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ENHANCED STRUCTURE, COMPOSITION, AND PROPERTIES OF $CUCR_{1-X}O_2$ THIN FILMS

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Abstract

$CuCr_{1-x}O_2$ thin films was synthesized by a sol-gel technique. In this study structural, optical and electrical properties of $CuCr_{1-x}O_2$ films (x = 0, 0.1, 0.15, 0.2, 0.3) which exhibited p-type properties, were investigated. Using Combustion chemistry, films are solution processed at150^o c which is lower than most recent efforts. Smooth and homogeneous thin films are obtained at the pretreated temperature at 450^{o}c. $CuCr_{1-x}O_2$ thin films have been annealed at different temperatures (from 600 to 900^{0}c). The films were characterized by XRD, FE-SEM, FTIR and Hall Effect measurement. The optical band gap as determined from FTIR measurements is observed ranging between 3.12 and 3.2 eV the lowest resistivity was obtained with annealing at 800^{0}c, 92.85 Ω cm respectively. The results exhibited Superior optoelectronic Characteristics with interesting temperature-dependent copper delafossite thin films.

INTRODUCTION: CuCrO2films with p-type conductivity are broadly used as critical components used in both light emitting device Mechanism In this contemporary work, we have adapted CuCrO2 thin films with different concentration of cr+3 (0.05M, 0.1M, 0.15M, and 0.2M,0.3M) on Glass substrate by simple sol-gel spin coating Method. Different members of the copper delafossite family exhibit both good transparency and p-type electrical conductivity [1-5]. The latter are therefore of great interest in optoelectronics, in particular for developing transparent light-emitting diodes. However, delafossites often require heat treatments at high temperature (≥600 ◦C for CuCrO2) in order to achieve sufficient electronic and optical properties from the point of view of technological applications [6-12]. This constraint therefore excludes the use of many usual substrates of polymer type and even ordinary glass [13-17]. However, the techniques of direct writing laser, which make it possible to strongly heat a layer absorbing the wavelength of the laser, while only slightly raising the temperature of a transparent substrate, could make it possible to circumvent this limitation[18-19]. The control of the laser spot on a micron scale would also allow the production of specific patterns, sometimes required by transparent electronics.

1. Experimental:

In this exercise specified amount of Cu $(CH_3COO)_2H_2O$ (99%) and $Cr(NO_3)_3 9H_2O$(99%˙)were fused in 20ml propionic acid. The metallic ion (Cu^{2+} and Cr^{3+}) concentrations were 0.05M 0.1M, 0.15M and 0.2M (Cr^{3+})· The admixtures were stirred for many hours in order to get a transparent solution. The solution was spin-coated onto Glass substrates at a rate of 8000 r/min, Preheated at 400–550 °C for 30 min in air. Later repeated the above illustrate procedure five times, all the films were finally sintered in a furnace 900^0c.

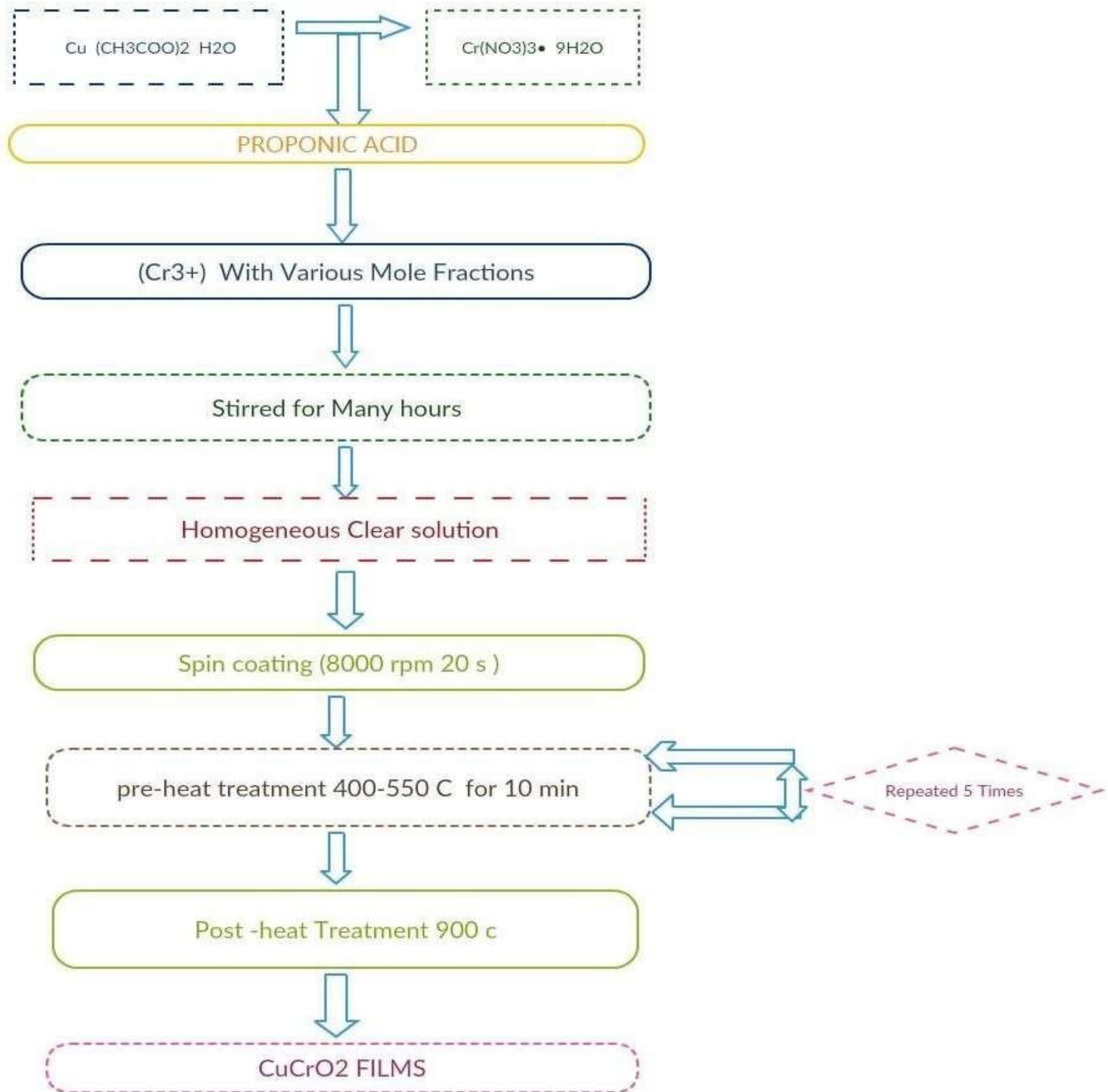

Figure1.1: The Flowchart for the preparation of the $CuCrO_2$ thin films by the sol-gel spin-coating method.

. Results and Discussion:

XRD STUDY:

This Shows the XRD results of the $CuCrO_2$ films pretreated at varying temperatures (400–900 °C), sintered at 900 °C. From the XRD results, it can be erect that the films pretreated at temperatures of 400–900°C are Composed of single Structured $CuCrO_2$ phase, as shown by D in Fig. 1.2 without any detectable undesired phases. Moreover, it can be observed that the peak at 31.4° is especially sharp and have a compelling lower line width than the other signals

Sherrer formula: $D = K\lambda / \beta\cos\theta$.
Where λ is the wavelength of CuKα radiation (0.154nm),
k =0.9 is the shape factor
Θ is the Bragg angle and
β is the experimental full-width at half maximum on the respective diffraction peak
The Crystalline size Calculated by applying the Scherer formula Associated to the peaks at 31.6^0 and Corresponding to the (003). The Crystalline size also increases from 29nm to 78nm

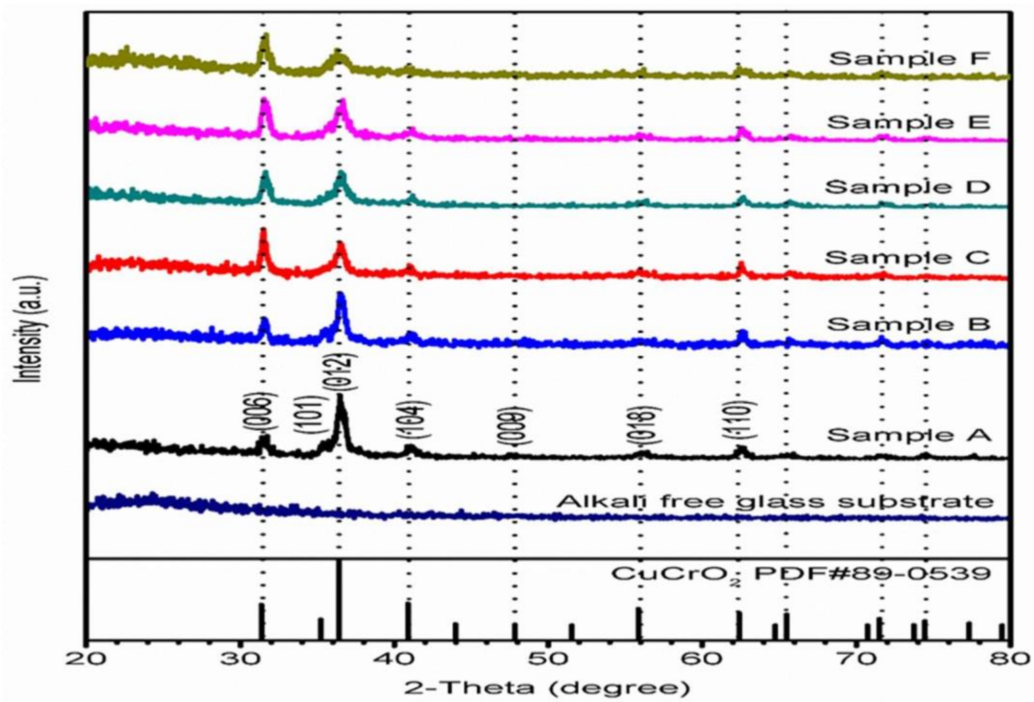

Figure 1.2 shows the XRD patterns of the sol-gel derived films. After sintering at 600℃ in N2 atmosphere for 1h phase pure $CuCr_{1-X}O2$ films (R3M, JCPDS #C89-6744) are obtained above 700℃ ,800 ^{0}C and 900 C (003), (006) diffraction peaks appeared .

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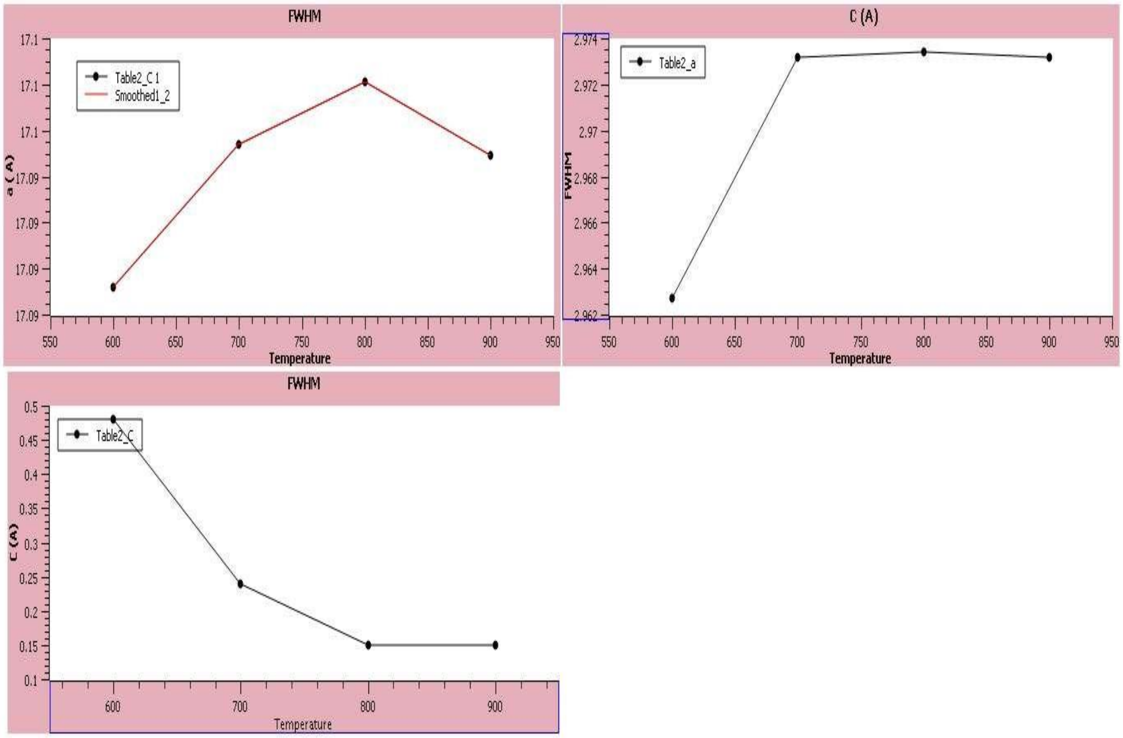

Figure1.3 Shows the Lattice Parameters (a and c) Through Temperature and FWHM

Figure 1.3 Shows the variations in the FWHM and the crystalline size as a function of annealing temperature obtained by (006) signal at 31.4°. The values of the full width at half Maximum (FWHM) for the (006) diffraction peak were 0.48(600℃), 0.24 (700℃) 0.15 (800℃), and 0.15 (900℃).

Table: 1.1 Lattice parameters a and c of $CuCrO_2$ films with different annealing temperature

$CucrO_2$ films	600℃	700℃	800℃	900℃
a(A°)	2.9627	2.9732	2.9734	2.9732
c (A°)	17.0892	17.0954	17.0981	17.0949

3. Morphology and Compositional Analysis

The SEM images of Surfaces of $CuCrO_2$ Films 0.2M the surfaces of thereare smooth and fine particles. No cracks exist at the surface. As a result, we could assume that the crystallinity of CuCoO2 retains a structure mostly constituted of nanocrystals smaller than 15 nm in diameter

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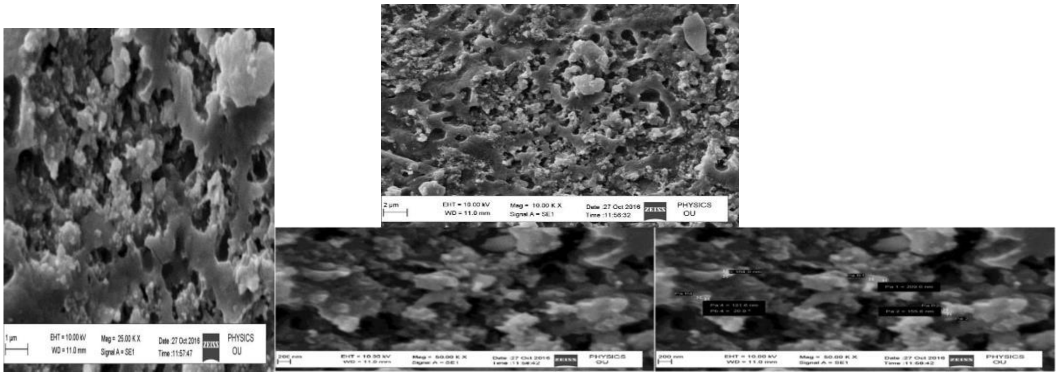
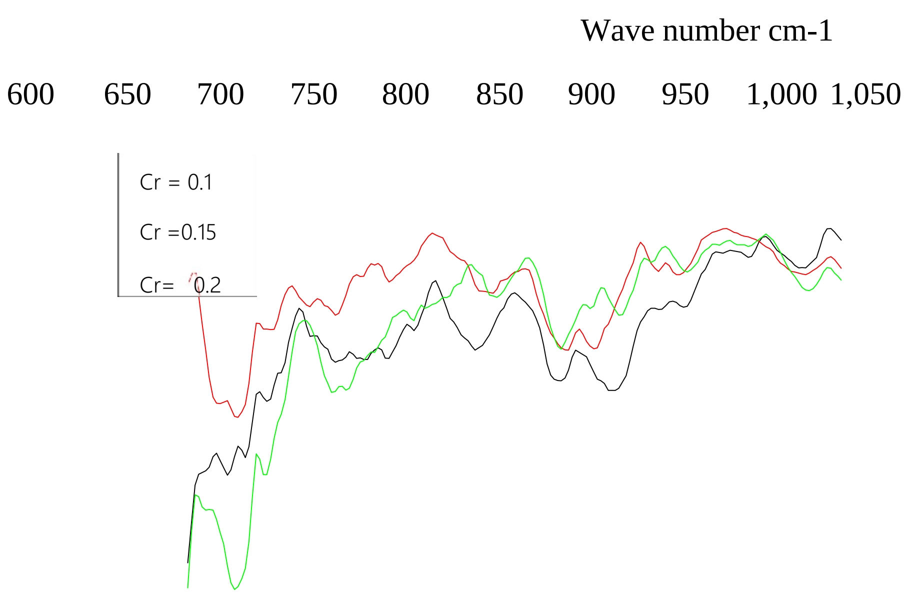


Figure 1.5 SEM IMAGES OF 0.2 M

4. Optical study:

The FT-IR spectrum of the $CuCrO_2$ Films is shown in Fig. 1.5 Shows one weak (958 cm^{-1}) and five strong bands (675,734,750,765 and 781 cm^{-1}) could be assigned to the Cr^{III}–O, and M–O bond stretching frequencies of the $CuCrO_2$ Films.The FT-IR spectrum of the $CuCrO_2$ films good agreement with Experimental value.

FTIR GRAPHS $CUCrO_2$ FILMS



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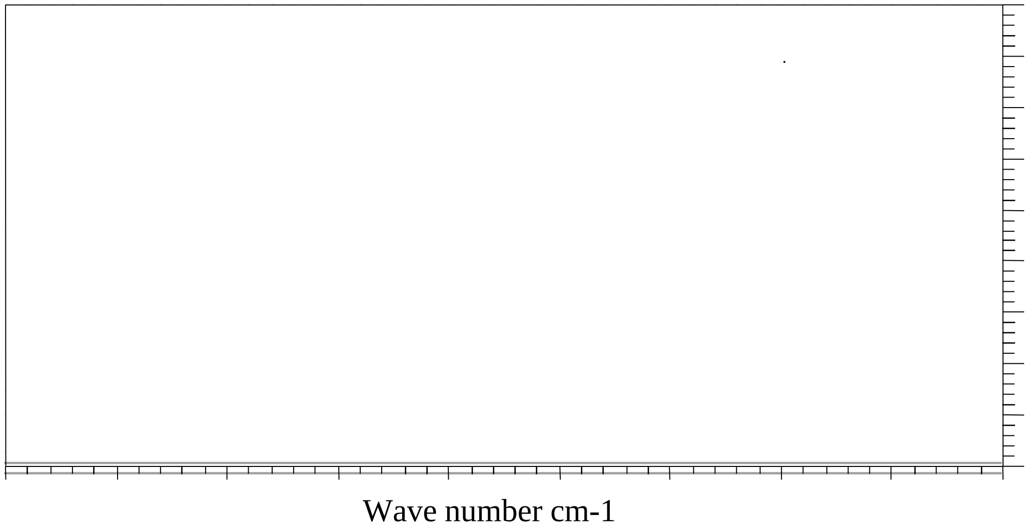


1.6 FTIR SPECTRUM OF $CuCrO_2$ FILMS Cu =0.2 M AND Cr = 0.1 M, 0.15M AND 0.2 M

5. Thermo electric Properties and Conductivity

In figure 1.7 we show the electrical transport measurements on the same films annealed at various temperatures 600-900 ^{0} C. As shown in Figure 3a, for all the films the T dependence of resistivity shows a purely semiconducting behavior with dU/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 CuCr2O4 to CuCrO2. 31 The resistivity of the film with maximum proportion of CuCrO2 (i.e. film annealed at 900 ^{0} C) matches well with the values reported in literature.

Figure 1.8 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 ± 10 PV/K. This is comparable (~ 350 PV/K) to the value reported by T. Okuda et al. 18-20 for powder samples of Mg doped CuCrO2. However, much higher (~ 1200 PV/K) values have been reported by Benko, Koffyberg11 and Y. Ono et al.18 for bulk powdered samples of Ca and Mg doped CuCrO2 respectively. This is believed to be related to the large resistivity differences 32 of their materials (~ 100: cm) to the films we measured (~ 1.0: 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.

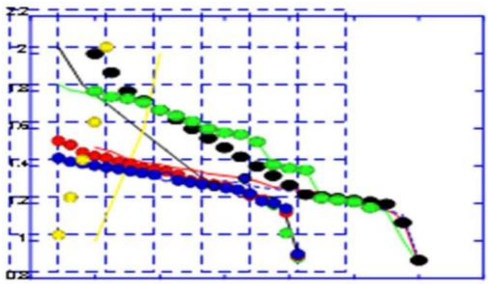


Figure 1.7 Temperature Dependent Resistivity with Concentration

We can use four probe techniques to measure the potential drop between two electrodes when a constant known current flows between other two electrodes and then calculating conductivity using the geometry of electrodes. Delafossite characteristic diffraction peaks were obtained as a function of the thermal treatment. The electrical conductivity was optimized until 1.6 S cm^{-1} is good agreement with literature value.

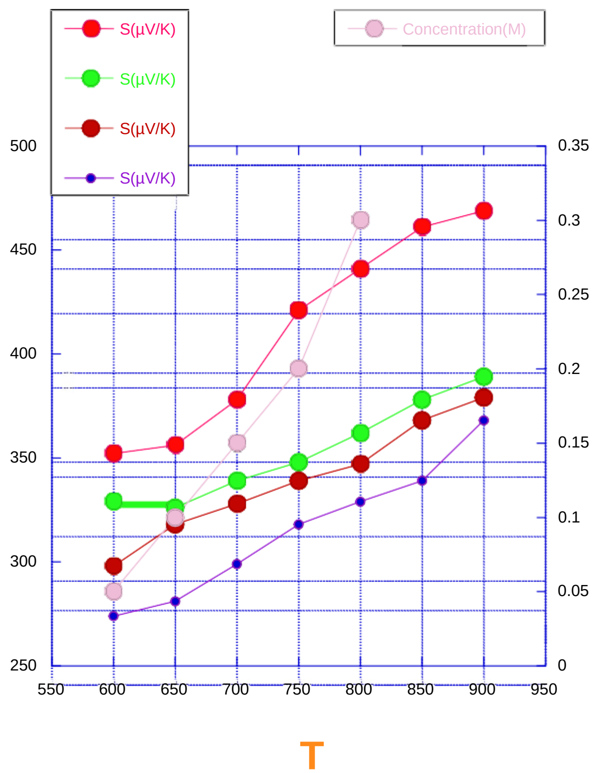


Figure 1.8 Temperature dependence Seebeck coefficients with Concentration

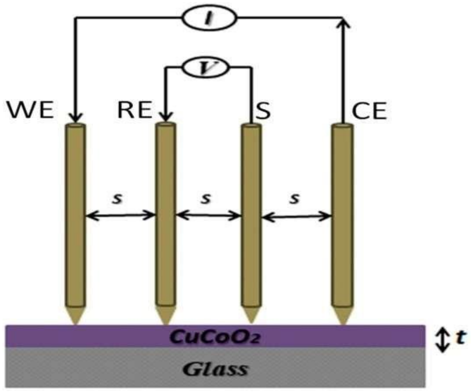
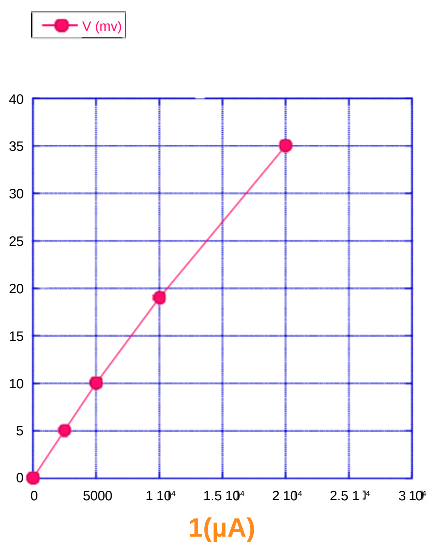


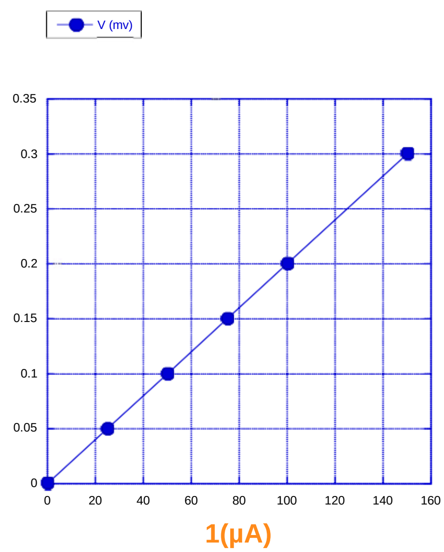
Figure 1.9 Four Probe Point Experiment

The experimental procedure used is the following. The four point probe is attached to a source meter that may supply a certain current. A source meter's current (I) flows through the two outer probes, and a voltammeter can measure the voltage (V) across the two inner probes. Plotting the voltage measured for each current intensity permit us determine the sheet resistance, Rs, such as is shown in Figure 2.1, 2.2 and 2.3

2.1: $CuCrO_2$ _ 0.1 M I-V



2.2: $CuCrO_2$_0.2 M I-V



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2.3 $CuCrO_2$_ 0.3 M I-V

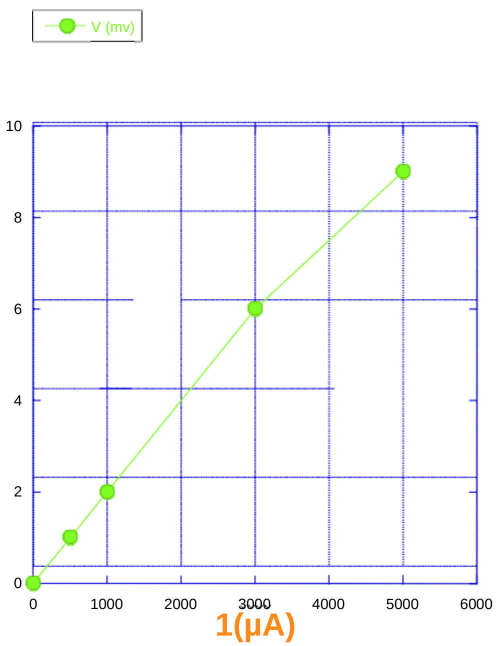

Table 1.2: The electrical properties of the CuCrO2 thin films determined at annealing temperature

Samples	*Sheet Resistivity(□s)* ×*10*$^{-3}$ **(Ω.cm)**	*Sheet resistance(Rs)* **(Ω)**	*Sheet Conductivity* ×*10*^{3} **(S.cm^{-1})**
CuCrO2_0.1 M	0.117 ±0.002	8.19±0.05	8.9±0.2
CuCrO2_0.2 M	0.108±0.002	7.79±0.04	9.6±0.2
CuCrO2_0.3 M	0.119±0.002	8.17±0.04	8.7±0.2

5. Conclusions

In this work, we presented the structural, optical and electronic transport properties of $CuCrO_2$ thin films fabricated through an Sol-gel Method. 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

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family for potential TCO applications. The as-deposited films exhibited smooth homogeneous surfaces but were non-crystalline; annealing at 600-900 ^{0}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.

References:

- R. W. Johnson, A. Hultqvist, and S. F. Bent, *Materials Today* 2014, 17 (5), 236.
- V. Miikkulainen, M. Leskelä, M. Ritala, and R. L. Puurunen, *Journal of Applied Physics* 2013. 113, 021301.
- S. Seki, Y. Onose and Y. Tokura, *Phys. Rev. Lett*., 2008, 101, 067204.
- H. Kawazoe, M. Yasukawa, H. Hyodo, M. Kurita, H. Yanagi, and H. Hosono, *Nature* (London),1997, 398, 939.
- H. Yanagi, T. Hase, S.Ibuki, K. Ueda, H. Hosono, *Appl. Phys. Lett*,. 2001, 78, 1583. [6] N. Duan, A. W. Sleight, M. K. Jayaraj, and J. Tate, *Appl. Phys. Lett.*, 2000 77, 1325.
- H. Kawazoe, H. Yanagi, K. Ueda, and H. Hosono, *MRS Bull*., 2000, 25, 28.
- R. Nagarajan, N. Duan, M. K. Jayaraj, J. Li, K. A. Vanaja, A. Yokochi, A. Draeseke, J. Tate, and A. W. Sleight, *Int. J. Inorg. Mater*., 2001, 3, 265–270.
- M. Snure and A. Tiwari, *Appl. Phys. Lett.*, 2007, 91, 092123.
- F. A. Benko and F. P. Koffyberg, *Mater. Res. Bull*., 1986, 21, 753–757.
- C. Rastogi, S. H. Lim, and S. B. Desu, *J. Appl. Phys.*, 2008, 104, 032712.
- D. Li, X. D. Fang, Z. H. Deng, S. Zhou, R. H. Tao, W. W. Dong, T. Wang, Y. P. Zhao, G.Meng, and X. B. Zhu, *J. Phys. D: Appl. Phys*., 2007, 40, 4910–4915.
- D. O. Scanlon and G. W. Watson, *J. Mater. Chem*., 2011, 21, 3655.
- R. Bywalez, S. Gotzendorfer, and P. Lobmann, *J. Mater. Chem.*, 2010, 20, 6562–6570.
- Y. Ma, X. Zhou , Q. Ma, A. Litke, P. Liu, Y. Zhang, C. Li, and E. J. M. Hensen, *Catal Lett*, 2014, 144, 1487–1493.
- S. Zhou, X. Fang, Z. Deng, D. Li, W. Dong, and R. Tao, *Sensors and Actuators B*, 2009, 143,119.
- Y. Ono, K. Satoh, T. Nozaki, and T. Kajitani, *Jpn. J. Appl. Phys.*, 2007 46, 1071–1075.
- T. Okuda, N. Jufuku, S. Hidaka, and N. Terada, *Phys. Rev. B*, 2005, 72, 144403.
- K. Hayashi, K. Sato, T. Nozaki, and T. Kajitani, *Jpn. J. Appl. Phys*., 2008, 47, 59–63.
- G. B. Dong, M. Zhang, X. P. Zhao, H. Yan, C. Y. Tian, and Y. G. Ren, *Appl. Surf. Sci*., 2010,
- 256, 4121-4124.
- X. S. Zhou, F. T. Lin, W. Z. Shi, A. Y. Liu, *J. Alloys Compd*., 2014, 614, 221-225.

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