A LOW-PRESSURE R.F. OXYGEN PLASMA AS A TOOL FOR OXIDATION: THE TREATMENT OF COPPER FOILS.

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Abstract

Copper foils are oxidized in a RF oxygen plasma. The oxides formed are identified by their reflectance spectra in the UV-visible and IR range and from the photoluminescence spectra. An electrochemical study confirms the formation of a non-stoichiometric "precursor" oxide Cu_xO, the two copper (I) oxides ($Cu_{2-x}O$ and Cu_3O_2) and the cupric oxide which are formed by thermal oxidation at low temperature.The thickness of the oxide layer depends on the time exposure to the plasma and on the position of the sample for given treatment parameters; it evidences that the plasma treatment is much more efficient than the thermal treatment at low temperature.

Introduction

The chemical properties of a plasma are investigated in the case of an Oxygen RF plasma in the range 10^{-2} torr which is suitable to study the oxidizing properties. We selected Copper which leads to several oxides as a convenient indicator to evidence these properties and to precise the influence of the discharge parameters (e.g., induced power, gas pressure and flow, distance between the sample and the 1st coil). The choice of copper was also governed by its universal use in the electrotechnical industries and by the fact that oxides often form in relation with electric discharges and breakdowns.

In addition, the copper oxides raise up increased interest due to their use as a catalyst in methanol synthesis [1], as a component in solar cells [2] or in high temperature superconductors [3]. They are usually prepared by thermal oxidation of copper, electrodeposition or reactive sputtering for Cu_2O [4-5], sputtering or thermal CVD for CuO [6].

Previous studies on the thermal oxidation of copper films at low temperature [7] evidenced the formation of several oxides which were characterized by their reflectance spectra in the UV, visible and IR ranges and the photoluminescence spectra. One of our purpose is to check whether the same oxides are formed by plasma oxidation and hence a large part of this work will be devoted to analysis problems. We also plan to precise the influence of the various working parameters on the resulting oxides, both on the nature

and on the thickness of the layer. This enables us to compare the efficiency of the two methods for the preparation of copper oxide layers.

Experimental

The 13.56 MHz inductively coupled plasma device is conventional, except that the reactor is a pyrex glass tube.The treated copper foils are disposed on a water-cooled quenching head at fixed distance from the 1st coil. O_2 pressure is stabilized at 10^{-2} torr.

The Cu.A samples (1.13 cm^2 area; 0.3 mm thickness) are first cleaned in nitric acid, mechanically polished, washed and rinced in absolute ethanol and dried before exposure to the plasma.

The reflectance spectra were performed on a Perkin Elmer Lamda 9 or a Beckman 5240 UV-Vis-NIR spectrophotometers equipped with an integrating sphere. IR spectra were recorded on a Nicolet 710 FTIR spectrophotometer and photoluminescence measurements were performed on a Jobin-Yvon 3C.

The electrochemical cell fitted with a Pt auxiliary electrode and a SCE reference electrode is filled with (0.1 M) $Na_2B_4O_7$ as the electrolyte since at pH: 9 the solubilities of the various copper oxides and hydroxides are minimum.

Results and Discussion

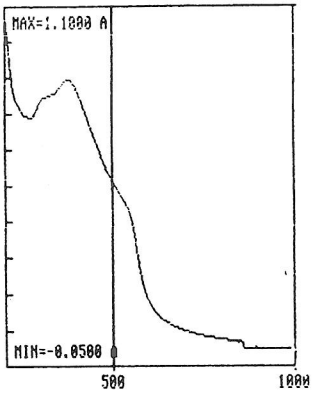
We varied the treatment conditions and we report here results relevant to various time exposures, various distances *d* (sample-1st coil) and various values of the electric power. All the results gathered are arguments in favour of a kinetic scheme for the oxidation process.

Precursor oxide Cu_xO. For short treatments and low electric power and long distances *d*, a precursor oxide Cu_xO forms. Its crystalline structure [7] is that of Cu_2O but the UV-vis. reflectance spectrum differs from that of metallic copper only by an absorption band in the 360-380 nm range (Fig. 1). This (0-I) mixed valency non stoichiometric compound results from the scattering of intersticial Cu(0) in the Cu(I) oxide phase. Its electrochemical reduction curve is characterized by a peak at -0.55 V/ SCE corresponding to the reduction of Cu(I), as illustrated by Fig. 2 which refers to a 5 minutes plasma treated sample. The influence of the electric power on the formation of the precursor is examined: for increased electric power of the plasma the reduction peak moves towards more negative potentials and tends to the reduction peak of Cu_2O (-0.85V/ SCE).

Copper (I) oxides: $Cu_{2-x}O$ and Cu_3O_2. The UV-vis. spectrum of $Cu_{2-x}O$ is characterized by an absorption band between 400 and 580 nm related to the occurrence of non-stoichiometric defects. The IR reflectance spectra of Cu_2O presents two bands around 650 cm^{-1} (LO mode) and 610 cm^{-1} (TO mode). Although Cu_3O_2 is a gross

structure of Cu_2O. Lenglet [9] pointed out the different optical properties between these oxides which can be characterized only by their photoluminescence spectra (Fig. 3) under excitation at 530 nm for 10 minutes: an intense emission band at 760 nm is attributed at Cu_3O_2 and the other (820 nm) less intense at Cu_2O .

The reduction voltammogram presents a minor peak near to -0.5 V/SCE which is attributed to the reduction of the precursor oxide, and a major peak near -0.85 V/SCE which is assigned to the reduction of Cu_2O and Cu_3O_2.



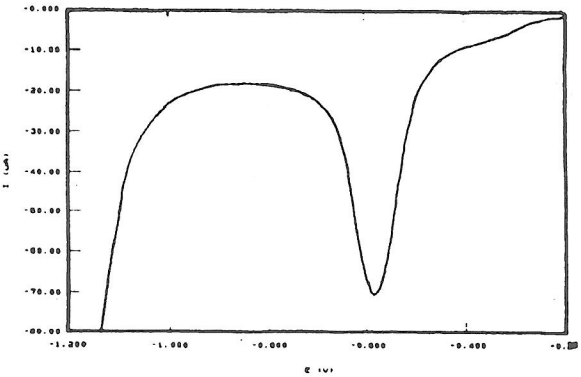
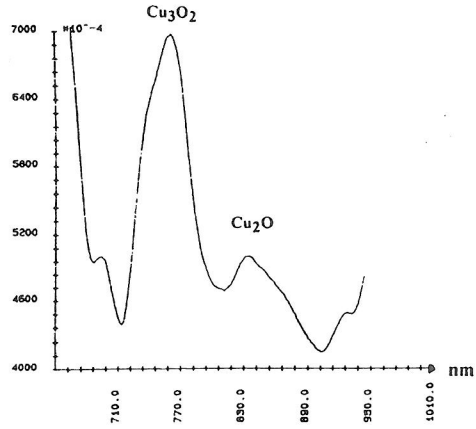


Fig. 1- *UV-vis spectrum (wavelengths in nm) of Copper treated for 5 minutes at d = 20 cm (P = 100W) showing the precursor oxide .*

Fig. 2- *Reduction voltammogram E vs.SCE of the precursor oxide (Electrolyte : 0.1M $Na_2B_4O_7$, pH = 9.2; Sweeping speed: 0.5 mV.s^{-1}; Plasma treatment : exposure time 5 minutes, d = 5 mm, P = 300 W, oxygen pressure 2 mbars).*



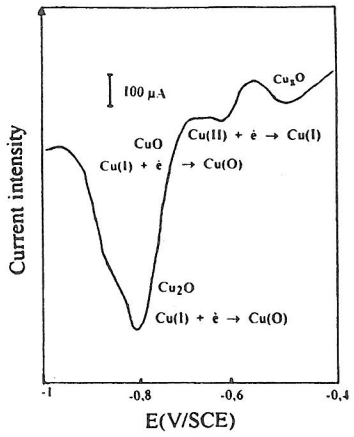


Fig. 3- *Photoluminescence spectrum (wavelength, nm.) of Cu(I) oxides (P:200 W; d:10; t: 15mn).*

Fig. 4- *Voltammogram (E, V/SCE) of plasma treated Cu (200W; t:30 min; d:20 cm).*

Copper (II) oxide or cupric oxide CuO. Cupric oxide is characterized by a sharp absorption rise in the range 700-800 nm. Besides it is known [10] that the electroreduction of CuO induces two peaks. Fig. 4 illustrates the electrochemical reduction of a sample treated for 30 minutes (plasma power 200W ; d = 20 cm) . Peaks at - 0.65 V/SCE and - 0.75 V/SCE are respectively assigned to the first and second reduction step of CuO while the major peak near -0.80 V/SCE is attributed to the reduction of cuprous oxide Cu_2O.

Influence of the treatment parameters.

The oxides formed depend strongly on the working conditions of the plasma. Several parameters were varied: the time exposure, the position of the sample (distance d) and the plasma power. The evolution of the various analytical characteristics of the oxides with the mentioned parameters can be summarized as follows. The precursor oxide is always formed. Increasing the time exposure or the electric power and decreasing the d values lead to limited quantities of the precursor oxide which disappears in favour of the copper (I) oxides Cu_2O and Cu_3O_2: the electroreduction peak moves towards lower potentials with increasing intensities (Table 1).

Power (W):	100	200	300
Ep (V/SCE):	-0.52	-0.55	-0.60
Ip (μA):	30	60	70

Table 1. *Influence of the electric power of the plasma on the position and the intensity of the electroreduction peak of the oxide layer (d = 5 cm; plasma treatment: 5 minutes)*

An increase of the treatment time induces an evolution of the FTIR spectra.The intensity of the W_L peak at 650 cm^{-1} decreases while that of the W_T peak at 610 cm^{-1} increases as Cu_2O forms and becomes prominent in the oxide layer. For longer exposures CuO forms and the relevant 510 cm^{-1} band increases.

Determination of the film thickness.

The film thickness is determined from interferometry techniques. It increases with the time exposure for given plasma conditions, and on a first approximation, the thickness e(μm) varies as kt^2 for the very first minutes of the treatment. Also, it depends on the distance d target-to-1st. coil and decreases as d increases for fixed treatment durations. For example, an oxide layer 1μm thick results from a treatment of 18 minutes at a distance of 5 cm, 23 minutes at 10 cm or 30 minutes at 20 cm.

At this juncture, it may be mentioned that the variations of the intensity of the reduction peak follows variations with the treatment duration similar to the thickness of the oxide layer. Both effects are interpreted in terms of plasma efficiency, since the smaller is d and the longer is the time exposure, the higher is the plasma efficiency.

Conclusions.

The association of non-destructive and destructive techniques such as optical and electrochemical methods (i.e. linear potential sweep voltammetry) allows to identify with an excellent agreement the various oxides formed on the surface of a copper foil when it is exposed to an oxygen plasma (Table 2). These techniques allow us to identify two

Copper oxide		UV-vis. (nm)	FTIR (cm^{-1})	Photoluminescence (nm)	Reduction peak E (V/SCE)
Cu(I)	Cu_4O	320-380	-	-	Cu^+ --> Cu -0.55±0.05
	Cu_2O	400-580	650 W_L	720-820	
	Cu_3O_2	-	610 W_T	740-760	Cu(I) --> Cu -0.95±0.1
Cu(II)	CuO	700-800	620; 580; 550; 510 W_L 605;530;470W_T		Cu^{2+} --> Cu^+ -0.65±0.05 Cu^+ --> Cu -0.80

Table 2- *Synopsis of the analytical characteristics of the copper oxides*

steps in the oxidation process, the first one is the formation of the precursor oxide and the second, the growth of complex films constituted by an intimate mixture of copper (I) and (II), i.e., Cu_2O, Cu_3O_2 and CuO. The scheme of the oxidation mechanism remains to be precised, since we have only identified the oxides formed as reported and the gaseous species present in the plasma by means of their emission lines: atomic oxygen was characterized by the 777.4 nm $O(^5P)$ triplet and the 844.6 nm $O(^3P)$ singlet.

A comparison between the plasma treatment and the classical thermal oxidation can be derived (Table 3) from these experiments on the basis of the thickness of the oxide layer formed since the nature of the oxides formed and the sequence of their formation are similar. Besides the starting material is the same for both techniques: and the Cu(A) sample is polished in both cases. It clearly appears that the plasma treatment leads to similar thicknesses of the oxide layers for much shorter times, which illustrates the well known efficiency of this process. In addition, this work evidences the formation of the precursor oxide as a major species at the surface, and this feature

presents an obvious interest for the adhesion of polymers on copper surfaces.

Th. 200:	0.1 μm (t= 2h);	0.2 μm (t= 8 h);	0.35 μm (t=16 h)
Pl.(d:10)	0.15 μm (t= 5 min)	0.25 μm (t= 10 min)	0.37 μm (t= 15 min)
Th.300:	0.25 μm (t= 10 min)	0.8 μm (t=20 min)	0.90 μm (t= 30 min)
Pl.(d: 5)	0.25 μm (t=7 min)	0.8 μm (t=13 min)	0.90 μm (t= 17 min)

Table 3. *Comparison between thermal and plasma treatments of Copper. on the basis of the thickness of the oxide layer and the treeatment time.Th.200 and Th.300 refer to thermal processes at 200°C and 300°C respectively of annealed (1 hour; 210°C) samples; Pl. (d:10) and (d:5) refer to oxygen plasma treatments at 300 W at distances d= 10 cm and d= 5 cm respectively.*

Literature Cited

1- G.C. Chinchen, P.D. Denny, J.R. Jennings, M.S. Spencer, K.C. Waugh; *Appl. Catal. 1* (1988) 36

2- S. E. Hornstrom, S.E. Karlsson, A. Roos, B. Westerstrandh, A. Kauf; *Solar Energy Mat. 9* (1984) 367.

3- P. Luzeau, X.Z. Xu, M. Lagues, N. Hess, J.P. Coutour, M. Nanot, F. Queyrous, M. Touzeau, D. Pagnon; *J. Vac. Sci. Technol. A 8* (1990) 3938

4- N. Economou, R.S. Toth, D.Trivich; *Proc 1st Photovoltaïc Solar Energy Conference of the CEC* (Dordrecht, The Netherlands 1970) 1180.

5- G. Beensh-Marchwicka, L. Krol-Stepniewska, M. Slaby; *Thin Solid Films 88* (1982) 33.

6- H. Suhr, C.Dehr, H. Holzschuh, F. Schmaderer, G. Wahl, T. Kruch, A. Kinnen; *Physica C 784* (1988) 153.

7- J.M. Machefert, M. Lenglet, D. Blavette, A. Menand, A. D'Huysser; *Structure and Reactivity of Surfaces*, Elsevier, Amsterdam (1989), 625.

8- M. Lenglet, K. Kartouni, D. Delahaye; *J. Appl. Electrochem. 21* (1986) 697

9- M. Lenglet; *Proc. 1st Int. Symp. on Control of Copper and Copper Alloys Oxidation* (Rouen, France, 1992) 163

10- R.L. Deutscher, R. Woods; *J. Appl. Electrochem.16* (1980) 413