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COPPER AND COPPER OXIDE THIN FILMS OBTAINED BY METALORGANIC MICROWAVE PLASMA CVD

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ABSTRACT : Microwave Plasma Enhanced Chemical Vapor Deposition (MPECVD) is an innovative technique allowing the direct preparation, at low temperature, of different valence states of copper (Cu^0 , Cu^{I} , Cu^{II}). The precursor used is a volatile metalorganic one (copper acetylacetonate) with helium as a carrier gas. The precursor is then transported in a remote plasma of Ar, Ar/ O_2 or Ar/ N_2O gas at low pressure. A judicious choice of the process parameters - microwave power, substrate temperature and nature of the oxidant gas (N_2O or O_2)- allows to favour the formation of metallic copper, Cu_2O or CuO . Copper and its oxides have been deposited as thin films on silicon and magnesium oxide single crystals. The techniques used for the characterization of the as deposited polycrystalline films are X-ray diffraction, Auger Electron Spectroscopy and Scanning Electron Microscopy.

I- INTRODUCTION

The discovery of high temperature superconductors in the systems La-Cu-O, Y-Ba-Cu-O, Bi-Sr-Cu-O and Tl-Ba-Ca-Cu-O has initiated some important research on single oxide phases. As copper oxide is found in all high T_c superconductors, copper (II) oxide thin layers can be considered as good models for studies directed towards the improved formation of thin films of the copper oxide based high T_c superconductors [1].

Among the techniques used for copper and copper oxide deposition, one can distinguish : spray pyrolysis of a salt solution [2], RF sputtering of copper and copper oxides [3], metal organic Chemical Vapor Deposition [4], plasma enhanced CVD [5] and laser CVD [6].

The purpose of this work was to use a method able to lead to copper and copper oxides thin layers at low temperature. A new technique has been investigated : metalorganic microwaves plasma enhanced chemical vapor deposition (MOMPECVD). Microwave plasmas was initially employed for semi-conductor etching [7], but the technique has also been developed for thin film deposition. Among the various materials prepared, one can mention diamond [8] and even

YBaCuO superconductors [9]. In this study, this innovative technique has been used for the synthesis of copper and copper oxides thin films from volatile organometallic precursors.

II- EXPERIMENTAL

A schematic drawing of the deposition reactor is shown in figure 1.

Figure 1 : Schematic representation of the deposition system

The microwave power was supplied by a 2,45 GHz generator, through a wave guide structure crossed by a quartz tube. Impedance matching was performed on the wave guide by a mechanical system consisting of one short-circuit and three plungers.

Argon or argon/oxidant gas mixture was admitted at low pressure into the reactor through the quartz tube where the plasma was generated. This plasma diffused into the reaction chamber where the heated substrate holder was located.

The copper source used for this study was copper(II) acetylacetonate ($\text{Cu}(\text{Acac})_2$) and was purchased from Strem Chemicals. This solid precursor was placed into a steel container, volatilized by heating to 160°C , and fed into the reaction chamber, just above the substrate, with helium as a carrier gas. The delivery line was heated to prevent any condensation of the product before the deposition zone. The oxygen sources were N_2O and O_2 . (100) Si and (100) MgO monocrystalline substrates were used.

The typical deposition parameters were :

Argon partial pressure : 0.2 mbar
 Oxidant gas partial pressure : 0.2 mbar (leading to ratio Ar/N₂O or O₂ = 1)
 Precursor temperature : 160 °C
 Carrier gas flow : 30 sccm/min
 Total pressure : 0.6 mbar
 Substrate temperature : 150°C to 300 °C
 Microwave power: 60, 100 or 200 W

An Inel curved position sensitive detector for X-ray diffraction has been used for the film characterization. 10% impurities can be detected with this apparatus.

III- RESULTS AND DISCUSSION

We have studied the effect of microwave power, substrate temperature and gas phase nature on the composition and crystallinity of the films. In all cases polycrystalline layers were obtained. Similar results have been obtained on silicon and magnesium oxide substrates. We have to notice that in quite all the samples impurities like oxygen, carbon and chlorine (coming from the precursor) have been evidenced in Auger spectra.

1- Microwave power

In the studied microwave power range (60-200 Watts) this parameter has no drastic effect on the film composition and crystallinity (Fig. 2). This fact could be explained as we are working with a remote plasma. The precursor vapor is not directly decomposed in the plasma, but reacts with activated species extracted from the plasma source.

2- Substrate temperature

As shown in figure 2 the copper oxidation state increases when the substrate temperature decreases with or without oxidant gas in the system. For a better comparison, figure 2a give the reference X-ray spectra of Cu, CuO and Cu₂O powders.

In an Ar discharge, without oxidant gas (Fig. 2a), a sample containing mainly metallic copper could be obtained at a temperature higher than 260°C-300°C whereas, at 150°C, Cu₂O dominated.

When an oxidant gas (N₂O or O₂ in our case) was added to the system (Fig. 2b), Cu₂O was obtained at 300°C but CuO appeared when the substrate temperature was decreased to 250°C. No important difference was noticed between the effect of O₂ and N₂O on the results.

These results are very surprising if compared to those of Larson [10] who provided evidence for the reduction of CuO to Cu₂O when heating at 250°C in vacuum.

In order to study in more detail the composition of the films, Auger Electron Spectroscopy analysis has been performed on the samples and confirms the X-ray diffraction results.

As shown in figure 3, the presumed metallic copper sample gives the same spectrum as a metallic copper reference. The others samples show the characteristic transitions L₂₃M₄₅M₄₅ of Cu(I) and Cu(II).

Figure 2 : XRD patterns of films deposited a) in Ar plasma b) in Ar/ N_2O plasma

In all the samples, oxygen and carbon impurities were noticed. In the case of metallic copper, the spectrum is representative of an interaction between Cu and O. It could be due to a solid solution of oxygen in copper or a O/Cu stoichiometry less than that required by Cu_2O .

From Oehr and Suhr [5], it is known that H_2 is necessary for the preparation of copper metallic films, indeed organometallic containing oxygen, such as acetylacetonates or alkoxy compounds often lead to oxide films rather than to metals.

Figure 3 : Comparison of the Auger $L_{23}M_{45}M_{45}$ emissions of copper for Cu, CuO and Cu_2O thin films.

3- Film texture

The deposited films have been observed by scanning electron microscopy. As shown in figure 4, the surface aspect of copper and copper oxides films are very different. Cu_2O always presents a very granular texture (Fig. 4a) which seems very porous. Compared to this morphology CuO films were more compact (Fig. 4b). Metallic copper films have a characteristic texture with small cracks and they do not seem to be very compact (Fig. 4c). No effect of the substrate has been evidenced on the film texture. In all cases, a good adherence has been observed on silicon and MgO substrates.

The layers obtained with a 60 minute deposition were about $0.2 \mu\text{m}$ thick. The corresponding deposition rates are very low and will have to be improved by increasing the precursor flow.

(a)

(b)

(c)

Figure 4 : Scanning electron micrographs of surface and cleaved cross sections of a) Cu_2O - b) CuO - c) Cu deposited films.

CONCLUSION

Metallorganic Microwave Plasma Enhanced Chemical Vapor Deposition seems to be a suitable technique to favour the deposition of metallic copper (without H_2) and copper oxides. It allows a good control of the oxygen stoichiometry and should be very convenient for the formation of high T_c superconductors at low temperature.

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REFERENCES

- /1/ LAURIE A.B., NORTON M.L., Mat. Res. Bull., 24 (1989) 1521
- /2/ DESISTO W., SOSNOWSKI M., SMITH F., DELUCA J., KERSHAW R., DWIGHT K. and WOLD A., Mat. Res. Bull., 24 (1989) 753
- /3/ BOHER P., HOUDY P., SCHILLER C., VAN IJZENDOORN L.J., Thin Solid Films, 174 (1989) 91
- /4/ LAURIE A.B., NORTON M.L., Mat. Res. Bull., 24 (1989) 213
- /5/ OEHR C., SUHR H., Appl. Phys. A, 45 (1988) 151
- /6/ HOULE F.A., JONES C.R., BAUM T., PICO C., KOVAC C.A., Appl. Phys. Lett., 46 (2) (1985) 204
- /7/ MAHI B., ARNAL Y., POMOT C., J. Vac. Sci. Technol., B5 (3) (1987) 657
- /8/ VANDENBULKE L., BOU P., HERBIN R., CHOLET V., BENY C., Journal de Physique, Coll. C5, 50 (1989) C5 177
- /9/ EBIHARA K., KANAZAWA S., IKEGAMI T., SHIGA M., Proc. of the 9th Inter. Symp. of Plasma Chem., (1989) 1509
- /10/ LARSON P., J. of Electron Spectroscopy and Related Phenomena, 4 (1974) 213