

## Nanostructuration in Ag-Cu-O sputtered films by controlling their oxygen and/or their silver concentrations

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### Abstract

Ag-Cu-O films were deposited on glass substrates using two reactive sputtering processes. In the first one, a silver-copper target ( $\text{Ag}_{60}\text{Cu}_{40}$ ) was sputtered in various Ar- $\text{O}_2$  reactive mixtures (sputtering process). The oxygen content in the films was fixed by the oxygen flow rate introduced in the deposition reactor. In the second process, silver and copper targets were cosputtered in an Ar- $\text{O}_2$  reactive mixture (cosputtering process). The silver content in the films was fixed by the current applied to the silver target. The adjustment of these two deposition parameters allowed the deposition of nanostructured metal/oxide composite coatings: nc-Ag and nc-silver-copper oxides.

**Keywords:** reactive sputtering, silver-copper oxides, nanostructured films

### 1. Introduction

Although copper and silver are situated in the same column of the periodic table, the first silver-copper oxide ( $\text{Ag}_2\text{Cu}_2\text{O}_3$ ) was discovered in 1999<sup>1</sup>. This oxide crystallizes in the same tetragonal structure than paramelaconite ( $\text{Cu}_4\text{O}_3$ ) where Cu(+I) ions are substituted by Ag(+I) ones. Since this date, a second silver-copper oxide was synthesised ( $\text{AgCuO}_2$ ) that crystallizes in a monoclinic structure<sup>2</sup>. These oxides were obtained in powder form using coprecipitation methods. However, this process leads to the formation of compounds where the Ag/Cu atomic ratio is constant. Recently, it was demonstrated that the reactive sputtering process can be successfully used to deposit silver-copper oxides with various silver to copper atomic ratios<sup>3</sup>. These films were synthesized using deposition conditions where the amount of oxygen available in the reactor was not limitant compared to those of silver and copper. Since the reactivity of sputtered silver atoms with oxygen atoms is lower than that of copper<sup>4</sup>, the control of the oxygen or silver concentration in the deposition reactor may induce the formation of biphased coatings: metal and oxide. In order to check this hypothesis, Ag-Cu-O films have been deposited by reactive magnetron sputtering using two distinct processes.

### 2. Experimental details

Ag-Cu-O films were deposited on glass substrates using two kinds of reactive magnetron sputtering processes: the sputtering of a composite  $\text{Ag}_{60}\text{Cu}_{40}$  target (SP) and the cosputtering of silver and copper targets (CSP). In both processes, the substrate-target distance was fixed at 50 mm and the target dimensions were 50 mm diameter and 3 mm thick. The argon flow rate was fixed to 30 sccm. The substrates were placed on a rotating substrate holder to ensure film thickness and chemical composition homogeneities. Films were deposited without external heating. In SP, the current applied to the  $\text{Ag}_{60}\text{Cu}_{40}$  target was fixed at 0.15 A. Only the oxygen flow rate was varied in the 0-24 sccm range. The total pressure during deposition was ranging between 0.5 and 1 Pa. On the other hand in CSP, the oxygen flow rate and the current applied to the copper target were fixed at 10 sccm and 0.3 A, respectively. The current applied to the silver

target was ranging between 0 and 0.16 A. Using these deposition conditions, the total pressure in the deposition chamber was 0.5 Pa.

The film composition was estimated from energy X-ray dispersive spectroscopy analyses (EDS) coupled to a field-effect scanning electron microscope. The films structure was investigated by X-ray diffraction in  $\theta/2\theta$  mode using a Co  $K\alpha$  radiation.

### 3. Results and discussion

#### 3.1. Ag-Cu-O films deposited using the sputtering process

Whatever the oxygen flow rate, the silver to copper atomic ratio in the deposited films ( $1.51 \pm 0.10$ ) is close to that of the target (1.5). The increase of the oxygen flow rate induces a continuous increase of the oxygen concentration in the deposited films (Fig. 1).

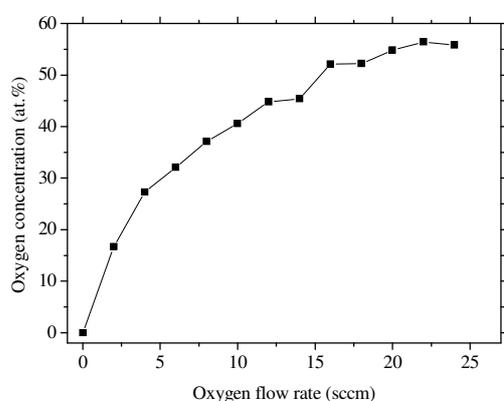


Fig.1. Influence of the oxygen flow rate on the oxygen content of Ag-Cu-O films deposited using SP.

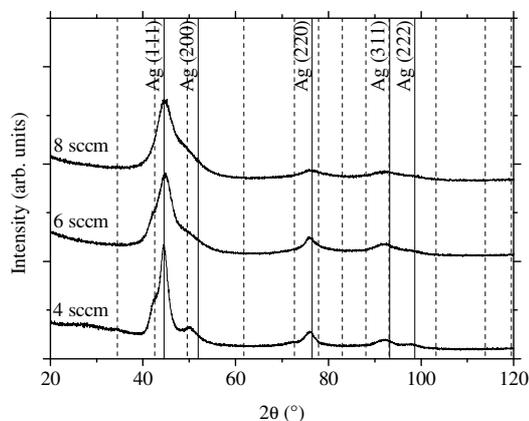


Fig.2. X-ray diffractograms of Ag-Cu-O films deposited using SP with an oxygen flow rate of 4, 6 and 8 sccm. Vertical dash lines are related to the theoretical positions of diffraction lines of  $\text{Cu}_2\text{O}$ .

When the oxygen flow rate is lower than 4 sccm, the deposited films crystallise in a fcc structure with a lattice constant ranging between those of copper and silver, indicating the formation of an Ag-Cu-(O) solid solution. For higher values of oxygen flow rates, new diffraction peaks are noticed that have been assigned to  $\text{Cu}_2\text{O}$  (Fig. 2). Furthermore, the intensities ratio of  $\text{Cu}_2\text{O}$  peaks to Ag ones increases with the oxygen flow rate. These results suggest that the amount of oxygen in the deposition reactor is not high enough to oxidised both silver and copper atoms. Since the reactivity of copper with oxygen atoms is higher than that of silver, copper atoms are oxidised while silver ones remain metallic. The full width at half maximum of the Ag (111) diffraction peak increases with the oxygen flow rate, indicating the refinement of the silver grains.

When the oxygen flow rate is 10 sccm, a new kind of diffractogram is observed (Fig. 3). Broad silver diffraction peaks with low intensity are still detected. On the other hand, a new diffraction peak is noticed close to  $47.8^\circ$ . This position cannot match with that of  $\text{Cu}_2\text{O}$  or  $\text{Ag}_2\text{O}$  peaks but indicates the formation of a silver-copper oxide with a cuprite-like structure. Since this position is closer to that of  $\text{Cu}_2\text{O}$  than that of  $\text{Ag}_2\text{O}$ , this oxide is copper rich. This result indicates that the use of 10 sccm oxygen allows the partial oxidation of the sputtered silver atoms. The remaining amount of silver is kept in the metallic state in the form of very fine grains. Further increase of the oxygen flow rate leads to the formation of X-ray amorphous films (Fig. 4). The  $2\theta$  position of the maximum intensity is shifted to lower values when the oxygen flow rate increases, indicating

a possible structural evolution of the deposited films. Since silver diffraction peaks seems to be no longer observed, the use of 12 sccm seems to be sufficient to oxidise the main part of the sputtered silver atoms.

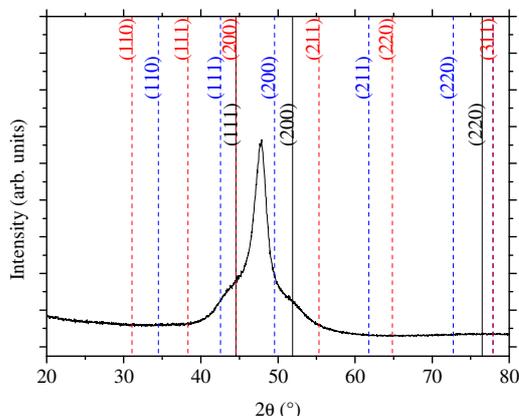


Fig.3. X-ray diffractogram of the film deposited using SP with 10 sccm oxygen. Black, red and blue vertical lines are related to the theoretical positions of Ag, Ag<sub>2</sub>O and Cu<sub>2</sub>O diffraction lines, respectively.

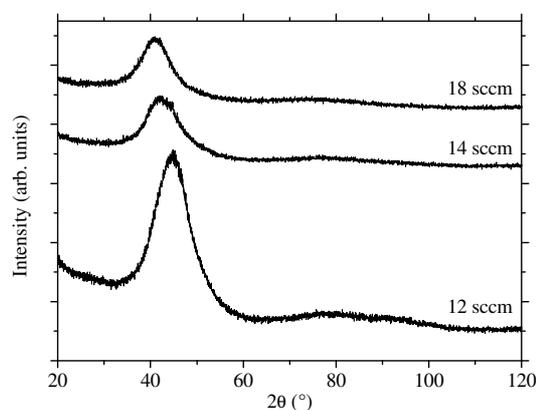


Fig.4. X-ray diffractograms of Ag-Cu-O films deposited using SP with 12, 14 and 18 sccm oxygen.

### 3.2. Ag-Cu-O films deposited using the cosputtering process

Ag-Cu-O films have also been synthesised using a cosputtering process where the current applied to the copper target and the oxygen flow rate were kept constant whereas the current applied to the silver target ( $I_{Ag}$ ) varied. Then, the composition of Ag-Cu-O films has been controlled by the current applied to the silver target. The increase of this deposition parameter induces a silver enrichment of the films and a progressive decrease of the film oxygen content due to the increasing flow of metallic sputtered atoms. However, within the current range applied to the silver target tested in this study, the oxygen concentration remained higher than 40 at. %.

When  $I_{Ag} = 0$  A, the use of 10 sccm oxygen leads to the deposition of copper oxide with a paramelaconite structure (Cu<sub>4</sub>O<sub>3</sub>) (Fig. 5). Such compound is formed by reactive sputtering when the oxygen flow rate is ranging between those necessary for the deposition of Cu<sub>2</sub>O and CuO<sup>5</sup>. The X-ray diffractogram of silver-free films clearly shows that paramelaconite films grow with a preferred orientation in the [001] direction. Incorporation of silver into Cu<sub>4</sub>O<sub>3</sub>-based films slightly modifies the X-ray diffractogram (Fig. 5): the strong preferred orientation in the [001] is lost and the paramelaconite diffraction peaks are slightly shifted towards lower values of  $2\theta$ , indicating a partial substitution of some Cu(+I) atoms by Ag(+I) ones to form Ag<sub>2-x</sub>Cu<sub>2+x</sub>O<sub>3</sub>. From the Ag/Cu atomic ratio estimated by EDS, the following film formulas have been proposed for films deposited with  $I_{Ag} = 0.04, 0.06$  and  $0.08$  A<sup>6</sup>: Ag<sub>0.6</sub>Cu<sub>3.4</sub>O<sub>3</sub>, Ag<sub>0.9</sub>Cu<sub>3.1</sub>O<sub>3</sub> and Ag<sub>1.2</sub>Cu<sub>2.8</sub>O<sub>3</sub>. It is worth of noting that the silver concentration increase comes with an enlargement of the diffraction peaks indicating a refinement of the paramelaconite-like grains. Single Cu<sub>4</sub>O<sub>3</sub> films have a mean crystal size estimated from the full width at half maximum of the (004) diffraction peak close to 8 nm whereas that of Ag<sub>1.2</sub>Cu<sub>2.8</sub>O<sub>3</sub> films is close to 6 nm.

When the current applied to the silver target exceeds 0.08 A, silver diffraction peaks are observed by XRD (Fig. 6). This result suggests that the oxygen flow rate introduced into the deposition chamber is not sufficient to oxidise all the silver sputtered atoms. Then, the excess of silver atoms is deposited in metallic form. Further increase of  $I_{Ag}$  firstly induces an improvement of the

diffracted intensity of metallic silver nanograins and finally a decrease of the intensity of paramaleconite-like diffraction peak intensity. When  $I_{Ag} = 0.16$  A, the crystal size of the silver grains has been estimated to approx. 2 nm.

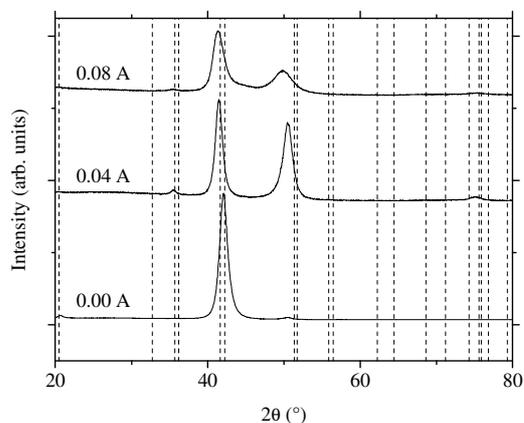


Fig.5. Effect of the current applied to the Ag target on the X-ray diffractograms of Ag-Cu-O films deposited using CSP. Vertical dash lines are related to the theoretical positions of  $Cu_4O_3$  diffraction peaks.

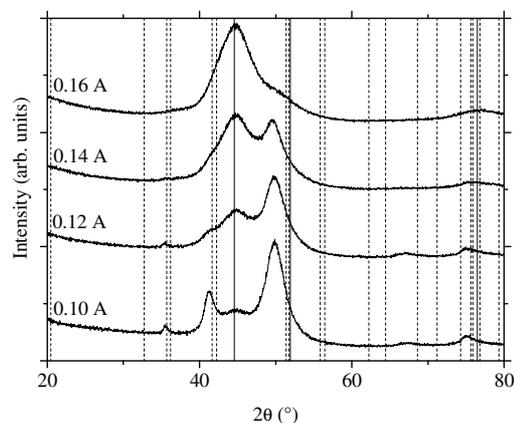


Fig.6. Influence of  $I_{Ag}$  on the X-ray diffractograms of Ag-Cu-O films deposited using CSP. Vertical solid and dash lines are related to the theoretical positions of Ag and  $Cu_4O_3$  diffraction peaks, respectively.

#### 4. Conclusion

Ag-Cu-O films have been deposited on glass substrates using two processes: reactive sputtering of a composite  $Ag_{60}Cu_{40}$  target (SP) and reactive cosputtering of silver and copper targets (CSP). In SP the films composition has been controlled by the oxygen flow rate introduced in the deposition chamber. As a function of the oxygen flow rates, the films exhibit various structures: Ag-Cu-(O) solid solution, nc-Ag + nc- $Cu_2O$ , nc-Ag + nc  $(Ag,Cu)_2O$  and finally X-ray amorphous. On the other hand, in CSP, the current applied to the silver target controls the films composition. As a function of this deposition parameter, the following structures have been observed:  $Cu_4O_3$ ,  $Ag_{2-x}Cu_{2+x}O_3$  and finally nc-Ag + nc- $Ag_{2-x}Cu_{2+x}O_3$ .

Whatever the process, the results clearly show that the occurrence of a nanocrystalline metallic silver phase in the films can be controlled by adjusting the oxygen and/or the silver concentrations.

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