Magnetoresistance of CuCrO_2-based delafossite films

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Abstract. Oxides with the delafossite structure (space group R̅3m) are of interest as wide-bandgap semiconductors, and as multiferroics. Well oriented c-axis films of CuCrO_2 and CuCr_{0.9}Mg_{0.1}O_2 have been produced on c-cut sapphire by PLD at elevated temperatures (650 °C). The lattice parameters for CuCrO_2 are a = 299.6 pm and c = 1719.7 pm. The end member is insulating at room temperature with ρ ≳ 1000 Ω m whereas the Mg-doped oxide is a degenerate p-type semiconductor with ρ ≈ 1.5 × 10^{-4} Ω m. There is a resistivity anomaly at T_N. A large negative magnetoresistance, which reaches its maximum value (≈ 300 %) in 14 T at about 2 K, persists throughout the temperature range where magnetic short range order is significant.

1. Introduction

Practical transparent conducting oxides (TCO) applications are dominated by just a few materials, including In_2O_3, SnO_2, ITO and ZnO, which are used principally for architectural glazing and in flat panel displays (FPDs). To date TCOs have been used in a passive electrical manner, as transparent electrodes or resistors. The demand for new materials is heightened by the promise of novel device applications in the emerging field of transparent electronics. The problem facing researchers in this area is the apparent lack of p-type materials available to them, since all of the commercially used, high-performance TCOs mentioned above are n-type conductors. In 1997, the report of transparent p-type conducting thin films of CuAlO_2 with the delafossite crystal structure [1], and the subsequent development of the "Chemical Modulation of the Valence Band" (CMVB) [2] design concept, have brought this class of material to the forefront of transparent semiconductor research.

Delafossite compounds belong to a family of ternary oxides with the general formula A^{+1}B^{+3}O_2. Some of these compounds have been well studied, most notably CuAlO_2 and CuFeO_2. Recently, attention has turned to copper chromite, CuCrO_2, which reportedly has a bandgap of 3.1 eV [3] and the highest p-type conductivity among the delafossites, 220 S/cm when doped with 5% Mg [4] deposited by rf sputtering. The p-type nature of this material has thus far only been confirmed by measurement of the Seebeck coefficient since the mobility is too low for direct measurement of the Hall effect. Films with a thickness of 250 nm have been reported to be 50 % transparent to visible light [3]. CuCrO_2 thin films have been fabricated by rf sputtering [5] low pressure Metal-Organic CVD [6], sol gel [7], pulsed laser deposition [8] and recently by chemical spray pyrolysis [9]. CuCrO_2 is also reported to exhibit both antiferromagnetic [10] and ferroelectric [11] behaviour below its Néel temperature, T_N = 25 K. The magnetic structure and the mechanism responsible for the ferroelectricity are still under investigation. Here we focus on the magnetoconductance of these delafossite films.
2. Experimental procedure
Thin films of undoped and Mg-doped CuCrO$_2$ were grown on single crystal Al$_2$O$_3$ (0001) substrates by PLD. The source targets were made from sintered pellets of CuCr$_{1-x}$Mg$_x$O$_2$ ($x = 0, 0.02, 0.05, 0.10$) powder prepared by solid state reaction. The doping concentration in the thin films was assumed to be equal to the nominal Mg concentration in the source target. A 248 nm wavelength KrF excimer laser with a pulse duration of approximately 25 ns and laser fluence of 1.9 Jcm$^{-2}$ was used for ablation. A wide range of oxygen background pressure ($1 \times 10^{-3}$ µbar to 100 µbar) and temperature ($500^\circ$C to $700^\circ$C) combinations were investigated to optimize single phase thin film growth.

The thin film samples were characterized structurally by x-ray diffraction using a Philips X’Pert Pro MPD diffractometer with Cu K$_{\alpha}$ radiation of wavelength 154.056 pm. The thickness of the thin films was determined by x-ray reflectivity (XRR). UV-visible optical spectroscopy was carried out in the range 200 nm - 900 nm. Conductivity and magneto-transport of the reasonably conductive samples were measured in the Van der Pauw configuration using In contacts and Au wire. Transport measurements were carried out in a Quantum Design PPMS (Physical Properties Measurement System) in the temperature range 2 K to 300 K in fields of up to 14 T.

3. Results and discussion
Optimum growth was achieved at high temperatures and in relatively high oxygen partial pressures, and was found to be extremely sensitive to both parameters. XRD phase analysis of the 0, 5 and 10 % Mg-doped samples, shown in Fig.1, confirmed the growth of highly crystalline, rhombohedral CuCrO$_2$ thin films with $R\bar{3}m$ space group symmetry. Most traces of the Cu$_2$O impurity phase were eliminated. The films were predominantly c-axis oriented, with a very minor additional Bragg peak in the (101) orientation.

![Figure 1](image1.png)

**Figure 1.** 2θ-ω scans of 0, 5, 10% Mg-doped films. * Indicates the substrate, unidentified peaks are Cu $K_{\beta}$ and W $L_{\alpha}$ peaks.

![Figure 2](image2.png)

**Figure 2.** $\phi$ scan of a CuCrO$_2$ thin film in the (104) direction and the (113) direction of the Al$_2$O$_3$ substrate.

In-plane $\phi$ scans were carried out in the CuCrO$_2$ (104) direction and in the Al$_2$O$_3$ (113) direction as shown in Fig.2. The mismatch between the CuCrO$_2$ (104) and Al$_2$O$_3$ (104) planes is 13.5%. Twinning of the delafossite (104) plane is responsible for the six-fold symmetry in the $\phi$ scan and the in-plane axes are rotated by 30° relative to the sapphire substrate to relax the lattice reducing the mismatch to 5.8%, hence the coincidence of the CuCrO$_2$ (104) and Al$_2$O$_3$ (113) peaks. The lattice parameters for the undoped film were determined to be $a = 299.6$ pm.
and $c = 1719.7$ pm, while the 10% Mg-doped had $a = 297.3$ pm and $c = 1705.4$ pm. Narrow rocking curves and the observation of Kiessig fringes about the primary diffraction peak in some of the films confirmed the high crystalline quality of the samples.

The bandgaps of the thin film samples, whose optical spectra are shown in Fig.3, were calculated from Tauc plots of $\alpha h\nu^{1/n}$ against $h\nu$ where $n = 1/2$ for a direct transition, and $n = 2$ for an indirect transition. The optical bandgaps were in the range 3.1 - 3.2 eV and were observed to be direct for all of the samples measured. The transparency of the samples, defined to be the average transmittance (%) over the visible range, was measured to be 60 % for the 63 nm thick undoped CuCrO$_2$ sample, the 5 % Mg-doped CuCrO$_2$ which was 27 nm thick was 65 % transparent, and the 10 % Mg-doped sample was 47 % transparent with a thickness of 40 nm. The undoped CuCrO$_2$ sample exhibited a sharp absorption compared to the other samples. The fringe just after the absorption edge has been identified as the first thickness fringe and is not related to any change in the absorption coefficient.

![Figure 3. UV-visible spectrometry of 0, 5 and 10% Mg-doped CuCrO$_2$ thin films.](image3)

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![Figure 4. Evolution of the conductivity of a 40 nm thick 10 % Mg-CuCrO$_2$ film with temperature in various magnetic fields.](image4)

![Figure 5. Transverse Magnetoconductance measured on a 135 nm thick 10 % Mg-doped CuCrO$_2$ film at various temperatures.](image5)

The temperature dependence of the resistance of a 40 nm thick 10% Mg-doped CuCrO$_2$ thin film was measured in order to investigate the nature of the conductivity. The room temperature conductivity of the sample was 25 S/cm, lower than the 50 S/cm previously reported for 5% Mg-doped CuCrO$_2$ films grown by PLD [8]. The samples were exposed to atmosphere
for a considerable time prior to transport measurements, this may account for the reduced conductivity. Fig.4 shows the evolution of the conductance, $\sigma$, with temperature in various applied magnetic fields. The feature around 25 K is due to the antiferromagnetic transition.

The magnetoconductance of a thicker 10 % Mg-doped sample was measured at various temperatures between room temperature and 2 K. Fig.5 shows the transverse magnetoconductance of a 135 nm thick film measured in a field of up to 14 T. The sample exhibited positive magnetoconductance of up to 300% in fields of $\pm$ 14 T at a temperature of 2 K. The activation energy of the acceptors is small enough ($\sim$ 3 meV), and influenced by the antiferromagnetic exchange energy to a sufficient degree, to command a substantial change of carrier concentration, which can account for this large magnetoconductance effect. The inset on Fig.4 demonstrates three clear regions of temperature activation of the high-field linear slope of the magnetoconductance - one below $T_N$, a second below the compensation point (where the effective carrier concentration changes sign), and a third high temperature region where the system is close to degenerate semiconductor.

The basic effective transport parameters (resistivity, mobility and electronic carrier concentration) are presented in Table 1. Data is available only for the interval 100 - 300 K, since the high sample impedance prohibits artefact-free low temperature measurements.

| Temperature (K) | Resistivity ($\Omega\cdot$cm) | Mobility (cm$^2$V$^{-1}$s$^{-1}$) | Carrier Concentration (cm$^{-3}$) |
|-----------------|--------------------------|------------------------|-----------------------------|
| 100             | 0.061                    | 0.032                  | -3.19-$10^{21}$             |
| 150             | 0.033                    | 0.0053                 | -3.5-$10^{22}$              |
| 200             | 0.023                    | 0.054                  | 5-$10^{21}$                 |
| 300             | 0.015                    | 0.042                  | 1-$10^{22}$                 |

Table 1. AC Hall effect data of a 10% Mg:CuCrO$_2$ thin film (135 nm) at various temperatures.

4. Conclusion

Highly crystalline $c$-axis oriented thin films of the ternary delafossite oxide CuCrO$_2$ and its Mg-doped counterpart have been fabricated by PLD. The bandgaps are between 3.1 and 3.2 eV and they appear to be direct transitions. Semiconducting behaviour has been observed with $\sigma =$ 25 S/cm at 300 K. The large positive magnetoconductance of $\approx$ 300 % measured in 14 T at 2 K is associated with the effect of the external magnetic field on the O/Cr acceptor states responsible both for the hole conduction and antiferromagnetic order. AC Hall effect data indicates $p$-type conduction with a compensation temperature above 150 K.

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