Growth and Microtopographic Study of CuAlS₂ Single Crystals

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Abstract. CuAlS₂ single crystals were grown by chemical vapour transport (CVT) technique in a close-spaced geometry. The elemental composition of the as-grown CuAlS₂ single crystals was determined by energy dispersive analysis of X-ray (EDAX). The crystal structure and lattice parameters were determined by X-ray diffraction (XRD). The optical band gap was determined from absorbance spectrum. Defects, growth mechanism, etc. were studied from the microstructure analysis. The obtained results are discussed in details.

Keywords: CuAlS₂, single crystals, chemical vapour transport, microstructures.


INTRODUCTION

The I–III–VI₂ chalcopyrite compounds (I = Cu, Ag; III = Al, Ga, In; and VI = S, Se, Te) have generated much interest due to their use in photovoltaic, optical detectors, solar cells, light emitting diodes and nonlinear optics [1,2]. Among chalcopyrite semiconductors, CuAlS₂ has the widest band gap of 3.49 eV [3] making it a promising and suitable material for blue to ultraviolet light emitting device.

In this paper the authors report single crystal growth, characterization and microstructure study of CuAlS₂ single crystals.

EXPERIMENTAL

Single crystals of CuAlS₂ were grown by chemical vapour transport (CVT) technique using iodine (I₂) as a transport agent. Copper (99.999%), aluminium (99.97%) and sulphur (99.999%) [Johnson-Mathey Chemicals Ltd., UK] were taken in stoichiometric proportion and sealed in an evacuated (~10⁻⁶ Torr) quartz ampoule. The compound synthesis was carried out by slowly heating the ampoule upto 1000 °C and maintaining it for 24 hrs. The synthesized compound was homogenized by grinding with agate mortar and then transferred into evacuated (10⁻⁶ Torr) quartz ampoule with 10 mg/cm³ of iodine as transporting agent. The CVT growth was carried out by maintaining the temperatures of source zone at 850 °C and the growth zone at 780 °C. The ampoule was maintained at these temperatures for 10 days. The as-grown single crystals were in the form of needles, Figure 1. They were shining bluish-black in colour with well-defined {112} face formed by interconnection of many tetragonal unit cells as shown in Figure 1b.

RESULTS AND DISCUSSIONS

The composition of the as-grown CuAlS₂ crystal was determined by Energy Dispersive Analysis of X-ray (EDAX) technique attached to a Philips Electron Microscope XL-30, Figure 2. The atomic and weight % obtained using EDAX along with standard data in bracket is tabulated in Table 1. The EDAX data shows that the as-grown CuAlS₂ single crystals are near stoichiometric.
TABLE 1. EDAX data.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>43.29 (41.09)</td>
<td>26.76 (25)</td>
</tr>
<tr>
<td>Al</td>
<td>16.34 (17.44)</td>
<td>23.79 (25)</td>
</tr>
<tr>
<td>S</td>
<td>40.37 (41.47)</td>
<td>49.45 (50)</td>
</tr>
</tbody>
</table>

FIGURE 3. X-ray diffraction pattern.

Figure 3 shows the XRD of the as-grown CuAlS₂ taken employing Philips X-pert-MPD X-ray diffractometer. All the peaks of XRD could be indexed as that of CuAlS₂ with tetragonal unit structure. The determined lattice parameters, \( a = b = 5.325\,\text{Å} \) and \( c = 10.39\,\text{Å} \) are in good agreement with the reported values [JCPDS Card No. 25-0014].

FIGURE 4. Plot of \((ahv)^n\) versus \(hv\) for the CuAlS₂ single crystals.

The optical energy bandgap \(E_g\) of the as-grown CuAlS₂ was determined from the optical absorption spectrum obtained using PerkinElmer Lambda -19 UV-Vis-NIR Spectrophotometer. The absorption spectrum was analyzed using the below equation for the near-band edge absorption [4].

\[
(ahv)^n = A(hv - E_g)
\]  

(1)

Where, \(n\) characterizes the transition. For direct allowed and forbidden transitions, \(n = 2\) and \(2/3\) respectively, and \(n = 1/2\) and \(1/3\) for indirect allowed and forbidden transitions respectively. It is observed that for the as-grown CuAlS₂ single crystals, the absorption can be satisfactorily explained with \(n=2\). A plot of \((ahv)^n\) versus \(hv\) is shown in Figure 4. The intercept of the straight line on the \(hv\) axis gives the direct optical bandgap value \(E_g \approx 3.07\,\text{eV}\). This value is in good agreement with the reported value [5].

The fresh as-grown surfaces of CuAlS₂ single crystals grown by CVT were examined under a Carl Zeiss ‘Axiotech 100 HD’ optical microscope for their microstructures. Figure 5 (a, b) shows the photographs of the most common microstructures visible on faces of the as-grown CVT CuAlS₂ single crystals.

FIGURE 5. (a) Eccentric growth spirals initiating from the boundary edge of a sub crystal inclusion (b) Dislocations along the step lines.

A large surface view shows grouping of eccentric growth spirals initiating from the boundary edges of a sub crystal inclusion, Figure 5a. The large number of layers progressing in all directions clearly indicates that the growth is rapid. The perfectly flat sub crystal surface and growth layers progressing in all direction clearly indicate that the growth is by a two dimensional layer mechanism of lateral spreading.

Figure 5b shows dislocations along the step lines of the layers. It is clearly seen that the step lines get modified due to the dislocations on the line.

CONCLUSION

Single crystals of CuAlS₂ were grown by chemical vapour transport (CVT) technique using iodine as transporting agent. The EDAX analysis showed that the as-grown single crystals are nearly stoichiometric. The XRD shows that the single crystals possess tetragonal unit cell structure. The determined lattice parameters are in perfect agreement with the reported data. The as-grown CuAlS₂ single crystals possess direct bandgap of 3.07 eV, which is in good agreement with the reported data. The surface microstructure showed that the growth of single crystal happens by layer growth mechanism.

REFERENCES