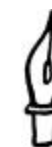
ANALELE UNIVERSITATII BUCURESTI

Department of Physical Chemistry
4-12 Regina Elisabeta Blvd, District 3, Bucharest
phone: +40-21-3143508; fax: +40-21-3159249
ISSN: 1844-0401

ARS DOCENDI PUBLISHING HOUSE
Sos. Panduri 90, District 5 Bucharest
phone/fax: +40-21-4102575
e-mail: arsdocendi@yahoo.com



INFLUENCE OF Nd_2O_3 IN COPPER AND COPPER COMPOSITE COATINGS OBTAINED BY ELECTROLESS PLATING

C. Iticescu *, M. Murarescu and G. Carac

abstract: copper and Cu/Nd_2O_3 composite coatings were deposited by electroless plating method using copper electrolyte alkaline solutions. Formaldehyde was used as reducing agent. Carbon steel was used as support for deposition. The concentration of Nd_2O_3 was between 5-50g/L in solution. There is a strong dependence on many factors like the nature of electrolyte and concentration of the dispersed phase in bath as well as the electrolysis conditions. The embedded particle of dispersed phase in the copper matrix determines changes of surface coatings and also of their properties. Morphology is an important property of electrodeposited composite coatings and was studied by scanning electron microscopy method (SEM).

key words: Nd_2O_3; copper; composite**;** electroless; morphology

received: May 12, 2009 *accepted*: May 20, 2009

1. Introduction

Pure copper and copper composite coatings can be deposited by wet chemical plating techniques such as electroplating and electroless plating. These techniques have the advantage of low cost of tools and materials, low processing temperature, high quality material and high throughput of the process. Chemical plating has a very high selectivity, uses a very thin seed layer, and has excellent step coverage and good trench filling capability that does not need any electrical contacting of wafers during deposition.

Advantages of electroless plating include excellent uniformity, bulk processing capability and ability to produce unique catalytic coatings. The main disadvantages of electroless plating method is the fact that thin layers were obtained and the working time is long [1,2]. By this consideration, the obtaining of composite layers by electroless plating methods was less studied. Another consideration consists in the instability of solutions of depositions and low deposition speed that interaction create a bigger activity of copper reducing reaction represent another reason of study.

They are thus suitable methods for low-cost processing. Electroless plating occurs simply by immersion of the samples in a plating bath. No rectifiers, batteries or anodes are

* "Dunarea de Jos" University of Galati, *corresponding author e-mail*: *catalina.iticescu@ugal.ro*

© 2009 ***Analele Universității din București***

involved. The essential elements of the solution are soluble metal salt, and reducing agent, additives such as complexing agents, buffers, bath stabilisers and rate promoters.

Electroless plating is an autocatalytic process; that means that metal deposition serves to catalyse the reaction [3,4].

Aiming at compactly selective metallizing, copper can be deposited from aqueous solutions under the action of several reducers such as formic aldehyde, boron hydride, hydrazine, potassium hypophosphite or of several redox pairs such as: Fe (II) / Fe (III), Ti (III) / Ti (IV), Cr (II) / Cr (III), V (II) / V (V). For practical applications, formic aldehyde and boron hydride are used with the best results [5].

In this study we used formic aldehyde as reducer. The copper chemical deposition can be performed from alkaline solutions only, and reacts according to the chemical equation below:

$$Cu^{2+} + 2HCHO + 4OH^{-} \rightarrow Cu + 2HCOO^{-} + H_2 + 2H_2O$$

Molecular hydrogen occurs from the reaction, the Cu / H_2 ratio being 1 [6].

Cooper coatings by electroless plating have been obtained. The paper presents studies on the influence of some factors involved in electroless plating of copper. Ions in the electrolyte have an important role in the transport of Cu^{2+} ions to the cathode surface.

2. Experimental

The copper electroless plating has been prepared using an electrolyte with the chemical composition: $CuSO_4 \cdot 5H_2O$ – 30g/L; Na_2CO_3 anh. – 12g/L; Na and K – tartrat 150g/L, NaOH –50g/L, EDTA – 6g/L [7]. The formic aldehyde (37%) was used as reducing agent and its amount was 20 g/L HCHO. The *p*H of the electrolyte was 13,5 at the temperature of 20-25^{0}C [7]. Carbon steel was used as metallic support for copper deposition. In the electrolyte there were added particles of Nd_2O_3 with a concentration between 1÷50g/L.

Therefore, the plating bath is capable of plating receptive surface, including plating tank and equipment surfaces. To maintain a constant plating rate, high control of pH and temperature are necessary. Metal and reducing agent concentration must also be kept at optimal specified levels [8].

Deposition of copper was obtained on carbon steel as metallic support with an effective area of 25 cm^2. The samples were cleaned mechanically by polishing with abrasive papers, organically (with acetone) and chemical degreased (at 70-80^{0}C for 5 minutes in alkaline solution), washed with hot distilled water and finally, for the activation of surface, treated with HCl 15% (2 minutes) [9].

Copper chemical deposits from electrolyte with and without particles in suspension were tested by optical microscopy in cross section.

Surface morphology and composition were studied by scanning electron microscopy (SEM) with an X-ray analyzer (EDXS) from Leo Instruments.

The results are compared with pure copper coatings to understand the effects of particles dispersed on the microstructure and properties of composite coatings during the electroless crystallization.

3. Results and discussions

3.1. The optimisation of copper electrolyte

Solution factors, such as the presence of stabilizers, can strongly influence the deposit uniformity. The state of the metal ion is of great importance to the behaviour of the electroless solution. In aqueous solutions Cu^{2+} ions should be more accurately represented as aqua- metal copper ions. Complexation of Cu ions with EDTA occurs, because the ligand is a stronger base than water. Not all of the metal ion species in solution will be active for electroless deposition. The autocatalytic reaction depends on the nature and content of the stabilizer additive used in solution. EDTA as a stabilizer additive was used in our solution (Fig. 1). The optimal content of EDTA in solution was of 6g/L.

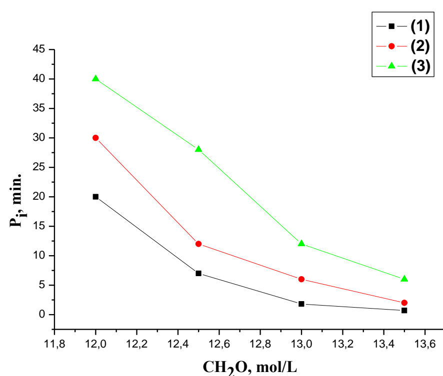


Fig. 1 *Period of induction in copper electrolyte with stabilizer concentration:*
1) 4g/L EDTA; 2) 6g/L EDTA; 3) 10g/L EDTA

For electroless plating, alkaline solution with pH bigger than 12 was used. No change of *p*H electrolytes was observed during of deposition processes. For *p*H values inferior to 12, because of some secondary reactions, the reduction of copper cannot take place. The rate of copper reduction is smaller for lower temperatures and larger for higher temperatures resulting in many pores and exfolling layers.

It was studied the influence of HCHO content for the same stabilizer (6g/l EDTA) in electrolyte. The alkaline electrolyte is more stable when copper is reduced in less time. The content of reducing agent influences the electrolyte stability and the quality of the deposits. Good results were obtained using a reducing agent of 22,5 g/l HCHO. The results obtained are presented in the Fig. 2. Experiments using the electrolyte with particles in suspension were also made. It was observed that Nd_2O_3 particles have catalytic actions upon the copper reducing reaction. The periods of induction were smaller in these cases. The deposits from

the electrolyte with particles are more uniform and resistant if speed of deposition is lower. On the other hand a low speed is not appropriate.

The control of reduction speed is necessary. The copper reduction is partial in the case of using of reducing agent in a bigger amount. The reactions are:

$$Cu^{2+} + 2e^{-} \rightarrow Cu^{0}$$

$$Cu^{2+} + e^{-} \rightarrow Cu^{+}$$

The deposits presented different colours, depending by copper compounds and working condition.

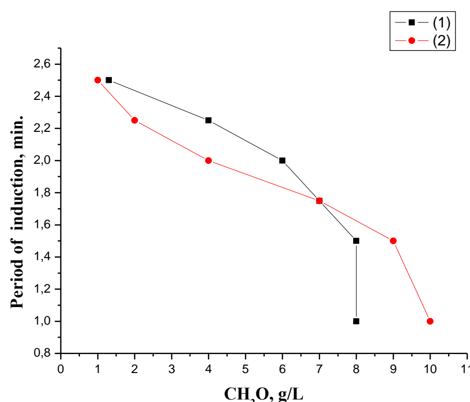


Fig. 2 *Period of induction in copper electrolyte with CH_2O concentration*

3.2. Structural aspects

The structure of copper coatings was investigated by light microscopy and scanning electron microscopy (SEM) in cross section. Thin layers of copper deposits between 3-18 μm were obtained. The layer thickness depends on the immersion time of samples in solution. The aspect of layers is not completely uniform but this can be explained by destruction of metallic support during the preparation of samples for optical analyses (Fig. 3).

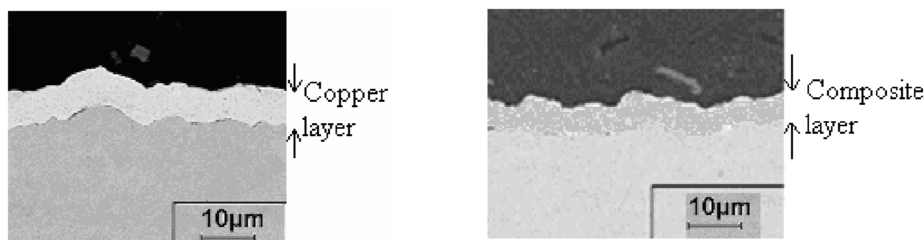


Fig. 3 *Optical microscopy for copper and copper composite deposition.*

Composites coatings structure is modified by the presence of Nd_2O_3 particles in copper matrix. SEM micrographs of composite layers obtained by chemical deposition are showed

in Fig. 6. An Nd_2O_3 particles agglomeration with their concentration increase was observed. The copper matrix structure is modified, the particles presence conduce to the surface polishing that was also demonstrated by the roughness measurements.

The presence of Nd_2O_3 particle affects the mechanism of the copper reduction by electroless plating. When Nd_2O_3 is added in solution, the particles of oxide were embedded in the copper deposits in a satisfactory amount. The results of the investigations confirm that Nd_2O_3 was embedded into copper matrix by electroless plating. The EDX analysis in point of Nd_2O_3 also indicated the presence of particles in copper matrix (Fig. 4).

From experimental date it was observed a growth amount of Nd_2O_3 in deposit with the amount of oxide in the electroless solution (Fig. 5).

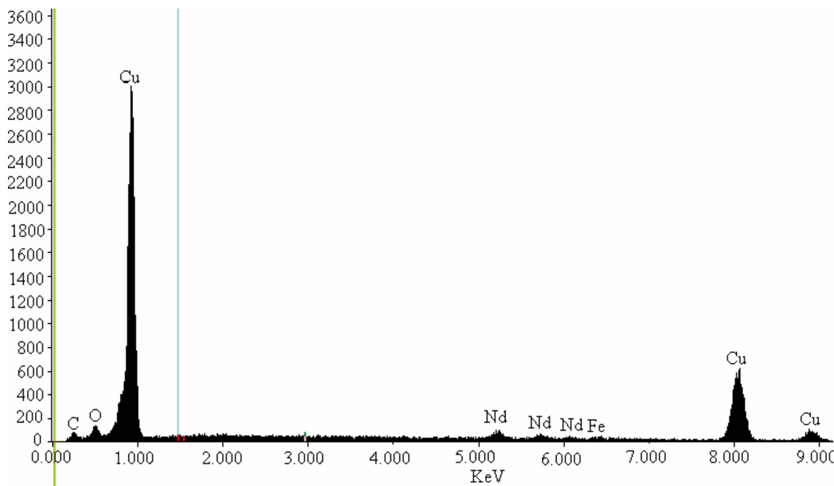


Fig. 4 *EDAX analysis (in point) on Nd_2O_3 particles included in copper matrix.*

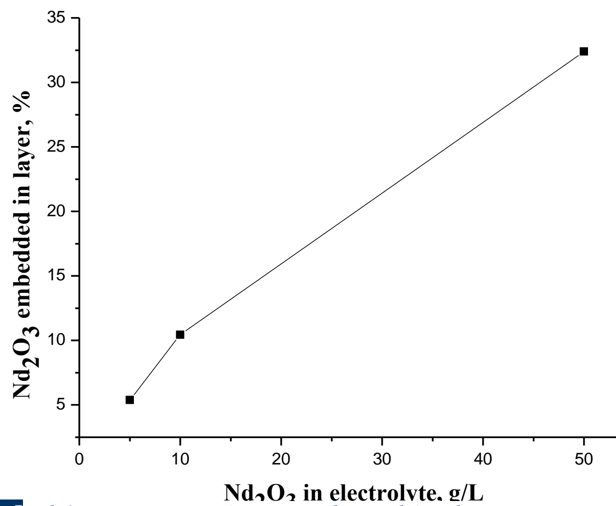


Fig. 5 *Nd_2O_3 amount content (percentage by weight) in the copper coatings.*

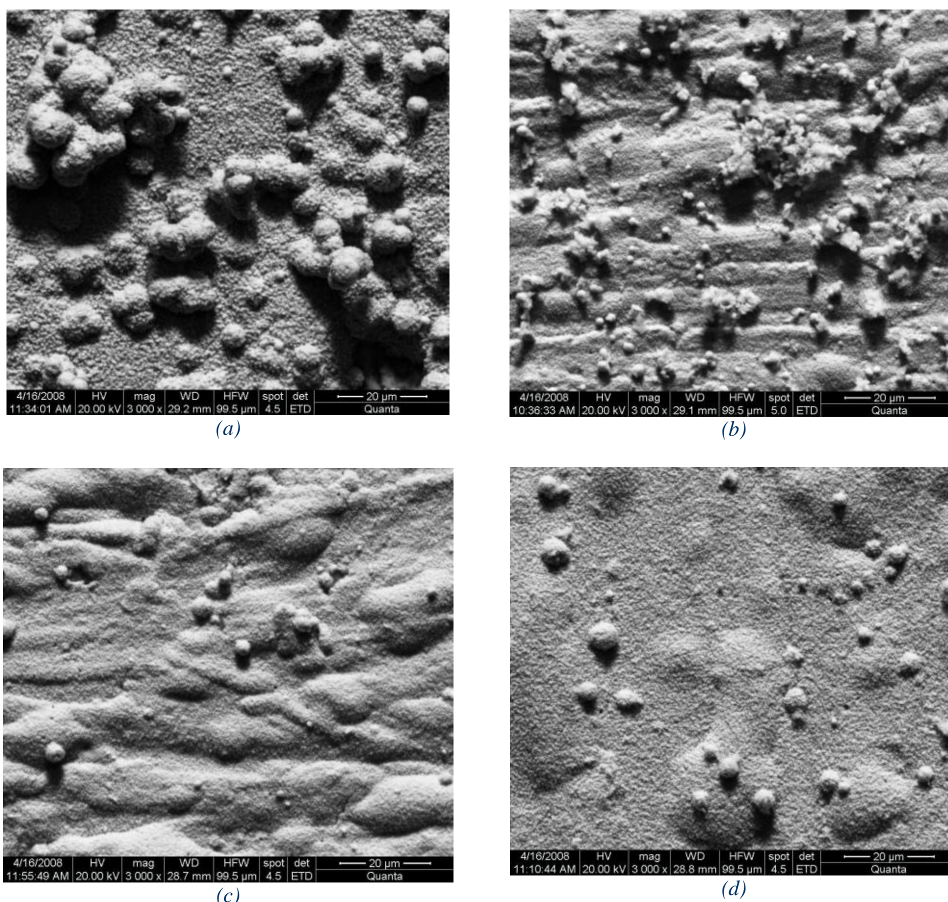


Fig. 6 *SEM micrographics:*
a) Cu; b) Cu-Nd_2O_3 (1 g/L in electrolyte); b) Cu-Nd_2O_3 (5 g/L in electrolyte); d) Cu-Nd_2O_3 (10 g/L in electrolyte)

4. Conclusions

1. The experiments were performed to study the obtaining of copper coatings matrix with and without Nd_2O_3 from a copper sulphate electrolyte with formaldehyde as reducing agent.

2. The period of induction is influenced by composition of electrolyte (concentration of EDTA, CH_2O, Nd_2O_3 and substrate).

3. The dispersed phase of Nd_2O_3 was included in copper layers in a small amount.

4. Were observed difference between morphologies of different types of composite coatings.

REFERENCES

1. Schlesinger, M. and Paunovic, M. (2000) **Modern Electroplating**, Fourth Edition, John Wiley & Sons, New York.
2. Shrestha, N. K., Sakurada, K., Masuko, M. and Saji, T. (2001) *Surface and Coatings Technology* **140**, 175.
3. Henry, J.R. (2007) *Metal Finishing* **105**(10), 350-60.
4. Aithal, R.K., Yenamandra, S., Gunasekaran, R.A., Coane, P. and Varahramyan, K. (2006) *Materials Chemistry and Physics* **98**, 95–102.
5. ***Concise Encyclopedia of Composite Materials** (1994) Anthony Kelly (Ed.), Churchill College Cambridge, U.K.
6. Searson, P.C. (2000) *Journal of the Electrochemical Society* **147**(7), 2571-5.
7. Iticescu, C., Cârâc, G. and Mitoseriu, O. (2003) *Annals of West University of Timisoara* **12**(3), 569-75.
8. Iticescu, C., Cârâc, G. and Mitoseriu, O. (2005) *Bulletin of the Polytechnic Institute of Iassy* **LI**(LV), 149-54.
9. Cârâc, G., Benea, L., Iticescu, C., Lampke, Th., Steinhäuser, S. and Wielage, B. (2004) *Surface Engineering* **20**(5), 353-9.