

Electroless displacement of cobalt by copper during Cu-Co nanomultilayers preparation

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In the present work, the quantification of the displacement reaction between Co and Cu²⁺ was studied. With the majority of electrolytes, the reduction potential of Cu²⁺ is higher than the oxidation potential of Co. Consequently, if metallic cobalt is in presence of cupric ions an electroless displacement may occur through the chemical reaction: Cu²⁺ + Co → Cu + Co²⁺. Our experimental results correspond first to cobalt electrodeposits immersed in copper solution for different times and secondly to the preparation of copper-cobalt alloys nanomultilayers by pulsed polarization.

According to the pH, differences of compartment and morphology (observed by A.F.M.) were observed for immersing times larger than 5 minutes.

The use of a quartz micro-balance as cathode allows obtaining the mass variation of electroless deposit versus time. The mass increases during the first minutes of immersing, then stops for pH 2, meaning the interruption of chemical displacement. The rate of this reaction could be calculated by the equation 1

$$R = \Delta m / \Delta M \quad (1)$$

In which, R is the rate reaction (mol.s⁻¹.cm⁻²), Δm the mass variation of quartz per time unit (g.cm⁻².s⁻¹) and ΔM the difference between the copper atomic weight and the cobalt atomic weight (*i.e.* to 4.62 g.mol⁻¹). The evaluation of displacement rate for the first minute gives 2.8*10⁻⁹ mol.s⁻¹.cm⁻².

The analysis of Co²⁺ concentration (using absorption atomic) in the copper solution was measured after different times of immersion. A linear increasing of cobalt concentration appears for the first 30 seconds of immersion. The chemical rate calculus to this point gives 3.1*10⁻⁹ mol.s⁻¹.cm⁻².

In manner to be realist, the rate reaction value must be in accordance with the diffusion of Cu²⁺ ions. So, we have to compare this value with that obtained from electrochemical measure. The use of faraday law (equation 2) allows us to calculate the electrochemical rate.

$$j t = n F N \quad (2)$$

In which, j is the current density (A.cm⁻²), t the time (s), n the involved electron number, F the faraday constant and N the number of reduced copper mole per cm⁻².

With the limiting current value collected during copper electrodeposition (0.6 mA.cm⁻²), we find that the maximum of chemical displacement rate is 3.1*10⁻⁹ mol.s⁻¹.cm⁻². Consequently, our values obtained with the quartz microbalance (2.8*10⁻⁹ mol.s⁻¹.cm⁻²) and with absorption atomic measures (3.1*10⁻⁹ mol.s⁻¹.cm⁻²) are plainly compatible with an electroless displacement controlled by diffusion process.

At last, we have realized Cu-Co alloys multilayers by pulse polarization and the results exhibits that the electroless displacement is diffusion controlled during the first seconds. So, it may be negligible for 100 nm

layers but it may represent the half of one layer for thickness around 1 nm. These results were plainly in accordance with the displacement results from others studies [1-4].

1. S. Roy, M. Matlosz and D. Landolt, J. Electrochem. Soc., **141** (1994) 1509.
2. J. J. Kelly, P. E. Bradley and D. Landolt, J. Electrochem. Soc., **147** (2000) 2975.
3. J. J. Kelly, P. Kern and D. Landolt, J. Electrochem. Soc., **147** (2000) 3725.
4. D. M. Tench and J. T. White, J. Electrochem. Soc., **139** (1992) 443