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Defect chemistry of solar cell chalcopyrite materials

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The I-III-VI$_2$ chalcopyrite-structured compounds and related solid solutions are currently of interest for use as visible-light absorbing layers in thin-film solar cells. Depending on the deposition conditions and post-treatment, thin films of CIS and related materials might exhibit electronic or mixed ionic-electronic conductivity. They can be p-type or n-type semiconductors, due to the presence of point defects. The acceptor defects are copper- or indium-ion vacancies while the donor character is due to the copper- or indium – ion interstitials, and/or and/or sulphide ion vacancies. In addition to these simple defects, Raman studies, showed the presence of anti-site defects. The anti-site defects, related to the occurrence of Cu-Au ordering, deviate from the chalcopyrite structure and determine the quality of the CIS layer and the efficiency of the solar cell. In this paper the defect chemistry of CIS with deviations from stoichiometry and molecularity is addressed. The defect chemical equations, using the Kröger-Vink notation, are proposed for the CIS material as basis for explaining the defect formation and conduction mechanisms. A similar approach can be used to describe the defect structures of the related materials, like $CuGaS_2$, $CuInSe_2$, $Cu(Ga,In)S_2$.

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1. Introduction

The I-III-VI$_2$ chalcopyrite-structured compounds and related solid solutions are currently of interest for use as visible-light absorbing layers in thin-film solar cells. The fundamental optical and electrical properties of $CuInS_2$ (CIS) crystals and thin films have been investigated as well as targeting practical applications, e.g. in solar cells.

The reason for the choice of this material is that out of the many highly absorbing semiconductor compounds available, the grain boundaries in polycrystalline layers do not appear to be severely detrimental to device performance. Devices made using I-III-VI$_2$ compounds are found to be more stable than other thin-film devices [1]. The ternary Cu-chalcopyrite semiconductors $Cu(In,Ga)(Se,S)_2$ represent the absorber material for efficient thin-film solar cells that have been produced so far [2]. These semiconductors offer a wide range of band gap energies from 1.0 eV for $CuInSe_2$ to 2.4 eV for $CuGaS_2$. The optimum value for terrestrial solar cells is 1.5 eV, which corresponds with the band gap value of $CuInS_2$. Depending on deposition techniques, doping and post treatment, the CIS material can exhibit ionic, electronic (p-type or n-type) or mixed electronic-ionic conduction.

In many cases the physical properties of crystalline materials depend to a large extent on the presence of point defects. Thus, a prerequisite for specific applications is a thorough understanding of the materials' defect chemistry.

In this paper the defect chemistry of CIS with deviations from stoichiometry and molecularity will be addressed. The defect chemical equations, using the Kröger-Vink notation, are proposed for the CIS material as basis for explaining the defect formation and conduction mechanisms.

2. Experimental

The experiments carried out for this study contains two parts: CIS thin films synthesis by spray pyrolysis and their characterisation. The discussions of the results are based on the theory related to defect chemistry [3].

2.1 Synthesis of CIS thin films

An aqueous solution of copper chloride, $CuCl_2.2H_2O$ (Merck), thiourea $SC(NH_2)_2$ (Aldrich, 99%) and indium trihloride $InCl_3$ (Alfa Aesar, 99.999%) was used to prepare the precursor solution for the spray pyrolysis deposition. In order to obtain a deviation from molecularity in the film, the following values for the [Cu]/[In] ratios were used: 1 for the stoichiometric material, 1.64 for the for the Cu-rich material, and 0.75 for the In-rich one. A large excess of sulphur in the precursor solution was used: sulphur to copper molar ratio ([S]/[Cu]) of 6.

The solution was sprayed onto a heated Mo-coated glass substrates (325°C), using nitrogen as a carrier gas.

2.2 Characterization

The XRD patterns of the films were recorded using a Bruker D8 Advance Diffractometer with a monochromatic Cu Kα_1 source. The crystalline structure was also studied with a home-built Raman spectrometer with as excitation source a Spectra Physics Millennia Nd:YVO_4 laser with a wavelength of 532 nm.

2.3 The Kroger - Vink notation

The defect formation is represented in the form of defect lattice reactions using the Kröger-Vink notation. In the Kröger-Vink defect notation the dot (˙) represents an effective positive charge, the dash (‘) an effective negative charge and x zero-effective charge.

The CIS material is a ternary material and different types of defects can be expected in the lattice: cation and anion vacancies (V_{Cu}', V_{In}''', $V_S^{\cdot\cdot}$), interstitial ions ($Cu_i^{\cdot}$, $In_i^{\cdot\cdot\cdot}$, S_i''), and cation anti-site disorder (Cu-Au ordering). In general, intrinsic point defects are thermally generated in CIS according to a Schottky mechanism (the formation of cation and anion vacancies, presented in equation 1), the Frenkel mechanism (the displacement of a cation in an interstitial position and leaving behind a cation vacancy, equations 2, 3), or an anti-Frenkel mechanism (the displacement of an anion in an interstitial position and leaving behind an anion vacancy, equation 4). The anti-site disorder occurs when cations exchange places in the lattice, i.e. Cu_{In}'' and $In_{Cu}^{\cdot\cdot}$. The anti-site defects can form an ordered arrangement, which is referred to as the Cu-Au ordering ($_{Cu\text{-}Au}$CIS).

$$0 \leftrightarrow V_{cu}' + V_{In}''' + 2V_S^{\bullet\bullet} \qquad (1)$$

$$0 \leftrightarrow Cu_i^{\bullet} + V_{Cu}' \qquad (2)$$

$$0 \leftrightarrow In_i^{\bullet\bullet\bullet} + V_{In}''' \qquad (3)$$

$$0 \leftrightarrow S_i''' + V_S^{\bullet\bullet} \qquad (4)$$

3. Results

The recorded XRD patterns and the Raman spectra are presented in Figs. 1, 2 and 3.

For the stoichiometric CIS the XRD pattern (Fig. 1 a) the presence of CIS, Mo, and In_5S_4 is revealed. In the Raman spectra, the following phases were identified: CIS chalcopyrite structure, Cu-Au ordered CIS, ($_{Cu\text{-}Au}$CIS), Mo, Mo_2S_3, and a Cu-poor phase.

In the Cu-rich material (Fig. 2 a, and 2 b) the CIS chalcopyrite, the $_{Cu\text{-}Au}$CIS, and the Cu_2S and Cu_xS structures were identified.

In the In-rich material (Fig. 3a and 3b) the CIS chalcopyrite, the $_{Cu\text{-}Au}$CIS, and the In_2S_3 structures were identified.

All recorded XRD patterns revealed Mo-S related structures and an unidentified peak at 36.5°, which could not be assigned to a material.

4. Discussion

The XRD and Raman spectra revealed the formation of thin films comprising the CIS with the chalcopyrite structure and also the presence of Cu-Au ordering. In the Raman spectra the signals of these phases are present at 290 cm^{-1} (chalcopyrite $CuInS_2$) and at 305 cm^{-1} ($_{Cu\text{-}Au}$CIS) [4]. The presence of peaks in between these values is an indication of a mixture of both structures.

The formation mechanism of the $_{Cu\text{-}Au}$CIS phase can be explained considering the simultaneous formation of Frenkel disorder in both cation sub-lattices of CIS lattice (equations 2 and 3). The formation of the In interstitial and In vacancy (equation 3) is not energetically favorable, because of the high electric charge of the point defect, but this reaction is formally possible. If both reactions occur, in the Cu and In ions in interstitial positions and their vacancies are present. In this case, the Cu ion can occupy the In site and the In ion in the copper site. The process is presented in equation 5.

$$Cu_i^{\bullet} + V_{Cu}' + In_i^{\bullet\bullet\bullet} + V_{In}''' \rightarrow Cu_{In}'' + In_{Cu}^{\bullet\bullet} \qquad (5)$$

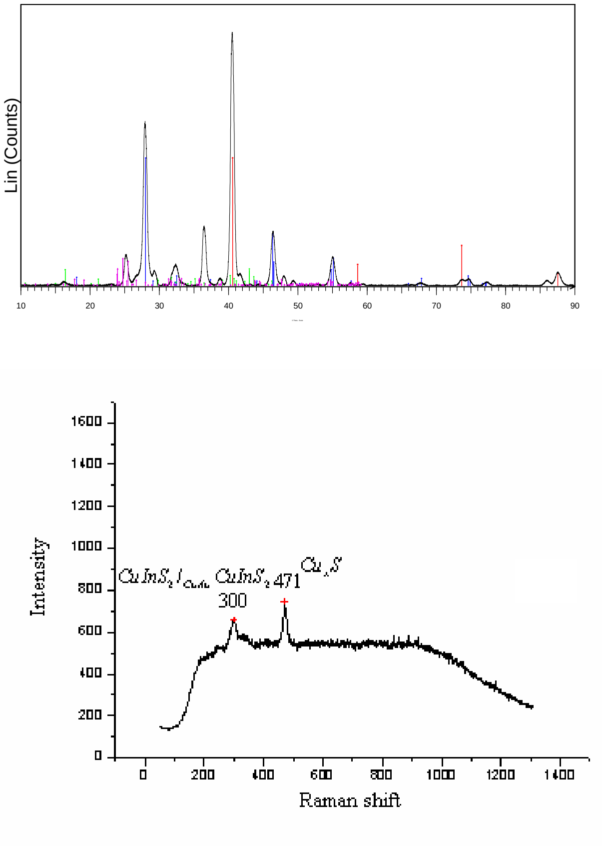

Fig. 1. The XRD pattern (a) and Raman spectrum (b) for stoichiometric CIS.

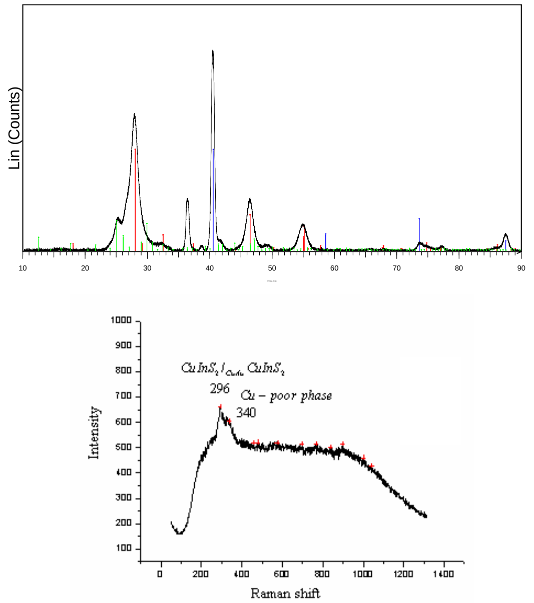

Fig. 2. The XRD pattern (a) and Raman spectrum (b) for Cu-rich CIS.

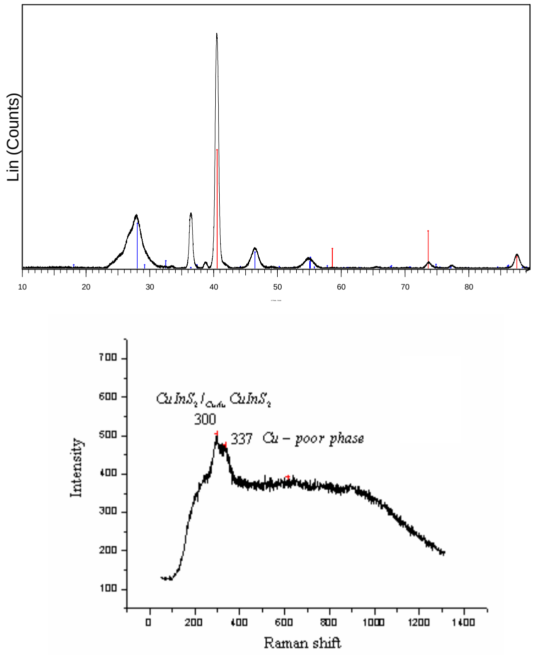

Fig. 3. The XRD pattern (a) and Raman spectrum (b) for In-rich CIS.

Here, it is assumed that the Frenkel disorders represent an intermediate situation.

This is not surprising as the ionic radii are very close (74 nm for Cu and 76 nm for In [5]). Thus, the Cu-Au ordering can be present in every CIS lattice. This type of disorder will not be predominant because the involvement of the In defects, which are energetically not favorable.

The structural characterization of the stoichiometric CIS revealed the presence of copper-poor phases. An explanation for this fact might be based also on the Frenkel disorder mechanism. The copper ions are displaced from their normal lattice positions, occupying an interstitial position and probably moving to the surface to form a copper oxide (equation 6) thus the copper content being depleted.

$$Cu_i^{\bullet} + \frac{1}{2}O_{2(g)} \rightarrow CuO_{(s)} + h^{\bullet} \qquad (6)$$

During this process holes are generated, compensating the effective charge of the copper vacancies in the material, hence the p-type conduction can occur.

In the case of the Cu-rich material, several defect reactions presented in equations 7, 8 and 9 can describe this composition.

$$Cu_2S \xrightarrow{CuInS_2} 2Cu_{Cu}^{x} + 2V_{In}^{'''} + S_S^{x} + 3V_S^{\bullet\bullet} \qquad (7)$$

$$Cu_2S \xrightarrow{CuInS_2} Cu_{Cu}^{x} + Cu_i^{\bullet} + V_{In}^{'''} + S_S^{x} + V_S^{\bullet\bullet} \qquad (8)$$

$$Cu_2S \xrightarrow{CuInS_2} Cu_{Cu}^{x} + Cu_{In}^{''} + S_S^{x} + V_S^{\bullet\bullet} \qquad (9)$$

The most energetically favorable is equation (9), because it involves the smallest number of defects with low electric charges. The probability of occurrence of the other equations is not completely excluded.

The incorporation of In_2S_3 in the CIS lattice, in the case of In-rich material can be described with equations 10, 11 and 12. From this group of equations, equation (12) might be the preferred one, without completely excluding the other lattice reactions.

$$In_2S_3 \xrightarrow{CuInS_2} 2V_{Cu}^{'} + 2In_{In}^{x} + 3S_S^{x} + V_S^{\bullet\bullet} \qquad (10)$$

$$In_2S_3 \xrightarrow{CuInS_2} V_{Cu}^{'} + In_{In}^{x} + In_i^{\bullet\bullet\bullet} + 2S_S^{x} + S_i^{''} \qquad (11)$$

$$In_2S_3 \xrightarrow{CuInS_2} In_{Cu}^{\bullet\bullet} + In_{In}^{x} + 2S_S^{x} + S_i^{''} \qquad (12)$$

As mentioned in the experimental part, the precursor solution contains excess sulphur. One of the reasons is that the sulphur ions act as reducing agent for the Cu(II) – as present in the precursor solution to Cu(I) – as present in the CIS lattice. In this case, the sulphur ions are oxidized to sulphur atoms which should be present in the aerosol mixture inducing thus in the lattice deviation from stoichiometry, described by equations 13-15.

$$S_{2(g)} \rightarrow V_{Cu}^{'} + V_{In}^{'''} + 2S_S^{x} + 4h^{\bullet} \qquad (13)$$

$$\frac{1}{2}S_{2(g)} + V_i^{x} \rightarrow S_i^{''} + 2h^{\bullet} \qquad (14)$$

$$\frac{1}{2}S_{2(g)} + V_S^{\bullet\bullet} \rightarrow S_S^{x} + 2h^{\bullet} \qquad (15)$$

Considering equation (14) the formation of segregated Cu_2S and In_2S_3 phases as identified in the XRD and Raman spectra can be explained. For CIS lattice the Frenkel disorders have been considered to explain the occurrence of interstitial cations. The formation of the new phases is presented in equations 16 - 19.

$$2\mathrm{Cu}_i^{\bullet} + \mathrm{S}_i^{''} \leftrightarrow \mathrm{Cu}_2\mathrm{S}_{(s)} \tag{16}$$

$$2\mathrm{Cu}_i^{\bullet} + \mathrm{S}_S^{x} \rightarrow \mathrm{Cu}_2\mathrm{S}_{(s)} + \mathrm{V}_S^{\bullet\bullet} \tag{17}$$

$$2\mathrm{In}_i^{\bullet\bullet\bullet} + 3\mathrm{S}_i^{''} \leftrightarrow \mathrm{In}_2\mathrm{S}_{3(s)} \tag{18}$$

$$2\mathrm{In}_i^{\bullet\bullet\bullet} + 3\mathrm{S}_S^{x} \rightarrow \mathrm{In}_2\mathrm{S}_{3(s)} + 3\mathrm{V}_S^{\bullet\bullet} \tag{19}$$

Combining a deviation from stoichiometry and from molecularity, (equations 20 and 21), the p-type conduction of the CIS material can again be shown.

$$\mathrm{Cu}_2\mathrm{S} + \frac{1}{2}\mathrm{S}_{2(g)} \xrightarrow{\mathrm{CuInS_2}} \mathrm{Cu}_{Cu}^{x} + \mathrm{Cu}_{In}^{''} + 2\mathrm{S}_S^{x} + 2h^{\bullet} \tag{19}$$

$$\mathrm{In}_2\mathrm{S}_3 + \frac{1}{2}\mathrm{S}_{2(g)} \xrightarrow{\mathrm{CuInS_2}} 2\mathrm{V}_{Cu}^{'} + 2\mathrm{In}_{In}^{x} + 4\mathrm{S}_S^{x} + 2h^{\bullet} \tag{20}$$

It has to be mentioned that a deviation from stoichiometry is more likely to occur when the materials are annealed in a sulfur atmosphere, which was not the case in the work presented here. But still, the presence of sulfur in the precursor solution might induce these processes.

5. Conclusions

The study presented in this paper was focused on the description of the defect chemistry of $CuInS_2$. Stoichiometric CIS, Cu-rich and In-rich materials have been prepared.

The thin films were prepared using the spray pyrolysis technique and they were analysed by XRD and Raman spectroscopy. The structural analysis revealed different phases in the thin films. The formation of these phased was explained using defect chemical lattice reactions.

A combined deviation from stoichiometry and from molecularity illustrates the complexity of the defect chemistry of CIS.

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