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Corrosion resistance of electrochemical copper coating realized in the presence of essential oils

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ABSTRACT

Copper coating was developed electrolytically on interconnections in technology used in wafer level packaging. These coatings are adherent and uniforms, the deposition rate reached 23 µm/h. The quality of the deposits was improved by the addition of a cinnamon extract in the plating bath. The morphology of the coatings was evaluated by scanning electron microscopy. The anti-corrosion properties of copper coatings in the absence and presence of different cinnamon extract concentrations were studied in a 3% NaCl solution using the potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and scanning electron microscope (SEM). The result showed that the presence of 150 ppm cinnamon improves the corrosion resistance of the copper substrate.

Keywords: Coating; copper; extract of cinnamon; Corrosion; Potentiodynamic polarization; electrochemical impedance spectroscopy (EIS); 3%NaCl

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INTRODUCTION

The electrodeposition is a widespread industrial method for metals or metal alloys deposition with varied applications ranging from anti-corrosion treatment on large surfaces (e.g. steel zinc electrodeposition) to advanced electronic industries (copper deposit on chips, magnetic heads, etc…)**[1]**. In the microelectronics industry, the copper coating is an excellent choice as underlayment. It has a very high plating efficiency with excellent coverage even on difficult substrates to be coated. Indeed, in some processes, the deposition of aluminum is carried out by CVD on copper coating **[2, 3].** Copper and its alloys can be electrodeposited from various electrolytes including aqueous citrate **[4]**, sulfate **[5–7]**, pyrophosphate **[8]**, oxalate **[9]**….

Copper and its alloys are highly corrosion resistant in chloride medium. So, they are widely employed in industrial applications such as heat exchangers and electronic devices. A good corrosion resistance of these materials is due to two reasons. Firstly, in acidic medium, the standard potential of Cu|Cu(I) is more positive than the hydrogen evolution potential. The spontaneous corrosion potential of copper will be therefore located in the immunity region in absence of dissolved oxygen **[10]**. Secondly, in neutral medium, a uniform and an adherent film formed at the metal surface by corrosion products acts as a barrier layer against aggressive medium. In spite of this self-protective effect, copper and copper alloys may undergo a damage in different situations. For instance, in chloride medium, the corrosion properties of copper are markedly modified by the formation of copper–chloride complexes [**11**]. Deslouis et al. concluded that in NaCl 3% medium the current density is depending on the chloride concentration, potential and rotation speed of the electrode **[12]**. The favorable effects of organic addition agents on the properties of electrodeposits have been known for a number of years **[13-16].** Organic additives, such as thiourea **[17, 18]**, gelatin **[19–23]** and animal glue **[24]** are widely used in copper electrodeposition since they can produce smooth and bright copper deposits. The presence of additives in electroplating baths also produces a better leveling effect on the surface of deposits and affects the diffusion of reactants in solution **[25-30].** Recently, considerable attention has been paid to substances that can be used in industry with a low toxicity **[31, 32–36]**.

The aim of this work is to study the corrosion resistance of copper coating electroplating connections used in wafer level packaging technology in a 3% NaCl solution in the presence of an essential oil by using the potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and scanning electron microscope (SEM).

MATERIALS AND METHODS

Electrolysis cell

The electrolysis cell was a borrosilcate glass (Pyrex®) cylinder closed by cap with five apertures. Three of them were used for the electrodes: Copper interconnects used in wafer level packaging technology (Figure 1) as working electrode, Pt plate as the counter while Ag/AgCl was used as the reference electrode. All potentials are referred with respect to this last electrode. All solutions used through these experiments were freshly prepared from analytical grade reagents and distilled water. The temperature was held at 25 ± 2 °C. The substrates are degreased in an ethanol bath and rinsed with deionized water and then pickled in a 1M sulfuric acid bath and rinsed again with deionized water. All corrosion tests were performed in 3%NaCl solution. The optimal conditions are: $CuSO_4$ 15 g/L at pH=1.5 and the current density applied is -17mA/cm^2. To improve the quality of the coating, a cinnamon extract was added to baths. The extraction of cinnamon is carried out in our laboratory. Initially, we prepared the deposit on the substrates in the presence of essential oil at different concentrations to achieve a uniform deposition and the same thickness of approximately 22µm / h.

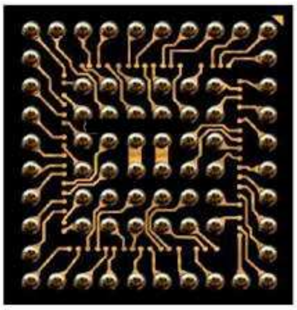

Figure 1: Interconnections of Cu used in wafer level packaging technology

The deposition rate R was determined gravimetrically according to the relationship:

$$R\ (\mu m/h) = (m_f - m_i) / (\rho \times s \times t)$$

m_i: Initial mass (g), m_f : Final mass (g), ρ: Density of copper (g/cm^3), s: Substrate surface (cm^2), t: Deposition time (s)

Electrochemical measurements

The electrochemical measurements were carried out using Potentiostat/Galvanostat/Voltalab PGZ 100 monitored by a personal computer. Corrosion current density, icorr, and the corrosion potential, Ecorr were obtained from the Tafel extrapolation method. The protective efficiency E (%) from the polarization curves was calculated from the following equation:

$$E\% = \left(1 - \frac{i_{corr}}{i_{0corr}}\right) \times 100 \qquad (1)$$

Where i_{0corr} and i_{corr} are respectively the corrosion current values without and with essential oil in the solution.

The electrochemical impedance spectroscopy measurements were carried out over a frequency domain from 100 KHz to 10 mHz. Resistance polarization (Rp) was calculated from the linear polarization method. The EIS spectra analysis was performed using Boukamp impedance analysis software [37]. The charge transfer resistance Rct is obtained from the diameter of the semicircle in Nyquist representation. The protective efficiency E% via the impedance curves of the coating was found from the following relationship:

$$E\% = \left(1 - \frac{R_{oct}}{R_{ct}}\right) \times 100 \qquad (2)$$

Where R_{0ct} and R_{ct} are respectively the charge transfer resistance values without and with alloy coating of substrate, respectively.

Characterization

The surface morphology was characterized by scanning electron microscopy (SEM) using LEO1530 FEG Scanning Electron Microscope.

RESULTS AND DISCUSSION

Chronopotentiometry

Figure (2) shows the chronopotentiograms with and without extract of cinnamon. The potential for copper electrodeposition in the absence of extract of cinnamon is equal to -0.20 V. The addition of 100 ppm cinnamon extract causes a slight displacement of this potential to -0.24 V indicating a small variation in the deposition rate.

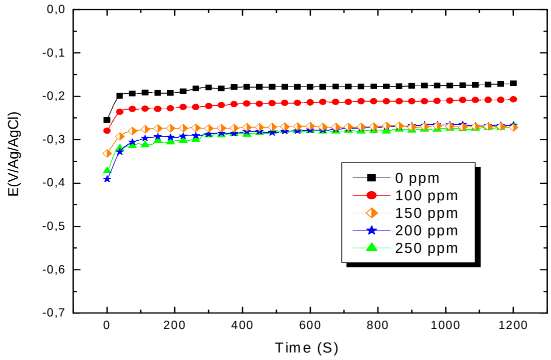

Figure 2: Chronopotentiometric curves with and without cinnamon extract at -17mA/cm^2

Effect of cinnamon concentration on the deposition rate

Figure (3) shows the variation of the deposition rate at different cinnamon extract concentrations. It may be noted that the addition of cinnamon does not really impact the deposition rate which remains 20 µ/h but it affects the quality of the coating (Table 1). Indeed, we observed a significant improvement in the quality of the coating with a concentration of 100 ppm.

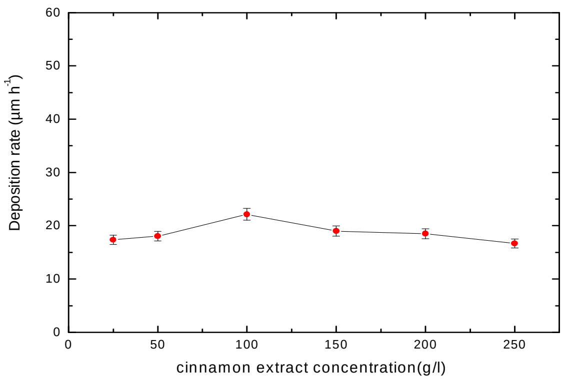

Figure 3: Effect of cinnamon concentration on the deposition rate

The coatings aspect was visually appreciated. The number 5 was assigned to the brighter and more uniform coating, whereas the number 1 was given to the heterogeneous and burned one.

Table 1: Appearance of the coating with the cinnamon extract at pH=1,5

C (extract) ppm	C($CuSO_4$) en g/l	I (mA/cm²)	Appearance
0	15	-17	3
25	15	-17	3
50	15	-17	3
100	15	-17	5
150	15	-17	4
200	15	-17	3
250	15	-17	3

Corrosion study
Potentiodynamic polarization
Figure 4 shows the stationary polarization curves of copper deposits in 3% NaCl. These deposits were developed in the presence of various essential oil concentrations in the plating bath. We observe a decrease in both anodic and cathodic currents when the essential oil concentration in the plating bath increases. This would indicate an improvement in the corrosion resistance of the coatings. We will try to confirm this hypothesis by calculating the corrosion current.

The corrosion current density can be evaluated by applying the Stern–Geary relationship [38]. The regression calculation using non-linear least-square method was applied to evaluate the corrosion parameters: i, i_{corr}, E_{corr}, ba and bc that are respectively the experimentally observable current density, corrosion current density, corrosion potential where the overall current is zero, the Tafel coefficient of anodic and cathodic process. The electrochemical corrosion parameters obtained from the Tafel polarization curves are given in Table 2.

We notice a significant decrease in corrosion current between the coating produced without additive in the deposition bath and deposits developed in its presence. Also the corrosion resistance of the coatings improves with increasing concentration of the additive in the elaboration bath. Thus, the corrosion current is equal to 1,5μA/cm^2 in the presence of 150 ppm of the extract of cinnamon and the corrosion inhibition efficiency (E%) reaches 85% (table 2).

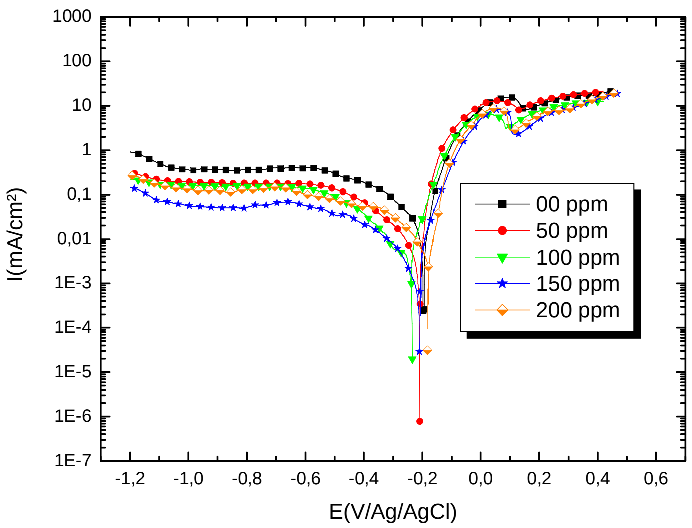

Figure 4: Stationary polarization curves on copper behavior in the presence and absence of essential oil at different concentrations in a 3%NaCl solution

Table 2: Corrosion characteristics of coating copper in 3% NaCl solution

Concentration	Ecorr mV/Ag/AgCl	Icorr μA/cm²	-bc mV/dec	ba mV/dec	E%
00ppm	-194	10	92	45	-
50ppm	-205	5.83	90	47.5	**41**
100ppm	-230	3.3	85	50	**67**
150ppm	-204	1.5	71	75.4	**85**
200ppm	-184	2.8	77	31	**72**

3.3.2. Electrochemical impedance spectroscopy
The corrosion resistance performance of copper electrodeposited was also investigated by the EIS. The impedance spectra of coating realized with and without cinnamon extract in 3%NaCl solution are represented on figure 5**.** Although the curves in the Nyquist plot appear to be similar with respect to their shape, they considerably differ in their sizes. The capacity loop at the high frequency represents the coating response, while the loop at the low frequency is associated with simultaneous physicochemical phenomena at the metal/coating/solution interface or diffusion phenomena of the oxidant chemical species through the porous coating **[**34-35, 39-40**]**. Then, the high frequency loop gives the double layer capacitance (C_{dl}) and the transfer resistance (Rt) of the oxidation reaction of copper coating. The values of these two parameters were obtained by fitting using a simple equivalent circuit R

(R_TC_{dl}). The R_{ct} and C_{dl} values of the coatings are compiled in Table 3. It is established that high values of R_{ct} imply a better corrosion protective ability **[39, 41]**.

Thus, we note that coatings elaborated in baths containing the additive have a resistance which is much higher in NaCl 3% solution than that of the coating elaborated in the basic bath.

Moreover, this resistance is maximal for a concentration of cinnamon extract equal to 150 ppm and the efficiency reaches 84.5%. Thus, the EIS results confirm the conclusions of the polarization study.

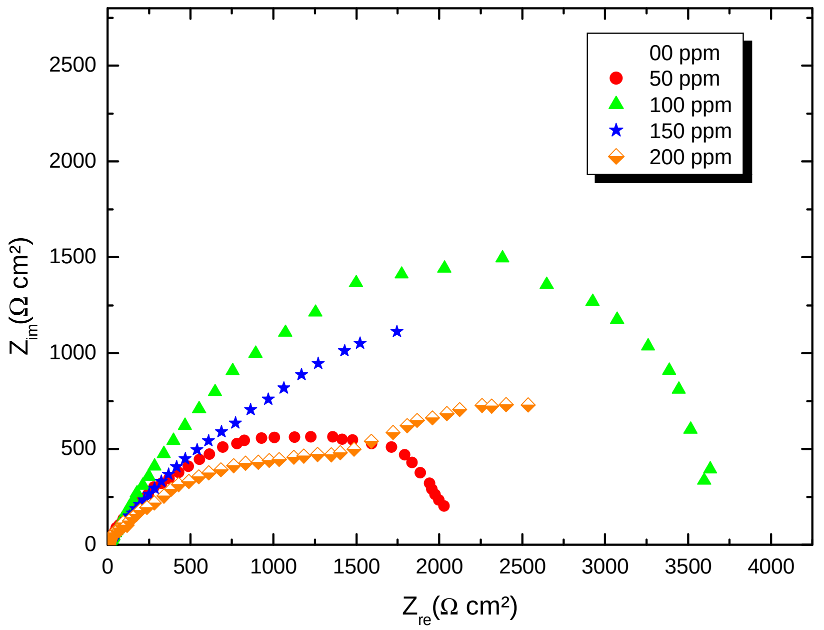

Figure 5: Nyquist plots of copper electrodeposition with and without cinnamon extract in 3% NaCl solutions

Table 3: Corrosion characteristics of copper with and without extract of cinnamon in 3% NaCl solution obtained from electrochemical impedance (EIS) studies

	R_s(Ω.cm²)	C_{dl}(μF/cm²)	R_p(Ω.cm²)	E%
00ppm	5	990	1235	-
50ppm	8	246	2088	**41**
100ppm	6	230	3800	**67.5**
150ppm	7	210	7950	**84.5**
200ppm	5	226	4155	**70**

3.2.3. Scanning Electron Microscopy

The morphology of copper surface electrodeposited on interconnects from electrolytes with and without cinnamon extract immersed for 24h in 3% NaCl solution was characterized. Thus, we observed that the surface of the copper coatings produced in the bath without additive is attacked. We note the presence of cracks, pitting and micropitting (fig.6a). Indeed, it is known that the copper dissolution in a chloride medium occurs according to the following process: oxidation of Cu to Cu^+, reaction of Cu+ with Cl^- to generate CuCl and the transformation of the CuCl to $CuCl^-_2$. This induces an attack of the copper surface **[43, 44].** By contrast, on the copper surface obtained in the presence of 150 ppm cinnamon, this corrosion process is not initiated, the surface was more regular, no porous and smooth (fig.6b).

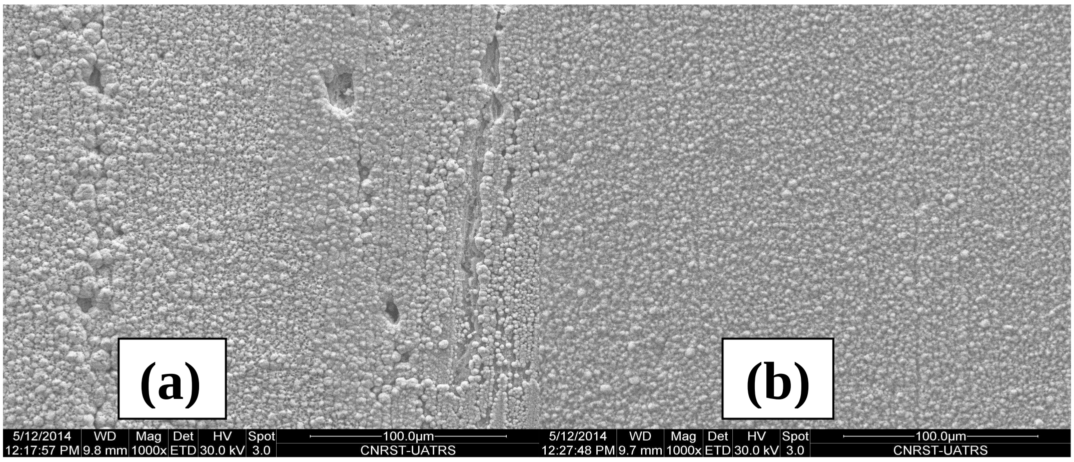

Figure 6: Micrograph (SEM) of copper deposit realized (a) Without and (b) with 150 ppm of cinnamon extract immersed in 3% NaCl for 24h

CONCLUSION

The study focused on the corrosion resistance of copper coatings developed on interconnections. It showed that this resistance was remarkably improved when such deposits were made in the presence of extract from "Cinnamon". Indeed, we recorded a significant drop of corrosion current and a significant increase of the transfer resistance. The efficiency was 85% at a concentration of the extract of Cinnamon 150 ppm.

Furthermore, the observations in scanning electron microscopy confirm these results. The samples prepared in the presence of Cinnamon extract showed a practically intact surface after spending 24 hours in 3% NaCl. On the contrary, those prepared without the additive were attacked and their surface has many pits.

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