

Zn incorporation in CuInSe₂: Particle size and strain effects on microstructural and electrical properties

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Abstract. Incorporation of the doping element Zn in the temperature range (550–700 °C) and the impact on structural and electrical properties of CuInSe₂ material are investigated. X-ray diffraction patterns showed the chalcopyrite nature of the pure and doped CuInSe₂ and revealed that diffusion temperature governs particle size as well as tensile strain. The calculated lattice parameters and cell volumes revealed that Zn diffuses in CuInSe₂ by substitution on Cu sites. Electrical properties of the material have been investigated using a contact-less technique based on high frequency microwave (HF). It is found that Zn atoms influence the defect equilibrium resulting in the conversion of the conduction type. The conductivity of the samples has been found increasing as the diffusion temperature increases.

Keywords. CuInSe₂; doping; zinc; Williamson–Hall; high frequency.

1. Introduction

In recent years, the chalcopyrite CuInSe₂ (CIS) has been investigated as a promising top candidate for use as a cell in photovoltaic systems because, it has a direct bandgap of 1 eV which perfectly matches the solar spectrum for energy conversion and a high absorption coefficient $> 10^4 \text{ cm}^{-1}$. CuInSe₂ is I.III.VI₂ compound semiconductor and in general, this material displays *n*- or *p*-type conductivity. Currently, the energy conversion efficiency of the best CuInSe₂-based solar cell has reached 19% (Green *et al* 2007). However, several studies have been reported that during the production process of the cell *p*-CuInSe₂/*n*-CdS/ZnO (Al), interdiffusion of the elements via different interfaces may occur (Wada *et al* 1998; Heske *et al* 1999; Nakada and Kunioka 1999; Nakada 2000; Nakada and Mise 2001; Haug *et al* 2003; Nishiwaki *et al* 2003; Platzer-Björkman *et al* 2003). Interdiffusion of the elements across the interface is major problem which deteriorates the production quality of CuInSe₂. When, it diffuses in CuInSe₂, Zn acts as a donor and allows changing the conduction type and increasing in the conductivity (Benabdeslem *et al* 2005). Improvement of cell performance can be achieved by a better understanding of the mechanisms involved in the incorporation of

Zn in CuInSe₂ and the role of this element in the properties of the absorber. In the present work, we report on the effect of Zn diffusion on the lattice structure, composition and the conductivity in bulk CuInSe₂ samples.

2. Experiments

Ingots of CuInSe₂ were prepared by melting in vacuum a stoichiometric mixture made from pure Cu, In and Se elements as described (Benabdeslem *et al* 2005). To carry out the Zn-related diffusion study, 0.5 mm thick circular wafers were cut from the central part of the CuInSe₂ ingot and used as substrates on which Zn layers were deposited by evaporation at 2×10^{-6} Torr. The specimens were then heated in ambient air at temperatures in the range (550–700 °C). The thickness of Zn layer measured with vibrating quartz was 0.8 μm. The structural properties of the samples were characterized by X-ray diffraction (XRD) by means of a Phillips X-ray diffractometer powder using CuKα₁ radiation. The structural information was probed by SEM whereas the composition and the depth profiling by EDS. Zn content (in the bulk of each CuInSe₂ piece) was measured along the thickness of the samples. The conduction type and the material conductivity were determined by respectively, the thermal probe method and the high frequency technique (HF) in a contactless way based on microwave resonance cavity (Gire *et al* 1997; Gevrey *et al* 2001; Benabdeslem *et al* 2007).

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3. Experimental

3.1 Structural properties

The homogeneity of the as grown ingot was further confirmed by taking extra concentration profiles of the different elements along growth and radial axes of the ingot. When compound semiconductors are grown, stoichiometric deviations can occur in the different parts of the ingot (first zone to freeze, middle and last zone to freeze) and this is due to the difference in vapour pressures of the constituent elements. For this reason, only the samples cut from the middle part of the compound with the correct composition were considered in this study. In order to confirm the existence of Zn inside the CuInSe₂ crystals, diffusion profiles of Zn were conducted by EDS as illustrated in figure 1. Zn signals showed gradual profiles of diffusion for all samples. The diffusion profiles obtained were in good agreement with an erfc fitting. X-ray diffraction analysis of CuInSe₂ samples reported in figure 2 confirmed that Zn-doped and pure CuInSe₂ specimens crystallized in the chalcopyrite structure (JCPDS file card number 40-1487). With increasing diffusion temperature, the diffraction peaks became narrow. The line shrinking can be caused by both an increase in crystallite size and a decrease in lattice strain. It should be noted that XRD reflections are slightly right shifted as seen on the magnified (112) line. These internal stress modify the lattice parameters. Taking into account the quadratic form for the tetragonal system, the lattice constants *a* and *c* of the unit cell were calculated by the least-squares fit method (Cullity 1971). The obtained values reported in table 1 showed a decrease of the lattice parameters and according to Bragg's law this means a

slight contraction of the unit cell. This behaviour can be explained by the decrease of internal strain induced in the doped specimens. To estimate qualitative information regarding size and microstrain present in the doped samples. Williamson–Hall technique is used (Williamson and Hall 1953). In this method, both size and strain broadening are assumed to be Lorentzian:

$$\beta_{\text{total}} = \beta_{\text{size}} + \beta_{\text{strain}} = \beta \cos \theta = \frac{k\lambda}{D} + 4\varepsilon \sin \theta, \quad (1)$$

ε is the effective strain.

The size and strain were calculated for pure and Zn-doped CuInSe₂ using (112), (211) and (316) planes. The curve $\beta \cos \theta$ vs $4 \sin \theta$ shows approximately a linear variation as seen in figure 3. The effective crystallite size and strain are calculated using a linear equation; $y = A + \varepsilon x$. The slope of these lines gives strain ε while their intercept on y-axis shows the effective crystallite size *D*. The positive slope on Zn doping samples indicate the presence of tensile strains in the crystal lattice. As the temperature is increased, the average crystallite size increases while the strain calculated from the graph decreases (table 1). The increase in crystallite size observed may be attributed to the replacement of smaller ionic radius of Cu²⁺ (70 pm) with slightly higher Zn²⁺ (74 pm) (Shannon 1976). The dislocation density Δ is calculated using Williamsons and Smallman's equation (Padiyan *et al* 2002):

$$\Delta = \frac{1}{D^2}. \quad (2)$$

The dislocation density for the doped specimens shown in table 1 is highest among the studied crystals and for longer diffusion temperature, the density Δ decreases.

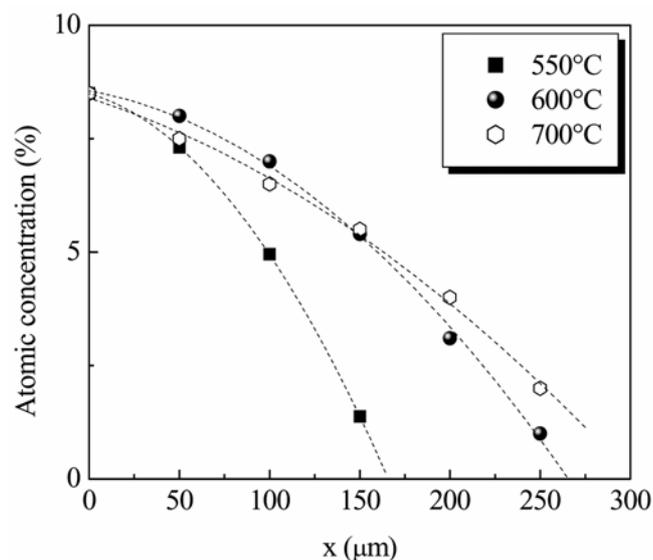


Figure 1. Concentration profiles of Zn in CuInSe₂.

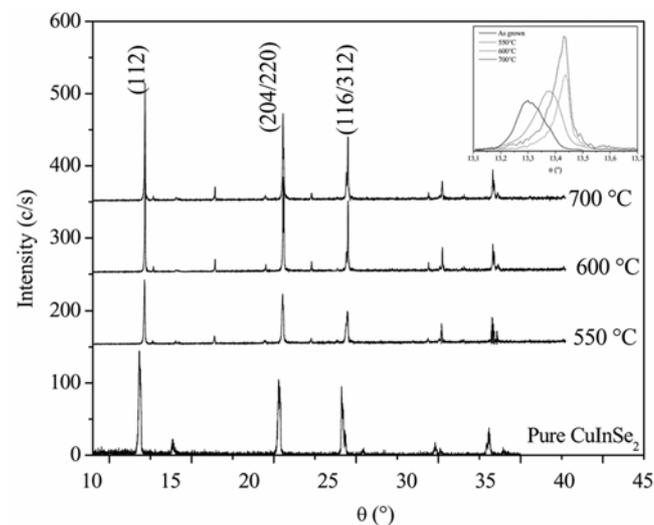


Figure 2. X-ray diffraction patterns of pure and Zn-doped CuInSe₂ crystals.

Table 1. Lattice parameters and volumes of as pure and Zn-doped CuInSe₂ crystals.

| | <i>a</i> (Å) | <i>c</i> (Å) | <i>cla</i> | <i>V</i> (Å ³) | W-H <i>D</i> (nm) | ϵ (10 ⁻⁴) | Δ (10 ¹⁵) (lines/m ²) |
|--------|--------------|--------------|------------|----------------------------|----------------------|--------------------------------|---|
| Pure | 5.91 | 11.71 | 1.98 | 409.99 | 25 | – | 1.60 × 10 ¹⁵ |
| 550 °C | 5.81 | 11.62 | 2.00 | 392.46 | 171 | 4.57 × 10 ⁻⁴ | 3.42 × 10 ¹³ |
| 600 °C | 5.77 | 11.61 | 2.01 | 387.20 | 250 | 5.87 × 10 ⁻⁵ | 1.60 × 10 ¹³ |
| 700 °C | 5.78 | 11.62 | 2.01 | 388.71 | 237 | 6.25 × 10 ⁻⁵ | 1.78 × 10 ¹³ |

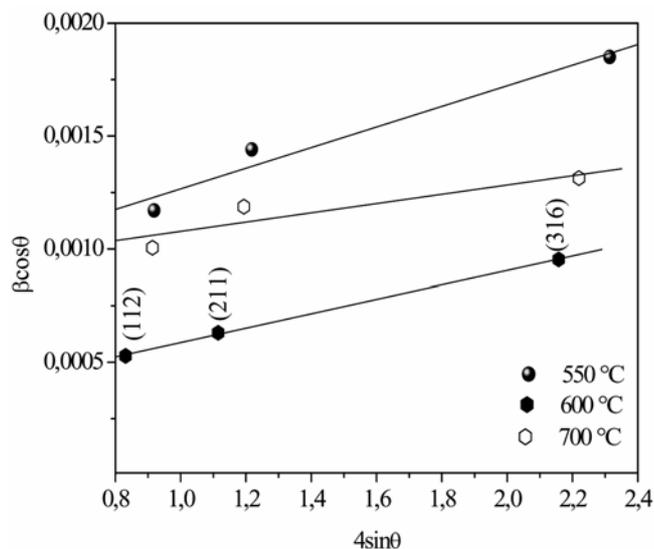


Figure 3. W-H analysis of Zn/CuInSe₂ at different diffusion temperatures.

Table 2. Composition of pure and Zn-doped CuInSe₂ crystals.

| Diffusion temperature | Cu (at%) | In (at%) | Se (at%) |
|-----------------------|----------|----------|----------|
| 550 °C | | | |
| P1 | 23.29 | 27.47 | 46.37 |
| P2 | 23.12 | 26.56 | 47.28 |
| P3 | 21.41 | 26.34 | 49.52 |
| 600 °C | | | |
| P1 | 28.10 | 25.70 | 43.50 |
| P2 | 25.30 | 25.50 | 42.50 |
| P3 | 22.20 | 24.80 | 41.70 |
| 700 °C | | | |
| P1 | 32.30 | 23.07 | 43.50 |
| P2 | 29.35 | 22.65 | 46.36 |
| P3 | 24.50 | 24.60 | 36.04 |

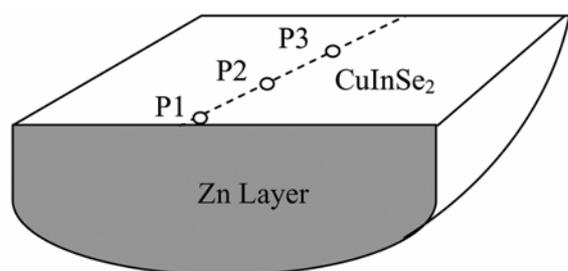


Figure 4. Positions of measured concentrations.

3.2 Composition analysis

Composition measurements were conducted on heated samples to determine the eventual changes in the content of different constituents in relation with the diffusion temperature. EDS analyses were made on several points labelled P1, P2 and P3 along the thickness of the doped samples as shown in figure 4. The elevated concentration of Cu near the surface is reported in table 2, may be explained by the fact that the copper element is extremely mobile due to its lower activation energy (0.35 eV), can migrate to the sample surface during the diffusion

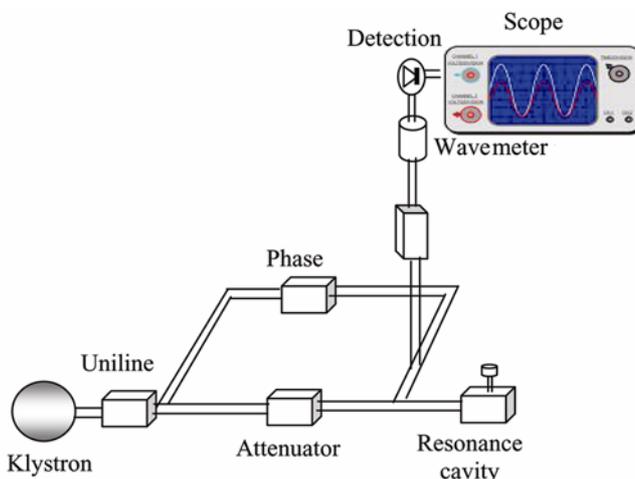


Figure 5. Experimental set up for HF conductivity measurements.

process. This behaviour is consistent with previous results, (Kenshole *et al* 1984). On the other hand, the In amount remains constant, whereas the decrease of Se is due to the sticking to the ampoule wall of this element is very volatile during the diffusion treatment. The variations in the content of the elements affect the properties of CuInSe₂ and deteriorate the production quality of absorbers.

Table 3. Electrical characteristics of as-grown and Zn-doped CuInSe₂ crystals.

| T (°C) | Time (h) | Type | $\chi'' \times 10^{-3}$ | $\sigma_{\text{HF}} \times 10^{-4}$ ($\Omega \text{ cm}$) ⁻¹ | δ (mm) |
|----------|----------|----------|-------------------------|---|---------------|
| Pure | – | <i>p</i> | 22 | 4.38 | 0.79 |
| 550 | 36 | <i>n</i> | 34 | 6.77 | 0.64 |
| 600 | 24 | <i>n</i> | 58 | 11.60 | 0.50 |
| 700 | 8 | <i>n</i> | 70 | 14.00 | 0.44 |

3.3 Electrical properties

The study of complex permittivity of materials at high frequencies is an interesting tool in estimating the conductivity. Microwave technique in the opposite way to the classical d.c. method does not need electrical contacts which cause parasitic resistance. The high frequency conductivity is generally a complex quantity: $\sigma_{\text{HF}} = \sigma_1 - i\sigma_2$ and can be determined from the measured values of the susceptibility as indicated by the following relation:

$$\sigma = \varepsilon_0 \omega \chi'' = 2\pi f \varepsilon_r \varepsilon_0 \chi'', \quad (3)$$

where ε_r is the permittivity of the free space ($8.85 \cdot 10^{-12}$ F/m) and ε_r the permittivity of the semiconductor material (for CuInSe₂, $\varepsilon_r = 3.9$). The electrical measurements based on the high frequency technique were performed at microwave frequency of 9192 MHz in a resonant cavity as shown in figure 5. The high frequency conductivity values of pure and Zn-doped CuInSe₂ specimens are summarized in table 3. The microwave assisted technique leads sometimes to high values of conductivity caused by the skin effect. The skin effect can be connected to the skin thickness using the equation:

$$\delta = \sqrt{\frac{2}{\mu_0 \sigma \omega}}, \quad (4)$$

μ_0 represents the magnetic permittivity ($4\pi \cdot 10^{-7}$) and ω the pulsation of the a.c. signal.

The obtained values of the parameter δ reported in table 3 showed that the skin thickness is more important than the thickness of the samples. Thus, the electrical measurements are not disturbed by the skin effect because the samples were well adjusted in the belly of the electrical field. Zn-doped CuInSe₂ samples were found *n*-type and conducting. V_{Cu} are more likely than V_{In} because copper might participate weakly in the covalent bonding. Thus, the increase in the conductivity might be due to the occupation of Cu vacancies sites by Zn atoms and consequently to the creation of donor levels close to the conduction band.

4. Conclusions

Zn diffusion into stoichiometric CuInSe₂ substrates under various temperatures (550–700 °C) has been investigated. The properties of CuInSe₂ were very sensitive to the diffu-

sion process. The migration of Zn in CuInSe₂ was confirmed by analysis of depth profiles and resulted in the deformation of the crystal lattice and hence reduced volumes (contraction of the cell lattice). The approach based on the deformation of the lattice crystal allows to confirm the diffusion kinetic of Zn in CuInSe₂ which operates substitutionally on Cu sites. Hyper frequency microwave measurements showed *n*-type properties of the doped CuInSe₂ crystals and as the diffusion temperature increases, the conductivity also increases. The factor responsible for this behaviour is thought to be Zn donors that occupy Cu sites.

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