OURNALOF

Ceramic Processing Research

Crystal growth of materials for photovoltaics

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An overview is given on the crystal growth of materials for thin film photovoltaic application such as chalcopyrites, e.g. $CuInSe_2$, and transition metal chalcogenides, e.g. MoS_2 . In order to study in detail their properties and their applicability as absorber materials high-quality crystals are prepared. Because of solid-solid phase transitions in the chalcopyrite systems the chemical vapor transport technique is useful to grow the crystals below these phase transition temperatures. To grow transition metal chalcogenides, not only halogen but also an excess of chalcogen is used in this technique. The main challenge here is the control of the composition of the gas phase as well as the optimization of the temperature field during the process.

Key words: Chalcopyrites, Transition metal dichalcogenides, Chemical vapor transport, Bridgman technique.

Introduction

Semiconducting materials based on chalcopyrite- and molybdenite-type compounds such as CuBX₂ (B = In, Ga; X = S, Se) and MX₂ (M = Mo, W; X = S, Se, Te) are of interest for photovoltaic applications because of their efficient light absorbance and appropriate electronic properties such as carrier mobility and doping behavior. These classes of compound semiconductors have band gaps E_g in the range 1-1.6 eV and high absorption coefficients leading to a typical absorption length L < 0.5 µm in the visible spectral range. They allow for tailoring of material properties with respect to conversion efficiency, availability and non-toxicity of the elements by chemical modification.

Using an optimized absorber material based on the chalcopyrite $Cu(In,Ga)Se_2$ with a band gap of 1.1 eV conversion efficiencies close to 20% were reported for a thin film solar cell [1]. Investigating CuInS₂ solid state cells, a conversion efficiency of 11.4% was reached [2]. In photoelectrochemical cells studying tungsten diselenide WSe₂ crystals as electrodes a conversion efficiency of 17% was obtained using high quality crystals. The average efficiency of this type of cell yielded 13-15% [3].

Besides their general suitability as absorber material in solar cells two-dimensional layered chalcogenides offer specific advantages as they provide atomically smooth and chemically inert van der Waals (0001) surfaces. The valence and conduction band edges of the layered Mo and W dichalcogenides are formed mainly from non-bonding metal d-states resulting in

*Corresponding author: Tel:+49-30-8062-2880 high photoelectrochemical stability [4]. The sulfides MoS_2 and WS_2 have the advantage to be composed of non-toxic and abundant elements compared to indium and selenium in chalcopyrites.

Chalcopyrites

The crystal structure of the chalcopyrites is named after the mineral "chalcopyrite – CuFeS₂", which crystallizes in a tetragonal body centered structure (I42d) as shown in Figure 1. It is based on the sphalerite structure where the zinc lattice sites are occupied by Cu and In(Ga) atoms in an ordered manner. For an accurate crystallographic description of



Fig. 1. Crystal structure $I\overline{4}2d$ of chalcopyrite-type compounds.

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Table 1. Lattice parameters, melting points and phase transition temperatures of CuBX₂ chalcopyrites (B=In,Ga; X=S,Se)

	CuInSe ₂	CuInS ₂	CuGaSe ₂	$CuGaS_2$
Space Group	1 4 2d	$I\overline{4}2d$	I 4 2d	$I\overline{4}2d$
a(Å) c(Å)	5.78 11.64	5.52 11.08	5.61 11.00	5.35 10.46
c/a	2.01	2.01	1.96	1.96
T_m (°C)	990 996	1050 1101	1102	1250
T_{ph} (°C)	810 822-826 (597)	$\begin{array}{c} 1040 \\ 1047 \end{array}$	1056	(1189)
	. ,	980 990		
$E_{g}\left(eV ight)$	1.04	1.53	1.68	2.43

the structure the lattice constant a_0 of the zincblende unit cell has to be doubled in the *c*-direction leading to a tetragonal cell. Deviation in the ratio c_0/a_0 from 2 indicates a shrinking or expanding of the unit cell due to different coordination of the metal atoms in (001) and (100) lattice planes. Lattice parameters, melting points and phase transitions temperatures for the chalcopyrites Cu(In,Ga)(S,Se)₂ are summarized in Table 1.

The phase diagrams of related pseudo-binary systems such as $Cu_2S-In_2S_3$ or $Cu_2Se-Ga_2Se_3$ show either a congruent or an incongruent melting behavior of the chalcopyrite phase as well as solid-solid-phase transitions. Studying the phase relations of $CuInS_2$, the pseudo-binary cut $Cu_2S-In_2S_3$ - shown in Figure 2, adapted from [5] - includes two solid-solid phase transitions. Passing the liquidus from the melt the material first crystallizes in a wurtzite-like structure at 1090 °C. At the solid-solid phase transition at 1047 °C the wurtzite-type phase converts into the sphalerite structure. Below 983 °C the room temperature modifi-



Fig. 2. Pseudobinary phase diagram $Cu_2S-In_2S_3$ according to Binsma [5]. The re-evaluated data measured by Binsma allow one to infer a deflected course of the liquidus line at the congruent melting point of $CuInS_2$. This behaviour is confirmed by our own differential thermal analysis data shown as open squares in the figure.

cation of a chalcopyrite-type structure is formed.

Considering the binary join $Cu_2Se-Ga(In)_2Se_3$ [6, 7], it can be concluded that the homogeneity range of the selenides $CuGaSe_2$ and $CuInSe_2$ extends up to 10 mole% into the direction of Ga_2Se_3 and In_2Se_3 , respectively. On the other hand, the homogeneity ranges of the corresponding sulfides, $CuInS_2$ and $CuGaS_2$, seems to be rather narrow, e.g. smaller than < 1 mole%, see [8].

Crystal growth of chalcopyrites

Chalcopyrite crystals are grown either by chemical vapor transport or by the Bridgman growth technique. The chemical vapor transport method is advantageous to grow crystals below their solid-solid phase transition temperatures. A disadvantage of this technique, however, is the accidental incorporation of the transport agent into the crystal lattice, leading to an additional doping of the material.

We use quartz glass ampoules in order to grow chalcopyrite crystals by chemical vapor transport. Stoichiometric ratios of highly pure elements are filled in the ampoule. Iodine as transport agent is added in the form of small crystals at a concentration of about 5 mg/cm³. After evacuating and sealing, the ampoule is kept at the growth temperature for 3 weeks. Large chalcopyrite crystals are obtained in a temperature field of $\Delta T = 850 \text{ °C-}750 \text{ °C}$. In this case the transport takes place from the hot to the cold end of the ampoule. Figure 3 shows an example of a CuGaSe₂ crystal. Obviously the (112) face appears as the predominant face of the crystal visible by an enhanced reflectivity in Figure 3. The simplified transport reaction, derived from mass spectroscopy, can be formulated as

$$CuGaSe_{2}(s) + 2I_{2}(g) \Leftrightarrow \frac{1}{3}(CuI)_{3}(g) + GaI_{3}(g) + Se_{2}(g).$$
(1)

Copper is mainly transported in the form of Cultrimers. Residues of adhesive copper iodide on the surfaces of the crystals can be removed by etching in



Fig. 3. Photograph of a large $CuGaSe_2$ crystal grown by chemical vapor transport using iodine. The reflecting surface is indexed as (112) crystal plane.



Fig. 4. Photograph of a $CuInSe_2$ ingot after crystallization in a pBN boat. Strongly reflecting areas indicate the presence of large single crystalline grains.

an ammonia solution.

Chalcopyrite crystals grown by the Bridgman growth technique can be achieved by slow cooling from the melt down below the solid-solid phase transition temperatures at e.g. 1-5 K/h. The elements are placed in a pyrolytic boron nitride (pBN) - or a glassy carbonboat in a closed quartz glass ampoule. The synthesis and the growth process are performed in one single step. After synthesis the material is heated to 50 degrees above the melting point in order to ensure the homogeneity of the melt. In order to suppress the decomposition of the chalcopyrite melt and within the growing crystal an additional (In,Ga)₂(S,Se)₃ source is held at 450 °C and 700 °C for the sulfides and for the selenides, respectively. According to the equilibrium gas phase equations

$$2\text{CuInX}_{2}(s) \Leftrightarrow \text{Cu}_{2}X(s) + \text{In}_{2}X(g) + X_{2}(g)$$

X = S, Se (2)

$$2CuGaX_{2}(s) \Leftrightarrow Cu_{2}X(s) + Ga_{2}X(g) + X_{2}(g)$$

X = S, Se (3)

the equilibrium is shifted towards the left side, the chalcopyrite phase, by forming In_2X or Ga_2X and X_2 -species caused by the additional source. Otherwise the melt would be slightly enriched by Cu_2X which is built into the lattice up to a certain concentration by occupying interstitial lattice sites.

After passing the lower solid-solid phase transition temperature the cooling rate can be increased to values up to 50 K/h. Crystalline ingots of about 10 cm length and 10 mm in diameter were obtained. They consist of large single crystalline grains, as becomes clearly visible in Figure 4.

Layered transition metal dichalcogenides

Transition metal dichalcogenides of the type MX_2 (M = Mo, W; X = S, Se, Te) have a hexagonal crystal structure according to the mineral "molybdenite -MoS₂" (*P6₃/mmc*), as depicted in Figure 5. They are



Fig. 5. Crystal structure $P6_3/mmc$ of molydenite-type compounds. The 2H-modification with a trigonal-prismatic coordination of the metal atom is shown.

formed by two-dimensional sandwich layers of covalently bonded X-M-X units which are separated from each other by weak van der Waals type interactions. In this class of layered compounds two structures are dominant. The coordination of the metal atom is either trigonal-prismatic or octahedral. One distinguishes between 1T-, 2H- and further modifications according to the periodically occurring sequence X-M-X in the cdirection. The symmetry of the modifications is denoted by trigonal (T), hexagonal (H), or rhombohedral (R). In Figure 5 the trigonal-prismatic coordination of the metal atom in the 2H-modification, namely a hexagonal structure of the type $P6_3/mmc$, is shown. Concerning the octahedral metal atom coordination, a 1T-modification is built up, crystallizing in the space group $P\overline{3}m$, displayed in Figure 6. As shown in Table



Fig. 6. Crystal structure $P\overline{3}m$ of layered compounds. The IT-modification with an octahedral coordination of the metal atom is depicted.

Table 2. Lattice parameters of transition metal chalcogenides MX₂ (M=Mo,W; X=S,Se,Te)

Material	$\begin{array}{c} \text{Band Gap} \\ E_g(eV) \end{array}$	Structure	Lattice Parameters	
		Structure	a (Å)	c (Å)
MoS ₂ (2H)	0.85-1.96	hexagonal P6 ₃ /mmc	3.16	12.294
$MoSe_2$ (2H)	1.1-1.64	hexagonal P6 ₃ /mmc	3.288	12.920
MoTe ₂ (2H)	0.9-1.17	hexagonal P6 ₃ /mmc	3.517	12.966
WS ₂ (2H)	2.07	hexagonal P6 ₃ /mmc	3.155	12.362
WSe ₂ (2H)	1.75	hexagonal P6 ₃ /mmc	3.286	12.976

2, the semiconducting compounds appear in the 2H-modification.

Crystal growth of layered compounds

We grow crystals of these layered materials by chemical vapor transport. Quartz glass ampoules loaded with pre-reacted MoX₂ or WX₂ powders are used. The halogens Cl₂, Br₂ and I₂ are filled in as transport agent at a concentration of 5 mg/cm³. Instead of foreign transport agents even a chalcogen excess might successfully accomplish the transport when used at a concentration of 5-10 mg/cm³. Crystal growth takes place in a temperature field of $\Delta T = 950-850$ °C for MoS₂/WS₂ and $\Delta T = 830-770$ °C for MoTe₂. The simplified transport reaction can be expressed as

$$MX_{2}(s) + Hal_{2}(g) \Leftrightarrow MHal_{4}(g) + X_{2}(g).$$
(4)

In the case that the chalcogen tellurium is to be transported the partial pressure of tellurium is not sufficient in order to accomplish the transport even at higher temperatures. Therefore, we suppose the following transport equation

$$MoTe_2(s) + 6Br_2(g) \Leftrightarrow MoBr_4(g) + 2TeBr_4(g).$$
 (5)

However, the amount of incorporated transport agent is particularly noticeable in this case. It was found to be in the range of 1-5 at% [9]. It is supposed that the incorporated halogen is located mainly within the van der Waals gap. This causes an increase of the lattice parameter c_0 depending on the amount of incorporated species in the crystal. MoTe₂ crystals grown with chlorine or bromine are n-type semiconductors. By proper selection of the transport agent it is possible to control the electrical properties of the crystals. Thus WSe₂ grown with bromine leads to n-type material. However, the crystals show a rather p-type behavior by using an excess of selenium as transport agent [10]. The vapor species serving for the transport of tungsten is assumed to be gaseous WSe₃ [11]. Crystals obtained with different transport agents show different typical dimensions. N-type WSe₂ crystals are usually up to 1



Fig. 7. Photograph of a large MoTe₂ crystal grown by chemical vapour transport. The (0001) surface has a size of about 20×10 mm².

mm thick while p-type WSe₂ crystals exhibit a thickness of about 10 μ m [10]. The quality of the crystals is strongly influenced by temperature, temperature gradient and transport agent. After a growth time of three weeks, WSe₂ and MoTe₂ crystals show van der Waals faces of about 20 × 10 mm² in size and MoS₂ of 5 × 5 mm², respectively. Figure 7 shows MoTe₂ crystals grown using chlorine as transport agent after a growth time of 150 hours.

So far, it is fairly difficult to grow reproducibly large sized WS_2 and MoS_2 crystals. The main challenge is to control the high nucleation rate in the beginning of the growth process. It can be affected by temperature and composition of the gas phase. As reported by Schäfer *et al.* [12] the transport of tungsten takes place via the formation of WX_4 (X=Cl, Br) using Br₂ and Cl₂ as transport agents. In the case of I₂ there is an oxygen-containing compound necessary. WO_2I_2 is formed in the presence of WO_2 or WO_3 . Only the presence of such a species can explain the transport observed.

In our own experiments an advantageous effect of MoO_2Br_2 in the gas phase is clearly shown. The crystal growth process is improved by adding MoO_2 or MoO_3 to the bromine transport agent. Transport of WS_2 with iodine alone occurs rather fast. The crystals grown in this way remain small. The transport rate can be reduced by adding WO_2 or WO_3 to the ampoule stimulating the growth of larger crystals. Typically heavily intergrown crystals of mm-size are produced. There is a need for optimizing concentration and composition of oxyhalogenides in the gas phase. Furthermore, an optimized temperature gradient for the growth process is to be found.

For the use of layered transition metal chalcogenides as absorbers in solar cells it is necessary to prepare thin-films with platelet-like crystallites oriented parallel to the van der Waals surfaces. The formation of thin and highly textured WS_2 layers was achieved by sulfurization of tungsten oxide WO_3 layers at 900 °C in an S/H₂-atmosphere [13]. The process benefits from the formation of a liquid nickel sulfide phase during the formation of WS_2 crystallites [14].

Summary

We have discussed the structure of chalcopyrites and transition metal dichalcogenides as interesting absorber materials for thin film solar cells. In order to obtain crystals that are sufficiently large for detailed analysis of their properties we employed chemical vapor transport as well as the Bridgman growth technique. For selected systems, the transport reaction equations are discussed and results presented.

Large chalcopyrite crystals are obtained using iodine as transport agent. The transition metal chalcogenides are grown by bromine or chlorine as transport agent. In the sulfide systems the addition of metal oxides improves the growth process. Even a chalcogen excess leads to good crystals. The selection of the transport agent controls the electrical properties of the crystals.

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