Growth and characterization of some I–III–VI\textsubscript{2} compound semiconductors

K. BALAKRISHNAN, B. VENGATESAN, P. RAMASAMY
Crystal Growth Centre, Anna University, Madras 600 025, India

Single crystals of CulnS\textsubscript{2}, CulnSe\textsubscript{2}, CulnTe\textsubscript{2}, CuGaS\textsubscript{2}, AgGaS\textsubscript{2}, CuInSSe, AgGaS\textsubscript{Se} have been grown by chemical vapour transport technique on the basis of a new general thermodynamical model which enables the minimum source temperature \( T_s \) and the minimum deposition temperature, \( T_d \), to be determined. X-ray analysis, X-ray photoelectron spectroscopic analysis, surface analysis, and microhardness studies have been carried out on the single crystals grown.

1. Introduction

Ternary and pseudo-ternary \( A'B'_2C' \) compounds are attracting attention from a fundamental point of view as a third generation of semiconducting materials after elemental and binary systems. These ternary and pseudo-ternary compounds are interesting for their possible applications in tuning lattice parameters and optical gaps [1] in order to obtain compounds tailored to meet specific photoconductive and non-linear optical demands. High-efficiency solar cells are often fabricated using single crystals of CuInS\textsubscript{2} and CuInSe\textsubscript{2} [2, 3]. In the present investigation, a general thermodynamic model to fix the minimum source temperature, \( T_s \), and the minimum deposition temperature, \( T_d \), for the efficient transport of ternary chalcopyrite compounds has been proposed. The proposed model has been verified experimentally with CuInS\textsubscript{2} and CuInSe\textsubscript{2}. Single crystals of some ternary chalcopyrite compounds, such as CuInS\textsubscript{2}, CuInSe\textsubscript{2}, CuInTe\textsubscript{2}, CuGaS\textsubscript{2}, AgGaS\textsubscript{2} and pseudo-ternary compounds, namely CuInS\textsubscript{Se} and AgGaS\textsubscript{Se}, have been grown by chemical vapour transport (CVT) using iodine as the transporting agent, and characterization studies, such as X-ray analysis, X-ray photoelectron spectroscopic (XPS) analysis, microscopic analysis and microhardness studies have been carried out for the single crystals grown.

2. Thermodynamic model

In the present work, an attempt has been made to consider thermodynamic analysis of the chemical vapour transport of ternary chalcopyrites by taking the elements as the source materials. Prediction of the minimum source temperature, \( T_s \), and the minimum growth temperature, \( T_d \), for the growth of ternary chalcopyrite compounds (CuInS\textsubscript{2} and CuInSe\textsubscript{2}) have been made on the basis of this proposed model. The model has been extended to predict the experimental conditions for the growth of CuInS\textsubscript{2} and CuInSe\textsubscript{2} with hydrogen iodide as the transporting agent. Further, this model can be used to study the minimum source temperature and growth temperature for other chalcopyrite compounds.

The components in stoichiometric proportions are converted into gaseous binary compounds by the reaction of the transporting agent. It is obvious that the gas phase during chemical transport of a ternary compound contains the same species as during hypothetical simultaneous transport of the components. The conditions under which deposition of the ternary compound will occur can be predicted if the \( \Delta G \) function of all possible solid to gas equilibrium reactions in the transport systems are known. A feasibility study of the transport of a ternary compound, therefore, reduces to the evaluation of the \( \Delta G \) functions of such reactions.

2.1. Application of the proposed model to CuInSe\textsubscript{2}

When the constituent elements, namely, copper, indium, selenium in the case of CuInSe\textsubscript{2}, are taken in stoichiometric ratio together with the transporting agent iodine at the source end, they react to form the gaseous binary iodides and selenium at high temperature. All these gaseous species diffuse to the colder growth zone due to the drop in temperature. At the growth zone they react back to form the ternary chalcogenide with the release of iodine. The iodine liberated diffuses back to the source end to form the metal iodides once again.

\[
\begin{align*}
\text{Cu(s)} + \text{In(s)} + 2\text{Se(g)} + 2\text{I}_2(g) & \rightleftharpoons \text{CuI}_2(g) + \text{InI}_3(g) + \text{Se}_2(g) \\
\text{CuInSe}_2(s) & \rightleftharpoons \text{CuI}_2(g) + \text{InI}_3(g) + \text{Se}_2(g)
\end{align*}
\]

As stated above, the gas phase during a chemical vapour transport reaction contains the same species as during a hypothetical transport of the constituent elements occurring simultaneously. The hypothetical transport reactions of the elements are as follows

\[
\begin{align*}
\text{Cu}(s) + \text{I}_2(g) & \rightleftharpoons \text{CuI}_2(g) \\
\text{In}(s) + \text{Se}_2(g) + 3/2 \text{I}_2(g) & \rightleftharpoons \text{InI}_3(g) + 1/2 \text{Se}_2(g)
\end{align*}
\]
In general, $\Delta G$ is given by the equation

$$\Delta G = \Delta G^\circ + RT \ln K_p$$  \hspace{1cm} (4)$$

where $\Delta G^\circ$ is the standard free energy change, $R$ the gas constant, $T$ the temperature, and $K$ the equilibrium constant. The source temperature is determined upon predicting the conditions under which CuI and InI$_3$ form (i.e., conditions under which the free energy change corresponding to the Equations 2 and 3 become negative). In the same way, the source temperature of CuInSe$_2$ with HI and CuInS$_2$ with I$_2$ and HI as the transporting agents and deposition temperatures have been predicted (Table I). The dependence of $\Delta G$ on temperature for a fixed iodine (transporting agent) concentration is represented in Fig. 1.

### 3. Experimental procedure

For the growth of crystalline ABC$_2$, high-purity elements A (Cu, Ag), B (In, Ga), C (S, Se, and S and Se in the case CuInSSe and AgGaSSe) in stoichiometric ratio and trace amounts of iodine have been taken in a quartz ampoule of 200 mm length and 10 mm diameter with a narrow extension to suppress the spurious nucleation. The ampoule was evacuated to a vacuum of $10^{-6}$ torr and then placed in a horizontal kanthal coiled double zone furnace and the zone temperatures were maintained steady, correct to $\pm 1^\circ$C by means of thyristorized controllers. The growth zone was cleaned, initially maintaining the temperature higher than the source zone for 24 h. After this the temperature gradient was reversed and the source temperature and deposition temperature were kept constant at two different values.

### 4. Results and discussion

Crystals of ABC$_2$ were deposited at the colder tip of the ampoule after about 100 h. The formation of ABC$_2$ may be due to the chemical reaction

$$A(s) + B_{(g)} + C_{(s)} + 2I_{2(g)} \rightarrow \text{ABC}_2(s) + 2I_{2(g)}$$  \hspace{1cm} (5)$$

In this way, single crystals of CuInS$_2$, CuInSe$_2$, CuInTe$_2$, CuGaS$_2$, CuInSSe, AgGaS$_2$, and AgGaSSe have been grown with different transporting agent concentrations. Table II gives the growth details of the single crystals grown. Figs 2–6 show the single crystals of CuInS$_2$, CuInSe$_2$, CuInSSe, CuInTe$_2$, and CuGaS$_2$, respectively.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Source</th>
<th>Transport agent</th>
<th>Predicted minimum $T_s$ (K)</th>
<th>Predicted minimum $T_d$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuInS$_2$</td>
<td>Cu:In:Se</td>
<td>I$_2$</td>
<td>901</td>
<td>835</td>
</tr>
<tr>
<td>CuInS$_2$</td>
<td>Cu:In:Se</td>
<td>HI</td>
<td>1250</td>
<td>1100</td>
</tr>
<tr>
<td>CuInS$_2$</td>
<td>Cu:In:S</td>
<td>I$_2$</td>
<td>1025</td>
<td>844</td>
</tr>
<tr>
<td>CuInS$_2$</td>
<td>Cu:In:S</td>
<td>HI</td>
<td>1640</td>
<td>1480</td>
</tr>
</tbody>
</table>

**Figure 1** The variation of $\Delta G$ with temperature for different iodine concentrations (CuInSe$_2$): (a) 1 mg cm$^{-3}$, (b) 2 mg cm$^{-3}$, (c) 3 mg cm$^{-3}$, (d) 4 mg cm$^{-3}$, (e) 5 mg cm$^{-3}$.

**Figure 2** Crystals of CuInS$_2$.  

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Source temperature $T_s$ (°C)</th>
<th>Growth temperature $T_d$ (°C)</th>
<th>Transporting agent</th>
<th>Size (mm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuInS$_2$</td>
<td>830</td>
<td>800</td>
<td>I$_2$</td>
<td>7 x 3 x 1</td>
</tr>
<tr>
<td>CuInSe$_2$</td>
<td>810</td>
<td>770</td>
<td>I$_2$</td>
<td>5 x 3 x 2</td>
</tr>
<tr>
<td>CuInTe$_2$</td>
<td>710</td>
<td>670</td>
<td>I$_2$ + TeCl$_4$</td>
<td>3 x 1 x 1</td>
</tr>
<tr>
<td>CuGaS$_2$</td>
<td>840</td>
<td>750</td>
<td>I$_2$</td>
<td>3 x 1 x 1</td>
</tr>
<tr>
<td>AgGaS$_3$</td>
<td>930</td>
<td>890</td>
<td>I$_2$</td>
<td>3 x 2 x 1</td>
</tr>
<tr>
<td>CuInSSe</td>
<td>950</td>
<td>900</td>
<td>I$_2$</td>
<td>3 x 2 x 1</td>
</tr>
<tr>
<td>AgGaSSe</td>
<td>935</td>
<td>855</td>
<td>I$_2$</td>
<td>4 x 2 x 2</td>
</tr>
</tbody>
</table>

**Table II** Growth details of the single crystals grown.