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Thin films preparation by rf-sputtering of copper/iron ceramic targets with Cu/Fe = 1: From nanocomposites to delafossite compounds

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Abstract

In the Cu–Fe–O phase diagram, delafossite $CuFeO_2$ is obtained for the Cu^I oxidation state and for the Cu/Fe = 1 ratio. By decreasing the oxygen content, copper/spinel oxide composite can be obtained because of the reduction and the disproponation of cuprous ions. Many physical properties as for instance, electrical, optical, catalytic properties can then be affected by the control of the oxygen stoichiometry.

In rf-sputtering technique, the bombardment energies on the substrate can be controlled by the deposition conditions leading to different oxygen stoichiometry in the growing layers.

By this technique, thin films have been prepared from two ceramic targets: $CuFeO_2$ and $CuO+CuFe_2O_4$. We thus synthesized either $Cu^0/Cu_xFe_{1-x}O_4$ nanocomposites thin films with various Cu^0 quantities or $CuFeO_2$-based thin films.

Two-probes conductivity measurements were permitted to comparatively evaluate the Cu^0 content, while optical microscopy evidenced a self-assembly phenomenon during thermal annealing.

Keywords: Delafossite; Nanocomposites; Sputtering; Thin films

1. Introduction

Cu–Fe–O system has been extensively studied [1–6]: the corresponding phase diagram at 1000 °C is reported in Fig. 1. This system contains 9 main species: 2 metals (Cu and Fe), 5 simple oxides (Cu_2O, CuO and FeO, Fe_3O_4, Fe_2O_3), and 2 mixed oxides ($CuFeO_2$, $CuFe_2O_4$). One can note that a complete solid solution noted $Cu_xFe_{3-x}O_4$ exists in between Fe_3O_4 ($x=0$) and $CuFe_2O_4$ ($x=1$). For the Cu/Fe = 1 ratio, the 2 main phases stabilized for the intermediate oxygen partial pressure ($-7<pO_2$ [Pa]<4) at $T=1000$ °C are the composite $Cu^0/Cu_xFe_{3-x}O_4$ and the delafossite $CuFeO_2$ (Fig. 1). Composites made of metal particles dispersed in an oxide matrix have received great attention due to their specific or improved mechanical, optical, electrical, thermal or magnetic properties [7–14]. In the form of thin films, these materials could be used for different technological applications, for instance in magnetic recording media or in electronic and optical devices. Delafossite compounds are an interesting family of materials by their quite low absorption in the visible spectrum and their p-type semi-conducting properties. For special composition, these two properties make delafossite oxides good candidates for p-type Transparent Conducting Oxides (TCO) applications such as transparent pn-junctions, transistors or diodes [15]. Final technological applications could be flat-panel displays, light-emitting diodes, etc [16]. To synthesize thin films of these two compounds, rf-sputtering is a very suitable method, because of its versatility in terms of apparatus configurations and parameters to vary.

In this work, we report the synthesis of $CuFeO_2$ and $Cu^0/Cu_xFe_{3-x}O_4$ thin films by rf-sputtering at room temperature on glass substrates. Moreover, we show that these two phases can be obtained by a proper adjustment of the deposition parameters, because the change in deposition conditions leads to similar effects than temperature and oxygen partial pressure modification.

2. Experimental details

2.1. Film deposition

All the films referred in this paper were synthesized either with an ALCATEL A450 apparatus for magnetron sputtered films or with an ALCATEL SCR650 apparatus for non-

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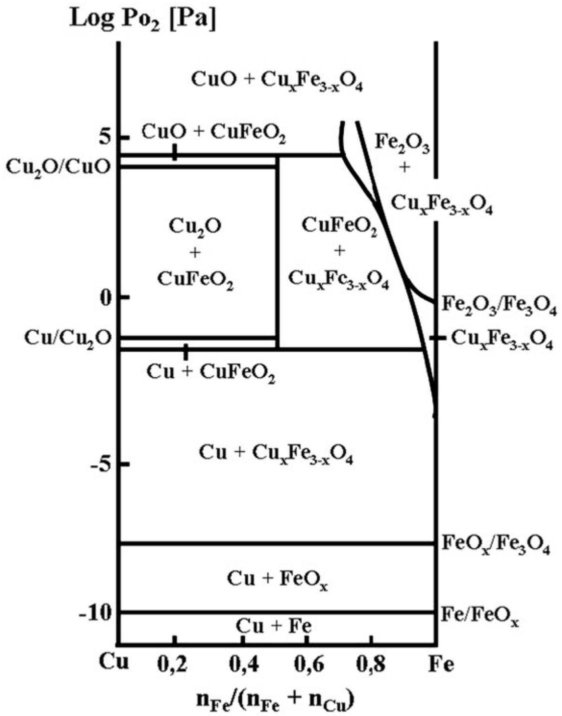

Fig. 1. Phase diagram of the Cu–Fe–O system at 1000 °C from [6].

magnetron sputtered films. The films were prepared from two ceramic targets with a diameter of 10 cm and a Cu/Fe ratio equal to 1. The first target (called A) is a pure $CuFeO_2$ ceramic with cuprous ions alone. Target B is made of CuO and $CuFe_2O_4$ phases in which cupric ions are predominant. All the films were deposited on glass substrates placed on a water cooled sample holder. No additional heating was performed during deposition. RF power was fixed at 200 W or 50 W whether magnetron is applied or not and gas (argon) pressure was fixed at 0.5 Pa. No external oxygen was introduced in the sputter chamber. Deposits were carried out with various target-to-substrate distances D ranging from 55 mm to 80 mm. The deposition conditions are summarized in Table 1.

2.2. Characterizations

Structural phase analyses such as Grazing Incidence X-Ray Diffraction (GIXRD) (grazing angle $\alpha = 1°$) and Electronic Diffraction (ED) were carried out with a Siemens D5000 diffractometer using the copper Kα radiation and a JEOL 2010 transmission electron microscope operating at 200 kV, respectively. As most of the as-deposited films were amorphous from GIXRD, post-deposition annealing treatments at 450 °C for 4 h under inert atmosphere were performed to crystallise the film's phases. A 2-probes method was used to acquire ln $R = f(1/T)$ plots from room temperature to 280 °C with a rate of 150 °C/h. Films cationic compositions were determined by a Cameca SX50 electron microprobe.

Table 1
Sputtering deposit parameters

Target	$A = CuFeO_2$		$B = CuO + CuFe_2O_4$
Magnetron	Yes	No	No
Rf-power (W)	50	200	200
Gas pressure (Pa)	0.5		
Target-substrate distance (mm)	70	55–80	55; 70
Substrate	glass		

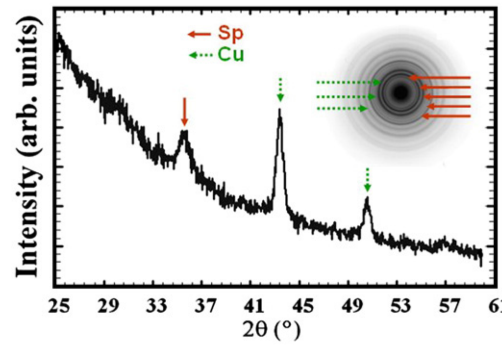

Fig. 2. Typical GIXRD and ED patterns of nanocomposites $Cu^0/Cu_xFe_{3-x}O_4$.

3. Results and discussion

We have shown in a previous paper [17] that thin films prepared from a $CuFeO_2$ target without magnetron always contain both metallic copper and spinel ferrite phases, whatever the target-to-substrate distance chosen. For instance, typical GIXRD and ED patterns are shown in Fig. 2 for the $D = 60$ mm sample. For all the samples, the Cu/Fe ratio is equal to 1, which means that the films have the same cationic composition than the target. In order to describe the deposition reaction, we can thus provide the following global equation:

$$CuFeO_2 \rightarrow \left(\frac{1}{3-x}\right) Cu_xFe_{3-x}O_4 + \left(\frac{3-2x}{3-x}\right) Cu + \left(\frac{1-x}{3-x}\right) O_2 \qquad 0 \le x \le 1 \tag{1}$$

During the sputtering process, the bombardment of the growing layer by energetic particles leads to samples with a

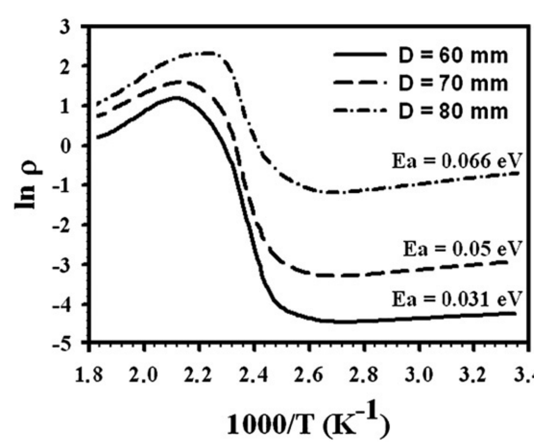

Fig. 3. Electrical resistivity versus temperature for nanocomposites samples prepared at $D = 60$, 70 and 80 mm and their respective activation energies.