Preparation of delafossite CuFeO$_2$ thin films by rf-sputtering on conventional glass substrate

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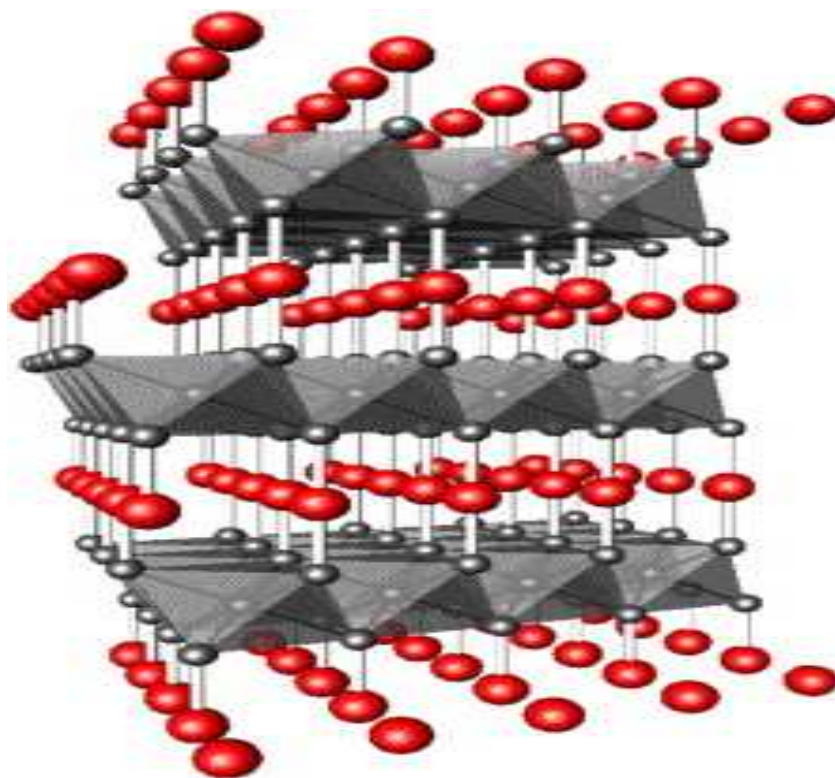
Abstract

CuFeO$_2$ is a delafossite-type compound and is a well known p-type semiconductor. The growth of delafossite CuFeO$_2$ thin films on conventional glass substrate by radio-frequency sputtering is reported. The deposition, performed at room temperature leads to an amorphous phase with extremely low roughness and high density. The films consisted of a well crystallized delafossite CuFeO$_2$ after heat treatment at 450 °C in inert atmosphere. The electrical conductivity of the film was 1 mS/cm. The direct optical band gap was estimated to be 2 eV.

Keywords: Delafossite; Oxide; Thin film; Rf-sputtering; Synthesis

Transparent conducting oxides (TCOs) are materials with high electrical conductivities and low optical absorptions for the visible light. Thin films of TCOs are used as transparent electrodes in technological applications including photovoltaic cells, flat panel displays and light emitting diodes [1]. Development of p-type TCOs will open up application possibilities that are simply not feasible with n-type materials alone, such as transparent diodes, transistors and p–n heterojunctions [2] and [3]. Delafossite oxides make up an interesting family of materials for these technological applications because of their p-type semi-conducting

properties and their quite low optical absorption for the visible radiations. ABO_2 delafossite structure presented in Fig. 1, can be viewed as the stacking of $[B^{3+}O_2^{2-}]_\infty$ layers made of two closely-packed oxygen planes having all octahedral sites occupied by B^{3+} cations, which are connected by planes of A^+ cations arranged as a triangular network. Each A^+ cation is coordinated linearly to two oxygen anions from the oxygen planes above and below. The stacking sequence of successive oxygen compact layers along the c axis leads to various polytypes of the delafossite structure. The delafossite structure exists for a large number of A and B cations [4] and [5]. Depending on the size of the B^{3+} cations, various available spaces for oxygen intercalation in the A^+ cations triangular network can exist.

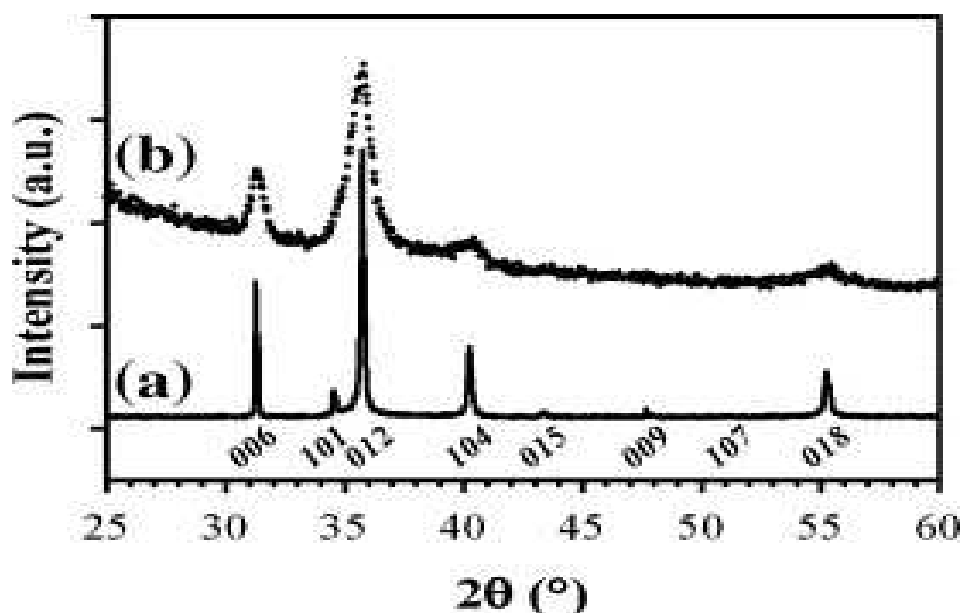Fig. 1. Delafossite type structure (3R-polytype).

Delafossite oxides powders are made of noble metals (Cu, Ag, Pd or Pt). It is then difficult to prepare them by high temperature solid state techniques because of their tendency to decompose before the formation reaction occurs. Quite narrow preparation conditions (temperature and oxygen partial pressure) [6], or cation exchange reactions [5], or "chimie douce" pathways as hydrothermal synthesis [7] are thus required. For similar reasons, it is also difficult to obtain delafossite oxide thin films especially by the well-known industrial

sputtering process [8], [9], [10] and [11]. Moreover, TCOs' practical applications require the use of conventional glass substrates which are not stable above 450 °C. All of these constraints make the synthesis of delafossite thin films by rf-sputtering on conventional glass substrates a real challenge. However, the preparation of $CuFeO_2$ delafossite thin films in these conditions is reported in this letter for the first time, opening real prospects for this family of materials.

In a first step, a pure $CuFeO_2$ powder was prepared from an intimate mixture of Cu_2O and Fe_2O_3. This mixture was grinded and heated at 1000 °C for 24 h several times. After 2 cycles, X-ray diffraction of this product showed pure delafossite $CuFeO_2$ (Fig. 2a). A 10 cm in diameter sputtering target was then prepared by pressing and heating a pellet of $CuFeO_2$ at 950 °C for 12 h in order to obtain 80% relative density.

Fig. 2. (a) XRD pattern of $CuFeO_2$ target. (b) GIXRD pattern of $CuFeO_2$ thin film deposited on conventional glass substrate.

The as-prepared ceramic target was placed in a sputtering chamber and pre-sputtered by an argon plasma for 10 min to remove surface contamination prior to film deposition. A pre-cleaned microscopic slide was used as a conventional glass substrate. The deposition conditions summarized in Table 1 were optimised in terms of target to substrate distance, apparatus geometry, internal gas pressure, rf-power and magnetron in order to keep constant the nominal oxygen stoichiometry of the target.
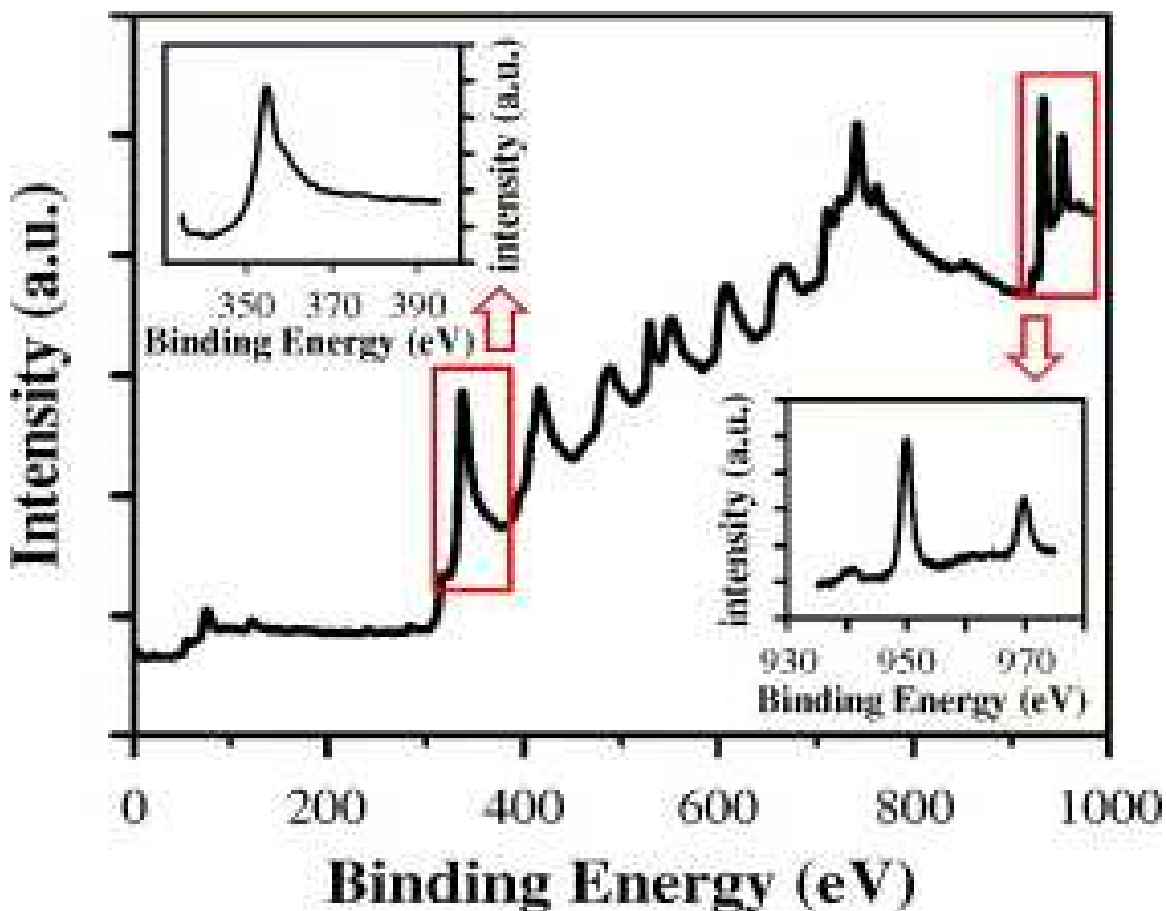
Table 1.

Summary of deposition parameters

Target composition	CuFeO$_2$
Substrate to target distance	5.5–9 cm
Substrate	Glass
Substrate temperature	RT
Magnetron	Yes
Sputtering power	0.9 W/cm^2
Sputtering gas/pressure	Ar/0.5 Pa
Deposition rate	39 Å/mn

The initially deposited thin film was amorphous from $\alpha = 1°$ grazing incidence X-ray diffraction (GIXRD) and electron diffraction (ED) measurements.

Electron scanning for chemical analysis spectra using a Mg Kα ($h_v = 1253.6$ eV) X-Ray source were acquired. The binding energies (BE) were referenced to the 1 s carbon peak (atmospheric contamination) at 284.6 eV. No satellite peak of Cu 2p$^{1/2}$ and Cu 2p$^{3/2}$ peaks (BE = 952.7 eV and 932.8 eV respectively) could be detected ([Fig. 3](#)), inducing the absence of Cu$^{+\mathrm{II}}$ species. The L$_3$VV Auger region of copper revealed only one peak (BE = 337.7 eV) assignable to Cu$^{+\mathrm{I}}$. This analysis showed the presence of solely + I oxidation number of copper in the as-deposited films.

Fig. 3. ESCA spectrum of CuFeO$_2$ thin film deposited on conventional glass substrate.
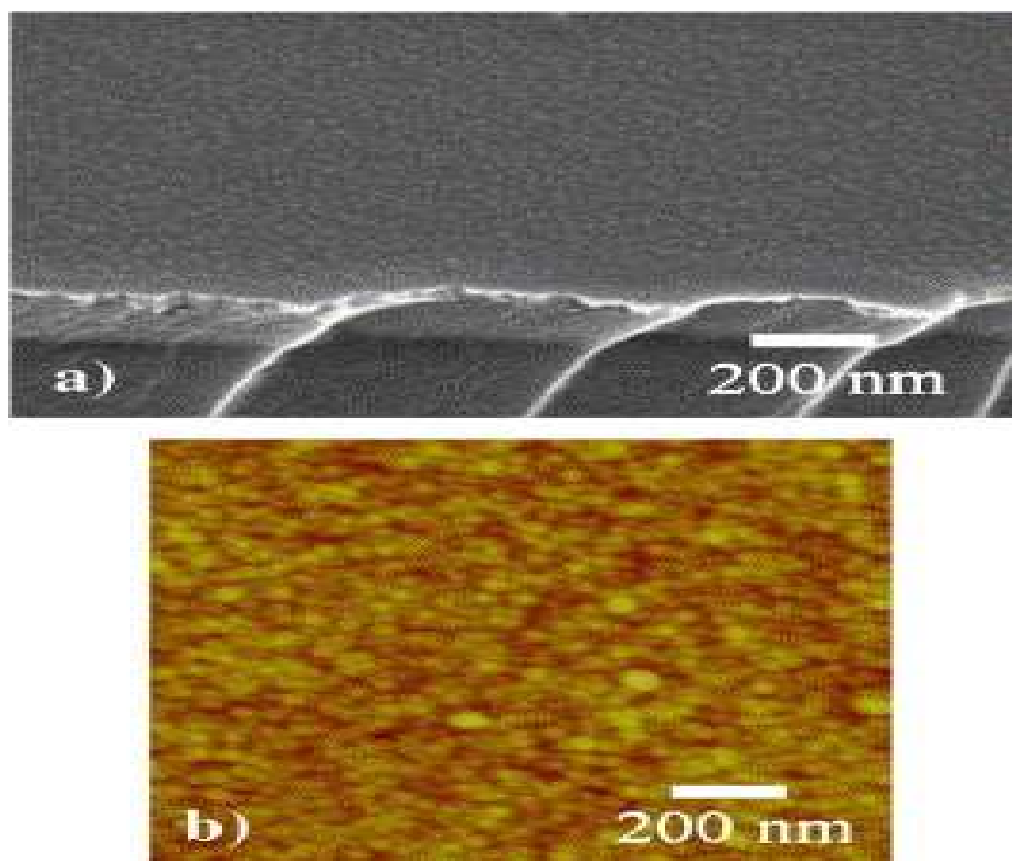

This was confirmed by the thermal annealing of films for 4 h at 450 °C under N$_2$ atmosphere which lead to pure polycrystalline CuFeO$_2$ (Fig. 2b). The main GIXRD peaks of the polycrystalline thin films did not indicate any particular preferred orientation despite of the high anisotropy of the delafossite structure. A Cu/Fe atomic ratio close to 1 was also measured by electron probe microanalysis in agreement with the relative content of metallic elements in delafossite.

However, as-deposited films are dark brown and electrical insulators showing a direct optical band gap of 2 eV. As for many iron oxides the optical transparency is less important for green and blue light than for red light. In this later spectral range the transparency is quite high. For instance, 30 nm thick films exhibit 70% transparency at 800 nm.

Scanning electron microscopy (Fig. 4a) and atomic force microscopy (Fig. 4b) revealed very dense thin films with very low roughness of 0.8 and 20 nm surface grain size for $d = 9$ cm substrate to target distance.

Fig. 4. (a) SEM and (b) AFM micrographs of as-deposited thin film deposited on conventional glass with $d = 9$ cm.

Annealing these films under air atmosphere at 450 °C for 4 h lead to a polycrystalline $CuFeO_{2+\delta}$ film. Four probe electrical measurements at room temperature showed an increase in conductivity up to $\sigma_{RT} = 1.03$ mS/cm when films are annealed at 450 °C for 6 h. A Hall effect could not be detected. p-type semi-conducting properties were however revealed by thermopower measurements. Calculated direct optical band gap, the lack of measurable Hall effect and the positive thermopower are in accordance with previous studies [12] for bulk $CuFeO_2$.

This increase in conductivity with air annealing treatment is correlated with a hopping mechanism which is favoured with the oxygen intercalation in the Cu^+ layers of the

delafossite leading to the $(Cu_{1-2\delta}^{+}Cu_{2\delta}^{2+})FeO_{2+\delta}$ formulae. This feature is common for delafossite $CuBO_2$ with large B cation as Y [13]. For smaller B cation as Fe, oxygen intercalation is forced and generates structural shear and defects [14]. Above a critical oxidation degree, the delafossite structure cannot accept anymore oxygen anions. Delafossite phase is then transformed into copper (II) monoxide and copper spinel ferrite. Especially after annealing treatment in air at 450 °C for more than 36 h, the X-rays pattern of the sample both display small and broad delafossite Bragg peaks on the one hand and the copper monoxide and spinel ferrite characteristic Bragg peaks.

The electrical conductivities of prepared films are still low compared to bulk reference. This is due to the defect structure generated by the forced oxygen intercalation and by the thin film microstructure [15]. However, the preparation of delafossite films on conventional glass substrate remains an interesting result for future technological applications of delafossite oxides, because the optical and electrical properties could be improved using the wide range of composition permitted in the copper delafossite structural family $CuBO_2$ on the one hand, and the possible improvement in microstructure due to the versatility of the sputtering process.

References

D.S. Ginley and C. Bright, *MRS Bull.* 25 (2000), pp. 15–18.

H. Kawazoe, H. Yanagi, K. Ueda and H. Hosono, *MRS Bull.* 25 (2000), pp. 28–36.

H. Kawazoe, M. Yasukawa, H. Hyodo, M. Kurita, H. Yanagi and H. Hosono, *Nature* 389 (1997), pp. 939–942.

R.D. Shannon, D.B. Rogers and C.T. Prewitt, *Inorg. Chem.* 10 (1971), pp. 713–718.

J.P. Doumerc, A. Ammar, A. Wichainchai, M. Pouchard and P. Hagenmuller, *J. Phys. Chem. Solids* 48 (1987), pp. 37–43.

S.C. Schaefer, G.L. Hundley, F.E. Block, R.A. Mc Cune and R.V. Mrazek, *Metall. Trans.* 1 (1970), pp. 2557–2563.

W.C. Sheets, E. Mugnier, A. Barnabé, T.J. Marks and K.R. Poeppelmeier, *Chem. Mater.* 18 (2006) (1), pp. 7–20.

T. Otabe, K. Ueda, A. Kudoh, H. Hosono and H. Kawazoe, *Appl. Phys. Lett.* 72 (1998), pp. 1036–1038.

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.* 3 (2001), pp. 265–270.

A.N. Banerjee, S. Kundoo and K.K. Chattopadhyay, *Thin Solid Films* 440 (2003), pp. 5–10.

N. Tsuboi, Y. Takahashi, S. Kobayashi, H. Shimizu, K. Kato and F. Kaneko, *J. Phys. Chem. Solids* 64 (2003), pp. 1671–1674.

F.A. Benko and F.P. Koffyberg, *J. Phys. Chem. Solids* 48 (1987), pp. 431–434.

B.J. Ingram, B.J. Harder, N.W. Hrabe, T.O. Mason and K.R. Poeppelmeier, *Chem. Mater.* 16 (2004), pp. 5623–5629.

E. Mugnier, A. Barnabé and Ph. Tailhades, *Solid State Ionics* 177 (2006) (5–6), pp. 607–612.

S. Capdeville, P. Alphonse, C. Bonningue, L. Presmanes and P. Tailhades, *J. Appl. Phys.* 96 (2004), pp. 6142–6146.

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