se\textsubscript{2} nanocrystals powder (namely, CuInSe\textsubscript{2} and CuIn\textsubscript{0.18}Ga\textsubscript{0.82}Se\textsubscript{2}). The results indicate that both CuInSe\textsubscript{2} and CuIn\textsubscript{0.18}Ga\textsubscript{0.82}Se\textsubscript{2} samples are crystalline with a single phase dominated mainly by tetragonal crystal structure with (112) preferred crystallographic plans. Similar results have been found for the CuIn\textsubscript{0.4}Ga\textsubscript{0.6}Se\textsubscript{2} sample (not shown). As shown in figure 2, a clear broadening and shift of all XRD peaks of CuIn\textsubscript{0.18}Ga\textsubscript{0.82}Se\textsubscript{2} samples relative to that of CuInSe\textsubscript{2} were observed. Also, the nanocrystals average sizes were calculated to be between 30 and 18 nm for CuInSe\textsubscript{2} and CuIn\textsubscript{0.18}Ga\textsubscript{0.82}Se\textsubscript{2} samples, respectively, using Sherer’s equation, $D = \frac{K\lambda}{\beta \cos \theta}$. This result was
also confirmed from TEM measurements (see Figure 3) where the average nanocrystals size was determined to be around 35 and 15 nm for CuInSe$_2$ and CuIn$_{0.18}$Ga$_{0.82}$Se$_2$ samples, respectively. In addition, TEM images show that the nanocrystals, in general, have “spherical” shape with approximately mono-dispersive size distribution. Independent optical absorption measurements indicate the high optical quality of the samples (not shown).

The PAL parameters ($\tau_1$, $\tau_2$, $I_1$ and $I_2$) for as-synthesized three samples of CuIn$_1$$_{1-x}$Ga$_x$Se$_2$ samples are shown in figure 4 and the results show that the first lifetime component $\tau_1$ values are ranged from 330.3 to 352.3 ps with intensity range of 96.94-98.78%. The measured $\tau_1$ values are greater than the calculated positron bulk lifetime, 235-240 ps [11,12]. This indicates that saturation trapping to vacancy-type defects occurs in all studied samples. These results mean that the concentrations of the vacancy defects are greater than the saturation trapping limit (~ $10^{15}$ cm$^{-3}$, that estimated by assuming a plausible defect specific trapping coefficient of $1 \times 10^{15}$ s$^{-1}$ [11]). The measured $\tau_1$ values are close to the reported values of theoretically calculated positron lifetimes for the Cu-Se, In-Se and/or Ga-Se divacancies in CuInSe$_2$ and CuGaSe$_2$ [11-13]. The results also show that the $\tau_1$ component for $x = 0.6$ and 0.82 samples is reduced by a mean percentage of ~6 % compared with that of $x = 0.0$ sample. This reduction in $\tau_1$ value can be ascribed to the following reasons: (i) change the size of trapping defects by incorporation of Ga$^{3+}$ ions of 0.076 nm radius instead of the In$^{3+}$ ions of 0.094 nm radius and (ii) change in the concentration and mobility of charge carriers by replacing In with Ga [17]. The high-intensity $I_1$ values (96.94-98.78%) of the lifetime component $\tau_1$ is consistent with the previous result of Ref. 12 which reported the presence of only one lifetime component in CuInSe$_2$ thin film. We also note that the variation of the $I_1$ values with Ga content is the same as in the case of the $\tau_1$. The observed decrease of $I_1$ values may be due to the decrease of defects caused by substituting the higher radius In$^{3+}$ ions with the lower radius Ga$^{3+}$ ions. At higher Ga content (x=0.82), the agglomeration of the defects is the dominant process that decreases the divacancies concentration and increases the large void as shown in the behaviour of $I_2$ (see figure 4).

By analysis of the lifetime spectra, very weak nanosecond lifetime component was also resolved. The values of this second o-Ps lifetime component $\tau_2$ are ranged from 993 to 1943 ps for the measured samples. The $\tau_2$ is attributed to pick-off annihilation of the Ps in the large voids present in the samples. The results indicate that the concentration of these large voids is too small as the intensity of $\tau_2$ is low with
a range of $I_2=1.27$-3.06%. The volume of these large voids was calculated according to Ref. 18 by assuming a spherical shape of these voids. Table 1 listed the radius and volume of the large voids in CuIn$_{1-x}$Ga$_x$Se$_2$ samples.

For comparison purpose, the measured experimental positron lifetimes for vacancy-related defects of Cu(In,Ga)Se$_2$ material systems, grown by different methods including expensive Bridgman and electrochemical techniques, and their reported values are listed in table 2. The high quality of the as-synthesized nanocrystals is confirmed as their measured $\tau_1$ values are comparable with those reported for annealed bulk samples [12] in spite that our samples were synthesized using simple and low-cost hot-injection method. We expect that, the quality of our synthesized samples can be enhanced by applying heat treatment which is currently under investigation.

![Figure 3](image)

**Figure 3.** Transmission electron microscopy images of as-synthesized (a) CuInSe$_2$ and (b) CuIn$_{0.18}$Ga$_{0.82}$Se$_2$ nanocrystals (insets: size distribution data).

| Ga content ($x$) | Radius ($R$, nm) | Volume ($V$, nm$^3$) |
|-----------------|-----------------|---------------------|
| 0.0             | 0.215           | 0.042±0.003         |
| 0.6             | 0.164           | 0.019±0.001         |
| 0.82            | 0.283           | 0.095±0.002         |

Table 1. The radius, $R$, and the volume, $V$, of the large voids for CuIn$_{1-x}$Ga$_x$Se$_2$ samples.

The calculated $S$- and $W$-parameters, for the CuIn$_{1-x}$Ga$_x$Se$_2$ samples, as a function of Ga contents are shown in Figure 5. The results indicate that the size and the concentration of the vacancy-type defects are reduced for the for the CuIn$_{1-x}$Ga$_x$Se$_2$ samples with Ga content of $x = 0.6$ and 0.82 as their $S$ values are decreased compared with that for $x = 0.0$ sample. In addition, the results show that the inverse behavior was found for the dependence of $W$-parameter on the Ga content. This opposite behavior may be due to the agglomeration of defects with Ga content. The correlation between $S$ and $W$ for CuIn$_{1-x}$Ga$_x$Se$_2$ samples with Ga content is presented in figure 6. The linear relation between the $S$- and $W$-parameters indicates that the defect type is similar for all studied samples regardless of the Ga content. This result is consistent with that of the PAL measurements.
Figure 4. The PAL parameters (τ₁ and τ₂ and their intensity I₁ and I₂) as a function of Ga content for CuIn₁₋ₓGaₓSe₂ samples.

Table 2. Experimental positron lifetimes for vacancy-type defects of Cu(In,Ga)Se₂ material systems.

|                        | τ₁ (ps) | I₁ (%) | τ₂ (ps) | I₂ (%) | Reference               |
|------------------------|---------|--------|---------|--------|-------------------------|
| **CuInSe₂ Samples**   |         |        |         |        |                         |
| CuInSe₂ (bulk), (as-grown) | 459±2.7 | 100    | -       | -      | [12]                    |
| CuInSe₂ (bulk), (annealed in Se-atmosphere) | 355±2.6 | 100    | -       | -      | [12]                    |
| CuInSe₂ (bulk), (annealed in S-atmosphere) | 276±6.1 | 100    | -       | -      | [12]                    |
| CuInSe₂ (bulk)        | 269±3   | 82     | 360±15  | 18     | [11]                    |
| CuInSe₂ (nanocrystals) | 352.3±1.7 | 98.78±0.15 |        |        | This work               |
| (as-synthesized)      |         |        |         |        |                         |
| **CuIn₀.₉₅Ga₀.₀₅Se₂ Samples** |         |        |         |        |                         |
| Cu(In₀.₉₅,Ga₀.₀₅)Se₂ (bulk) | 267±4 | 86±3   | 371±10  | 14     | [11]                    |
| CuIn₀.₄Ga₀.₆Se₂ (nanocrystals) | 332.0±2.0 | 98.2±0.4 |         |        | This work               |
| (as-synthesized)      |         |        |         |        |                         |
| CuIn₀.₁₈Ga₀.₈₂Se₂ (nanocrystals) | 330.3±2.0 | 96.94±0.10 |         |        | This work               |

a Grown by the electrochemical deposition processing technique.

b Grown by the vertical Bridgman method.

c Synthesized by the hot-injection method.
Figure 5. The DB parameters (S and W) as a function of Ga content for CuIn$_{1-x}$Ga$_x$Se$_2$ samples.

Figure 6. The S–W plot for CuIn$_{1-x}$Ga$_x$Se$_2$ samples.

4. Conclusion.
Colloidal nanocrystals CuIn$_{1-x}$Ga$_x$Se$_2$ (x = 0.0, 0.6 and 0.82) were synthesized using the solution-based hot-injection method. A single phase nanocrystals structure of the synthesized CuIn$_{1-x}$Ga$_x$Se$_2$ is confirmed through XRD and TEM measurements. From the results of PAL and DB measurements, it was found that Cu-Se, In-Se and/or Ga-Se are the dominant vacancy-type defects in the as-grown samples. The obtained parameters of PAL and DB measurements indicate that both techniques are highly sensitive to any microstructure changes occurred due to the addition of Ga to CuIn$_{1-x}$Ga$_x$Se$_2$ nanocrystals system. For a systematic study of the effect of Ga substitution and annealing on the structural defects in CuIn$_{1-x}$Ga$_x$Se$_2$ nanocrystals, additional samples with lower Ga content (i.e. x < 0.6) were synthesized and their characterizations are now in progress.
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