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 dispproponation 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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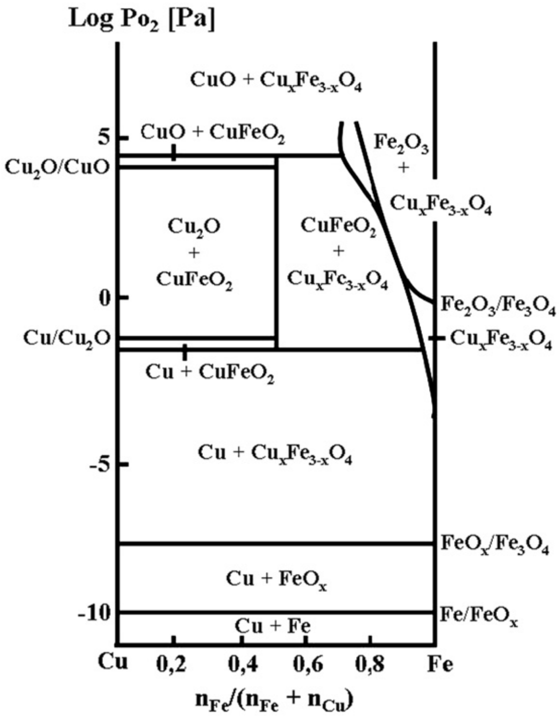

Fig. 1. Phase diagram of the Cu–Fe–O system at 1000 °C from [6].

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$_2$O$_4$
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		

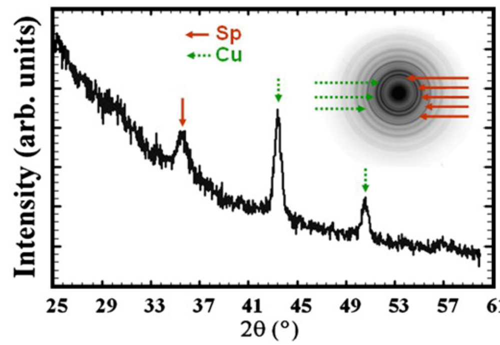

Fig. 2. Typical GIXRD and ED patterns of nanocomposites $Cu^0/Cu_xFe_{3-x}O_4$.

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:

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

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

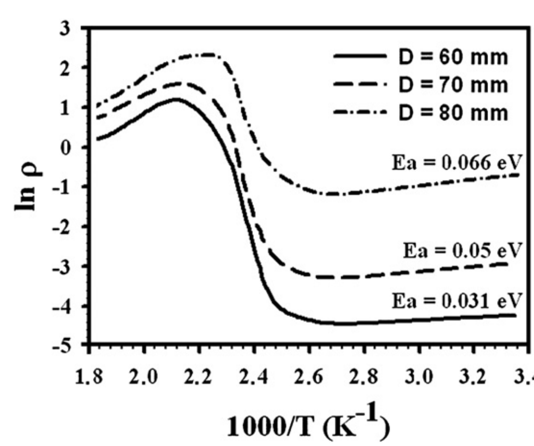

Fig. 3. Electrical resistivity versus temperature for nanocomposites samples prepared at $D=60$, 70 and 80 mm and their respective activation energies.

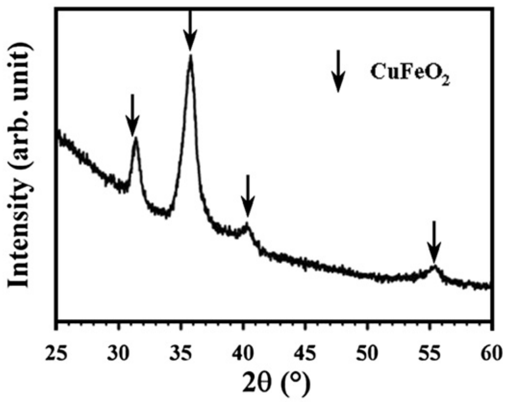

Fig. 4. GIXRD pattern of a delafossite thin film prepared from target A ($CuFeO_2$).

lower oxygen content than that of the target [18], due to the bombardment of the growing layer by energetic particles. This oxygen loss during the transfer to the condensed substrate can explain the formation of metallic copper from a Cu^+ containing target. Moreover, we have noticed that the thin films metallic copper content varies with target-to-substrate distance (D). Electrical measurements between 25 °C and 280 °C on thin films elaborated with $D=60$, 70 and 80 mm are shown on Fig. 3. The Cu^0 quantity can be comparatively estimated, by quantifying the activation energy at low temperature which is representative of the mixing of the metallic and semi-conducting parts, as well as the resistance jumps which correspond to the disappearance of the metallic part during the $Cu^0 \rightarrow Cu^{+II}$ oxidation [17]. One can notice that as the distance D increases, the metallic content decreases. When sputtering, energies of particles arriving to the substrate would be very different whether D is higher or lower than their free mean path λ. If D is higher, particles would have many collisions inside the plasma, leading to lower energies when condensing on the substrate than if $D<\lambda$. The growing layer is thus less bombarded in the case of high D, and less oxygen is ejected in the sputtering chamber. According to Eq. (1), a few loss of oxygen (i.e. high x) means a low metallic copper content in the films.

As explained above, oxygen loss and then copper reduction from target to substrate is due to the bombardment of the growing layer. In order to synthesize delafossite thin films, the oxygen loss and therefore this bombardment have to be reduced. In the sputtering parameters range, magnetron configuration can provide us this condition. Actually, by a magnet effect, it confines electrons near the target so the only species arriving on substrate are target and gas species. This configuration always leads to amorphous as-deposited samples. However, after a crystallisation at 450 °C under nitrogen flux, thin films exhibit pure delafossite GIXRD pattern (Fig. 4). This confirms that the effect of magnetron configuration decreases the bombardment of the growing layers and then tends to minimize the oxygen loss. Unfortunately, this configuration results in homogeneous as-deposited samples where Cu/Fe ratios are higher than 1, due to the preferential sputtering of copper rather than the iron one [19] in this configuration (see Fig. 5a). After the crystallisation treatment at 450 °C under nitrogen flux, important heterogeneities, concentrated on the sides of the slides are thought visible to the naked eye. At the homogeneous centred part of the films, the Cu/Fe ratio is strictly equal to 1 (area I Fig. 5b), corroborating the fact that delafossite $CuFeO_2$ can exist only in its stoichiometric composition [20,21]. Thin films sides microprobe analyses were performed and showed Cu/Fe values greater than 1 (area II Fig. 5b and inset). In a previous paper [17], we evidenced the high mobility of copper particles towards surface defects on films deposited on patterned substrates. When annealed at 450 °C under nitrogen atmosphere, a self-assembly phenomenon occurred and the metallic copper particles were gathered in the patterned regions, leaving the other parts of the film. This phenomenon can explain the higher copper concentration on the sides of the slide, if we consider them as the main surface defects toward which copper particles would migrate when annealed under nitrogen atmosphere. Even if magnetron configuration allows

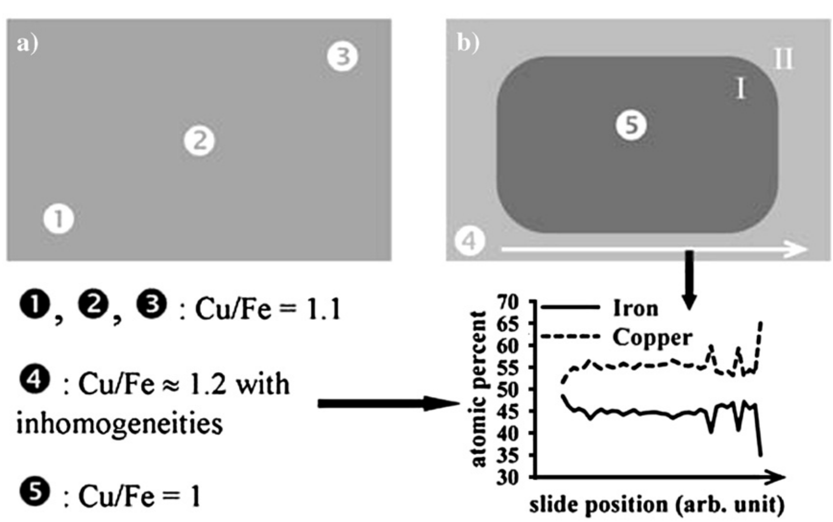

Fig. 5. Schematic view of a) as-deposited and b) annealed under inert atmosphere delafossite films prepared from target A ($CuFeO_2$). Cationic ratios Cu/Fe measured by electron probe analysis are indicated in various locations.

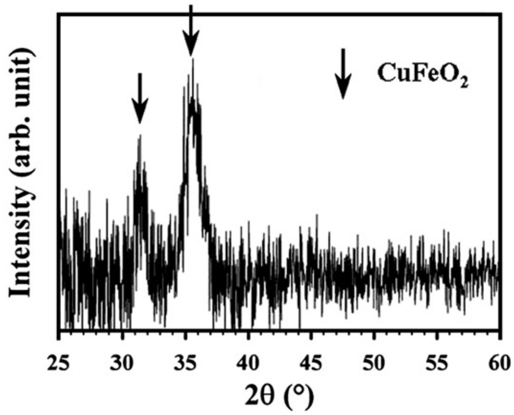

Fig. 6. GIXRD pattern of a delafossite thin film prepared from target B ($CuO+CuFe_2O_4$).

$CuFeO_2$ formation due to the almost correct oxygen stoichiometry, heterogeneities due to cationic non-stoichiometry are obviously a problem in terms of electrical or optical characterizations and thereafter for the applications aimed.

As described in the first part of this work, it is possible to synthesize films in this Cu–Fe–O system where the oxygen ratio is lower than that of the target but the cationic one keep unchanged. We then try to elaborate $CuFeO_2$ films in the first conditions but starting from an over-oxidized target (target B) in order to compensate the oxygen loss during the deposition process. The synthesis of delafossite films from target B can then be described by the following equation:

$$CuO + CuFe_2O_4 \rightarrow 2CuFeO_2 + \frac{1}{2}O_2 \quad (2)$$

As the oxygen amount to be ejected is quite important in Eq. (2), we first use the more energetical sputtering conditions we could, i.e. with the lower target to substrate D value. D equal to 55 mm was thus used as the starting target-substrate distance. These conditions lead again to the formation of nanocomposites $Cu^0/Cu_xFe_{3-x}O_4$ with the same characteristics as those obtained previously:

- Cu/Fe = 1,
- growing copper particles size with annealing under neutral atmosphere,
- tendency of these ones to migrate towards surface defects.

This result confirms that too much oxygen have been ejected despite the initial over-stoichiometry of the target. By the same mechanisms than those involved in the thin films previously obtained with the target A, the oxygen loss can be reduced by the increase of D. $D = 70$ mm was found to be the required distance. For this distance, the as-deposited films were amorphous but a usual annealing treatment under inert atmosphere, allows the crystallisation of pure $CuFeO_2$ (Fig. 6). Even after this treatment, delafossite films show a high optical homogeneity and microprobe analysis revealed a cationic ratio equal to the target one.

4. Conclusions

In this study, $Cu^0/Cu_xFe_{3-x}O_4$ nanocomposites and $CuFeO_2$ thin films have been prepared by rf-sputtering, from two different targets: ($CuFeO_2$) and ($CuO+CuFe_2O_4$).

Deposition conditions have been adjusted in order to elaborate either very reduced phases, ($Cu^0/Cu_xFe_{3-x}O_4$) or phases with the same oxygen content than that of the target ($CuFeO_2$). Moreover, this elaboration approach allows us to synthesize delafossite thin films from two different ways. Microstructural properties, homogeneity and specific oxygen stoichiometry of the delafossite phase can then be adjusted in connection with the physical properties.

The capability to elaborate $CuFeO_2$ thin films at room temperature on conventional glass substrate from a ceramic target presents an interesting result for future technological applications of delafossite oxides, such as p-type Transparent Conducting Oxides TCO. The optical and electrical properties could indeed be improved using the wide range of composition permitted in the copper delafossite structural family $CuBO_2$.

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