Structure, Electrical, and Thermal Properties Study of
CVT Grown CuAlS\textsubscript{2} Single Crystals

Sunil H. Chaki,* Kanchan S. Mahato,† and M. P. Deshpande

P. G. Department of Physics, Sardar Patel University,
Vallabh Vidyanagar-388 120, Gujarat, India
(Received February 16, 2014; Revised April 6, 2014)

CuAlS\textsubscript{2} single crystals were grown by the chemical vapour transport (CVT) technique using iodine as a transporting agent in a close-spaced geometry. The crystal structure, lattice constants, Miller indices, density, and %d errors of as grown CuAlS\textsubscript{2} were determined from X-ray diffraction (XRD). The crystalline nature was confirmed by the selected area electron diffraction (SAED) pattern of transmission electron microscopy (TEM). The scanning electron microscopy (SEM) images of the as grown surfaces of the single crystals showed the layer growth mechanism. The variation of resistivity with temperature was studied along the perpendicular to the c-axis using the four probes technique. The activation energy values were evaluated from the slopes of the resistivity variation with temperature plot. The Hall measurement data at ambient temperature were used to determine the resistivity ($\rho$), Hall coefficient ($R_H$), carrier concentration ($n$), Hall mobility ($\mu$), and conductivity type of the grown crystals. The hot probe method was used to confirm the conductivity type. Values of the Fermi energy ($E_F$), constant values ($\Lambda$), scattering parameter ($s$), Seebeck coefficient ($S$), effective density of states ($N_A$) and effective mass ($m_e^*$) were determined by the data of the Seebeck coefficient variation with temperature. The I-V characteristics study was carried out in dark as well as under white and UV illumination. The high pressure electrical resistance measurements have been performed on as grown single crystals up to a pressure of 5 GPa. It was observed that the resistance decreases with pressure up to some point, then afterward increases gradually with pressure. Thermogravimetric (TG), differential thermal analysis (DTA), and differential thermogravimetric (DTG) analysis were carried out on the as grown CuAlS\textsubscript{2} single crystals in an inert nitrogen atmosphere in the temperature range from room temperature to 1223 K. The kinetic parameters were determined employing non-mechanistic equations using the Broido and Coats-Redfern (C-R) relations.

DOI: 10.6122/CJP.20140428 PACS numbers: 61.05.cp, 81.10Bk, 81.70.Pg

I. INTRODUCTION

Ternary semiconducting compounds, such as CuAlS\textsubscript{2}, CuAlSe\textsubscript{2}, CuInS\textsubscript{2}, CuInSe\textsubscript{2}, CuGaS\textsubscript{2}, CuGaSe\textsubscript{2}, AgAlSe\textsubscript{2}, CdSiP\textsubscript{2}, and ZnSnAs\textsubscript{2}, have been widely investigated because of their potential applications in electro-optic, opto-electronic, and nonlinear optical devices. These compounds are promising candidates for solar cells [1], photovoltaic detec-

---

*Electronic address: sunilchaki@yahoo.co.in
†Electronic address: kanchan23_007@yahoo.co.in
tors [2], building blue and green light emitting devices [3], modulators, filters such as optical light eliminator filters [4], and optical frequency conversion applications in solid-state-based tunable laser systems [5]. Among these, CuAlS₂ has been used as an oxygen gas sensor working at room temperature [6], and it has been used in targeted “in vitro” imaging of cancer cells, which is an example of its potential for application in cancer diagnostics without any intrinsic toxicity rendered to cells [7].

The growth of CuAlS₂ single crystals by the chemical vapour transport (CVT) technique using iodine (I₂) as a transporting agent have been reported by Chaki et al. [8]. In this research paper, further study of the as grown CVT CuAlS₂ single crystals, like the determination of structural parameters by X-ray diffraction (XRD), crystalline nature by transmission electron microscopy (TEM), and surface microstructure study by scanning electron microscopy (SEM) were done. The electrical transport parameters and thermal kinetic parameters were evaluated.

II. RESULTS AND DISCUSSIONS

II-1. Structural analysis

Figure 1 shows the XRD spectrum of a CuAlS₂ single crystal taken employing an Philips X-pert-MPD X-ray diffractometer. All the peaks of the XRD could be indexed as that of CuAlS₂ with tetragonal unit structure.

The determined lattice parameters, $a = b = 5.325$ Å and $c = 10.391$ Å are in good
agreement with the reported values [JCPDS Card No. 25-0014]. Other parameters like the Miller indices, \(2\theta\) angle, inter planer spacing \((d)\), and \(\%d\) errors for each extreme peak were determined by Powder-X software. The obtained parameters are tabulated in Table I.

TABLE I: Miller indices, \(2\theta\) angle, inter planer spacing \((d)\), and \(\%d\) error determined for as grown CVT CuAlS\(_2\) single crystals.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>(hkl)</th>
<th>(2\theta)</th>
<th>(d) (Å)</th>
<th>(%d) Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuAlS(_2)</td>
<td>(101)</td>
<td>18.828</td>
<td>4.709</td>
<td>0.625</td>
</tr>
<tr>
<td></td>
<td>(112)</td>
<td>29.357</td>
<td>3.041</td>
<td>0.289</td>
</tr>
<tr>
<td></td>
<td>(103)</td>
<td>30.834</td>
<td>2.898</td>
<td>0.198</td>
</tr>
<tr>
<td></td>
<td>(211)</td>
<td>38.829</td>
<td>2.317</td>
<td>0.164</td>
</tr>
<tr>
<td></td>
<td>(220)</td>
<td>48.373</td>
<td>1.881</td>
<td>0.135</td>
</tr>
<tr>
<td></td>
<td>(204)</td>
<td>48.938</td>
<td>1.861</td>
<td>0.024</td>
</tr>
<tr>
<td></td>
<td>(312)</td>
<td>57.492</td>
<td>1.602</td>
<td>0.011</td>
</tr>
<tr>
<td></td>
<td>(116)</td>
<td>58.536</td>
<td>1.576</td>
<td>0.148</td>
</tr>
<tr>
<td></td>
<td>(400)</td>
<td>70.714</td>
<td>1.331</td>
<td>0.007</td>
</tr>
<tr>
<td></td>
<td>(332)</td>
<td>78.233</td>
<td>1.221</td>
<td>0.078</td>
</tr>
<tr>
<td></td>
<td>(413)</td>
<td>79.135</td>
<td>1.209</td>
<td>0.067</td>
</tr>
<tr>
<td></td>
<td>(316)</td>
<td>79.375</td>
<td>1.206</td>
<td>0.083</td>
</tr>
</tbody>
</table>

The \(\%d\) error is below 0.625\%, showing the material to be of single phase CuAlS\(_2\). The calculated X-ray density of the as-grown CuAlS\(_2\) single crystal came out to be 3.49 gm·cm\(^{-3}\). The calculated value of the X-ray density is in good agreement with the reported value 3.43 gm·cm\(^{-3}\) [9]. Figure 2 shows the selected area electron diffraction (SAED) pattern of as grown CuAlS\(_2\) single crystals recorded using a Philips, Tecnai 20 transmission electron microscope (TEM).

The SAED pattern shows spots, confirming that the as grown crystals are crystalline in nature. The rings were drawn only for simplicity to identify equidistant spots from the center. They were indexed as (112), (211), (220), (204), (312), (116), (400), and (332) associated with a tetragonal crystal structure. The indexed planes are in good agreement with the XRD planes.

Figure 3 shows the SEM images of the as-grown surfaces of CuAlS\(_2\) single crystals taken employing a JEOL JSM-5610LV scanning electron microscope. These were the common features observed on the surfaces of the as grown single crystals. Figure 3(a & b), clearly show layers on the surfaces of the single crystals. The perfectly flat sub crystal surfaces and growth layers progressing in all direction clearly indicate that the growth is by a two dimensional layer mechanism of lateral spreading. The large number of layers progressing in all directions clearly indicates that the growth is rapid.
II-2. Electrical transport properties analysis

The d.c. electrical resistivity variation with temperature in the temperature range from ambient to 390 K was studied for CuAlS$_2$ single crystal using a four probe set-up, Model DFP-02 (Scientific Equipment Services, Roorkee, India). Using the measured voltage at constant current, the resistivity ($\rho$) at each temperature perpendicular to the c-axis was evaluated by taking into consideration the correction factor. The log $\rho$ versus 1000/$T$ plot for as grown CVT CuAlS$_2$ single crystal is shown in Figure 4. The resistivity decreases with an increase in temperature, showing the semiconducting nature of the sample. The determined activation energy value from the slope of the plot is tabulated in Table II. The obtained value of the activation energy, 0.029 eV, is in good agreement with the reported value of 0.030 eV [10, 11].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature range (K)</th>
<th>Activation Energy $E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuAlS$_2$</td>
<td>311 to 390</td>
<td>0.029</td>
</tr>
</tbody>
</table>

The Hall effect analysis was carried out on the as grown CuAlS$_2$ single crystal by employing the Hall effect set up, DHE-22 (Scientific Equipment Services, Roorkee, India) at room temperature. Graphite conductive adhesive alcohol based (Alfa Aesar) paste was used for making the ohmic contacts in the van der Pauw geometry. The ohmic nature of the electrical contacts made on the sample were confirmed by measuring the I-V characteristic.
between the $R_{12.12}$, $R_{23.23}$, $R_{34.34}$, and $R_{41.41}$ contacts of the sample (Figure 5) for both polarities in the current range $-2\,\mu A$ to $+2\,\mu A$. The sample under investigation was kept in the magnetic field range of 0.1 T to 0.3 T, varying the magnetic field in steps of 0.01 T. The magnetic field modifies the path of the carriers which produce the Hall voltage. Figure 6 shows the graph of the Hall voltage ($V_H$) versus magnetic field ($B$). Using the
The Log $\rho$ versus $1000/T$ plot for CuAlS$_2$ single crystals.

value of the slope from Figure 6, the thickness of the sample $t = 15 \ \mu$m, and the constant current $I = 2 \ \mu$A, the Hall coefficient ($R_H$), the mobility of charge carriers ($\mu_H$), and the carrier concentration ($\eta$) were evaluated using standard formulae. The obtained values are tabulated in Table III, the negative Hall coefficient ($R_H$) confirmed the sample to be $n$-type in nature, and its carrier concentration comes out to be of the order of $10^{16}$ cm$^{-3}$, showing the sample to be a semiconductor. The electron mobility ($\mu$) value determined from the Hall effect measurement was 2.92 cm$^2$V$^{-1}$s$^{-1}$. The value is in good agreement with the reported value [11]. The $n$-type nature of the single crystals was also confirmed by the hot probe method.

<table>
<thead>
<tr>
<th>Resistivity $\rho$ (Ω·cm)</th>
<th>Hall coefficient $R_H$ (cm$^3$C$^{-1}$)</th>
<th>Carrier concentration $\eta$ (cm$^{-3}$)</th>
<th>Hall mobility $\mu$ (cm$^2$V$^{-1}$s$^{-1}$)</th>
<th>Semiconductor type</th>
</tr>
</thead>
<tbody>
<tr>
<td>28.96</td>
<td>−84.6</td>
<td>$7.38 \times 10^{16}$</td>
<td>2.92</td>
<td>$n$</td>
</tr>
</tbody>
</table>

The variation of the thermoelectric power ‘$S$’ as a function of temperature was measured using the experimental set up, TPSS-200, (Scientific Solution, Mumbai, India). The variation of the potential difference between the two probes keeping the temperature difference (ΔT) at 5 K was measured from 300 K to 573 K. The determined Seebeck coefficient ($S$) variation with the inverse of temperature ($1000/T$) is shown in Figure 7. The plot shows that the Seebeck coefficient values increase with temperature, showing the semi-
conducting nature of the samples. The absolute values of the Seebeck coefficient at all evaluated temperatures is negative, showing the sample to be \( n \)-type in nature. This result further corroborates the results of the Hall effect and hot probe methods.
FIG. 7: The plot of the Seebeck coefficient ($S$) versus $1000/T$ of as grown CuAlS$_2$ single crystal.

The values of the Fermi energy ($E_F$) and constant ($A$) were evaluated from the slope and intercepts of Figure 7, respectively. Using the value of ‘$A$’ and the carrier concentration ($\eta$) obtained from the Hall Effect measurements, the scattering parameter ($s$), effective density of states ($N_A$) and effective mass of electrons ($m_e^*$) were evaluated by employing standard equations. The calculated values are tabulated in Table IV.

TABLE IV: Values of the Fermi energy ($E_f$), constant ($A$), scattering parameter ($s$), room temperature Seebeck coefficient ($S$), effective density of states ($N_A$), and effective mass ($m_e^*$) of as grown CuAlS$_2$ single crystals.

<table>
<thead>
<tr>
<th>Fermi Energy ($E_f$) (eV)</th>
<th>$A$</th>
<th>Scattering constant ($s$)</th>
<th>$S$ ($\mu$V/K)</th>
<th>$N_A$ (cm$^{-3}$)</th>
<th>$m_e^*$ (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.055</td>
<td>-2.275</td>
<td>4.775</td>
<td>-14.21</td>
<td>$6.90 \times 10^{16}$</td>
<td>$8.3 \times 10^{-32}$</td>
</tr>
</tbody>
</table>

The I-V characteristics study on the CuAlS$_2$ single crystal was carried out in dark as well as under white and UV electromagnetic illumination. The I-V measurements under white illumination was made by using a 4 W lamp (Philips) having intensity on the sample surface of 6614 Lux. Whereas the UV illuminated I-V measurement was carried out employing a 4 W UV lamp (Model: UVSL-14P, Ultra-Violet Products Ltd. Cambridge CB4 1TG, UK) having an intensity of 31 Lux on the sample surface. The intensity measurement was done by a light Luxmeter (Model: MECO-930, MECO Meters Pvt. Ltd., Navi Mumbai, India). The recorded I-V characteristics in dark, for white, and UV illuminations are shown...
in Figure 8. The dark and white lines are near to overlapping with each other, while the UV illumination has a deviation. The slope of the UV illuminate line is less than the dark and white illumination. This indicates that UV illumination produces a larger number of electron–hole pairs. The reason being that the determined optical energy band gap of single crystal CuAlS$_2$ is 3.07 eV [8], which corresponds to a wavelength of ultra violet radiation ($\sim$ 404 nm). The bandgap of as-grown CuAlS$_2$ is in good agreement with the reported value [12].

FIG. 8: The I-V plots of CuAlS$_2$ single crystal in dark as well as under white and UV illumination.

The deviation in the I-V plot in the case of UV illumination is small compared to that of the dark and white illumination. This can be explained since, in accordance with the photoelectric effect, the generation of electron-hole pairs depends on the intensity of the source. Here, the intensity of the UV illumination is quite small, 31 Lux on the sample surface. Due to this, the I-V characteristic shows a minor variation compared to the dark and white illumination. In the case of the dark and white illumination, the sample just behaves as a simple resistor, unaffected by the external illumination, thus both I-V plots nearly overlap. The effect of the illumination on the CuAlS$_2$ single crystal shows that it can be used as a photovoltaic material for the UV range and also as a window material.

The high pressure d. c. electrical resistance variation with pressure up to 5 GPa was measured using the four probes method on CuAlS$_2$ single crystals. Figure 9 shows the variation of resistance with pressure for CuAlS$_2$ single crystals. In the pressure range from
ambient to nearly 1.75 GPa the resistance decreases with pressure. The rate of decrease is fast, and the decrease of resistance may be due to the charge carriers of the valence band contributing to the conduction band carriers. Above 1.75 GPa the resistance increases with pressure. The rate of increase is slow; this may be due to a phase change.

FIG. 9: A plot of the logarithm of the d. c. electrical resistance versus pressure of the as grown CuAlS$_2$ single crystal.

The high pressure resistance variation was measured in several independent runs and was found to have a similar behaviour.

II-3. Thermal analysis

The thermogravimetric (TG), differential thermogravimetric (DTG), and differential thermal analysis (DTA) curves were recorded for the as grown CuAlS$_2$ single crystals using a Seiko EXSTAR SII TG/DTA7200 thermal analyzer. The curves were recorded between ambient temperatures to 1223 K in an inert nitrogen atmosphere at a constant heating rate of 10 K min$^{-1}$.

The TG curve of as grown CuAlS$_2$ single crystals, Figure 10, shows a continuous weight loss in the analyzed temperature range of ambient to 1223 K. The total weight loss takes place in three steps. Step–I is between ambient to 600 K, Step–II lies between 601 K to 900 K, whereas Step–III lies between the temperatures of 901 K to 1223 K. The observed weight loss in the three steps are, Step–I has 1.74%, Step–II has 2.37%, and Step–III has 2.78%. The three TG steps of weight loss are also reflected in the recorded simultaneous DTG curve, Figure 10. The DTG has three peaks at 470.01 K, 687.23 K, and 1049 K. These peaks correspond to the three weight loss steps of the TG curve.

The simultaneous DTA, Figure 11, shows a general endothermic nature, since the curve lies below the base line all throughout the analyzed temperature range. The TG
weight loss and DTA endothermic nature may be due to sulphur loss. The weight losses in all three steps are minor, showing a loss of excess sulphur from the as grown CuAlS$_2$ single crystals. The kinetic parameters, like the activation energy, activation enthalpy ($\Delta H^*$), and Gibbs free energy change ($\Delta G^*$), calculated using the Broido [13] and Coats-Redfern relations [14], are tabulated in Table V for the three steps. The obtained positive values of the enthalpy ($\Delta H^*$) in all three steps confirms the absorption of energy by the system, corroborating the endothermic nature seen in the DTA. The positive values of the Gibbs free energy change ($\Delta G^*$) substantiates that the reaction is moving away from equilibrium, showing decomposition, as observed in the TG curve.

In addition to the endothermic DTA nature, this also shows a minor exothermic tip at 660 K. This DTA exothermic peak lies in the temperature range of Step–II of the TG curve. In this TG analysis temperature range, the values of the thermal activation energy calculated by both the Broido and Coats-Redfern relations are highest. That means that there is a minor decomposition of CuAlS$_2$ which releases heat, seen as an exothermic rise in the DTA curve.
III. CONCLUSIONS

The XRD analysis of the as grown CuAlS\textsubscript{2} single crystals showed them to possess tetragonal unit cell structure. The calculated X-ray density of as grown CuAlS\textsubscript{2} single crystal was 3.49 gm-cm\textsuperscript{-3}, in good agreement with the reported value of 3.43 gm-cm\textsuperscript{-3}. The SAED done through the TEM analysis of the as grown CuAlS\textsubscript{2} single crystals showed a spot pattern confirming the crystalline nature. The SEM images of the surfaces of the
as grown single crystals shows that the growth happened by the layer growth mechanism. The d. c. electrical resistivity variation with temperature in the temperature range from room temperature to 390 K showed a continuous decrease of resistivity with temperature, showing the semiconducting nature of the samples. The activation energy value obtained from the plot of resistivity versus temperature came out to be 0.029 eV, in good agreement with reported value of 0.030 eV. The room temperature Hall effect measurements showed the samples to be n-type in nature having carrier concentration of the order of $10^{16}$ cm$^{-3}$, further corroborating the semiconducting nature of the samples. The n-type nature of the semiconductor was confirmed by the hot probe method. The plot of the Seebeck coefficient values with temperature showed that the Seebeck value increases with temperature, further confirming the semiconducting nature of the samples. The absolute values of the Seebeck coefficient all through the analyzed temperature was negative, showing the samples to be n-type in nature. The high pressure d. c. electrical resistance variation with pressure up to 5 GPa, measured using the four probe method on CuAlS$_2$ single crystals showed that the resistance decreases with pressure up to nearly the pressure of 1.75 GPa. The rate of decrease is fast, and the decrease of resistance may be due to the charge carriers of the valence band contributing to the conduction band carriers. Above 1.75 GPa the resistance increased with pressure. The rate of increase is slow, this may be due to a phase change. The TG and DTG curves in the temperature range of ambient to 1223 K in inert atmosphere, clearly shows decomposition taking place by three steps. The weight losses in these three steps are small, showing that these might be arising due to the loss of excess sulphur from the CuAlS$_2$ single crystals. The simultaneous DTA curve shows an endothermic nature, with heat being absorbed during the decomposition.

Acknowledgements

One of the authors (KSM) is thankful to the University Grants Commission (UGC), New Delhi for the award of a Research Fellowship in Sciences for Meritorious Students (RFSMS) for carrying out the research work.

References


