

# Influence of Concentration on Structural Properties of Copper Iron Oxide Thin Films Synthesized Through Chemical Spray Pyrolysis Technique

E. Ashlyn Kirupa,

Department of Physics & Research Centre, Nesamony Memorial Christian College,  
Marthandam - 629 165

## Abstract

Copper Iron oxide ( $\text{CuFeO}_2$ ) of well ordered crystalline films were deposited on to glass substrates for various Cu:Fe concentrations 0.1:0.1, 0.15:0.15 and 0.2:0.2 M at the constant substrate temperature of 300 °C. Films which were characterized had a thickness of the order of few micrometers. Films deposited using optimized Cu:Fe precursor concentration (0.1:0.1M) and at the substrate temperature (300 °C) revealed well crystalline nature indexed for its rhombohedral phase. The diffraction peaks located at  $2\theta = 33.5$  and  $38.6^\circ$  corresponds to (1 0 1) and (1 0 4) reflection of  $\text{CuFeO}_2$  phase. The activation energy decreases as the concentration of the films increases. From the observed results it was evidenced that the concentration has strong influence on the structural and electrical properties of the spray pyrolysed copper iron oxide films.

**Keywords:** Thin films, Chemical vapour deposition, XRD, semiconductor.

## Introduction

In recent years, there has emerged significant interest in functional oxide materials [1]. One of the more important functionalities for electronic applications is that of the wide bandgap semiconductors [2-4]. Though there has been recent success in growing pn-homojunctions, the need still exists to examine alternative p-type transparent conductive oxides (TCO's) to couple with n-type to create successful top and bottom gated TFT's and transparent pn-junctions. Also TCO's have diverse industrial applications and are used to fabricate transparent electrodes in solar cells, active matrix liquid crystal displays, touch screen displays, and in inorganic or organic light emitting diodes in solid-state lighting. Perhaps the most promising group of candidates is the delafossites and they are a subset of the much larger group of  $\text{AMO}_2$  compounds. Delafossite polytype structure is one composed of an alternating stack of O-A-O "dumbbells" and  $[\text{MO}_6]$  edge sharing

octahedral and is divided between two polytypes the 3R rhombohedral crystal structure with the space group  $R\bar{3}m$  and the similar hexagonal structure 2H with the space group P63/mmc. So far only four cations are recognized to occupy the linearly coordinated  $A^+$  positions in the delafossite crystal lattice and are  $Cu^+$  and  $Ag^+$ , but in rare cases  $Pd^+$  and  $Pt^+$  [5-7].

Among the copper and silver based delafossites, copper ions coordinated in  $AMO_2$  structure still seem to be the most promising candidates to fulfill the demands for technical application and mass production. Among the delafossites, p-type TCOs are neither well studied nor systematically explored yet. The p-type films of delafossite structure in particular has been attracting an immense research interest because of its attractive properties, which have great potential for practical applications. Many sophisticated film deposition techniques were reported for the synthesis of multi-cation TCO thin films. But spray pyrolysis technique is one of the non-vacuum techniques which operates in open atmosphere. This method does not require either any high quality targets/substrates or require vacuum at any stage. Due to its merit of being cheap and simple, the deposition of the thin films were done by the spray pyrolysis technique.

Substrate temperature and precursor concentration are the parameters that has a crucial part in deciding the structural, morphological and electro-optical properties of thin films. Improved crystallinity and reduced resistivity have been proven by varying these parameters. Hence the prepared nanostructured thin films were characterized for evaluation of their structural, morphological and electrical properties by using various probes such as; XRD, EDAX, two probe. After identifying the qualities, the optimised films were engaged for device fabrication.

## Experimental Details

Cleaning the substrate surface is very important due to its effect on adherent thin film properties. Copper iron oxide nanostructures were spray pyrolytically synthesized on well cleaned glass substrates using copper chloride [ $CuCl_2$ ] (M.W.=170.48) and ferric chloride [ $FeCl_3$ ] (M.W.=162.21) dissolved in 50 % ethanol ( $C_2H_5OH$ ) and de-ionized water for various Cu:Fe concentrations 0.1:0.1, 0.15:0.15 and 0.2:0.2 M at the constant substrate temperature of 300 °C. All other optimized deposition conditions are listed in Table 1. The thickness of the films was measured using Stylus profiler model Mitutoya SurfTest SJ-301. The X-ray diffraction patterns of  $CuAlO_2$  films were obtained with an X-ray diffractometer (XPRT-PRO) using  $CuK\alpha$  (30mA, 40kV,  $\lambda=1.54060$ ) at a continuous scan type with step size 0.0330 ( $^{\circ}2\theta$ ). The chemical environment

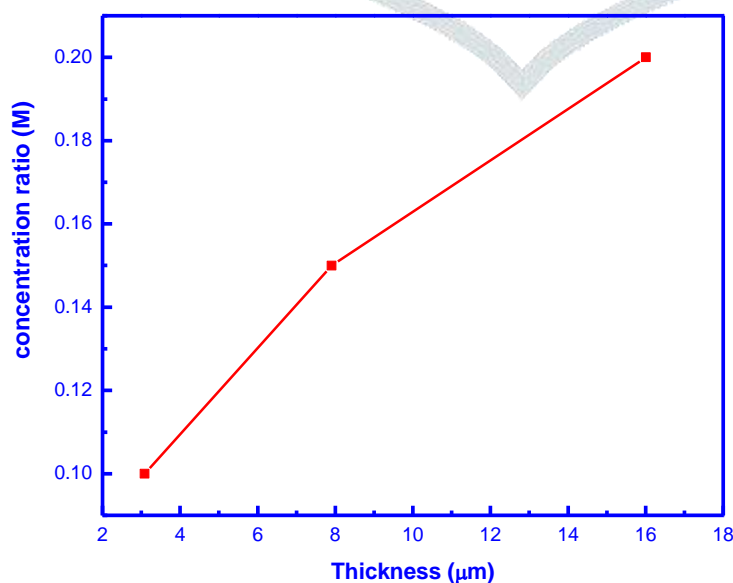
of the  $\text{CuAlO}_2$  films was investigated using VG Microtech Multilab ESCA 3000 spectrometer with a non-monochromatized  $\text{M}_g \text{K}_\alpha$  X-ray source at the vacuum level of  $10^{-10}$  Torr. The two probe technique was used for measuring electrical resistivity of  $\text{CuAlO}_2$  films using Keithley Source meter.

**Table 1 Optimized deposition parameters**

| Spray parameters                   | Optimized values                     |
|------------------------------------|--------------------------------------|
| Substrate temperature              | 300 °C                               |
| Volume of precursor                | 50 ml.                               |
| Solvent                            | 50 % Ethanol & 50 % de-ionized water |
| Spray rate                         | 0.5 ml/sec.                          |
| Concentration of precursor (Cu:Fe) | 0.1:0.1, 0.15:0.15 & 0.2:0.2 M       |
| Carrier gas pressure               | 0.3 kg/cm <sup>2</sup>               |
| Nozzle to substrate distance       | 30 cm.                               |

### Structural Analysis

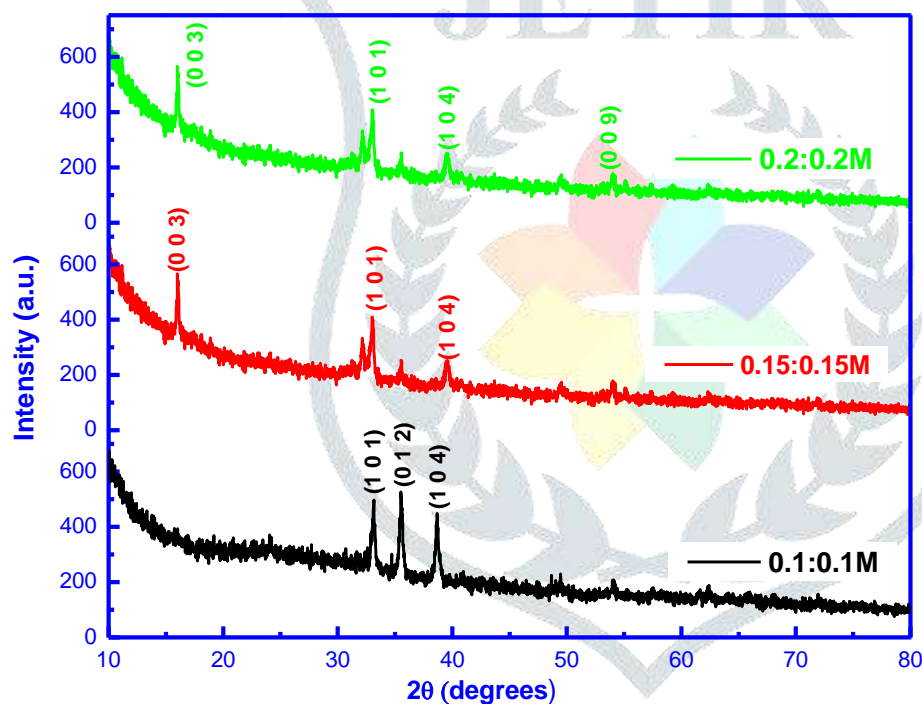
The thickness of the prepared films was measured using a stylus type profilometer and its variation with the concentration ratio is shown in Fig. 1. It shows an increase in thickness with the concentration and the values are 3.09, 7.91 and 16  $\mu\text{m}$  for the concentrations 0.1:0.1, 0.15:0.15 and 0.2:0.2 M respectively.



**Fig. 1 Variation of thickness with concentration ratio of  $\text{CuFeO}_2$  thin films**

It is noticed from the above figure that the growth rate increases with increase in molarity of the precursor solution. The continuous increase in growth rate with molarity indicates that the growth rate may be governed by the Cu and Fe-containing species. In spray pyrolysis technique, it is difficult to control the incorporation of O<sub>2</sub> into the film during the growth process because the film grows in atmospheric conditions. So the stoichiometry is controlled by the Cu and Fe species. Thin films formed at less concentration are of low thickness and contributes to higher transparency.

Fig. 2 shows the XRD pattern of CuFeO<sub>2</sub> thin films deposited at various precursor concentration ratio. XRD analysis identified the thin films of CuFeO<sub>2</sub> as delafossite structure and the 3R-delafossite phase is refined in the rhombohedral  $R\bar{3}m$  (N-166) space group using the hexagonal axes. The diffraction peaks located at  $2\theta=33.5^\circ$  and  $2\theta=38.6^\circ$  corresponds to (1 0 1) and (1 0 4) reflection of CuFeO<sub>2</sub> phase.



**Fig. 2 XRD patterns of CuFeO<sub>2</sub> thin films deposited at various concentrations**

The peak positions are in perfect match with the standard rhombohedral phase, which was similar to those reported by Adel et. al [8]. Calculated lattice parameters, unit cell volume and density are in good agreement with the JCPDS No: 75-2146 values ( $a = 3.0395 \text{ \AA}$ ,  $c = 17.7760 \text{ \AA}$ ,  $\rho = 5.507 \text{ g/cc}$ ,  $V = 136.94 \text{ \AA}^3$ ) and along with these parameters the calculated crystallite size, microstrain and dislocation density of the films are given in Table 2. With increasing film thickness, the crystallite size decreases which in turn decrease the crystallinity of the films as evidenced from the XRD pattern. This may be due to the vertical growth of the

grains. As supersaturation is attained very quickly, grains are very small because of secondary nucleation, just above the grains. On the other hand, both the microstrain and dislocation density increases as the concentration ascends. The decrease in the diffraction intensity as the concentration increases is assumed to be due to the decrease in the covalent bonding as the structural defects increase. With increasing film thickness, usually the grain size increases that lead to introduce fewer defects in the crystal lattice.

**Table 2 Structural parameters of CuFeO<sub>2</sub> thin**

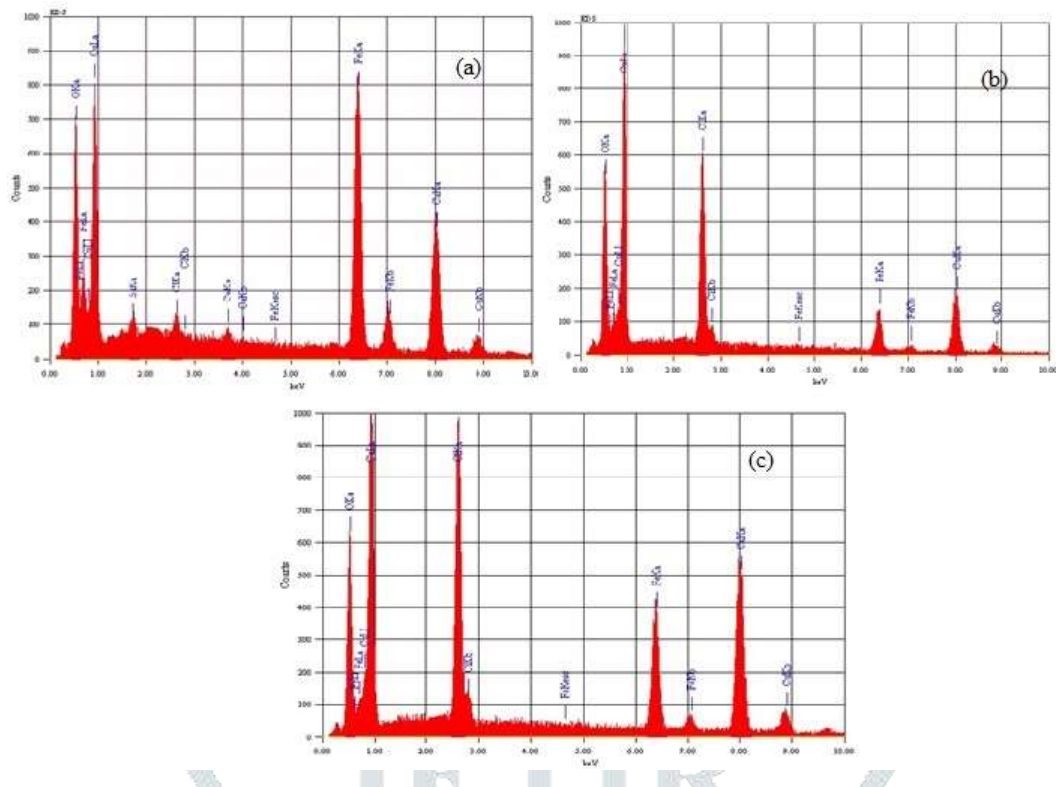
| A         | B                    | C      | D      | E    | F    | G     | H     |
|-----------|----------------------|--------|--------|------|------|-------|-------|
| 0.1:0.1   | a=3.0395<br>c=17.776 | 142.22 | 5.3010 | 51.8 | 3.77 | 3.73  | 0.628 |
| 0.15:0.15 | a=3.1734<br>c=16.287 | 142.00 | 5.3091 | 43.4 | 5.71 | 5.30  | 0.697 |
| 0.2:0.2   | a=3.1603<br>c=16.432 | 142.09 | 5.3057 | 28.7 | 67.7 | 12.10 | 1.158 |

A- Cu:Fe concentrations (M), B-lattice constants in Å, C-Unit cell volume in Å<sup>3</sup>, D-Density in g/cm<sup>3</sup>, E-Crystallite size in nm, F- Number of crystallites in 10<sup>16</sup> m<sup>-2</sup>, G -Dislocation density in 10<sup>14</sup> lines/m, H- Microstrain in 10<sup>-3</sup> lines/m<sup>2</sup>

However in the present study, grain size decreases with increase in film thickness, which may be due to the realignment of crystal basis especially in the (003) and (006) planes. Initiated growth in those planes diminishes the XRD intensity of the prominent planes (012) and (104). This embarked variation not only increases the defects parameters but also changes the surface morphology of the grains.

### Quantitative chemical analysis

Purity as well as the quantity of each element present in the CuFeO<sub>2</sub> compound was evaluated from the recorded EDAX spectra shown in Fig. 3. EDAX spectra clearly shows the only presence of Cu, Fe and O peaks with respective emission lines at 8.04 , 6.39 and 0.53 keV. This result proves the purity of the prepared samples, even without the trace of carbon as evidenced from the XPS studies. Hence the presence of carbon is in the non detectable range in EDAX instrumentation.



**Fig. 3 EDAX Spectra of CuFeO<sub>2</sub> thin films deposited at precursor concentrations (a) 0.1:0.1 M (b) 0.15:0.15 M (c) 0.2:0.2 M**

However, incorporation of other elements Ca, Cl and Si in feeble amount is unavoidable as X-rays penetrate deep into the glass substrates when thickness of the film is low. The elemental composition of the films deposited using precursors of different concentrations is presented in Table 3.

**Table 3 Elemental composition of CuFeO<sub>2</sub> thin films deposited using precursors of different concentrations**

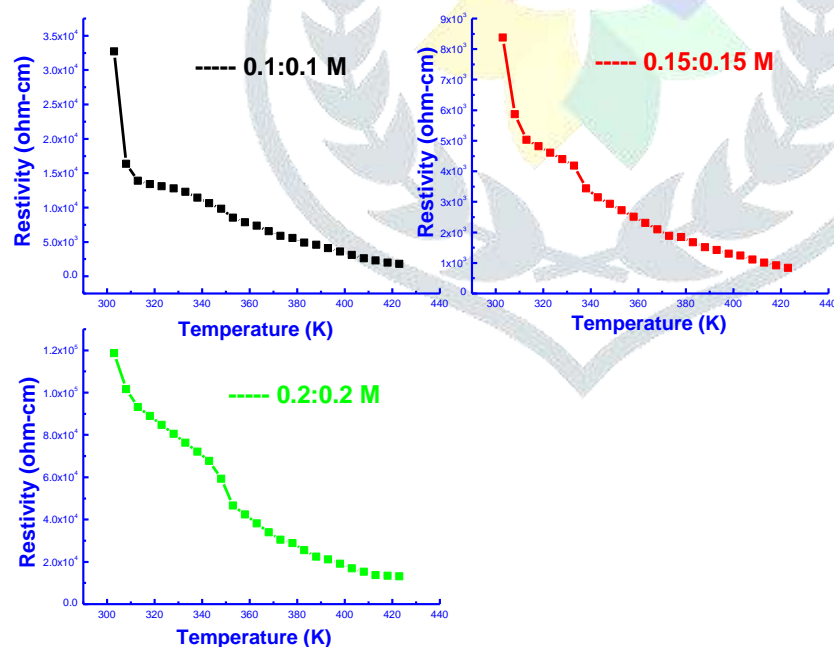
| Cu:Fe<br>Concentration<br>(M) | Elemental composition |        |               |        |               |        |
|-------------------------------|-----------------------|--------|---------------|--------|---------------|--------|
|                               | O K $\alpha$          |        | Fe K $\alpha$ |        | Cu K $\alpha$ |        |
|                               | Mass %                | Atom % | Mass %        | Atom % | Mass %        | Atom % |
| <b>0.1:0.1</b>                | 10.61                 | 30.13  | 48.08         | 39.11  | 39.11         | 28.05  |
| <b>0.15:0.15</b>              | 17.21                 | 40.17  | 15.79         | 10.56  | 45.75         | 26.88  |
| <b>0.2:0.2</b>                | 9.11                  | 25.12  | 21.29         | 16.82  | 51.92         | 36.05  |

From the above table it is known that the cation percentage dominates the anion content because the depositions are carried out at high temperatures in chemical spray pyrolysis technique. Also at higher concentrations, the atomic percentage of iron is very low and hence there may be realignment of cations that modify the crystal basis as evidenced from the XRD studies.

## Electrical studies

The p-type conductivity in  $\text{CuFeO}_2$  can be explained primarily from their electronic structure. A vital role played by the trivalent cation  $\text{Fe}^{+3}$  in delafossite oxides is the cause for developing p-type conductivity. In delafossite system, the O 2p states can be hybridized with cationic Fe 3d states so that the top of the valence band becomes more disperse and results in less localized holes allowing p-type conductivity with higher mobilities. Secondly, studies of both intrinsic and extrinsic defects have shown that the acceptor-type defects are more stable than donor defects, which is the reason for their p-type conductivity in delafossite structures [9-11]. The formation of crystal defects like copper vacancies and oxygen interstitials in the thin film are of natural thermodynamic consequences. Copper vacancies or oxygen interstitials are also responsible for intrinsic conductivity with both defects having low formation energies.

Fig. 4 shows the resistivity variation with temperatures in the measured range 300 to 423 K. The resistivity of the films decreases with rise in temperature, which confirms the semiconducting nature of the films.

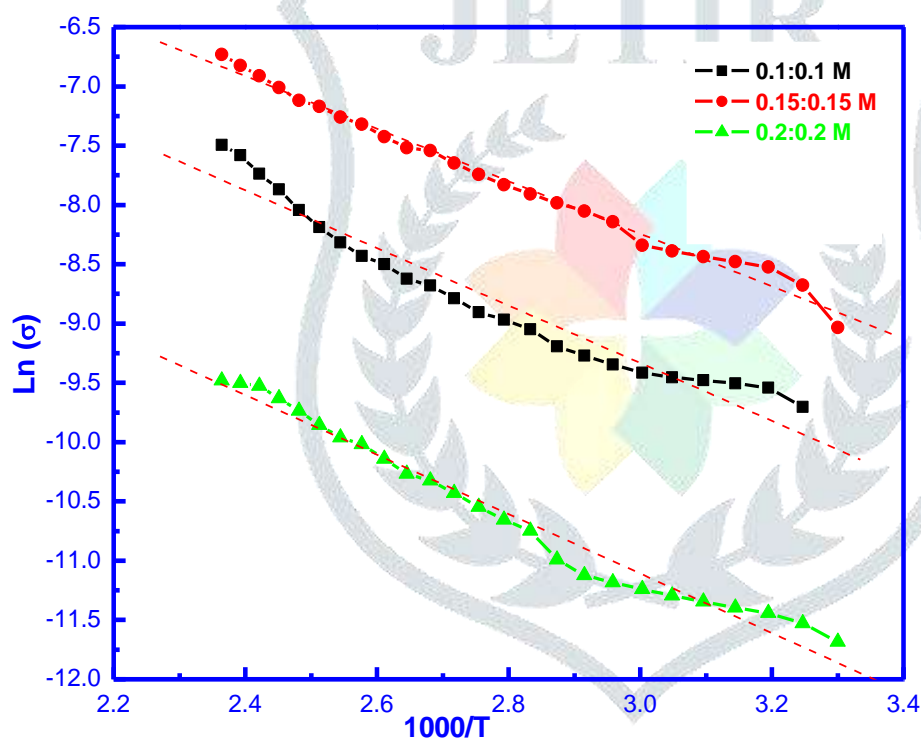


**Fig. 4** Variation of resistivity with temperature of  $\text{CuFeO}_2$  thin films deposited using precursors of different concentrations

The increase in conductivity with temperature is linked with a hopping mechanism, which is favoured with the oxygen intercalation in the  $\text{Cu}^{1+}$  layers of the delafossite ( $\text{CuBO}_2$ ). For smaller B cation like Fe,

oxygen intercalation is forced and generates structural shear and defects [12]. Above a critical oxidation degree, the delafossite structure cannot accept any more oxygen anions. Due to the mentioned effects, the electrical conductivities of prepared films are moderate compared to bulk reference. This is due to the defect structure generated by the forced oxygen intercalation and by the thin film microstructure [13]. Also, the polaron carriers can hop between the Cu sites and between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  sites in octahedral layer for electronic conduction.

For the p-type  $\text{CuFeO}_2$ , the activation energy corresponds to the energy required for the polarons to hop between the mentioned sites. The activation energy ' $E_a$ ' was determined from the slope of the Arrhenius plot given in Fig.5. The results show that the slopes are straight lines with negative slope indicating the positive value of activation energy of conduction.



**Fig. 5 Arrhenius plot of  $\text{CuFeO}_2$  films deposited using precursors of different concentrations**

The activation energy decreases from 0.483 and down to 0.440 and 0.438 eV for the films prepared using 0.1:0.1 M, 0.15:0.15 M, and 0.2:0.2 M precursor concentrations respectively, with the increase in film thicknesses. The increase in activation energy for the optimised film shows the decrease in density of Cu vacancies. Also, the value for  $E_a$  is found to decrease with an increase of precursor concentration. Decrement in activation energy with film thickness indicates the requirement of low energy to the polarons for hopping so that they can easily migrate for conduction. In addition, the results of activation energy show that the carrier



conductivity of the samples is thermally activated which occurs for polaron mechanism in semiconductor conduction.

Observed increase of activation energy with decreasing film thickness may be explained on two basis: (i) island structure theory and (ii) density of shallow traps. In island structure theory, charge carriers can tunnel between islands separated by a short distance [14]. This variation in activation energy could be attributed to the increased density of shallow traps with increase in porosity and the large surface area as a result of enhanced film thickness. These traps with short residence times may be filled with excitons at low temperature and could be later excited by raising the temperature upon thermal activation [15]. The charge carriers thus excited from the traps may adopt a hopping mechanism to cross the potential barrier and hence produce enhanced current [16,17].

Moreover in delafosite oxides, the electrical conductivity is moderate due to electron mobility. The electron mobility is much smaller that indicate electrons hopping between the Fe ions experience a much larger barrier than the holes hopping between the Cu ions (the Cu-Cu and Fe-Fe distances are identical). This mobility difference is probably related to the difference in coordination of the Fe and Cu ions in the delafosite structure. In the  $[\text{FeO}_2^-]$  layers, Fe ions are surrounded by an octahedron of oxygen ions and the electron must hop over a saddle-type configuration of the  $\text{O}^{2-}$  ions. On the other hand, the Cu ions are coordinated to two  $\text{O}^{2-}$  ions in a line parallel to the c-axis, but in the  $[\text{Cu}^{1+}]$  layers there are no oxygen ions which could form a large barrier for the hopping holes [18].

## Conclusion

Copper iron oxide thin films have been prepared using the chemical spray pyrolysis technique on glass substrates. The preparation conditions were optimised to obtain homogenous and good-quality  $\text{CuFeO}_2$  thin films. Films deposited using optimized Cu:Fe precursor concentration (0.1:0.1M) and at the substrate temperature (300 °C) revealed well crystalline nature indexed for its rhombohedral phase. The diffraction peaks located at  $2\theta = 33.5$  and  $38.6^\circ$  corresponds to (1 0 1) and (1 0 4) reflection of  $\text{CuFeO}_2$  phase. As the precursor concentration increases, crystallinity of the film decreases and hence the defect parameters dominate. The conductivity variations confirmed the semiconducting nature of the films.

## References

- [1] D.P. Norton, Mater. Sci. Eng. R 43 (2004) 39.
- [2] U. Ozgur, Y.I. Alivov, C. Liu, A. Teke, M.A. Reshchikov, S. Dogan, V. Avrutin, S.J. Cho, H. Morkoc, J. Appl. Phys. 98 (2005) 041301.
- [3] C.G. Granqvist, A. Hultaker, Thin Solid Films 411 (2002) 1.
- [4] D.S. Ginley, C. Bright, Mater. Res. Bull. 25 (2000) 15.
- [5] R.D. Shannon, D.B. Rogers, C.T. Prewitt, Inorg. Chem. 10 (1971) 713.
- [6] D.B. Rogers, R.D. Shannon, C.T. Prewitt, J.L. Gillson, Inorg. Chem. 10 (1971) 723.
- [7] C.T. Prewitt, R.D. Shannon, D.B. Rogers, Inorg. Chem. 10 (1971) 719.
- [8] Adel H.Omran Alkhayatt, S.M. Thahab , Inass Abdulah Zgair, Applied Numerical Mathematics and Scientific Computation Nov (2014) 165.
- [9] F.Z. Jie, S.L. Jie, L.Y. Hui, Chin. Phys. B 17 (2008) 4279.
- [10] L. Liu, Kewu, H. Gong, P. Wu, Chem. Mater. 17 (2005) 5529.
- [11] L. Liu, K. Bai, H. Gong, P. Wu, Phys. Rev. B 72 (2005) 125204.
- [12] E. Mugnier, A. Barnabe, Ph. Tailhades, Solid State Ionics 177 (2006) 607.
- [13] S. Capdeville, P. Alphonse, C. Bonningue, L. Presmanes, P. Tailhades, J. Appl. Phys. 96 (2004) 6142.
- [14] G.A. Neugebauer, Physics of Thin Films, Ed. G. Has and R. E. Thun, Academic Press, Inc., New York 1964 (p. 2)
- [15] R. Kripal, A.K. Gupta, S.K. Mishra, R.K. Srivastava, A.C. Pandey, S.G. Prakash, Spectrochim. Acta A 76 (2010) 523.
- [16] D. Ponniah, F. Xavier, Physica B 392 ( 2007) 20.
- [17] J. Merline Shyla, Ph.D thesis, University of Madras (Chennai, India, 2007).
- [18] F.A. Benko, F.P. Koffyberg, J. Phys. Chem. Solids 48 (1987) 431.