Optoelectronic properties of transparent p-type semiconductor CuₓS thin films

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Nowadays, among the available transparent semiconductors for device use, the great majority (if not all) have n-type conductivity. The fabrication of a transparent p-type semiconductor with good optoelectronic properties (comparable to those of n-type: InOₓ, ITO, ZnOₓ or FTO) would significantly broaden the application field of thin films. However, until now no material has yet presented all the required properties. Cu2S is a p-type narrow-band-gap material with an average optical transmittance of about 60% in the visible range for 50 nm thick films. However, due to its high conductivity at room temperature, 10 nm in thickness seems to be appropriate for device use. Cu2S thin films with 10 nm in thickness have an optical visible transmittance of about 85% rendering them as very good candidates for transparent p-type semiconductors. In this work CuₓS thin films were deposited on alkali-free (AF) glass by thermal evaporation. The objective was not only the determination of its optoelectronic properties but also the feasibility of an active layer in a p-type thin film transistor. In our CuₓS thin films, p-type high conductivity with a total visible transmittance of about 50% have been achieved.

1 Introduction

The quarrel amongst scientists for the production of a good transparent p-type semiconductor, suitable for device applications, has been around for quite some time now. First reports of a p-type transparent conductor go back to 1997 when Kawazoe et al. [1] reported CuAlO2 thin films. So far, the transparent p-type semiconductors available usually share fundamental problematic issues like low charge carrier concentration and very low carrier mobility [2]. The fabrication of p-type transparent semiconductor thin films with good optoelectronic properties would significantly boost the industry of thin films, especially if their fabrication is compatible with nowadays’ semiconductor processes. Several materials have been reported as very good p-type candidates, but none has yet gathered the required properties for application use [3].

Among the common p-type materials, the CuₓS system stands out mainly because of its excellent p-type conductivity, its low cost and non-toxicity [4]. CuₓS is a narrow-band-gap semiconductor material with a visible optical transmittance of about 60% for a 50 nm thick film [4]. However due to its very low resistivity at room temperature (≈10⁻⁴ Ω cm) CuₓS films with 10 nm in thickness seems appropriate for transistor use. These 10 nm films show an optical transmittance of about 85% in the visible range, rendering them as good candidates for p-type semiconductors [4]. Authors should point out the extensive work developed about this material a few years back, especially regarding photovoltaic applications [5, 6]. So being, there are numerous techniques for the deposition of CuₓS thin films [7, 8]. However, different techniques usually require different experimental approaches. In our work the CuₓS thin films were deposited by means of thermal evaporation of pure Cu2S powder in high vacuum. The as-deposited films were submitted to a mild heat treatment in order to achieve the required optoelectronic properties. Therefore annealings in several atmospheres and temperature ranges, as an effort to optimize the p-type conductivity of the material, were made.

2 Experimental

CuₓS thin films with an average thickness of 50 nm were obtained by thermally evaporating pure Cu2S powder onto previously cleaned bare alkali free...
(AF45) glass substrates. The vacuum chamber of the system was evacuated until a pressure of about $1 \times 10^{-3}$ Pa was achieved by means of an independent Edwards rotary/diffusion pump system. Authors should point out that the pressure raised one order of magnitude once the tungsten crucible’s temperature approached the Cu$_2$S melting point and once melted, the pressure quickly returned to its initial value. Previous works state that low evaporation rates enhance the stoichiometry of the deposited material [9]. The evaporation rate was therefore kept at 2 Å/s and there was no substrate heating during the process, although the radiated thermal energy from the crucible heated the samples to about 65 °C. The film thickness was measured in situ using an Edwards thickness monitor and the evaporation was stopped once 50 nm was achieved. Total thin film thickness was measured afterwards using a Sloan Dektak 3D stylus profiler and once 50 nm was achieved. Total thin film thickness was measured afterwards using a Sloan Dektak 3D stylus profiler and it was within experimental error in comparison to the thickness monitor. As for the annealings, several heat treatments in different atmospheres and temperature ranges were made. The vacuum annealings were carried out in an evaporation chamber with a base pressure of about $2 \times 10^{-3}$ Pa with temperatures ranging from 100 to 500 °C. As for the air annealings, they were performed on a common laboratory hot plate with temperatures varying from 100 to 310 °C. Optical measurements consisting of total transmittance, $T(\lambda)$ and optical band-gap determination were made using a Shimadzu UV-3100 spectrophotometer (190 nm < $\lambda$ < 2500 nm) without a bare substrate as reference. Temperature dependent electrical conductivity was also measured. Ohmic aluminium contacts were evaporated onto the samples soon after the thin films were grown, according to $I$–$V$ measurements. The apparatus consists of a Keithley 228A voltage source connected to a Peltier so that temperature is controlled. A Keithley 617 is used to apply both an electric field and measure the correspondent current between contacts. The measurement is done in primary vacuum (2 x 10$^{-3}$ Pa) to avoid surface conduction through adsorbed humidity during the preparation of the measurement. For the determination of the samples’ sheet resistance we used a Veeco FPP-5000 four-point probe (FPP) was also used. We should point out that this FPP-5000 is capable of determining the type of charge carriers in samples with less than 750 Ω/sq in average. Resistivity ($\rho$), mobility ($\mu$), carrier type and carrier concentration were also measured with a BioRad HL5500 Hall effect system in Van der Pauw geometry at room temperature with a constant magnetic field (0.5 T).

3 Results and discussion The 50 nm thick as-deposited films exhibit n-type conductivity at room temperature and a distinctive greenish colouration with a visible transmittance of about 55% (sample 1). In addition it was shown that the as-deposited films are in fact not tightly bonded to the substrate as one would expect from a thermal evaporation process. Vacuum annealings up to 500 °C and 1 h long did not change the sample’s properties from an optoelectronic point of view. However, after annealing in air for 5 min at 280 °C, the thin films changed their colouration to a lighter brownish colour whilst decreasing the visible transmittance to about 42% (sample 2), according to Fig. 1.

It is worth referring that the infrared reflection usually associated with free electrons decreased significantly with the air annealing [10]. The optical band-gap was inferred from the absorption spectrum of sample 2 by extrapolating the straight portion of the Tauc’s plot. It was assumed that Cu$_2$S is an indirect transition semiconductor and the band-gap was determined to be around 1.14 eV (Fig. 2) which is with accordance with other workers reports on similar materials [11]. Because it was difficult to get a straight portion of the Tauc’s plot of sample 1, optical band-gap determination has not been done.

Once the annealing was complete, the sheet resistance increased from 60 to 330 Ω/sq and p-type conductivity has been verified. However, samples which were air annealed longer than 5 min (not presented in this study) become highly resistive and the charge carrier type becomes inconclusive with the FPP device. Still regarding the conduction of these materials, it is important to remember that the FPP determines the semiconductor type using the Seebeck effect.
Once the p-type conductivity was verified by the FPP, Hall effect measurements were made on sample 2 to determine the carrier concentration and mobility, and to confirm the conduction type determined by the FPP. Table 2 resumes the obtained electrical properties for sample 2 (air annealed for 5 min, p-type).

Although the carrier mobility is relatively low compared to state of the art n-type semiconductors it is still well acceptable for p-type devices [1]. In addition it was proven not only that these p-type films are stable over an undetermined period of time (which to our knowledge and according to previous reported works is unusual), but also that the technique is simple and easily reproducible [12, 13].

### 4 Conclusions

Transparent p-type Cu$_2$S semiconductor thin films were deposited on AF glass by means of a high vacuum thermal evaporation. It was shown that a mild heat treatment in the presence of oxygen is an essential procedure in order to achieve a semiconducting p-type thin film. The first p-type thin films made with this technique are 3 months old and until now their electrical properties remain absolutely unchanged. Authors would also like to point out the unusual carrier concentration determined by the Hall effect on sample 2 which could explain to some extent the low resistance of these thin films (6.55 × 10$^{-4}$ Ω cm). Several characterization techniques such as XPS, SEM and XRD are scheduled and TFT’s based on this material are under development.

#### Acknowledgements

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#### References


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**Table 1** Optoelectronic properties of sample 1 (as-deposited) and sample 2 (air annealed).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Transmittance (@ 500 nm)</th>
<th>Sheet Resistance (FPP)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>54%</td>
<td>60 Ω/sq</td>
<td>n-type</td>
</tr>
<tr>
<td>Sample 2</td>
<td>40%</td>
<td>330 Ω/sq</td>
<td>p-type</td>
</tr>
</tbody>
</table>

**Table 2** Electrical properties of sample 2 (3 measurements).

<table>
<thead>
<tr>
<th>Sheet Resistance (Ω/sq)</th>
<th>Resistivity (Ω cm)</th>
<th>Hall Coefficient (cm$^3$/C)</th>
<th>Mobility (cm$^2$/V s)</th>
<th>Concentration (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>326</td>
<td>6.53 × 10$^{-4}$</td>
<td>30.3 × 10$^{-3}$</td>
<td>1.17</td>
<td>8.41 × 10$^{21}$</td>
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<tr>
<td>328</td>
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<td>25.8 × 10$^{-3}$</td>
<td>0.787</td>
<td>1.21 × 10$^{22}$</td>
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<tr>
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<td>6.55 × 10$^{-4}$</td>
<td>33.0 × 10$^{-3}$</td>
<td>1.01</td>
<td>9.47 × 10$^{21}$</td>
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