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Structural optical and electrical transport properties of ALD-fabricated CuCrO₂ films

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Abstract

We report the structural, optical and electrical transport properties of CuCrO₂ films deposited by atomic layer deposition. Copper tetramethyl heptanedionate (Cu(thd)₂) and chromium acetyl acetonate (Cr(acac)₃) have been used as the precursors for copper and chromium whereas ozone as the oxygen source. The effect of post-deposition annealing on the crystallinity of the films, band gap as well as electrical transport properties has been investigated. A direct band-gap of 3.10 eV was estimated from the UV visible spectrophotometric measurements for the films annealed at 800 °C in Ar environment. Electrical resistivity measurements show a semiconducting behavior. Seebeck coefficient shows an increasing trend with annealing temperature and with temperature sweep measurements.

Keywords: CuCrO₂, triangular lattice antiferromagnetism, band-gap, electrical transport, optical properties

1 Introduction

Atomic layer deposition (ALD) is a vapor-phase deposition technique capable of depositing variety of materials for thin films. The sequential and self-saturating growth nature of ALD; separate it from other vapor-phase deposition techniques e.g. charge vapor deposition (CVD) etc. It offers excellent conformality on high aspect ratio structures, Angstrom level thickness control, and tunable film compositions often at significantly lower temperatures¹². With the aforementioned advantages, ALD has emerged as a powerful tool for many industrial and research applications. So far most of the ALD processes that have been reported are either for metals or binary compositions, relatively less numbers have been reported for ternary compositions.

* All experimental work, analysis and writing (first draft).
† Editing suggestions and analysis.
CuCrO$_2$, which has been of interest for scientists because of its frustrated triangular lattice antiferromagnetism and multiferroicity$^{3,4}$ have become interesting again since the discovery of simultaneous p-type conductivity and optical transparency in thin films of CuAlO$_2$ in 1997.$^4$ Due to this paradigm shift towards “transparent electronics” subsequently, many other delafossite structures, including CuInO$_2$, CuScO$_2$, CuGaO$_2$, CuYO$_2$ and most recently CuBO$_2$ have been investigated as p-type transparent conducting oxides (TCOs). But to date the Mg-doped CuCrO$_2$ is reported to have highest conductivity (220 S cm$^{-1}$) among delafossite materials.

The reason why p-type TCOs are important is basically related to their less availability compare to n-type TCOs as well as to find matching p-type TCOs for the available n-type counterparts to fabricate transparent p–n and p–i–n diodes. In fact materials with bipolar dopability, a large gap, high conductivities and mobilities, will be a boom for optoelectronics industry. The earliest band gap measurement of CuCrO$_2$ by Benko and Koffyberg,$^{10}$ found it to possess an indirect band gap of 1.28 eV with an indirect allowed transition at 3.08 eV and a direct allowed transition at 3.35 eV. However the subsequent measurements of the band gap of CuCrO$_2$ has been debatable with various experimental groups reporting it to be both an indirect band gap$^{11}$ and a direct band gap semiconductor.$^{12}$ However, from the recent optical measurements the general consensus is that, it has the direct optical band gap in the range 2.95–3.30 eV, meaning CuCrO$_2$ is transparent to visible light.$^{13,14}$ Besides, the TCO applications CuCrO$_2$ have attracted attention for a range of other applications too. It has generated interest due to its catalytic abilities in hydrogenation reactions,$^{15}$ its ozone sensing properties,$^{16}$ and as a possible thermoelectric material.$^{17,18,19}$

Various thin film preparation methods have been reported for the preparation of CuCrO$_2$, such as reactive sputtering deposition$^{20}$, pulsed laser deposition$^{21}$, chemical solution deposition$^{22}$, and molecular beam epitaxy$^{23}$ and so on. No ALD process has been reported so far for CuCrO$_2$. In this work, we report the structural, optical and electrical characterizations of CuCrO$_2$ films deposited by ALD. Cu-Cr-O films were prepared by alternating exposure to copper tetramethyl heptanedionate (Cu(thd)$_2$), chromium acetyl acetonate (Cr(acac)$_3$) and ozone for copper, chromium and oxygen sources respectively.

2 Experimental Detail

Thin films of CuCrO$_2$ were deposited on 3.5 × 3.5 cm$^2$ borosilicate glass substrates. Copper 2,2,6,6-tetramethyl-3,5-heptanedionate (Cu(thd)$_2$) and chromium acetyl acetonate (Cr(acac)$_3$) have been used as the precursors for metal and ozone (produced with a Fischer model 502 laboratory ozone generator from oxygen (99.999%)) as an oxygen source. The commercial hot-wall flow-type F-120 ALD reactor from ASM Microchemistry Ltd., Finland is utilized for deposition operated under a nitrogen pressure of 2-3 mbar. Nitrogen (99.9995%) is used both as a carrier and purging gas and produced with a NITROX UHPN 3000 nitrogen generator. Cr(acac)$_3$ (97.5%) was procured from STREM Chemicals whereas Cu(thd)$_2$ was prepared from copper acetate (Fluka; 98%) and 2,2,6,6-tetramethyl heptane-3,5-dione (Fluka; > 98%) in our laboratory. The metal precursors Cu(thd)$_2$ and Cr(acac)$_3$ were sublimed from open glass boats held inside the reactor at 120 and 130 °C, respectively. Pulse and purge lengths for the metal precursors, ozone and N$_2$ were initially tested from 1 to 6 s, and then fixed to 2 s for all the three precursors and 3 s for the N$_2$ purge. Readers are suggested to read our full publication regarding detail ALD process and surface characterizations.$^{24}$ For crystallization the films were annealed at 600-800°C in a rapid thermal annealing (RTA) furnace PEO 601 (ATV Technologie GmbH) in Ar atmosphere.

The dc resistivity was measured in linear four-probe configuration. Seebeck coefficient was measured using our home made setup similar to the setup reported in Ref. $^{(25)}$. The spectrophotometric measurements were performed by Hitachi-U 2000 spectrophotometer in the wavelength range of 190-1100 nm. Crystal structure of the post-deposition annealed films was identified from grazing incidence
X-ray diffraction data (GIXRD; PANanalytical model X’pert Pro diffractometer, Cu Kα radiation). Film thicknesses were determined from X-ray reflectivity (XRR) patterns measured with the same diffractometer. Elemental composition of the films was determined from wavelength dispersive X-ray fluorescence spectroscopy (WD-XRF; PANanalytical AxiosMAX microanalysis system equipped with SST-mAX X-ray tube that virtually eliminates instrument drift). SuperQ software package from PANanalytical was used for the analysis of the XRF results.

3 Result and Discussion

In Figure 1 we show the XRD patterns of the films with the stoichiometric Cu/Cr ratio 1.02 after annealing the as-deposited films at different temperatures in argon (Ar) atmosphere for 5 minutes. The as-deposited film is non-crystalline and as expected the crystallinity of the films enhances with increasing annealing temperature. The film annealed at 700 °C contains small amounts of CuO and CuCr2O4 phases along with the CuCrO2 phase. By 800 °C the CuO and CuCr2O4 phases have transformed to CuCrO2 and a phase-pure CuCrO2 film is obtained.

![Figure 1. XRD patterns of as-deposited and annealed CuCrO2 in Ar at 600, 700, 750 and 800 °C. Red lines show the diffraction peaks matched with ICDD reference data for CuCrO2 (ICDD 74-0983) and CuCr2O4 (ICDD 26-0508).](image)
In Figure 2 we have shown the UV-vis spectra of the same films deposited on a borosilicate glass substrate. Thickness of the film is 125±2 nm determined from XRR measurements. Figure 2(a) shows the wavelength dependence of transmittance and reflectance data for the films along with the plain borosilicate glass substrate. It can be distinguished from XRD and transmittance measurements that the light transmittance is dominated by structural changes in the films with higher annealing temperature. Transmittance spectra of highest annealed film are more steeply sloped at a specific wavelength compared to the lower annealed films that consist of two-phase structure (CuO and CuCr2O4). The as-deposited film has a light transmittance of approximately 50 % in the wavelengths range 600–800 nm. In the same wavelength range transmittance of the films enhances with increased annealing temperature. The observed transmittance 74-79 % for the highest annealed sample is slightly better than the values (60-75 %) reported in literature for CuCrO2 films deposited by other deposition techniques. The reflectance values are not very conclusive with annealing temperatures and changes between 18-22% in the same wavelength range. The discrepancy in the transmittance measurements is largely attributed to the differences in point defects, grain sizes, void defects, surface conditions and film thicknesses.

![Figure 2](image_url)

**Figure 2.** (a) Transmittance and reflectance spectra for the Cu-Cr-O films annealed at various temperatures 600-800 °C deposited on a borosilicate glass substrate. (b) Direct bandgap of the films. Inset shows the absorption coefficient of the same as a function of wavelength.

From the film’s light transmittance and reflectance data the absorption coefficient (α) can be calculated at each wavelength as follows:

\[ \alpha = \left( \frac{1}{d} \right) \ln \left( \frac{1-R}{T} \right) \]  

where d is the thickness, R the reflectance and T is the light transmittance of the film.

The inset of Figure 2(b) shows the absorption coefficient as a function of wavelength. The characteristic absorption feature of the films is clearly visible with the sharp rise of the \( \alpha \) at a specific wavelength. It is observed that the peak (marked as I) due to sub-bandgap transition located at wavelength 350 nm with corresponding incident photon energy of 3.54 eV enhances with increased proportion of CuCrO2 at higher annealing temperature.

Such peaks have been mentioned to appear as sub-band gap transitions when the relationship, \( h \nu = E_g - E_k \) between an incident photon and a free exciton in the semiconductor is satisfied.
Here \( h \nu \) is the incident photon energy, \( E_g \) is the bandgap and \( E_b \) is the binding energy of the free exciton and \( k \) represents the wave-vector on the E–k diagram. On E–k diagram, sub-bands lie at lower energy positions. Thus sub-bandgap transitions are not, in general, capable of creating hole carriers to make any appreciable contribution to the electrical conductivity.

The following equation is used frequently to estimate the bandgap of a semiconductor material:

\[
(\alpha h \nu)^{1/n} = A(h \nu - E_g)
\]

where \( \alpha \) is the absorption coefficient and \( A \) is an arbitrary constant. For direct and indirect bandgaps \( n \) is taken as \( \frac{1}{2} \) and 2, respectively. From the graph \( (\alpha h \nu)^2 \) versus \( h \nu \) the direct bandgap of a material can be determined. As shown in Figure 2(b) the direct bandgap of our ALD CuCrO\(_2\) films enhances with higher annealing temperature. The larger band gap of the higher annealed films is due to the increased amount of CuCrO\(_2\) and the disappearance of CuO. The band gap is proportional to the CuCrO\(_2\) content of the film. The estimated band gap for highest annealed (800 °C) film is 3.09 eV, consistent with direct bandgaps of 2.95–3.55 eV reported in previous studies.\(^{20-25}\)

In Figure 3 we show the electrical transport measurements on the same films annealed at various temperatures 600-800 °C. As shown in Figure 3a, for all the films the T dependence of resistivity shows a purely semiconducting behavior with \( d\rho/dT < 0 \) as the temperature is increased. Annealing effect on the films is observed as the reduction in the total resistivity probably due to phase conversion of remnant CuO and CuCr\(_2\)O\(_4\) to CuCrO\(_2\).\(^{31}\) The resistivity of the film with maximum proportion of CuCrO\(_2\) (i.e. film annealed at 800 °C) matches well with the values reported in literature.\(^{15}\) Figure 3b shows the T dependence of Seebeck coefficient of the same films. The positive Seebeck values confirm the p-type conductivity of the films. Quantitatively the room temperature Seebeck values do not change much with higher annealing temperatures however show an increasing trend with values \(~ 300-325 \pm 10 \mu V/K\). This is comparable \((~350 \mu V/K)\) to the value reported by T. Okuda et al.\(^{18-20}\) for powder samples of Mg doped CuCrO\(_2\). However, much higher \((~1200 \mu V/K)\) values have been reported by Benko, Koffyberg\(^{11}\) and Y. Ono et al.\(^{18}\) for bulk powdered samples of Ca and Mg doped CuCrO\(_2\) respectively. This is believed to be related to the large resistivity differences\(^{32}\) of their materials \((~100 \Omega \text{ cm})\) to the films we measured \((~1.0 \Omega \text{ cm})\). It is to be mentioned that the T dependence of resistivity and Seebeck coefficient for all the films show similar character irrespective of their nature and remnant composition. It is probably due to the fact that the remnant compositions also show similar T dependence in their pure form.\(^{33,34}\) However, it is observed that the pure CuCrO\(_2\) film (800 °C annealed) shows an opposite trend reported for the bulk samples. For bulk samples Seebeck coefficient decreases as the temperature is increased above room temperature.\(^{18,20}\) This discrepancy may be related to the following reasons. (i) The large resistivity difference between the thin films and bulk samples.\(^{33}\) (ii) Is there any sub-band contribution? That has been seen in optical measurements. (iii) The other possible reason is the self-doping of copper at chromium sites that will introduce holes in the system. Because it has been reported that even a very small (1-2%) of Mg at chromium sites changes the electronic transport properties greatly moreover, a doping of 5% Mg reverses the trend completely and Seebeck coefficient increases with increasing temperature.\(^{18-20}\) However to verify this conjecture X-ray fluorescence spectroscopy (XPS) are required to check the site occupancy of the elements.
Figure 3. Temperature dependence of (a) resistivity and (b) Seebeck coefficient of the films annealed at various temperatures.

4 Conclusions

In this work, we presented the structural, optical and electronic transport properties of CuCrO$_2$ thin films fabricated through an atomic layer deposition process. Though the study was particularly intended to the growth of high-quality CuCrO$_2$ films the information of the process parameters and growth characteristics may also be useful for the deposition of other members of the CuAO$_2$ delafossite family for potential TCO applications. Our ALD process is based on Cu(thd)$_2$, Cr(acac)$_3$ and ozone precursors, and to get the desired Cu/Cr ratio for CuCrO$_2$ a super-cycle was employed with one Cu(thd)$_2$-O$_3$ and three Cr(acac)$_3$-O$_3$ sub-cycles. The as-deposited films exhibited smooth homogeneous surfaces but were non-crystalline; annealing at 600-800 °C in Ar then revealed crystalline CuCrO$_2$ films. With higher annealing temperature optical transmittance of the films improved to greater than 75% in the visible range with the direct bandgap of 3.09 eV. One higher-energy sub-band transition was observed at 3.54 eV. Electrical transport measurements confirm the p-type semiconducting behavior of the films. The observed T dependence of Seebeck coefficient show an opposite trend reported for bulk powder samples. The possible reason of copper self-doping at chromium sites needs good quality XPS measurements to check the site occupancy of the elements.
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