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Polycrystalline $CuGaSe_2$ Thin Films Grown by CVD with I2 as Transport Agent

A. Jäger-Waldau, N. Meyer, T. Weiss, S. Fiechter, M. Ch. Lux-Steiner
K. Tempelhoff [1] and W. Richter [1]

Hahn-Meitner-Institut Berlin, Glienicker Straße 100, 14109 Berlin, Germany
Phone: +49-30-8062 2604, FAX: +49-30-8062 3199, e-mail: jaeger-waldau@hmi.de
[1] Institut für Festkörperphysik, PN 6-1, Technische Universität Berlin, Hardenbergstraße 36, 10623 Berlin

1. Introduction

Chalcopyrites are well suited absorber materials for the preparation of high efficient thin film solar cells. In the system $Cu(Ga,In)(S,Se)_2$ the band gap can be varied by alloying from $E_G = 1.01$ eV for pure $CuInSe_2$ to $E_G = 2.40$ eV for $CuGaS_2$. Since successful realisation of $Cu(In,Ga)Se_2$ solar cells with efficiencies exceeding 16% has been reported [1], there is an increasing interest for materials with higher band gaps for a more optimised alignment with the solar spectrum, e.g. $CuInS_2$ [1, 2] single junction device.
$CuGaSe_2$ with a band gap of $E_G = 1.68$ eV is a well suited candidate for the top cell of a multi-junction device. In order to achieve this goal, the $CuGaSe_2$ cell has to be optimised first.
In this paper we report on the preparation of $CuGaSe_2$ thin films by a chemical vapour deposition (CVD) process with iodine as transport agent.

2. Experiments and Results

Thin films of $CuGaSe_2$ were deposited on 1×1 inch^2 float glass substrates by a CVD process. The schematic drawing of the deposition apparatus is shown in Fig. 1. An optical heating system combined with graphite susceptors was used to heat the reactor.

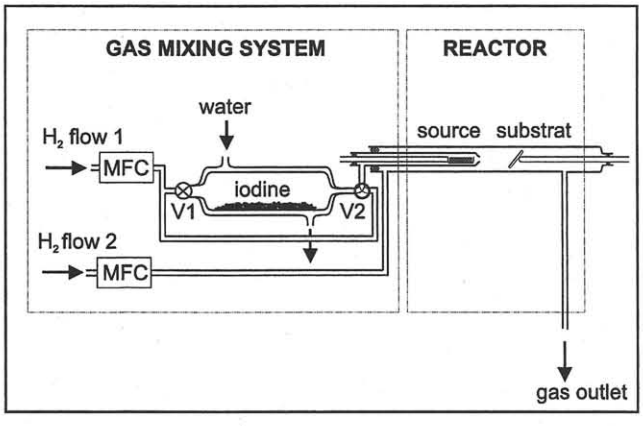

Fig. 1 Schematic drawing of deposition apparatus

As source material pressed $CuGaSe_2$ pellets were used. The $CuGaSe_2$ source material was prepared by synthesis of stoichiometric amounts of high purity elements (at least 5N). The elements were filled into a quartz glass ampoule which was evacuated and sealed. The reaction took place a furnace at a final temperature of 950°C.

Chemically cleaned glass substrates were placed in the reaction chamber approx. 35 mm away from the source material. Typically, the following deposition parameters were used. The temperature of the iodine source was kept at $T_{I2} = 80$°C, which corresponds to an iodine partial pressure in H_2-flow 1 of $p_{I2} = 19$ mbar. The source temperature was $T_{sc} = 600$°C and the substrate temperature was $T_{sub} = 550$°C. H_2 flow 1 and 2 were 100 ml/min each.
While heating up the system, the valves V1 and V2 (see Fig. 1) were in such a position that the H_2 flow 1 was bypassing the iodine source. Therefore, no iodine was present in the reaction chamber. After the temperature stabilised, the valves 1 and 2 were switched over and with H_2-flow 1 iodine was transported into the reactor. After a deposition period of typically 1 to 2 h the valves were switched again to bypass the iodine during cooling.
To determine structure and composition the prepared films were characterised by scanning electron microscopy (SEM), energy dispersive x-ray analysis (EDX) and X-ray diffraction (XRD). The films exhibited an average crystallite size of 3 to 5 µm. The EDX analysis was performed without standards. Within the experimental limits of this analysis the prepared films showed the stoichiometric composition of $CuGaSe_2$. A typical XRD diffractogram is depicted in Fig. 2. It can be seen that the film is single phase and exhibits the typical chalcopyrite structure.

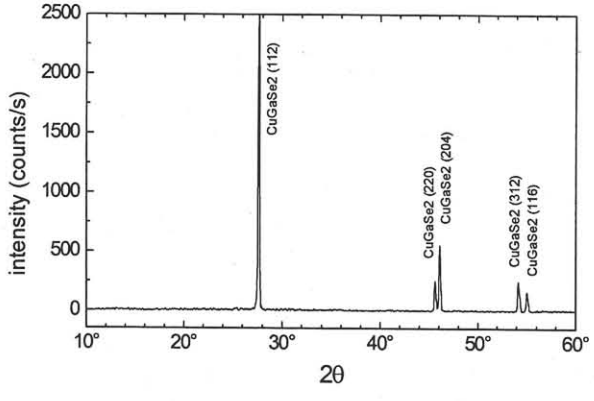

Fig. 2 XRD diffractogram of a $CuGaSe_2$ thin film

For comparison with the deposition conditions in a closed system [3], iodine was introduced into the reactor during the whole deposition process, including heating and cooling.
As shown in Fig. 3, the XRD measurements revealed, that the $CuGaSe_2$ films were no longer of single phase but exhibited an additional phase, which was identified as CuI.

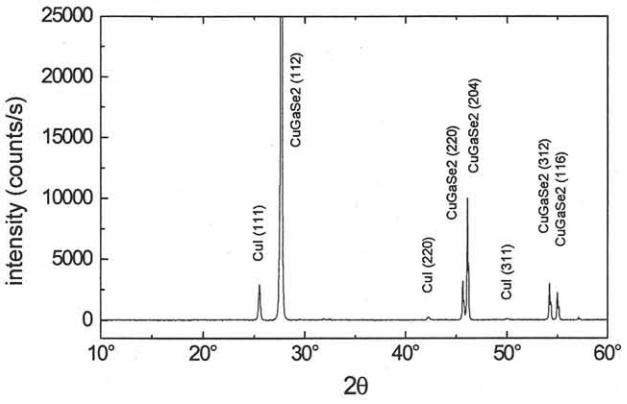

Fig. 3 XRD diffractogram of a $CuGaSe_2$ thin film prepared in presence of iodine during heating and cooling the reactor

In order to model the chemical processes involved in the system Cu-Ga-Se-I-H thermochemical calculations were performed for the system under equilibrium conditions. For this purpose the computer program ChemSage [4] and the thermochemical data listed in ref. 5 were used.
Since the thermochemical data for $CuGaSe_2$ are unknown, the standard entropy and enthalpy were estimated. The related values of the binaries Cu_2Se and Ga_2Se_3 were added and in order to take into account the new phase formation the sum of the standard enthalpies was multiplied by the factor 1.06. The coefficients to describe the molar heat were determined using the estimation published by Kubaschewski and Alcock [6]. The input parameters for this equation were the melting point and the molar heat at 298 K $C_p(298)$. The value of the melting point m_p of the synthesised $CuGaSe_2$ was determined by differential thermal analysis (m_p = 1380 K). $C_p(298)$ was calculated using formula and data given by Kubaschewski and Alcock [6] ($C_p(298)$ = 99.6 J/K mole). The resulting thermochemical properties of $CuGaSe_2$ are given in Table 1.

Table 1 Estimated thermochemical properties of $CuGaSe_2$

properties	values
standard enthalpy	ΔH_{298} = - 251 kJ/K mole
standard entropy	ΔS_{298} = 155 J/K mole
molar heat	$C_p = a + b \times 10^{-3} T + c \times 10^5 T^{-2}$
	a = 117 J/K mole
	b = 3.52 J/K² mole
	c = - 16.7 J K/mole

Input parameters for ChemSage calculations were the total pressure of the system $p_{tot.}$, the molar quantities of $CuGaSe_2$ $n_{CuGaSe2}$, iodine n_{I2}, hydrogen n_{H2}, and the temperature T. These parameters were chosen according to the deposition conditions in the CVD reactor. The result of the ChemSage calculation using p_{tot} = 1 bar, $n_{CuGaSe2}$ = 0.014 mole, n_{I2} = 0.0029 mole, n_{H2} = 0.48 mole for different temperatures is shown in Fig. 4.
In accordance with the calculation CuI was formed when iodine was present during cooling (T < 440°C). Under this conditions EDX measurements of the source showed only copper and iodine (Cu : I = 1 : 1) and the XRD diffractogram of the deposited film exhibited CuI as a secondary phase. Introducing iodine into the reactor only during the deposition period (T > 500 °C) the formation of Cu_2Se on the surface of the source was observed by EDX and XRD, while pure $CuGaSe_2$ films were obtained.

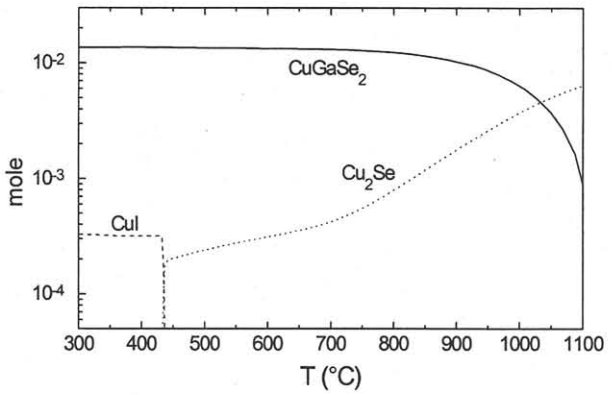

Fig. 4 Calculation of the amounts of the solid phases of the system Cu-Ga-Se-I-H under equilibrium conditions vs. temperature

3. Conclusion

Pure polycrystalline $CuGaSe_2$ thin films of chalcopyrite structure have been deposited by CVD on glass substrates with iodine as transport agent. However, if iodine is present during the heating and cooling period of the deposition process a secondary phase CuI is formed.
This experimental findings were confirmed by thermochemical calculations using ChemSage. The necessary values for the thermochemical data for the heat of formation ΔH_{298} and the standard entropy ΔS_{298} of $CuGaSe_2$ were estimated at ΔH_{298} = -251 kJ/Kmol and ΔS_{298} = 155 J/Kmol.

Acknowledgement

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