

Influence of pH Solution on Electroless Copper Plating Using Sodium Hypophosphite as Reducing Agent

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Received: 5 November 2011 / *Accepted:* 3 February 2012 / *Published:* 1 March 2012

The effect of pH solution on the electroless deposition of copper-rich Cu–Ni–P alloys, using hypophosphite as reducing agent, has been carried out. The deposition rate increased obviously with the increase of pH. The surfaces morphology, the roughness and the cristallinity depend many of pH. The kinetics of copper electroless was investigated by means of cyclic voltammetry and electrochemical impedance spectroscopy. The shape of voltammograms and impedance diagram depend also of the pH solution.

Keywords: Electroless, Copper, pH, Surfaces morphology, Cristallinity

1. INTRODUCTION

The copper plating has been widely used as interconnect materials for ultra large scale integration (ULSI) technology due to its low resistivity and high electromigration resistance [1,2]. The electroless deposition of copper is one of major process steps involved in electronic packages for the computer industry. It is also used for various metallization processes such as carbon nanotubes or hollow metal spheres [3,4].

Electroless copper plating as a non-electrolytic method of deposition from solution has been studied by some researchers [1-9]. Traditional electroless copper plating solutions often use formaldehyde as the reducing agent because of its low cost and the high quality of the deposit [10]. However, when formaldehyde is used as the reductant, the plating solution should have a high pH value [11]. Thus, some plating materials cannot be used along with formaldehyde because of the alkaline corrosion of the electrolyte. In addition to that, formaldehyde is a volatile toxic compound and the plating solution is easily decomposed. Therefore, non-formaldehyde electroless copper plating is preferred. Currently, glyoxylic acid [12–13], hypophosphite [5, 14-16], sodium bisulfate (NaHSO₃)

and the sodium thiosulfate pentahydrate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) [17], Co(II) [18], Fe(II)[19], borane-dimethylamine complex [20,21], etc, have been developed as substitutes for formaldehyde. Among these, the plating process using hypophosphite as the reductant has attracted considerable attention due to its low price, good bath stability, and relatively easy to control plating conditions. It may replace the formaldehyde electroless copper plating and may be applied in industries. However, the main difficulty results from the fact that the oxidation of hypophosphite is not catalyzed by copper [16, 22-24]. In alkaline solutions, this drawback is overcome by using additional catalysts, such as organic compounds or small amounts of mediators such as Ni^{2+} or Pd^{2+} ions [16, 23-24]. In acid solutions, several difficulties still remain, especially a low deposition rate due to slow oxidation of hypophosphite at these pH and the corrosion of the deposited copper layer [24]. So far, mainly Ni–Cu–P alloys have been obtained; however, high nickel contents reduce the conductivity of the layers [25, 26]. In the present work, the influence of pH on electroless copper plating using sodium hypophosphite as reducing agent is developed. The effect of solution pH on the plating rate, composition, morphology and structure of coatings are investigated. The voltammetric investigation and electrochemical impedance spectroscopy of the effect of pH are also realised.

2. EXPERIMENTAL WORK

A 200 ml cell thermostated was used. The substrates were iron plates ($S=3\text{cm}^2$), mechanically polished down to 1200 SiC paper, degreased in acetone, etched in 10% dilute sulfuric acid and rinsed with water, prior to the experiment. The deposition rate was estimated from the weight gain after a given immersion time (1–2h). The electrochemical measurements were carried out with a potentiostat (VoltaLab model PGZ100). The reference electrode was a saturated calomel electrode with all potentials referred. The morphology of the deposits was examined by scanning electron microscopy (SEM), the composition was estimated by EDX analysis, whereas the crystalline structure was determined by X-ray diffraction using a cobalt anticathode.

The electrolytes were made up of analytical grade chemicals. The solutions contained sodium hypophosphite as reducing agent, nickel sulfate and copper sulfate. Sodium citrate and ammonium acetate (or ammonium chloride) were added as complexing agents (Table 1). After the addition of all constituents, the solution pH is in the order of 6,8. It is adjusted by acetic acid or by ammonia in the range 5-9. The electrolytes were held at 78 ± 2 °C.

Table 1. Composition of the solutions, which contain in addition 0.081M $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 0.28M NaH_2PO_2 , H_2O and 0,3M $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$.

Electrolyte	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ M	$\text{CH}_3\text{CO}_2\text{NH}_4$ M	NH_4Cl M	pH
1	0.0016	1	0	5
2	0.002	1	0	5
3	0.0032	0	1	5

3. RESULTS AND DISCUSSION

3.1. Effect of solution pH on the rate deposition and the plating composition

The solution pH is a very important factor in the electroless deposition, indeed, it affects both anodic and cathodic reactions and various phenomena associated with the structure and composition of the metal-solution interphase. The major phenomena include; adsorption, potential zero charge, structure of the double layer, structure of ions species in the solution and the ionic strength of the solution. All these phenomena affect the rate of electroless copper deposition [27]. The influence of the solution pH, using bath 3, on the plating rate and the plating composition is shown in fig 1 and fig 2. The plating rate increases remarkably from 2 to 6.5 $\mu\text{m}/\text{h}$ when the solution pH increases from 5 to 9, this behavior can be justified by the effect of pH on the anodic reaction [22]. In our studies on the deposit of alloy Ni-P alloy in ammoniacal medium [28], we showed that in anodic range, a chemical reaction precedes charge transfer. This is a deprotonation reaction which can be written as:



The increase of pH solution enhances reaction (1) which supports the anodic process. In addition to that, the anodic oxidation of hypophosphite is the dominant factor in electroless deposition [22,29].

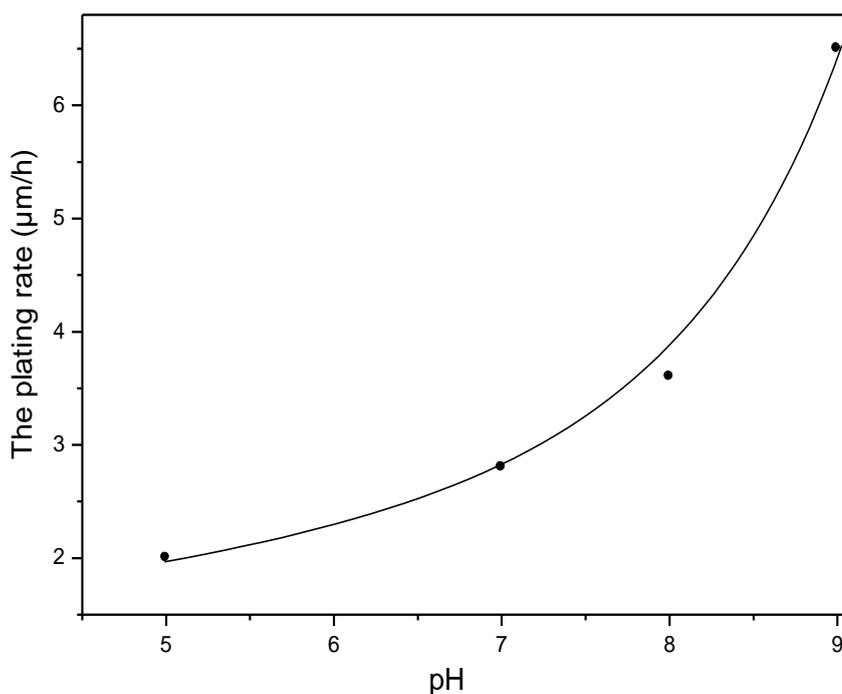


Figure 1. The effect of pH on the plating rate (Bath 3: 0.0032M Cu^{2+} , 0.081M Ni^{2+} , 0.3 M cit, 1 M NH_4Cl , 0.28M NaH_2PO_2 and $T = 78^\circ\text{C}$).

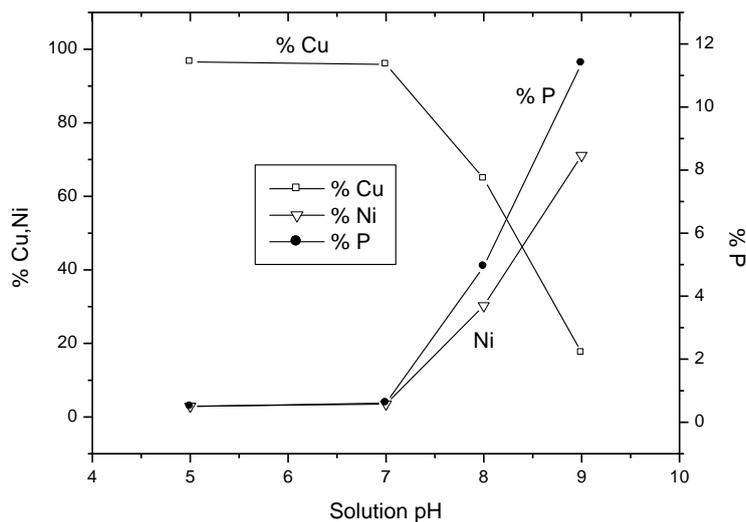


Figure 2. The effect of pH on the plating composition (Bath 3: 0.0032M Cu^{2+} , 0.081M Ni^{2+} , 0.3 M cit, 1 M NH_4Cl , 0.28M NaH_2PO_2 and $T = 78^\circ\text{C}$).

The content of both nickel and phosphorus increases and the content of copper decreases with the increasing of solution pH [15,30]. We note that in the pH range 7-9, the Cu content decreases significantly. This behavior can be justified by the change of the nature of the complex formed by Cu^{2+} with pH. In the pH range 4-10, the complex formed between citrate and Cu^{2+} is the dimer $[\text{Cu}_2\text{cit}_2]^{4-}$ [31]. Cu^{2+} forms also heteronuclear citrate complexes with Ni^{2+} . The most important among the formed compounds is the complex of the type $[\text{CuNicit}_2]^{4-}$ equivalent to the dimeric complex $[\text{Cu}_2\text{cit}_2]^{4-}$ in which one of the Cu^{2+} ions has been replaced by Ni^{2+} [32,33]. Ewa Beltowska-Lehman have also shown that in the pH range 6-8, the inert heteronuclear complex $[\text{CuNi}(\text{cit})_2]^{4-}$ is formed [34]. In our case, the decrease of the copper content may be due to rising solution pH, needs excess of ammonia solution addition, which is a kind of ligand that is able to form a good complex with Cu^{2+} , which decreases the free Cu^{2+} in the deposition boundary layer.

3.2. Effect of solution pH on the surface morphology and structure

The surfaces morphology of the deposits obtained from bath 3 at pH=5, and 9 was studied by means of Scanning Electron Microscopy (Fig 3). At pH=5, the micrograph shows that the copper deposit was nodular and the topography was rough. Moreover, the growth of this layer is perpendicular on the layer surface; this behavior is met in the case of plating controlled by the phenomenon of diffusion, which confirms that copper is discharged under diffusion control. The roughness and the porosity of the deposits decrease when the solution pH is raised from 5 to 9 and the copper content decreases remarkably from 97 wt% to 17.5 wt%. Furthermore, the morphology becomes nodular and compact because of high nickel content in the matrix.

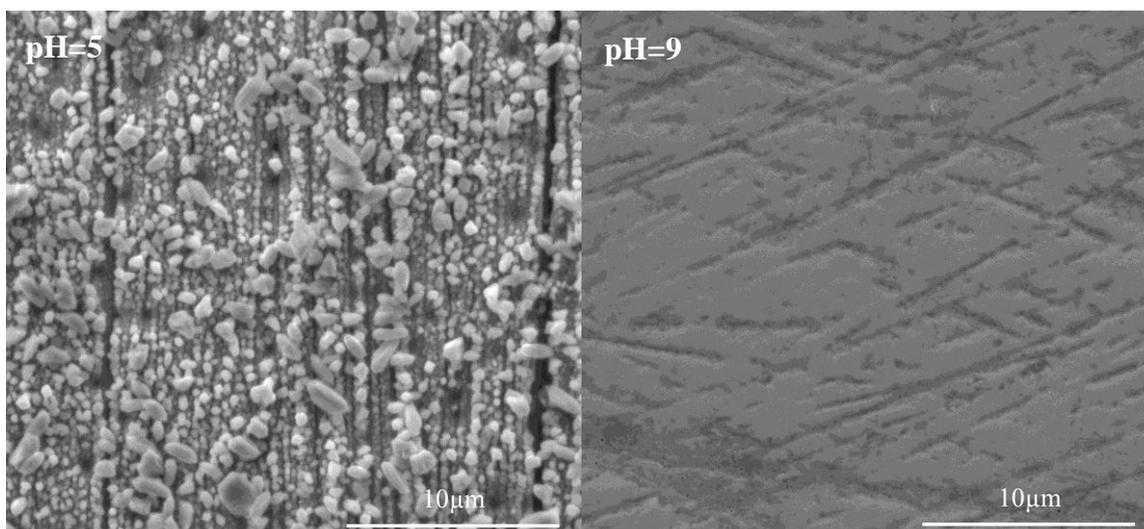


Figure 3. The effect of pH on the surface morphology (Bath 3: 0.0032M Cu^{2+} , 0.081M Ni^{2+} , 0.3 M cit, 1 M NH_4Cl , 0.28M NaH_2PO_2 and $T = 78^\circ\text{C}$).

The XRD patterns of the films deposits obtained at different pH solution are shown in fig 4. At pH 5, nearly pure copper (Ni-97Cu-0.5P) is deposited and also as shown in fig 4, it has a crystalline structure. When the pH solution increases from 5 to 9, we note that the peak broadness increases successively compared with the peak obtained at pH 5 and the Ni-17.5Cu-11.4P deposit is thought to be amorphous. This can be due to the increase of the phosphorus content from 0.5 to 11.4 wt% in the matrix. Indeed, it has been previously shown that the phosphorus content controls the structure of the Ni-Cu-P deposits, and the lower P deposits are crystalline, however they become amorphous once the phosphorus content is higher than 7 wt% [35, 36].

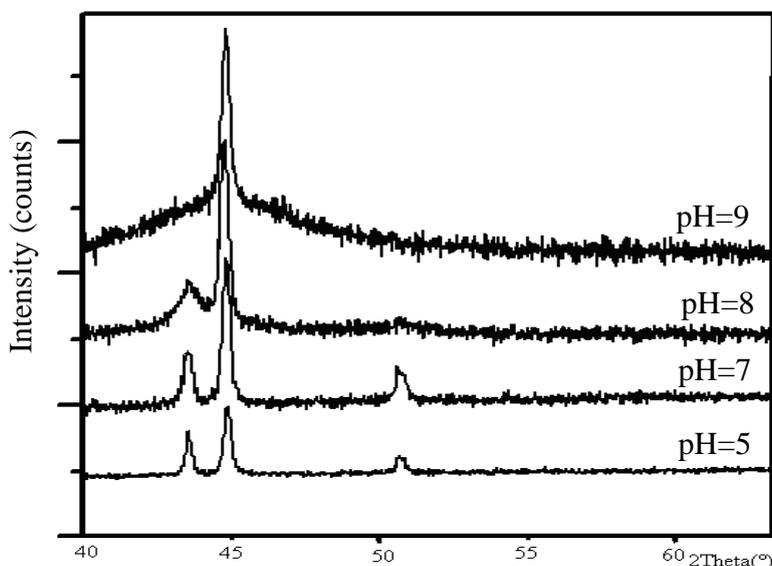


Figure 4. The XRD analysis of the Ni-Cu-P deposit obtained with various pH solution. (Bath 3: 0.0032M Cu^{2+} , 0.081M Ni^{2+} , 0.3 M cit, 1 M NH_4Cl , 0.28M NaH_2PO_2 and $T = 78^\circ\text{C}$).

3.3. Polarization behaviour

It is well known that the autocatalytic deposition of metals or alloys usually result from two half reactions: anodic oxidation of the reducing agent, here sodium hypophosphite, and the cathodic discharge of the metals. However, interactions often occur between these reactions [37, 38]. Cyclic voltammetry was carried out to characterize the effect of pH solutions on various redox processes. Fig 5 shows the voltammograms recorded at pH 5, 7, 8 and 9 (Bath 3). These voltammograms reveal the existence of:

- A cathodic peak K representing the reaction of reduction of Ni^{2+} , Cu^{2+} , H_2PO_2^- and H_3O^+ ions.
- A landing D, relating to the diffusion of ions Cu^{2+} .
- An anodic peak A located at -750 mV/s relating to the oxidation of H_2PO_2^- ions and hydrogen atoms adsorbed to the surface of the electrode.
- Two peaks B (at -100 mV) and C (at 250 mV) relating to the dissolution of the Ni–Cu–P deposit. According to literature, the first peak represents the dissolution of the crystalline phase of alloy, and the second one represents the dissolution of the amorphous phase [30].

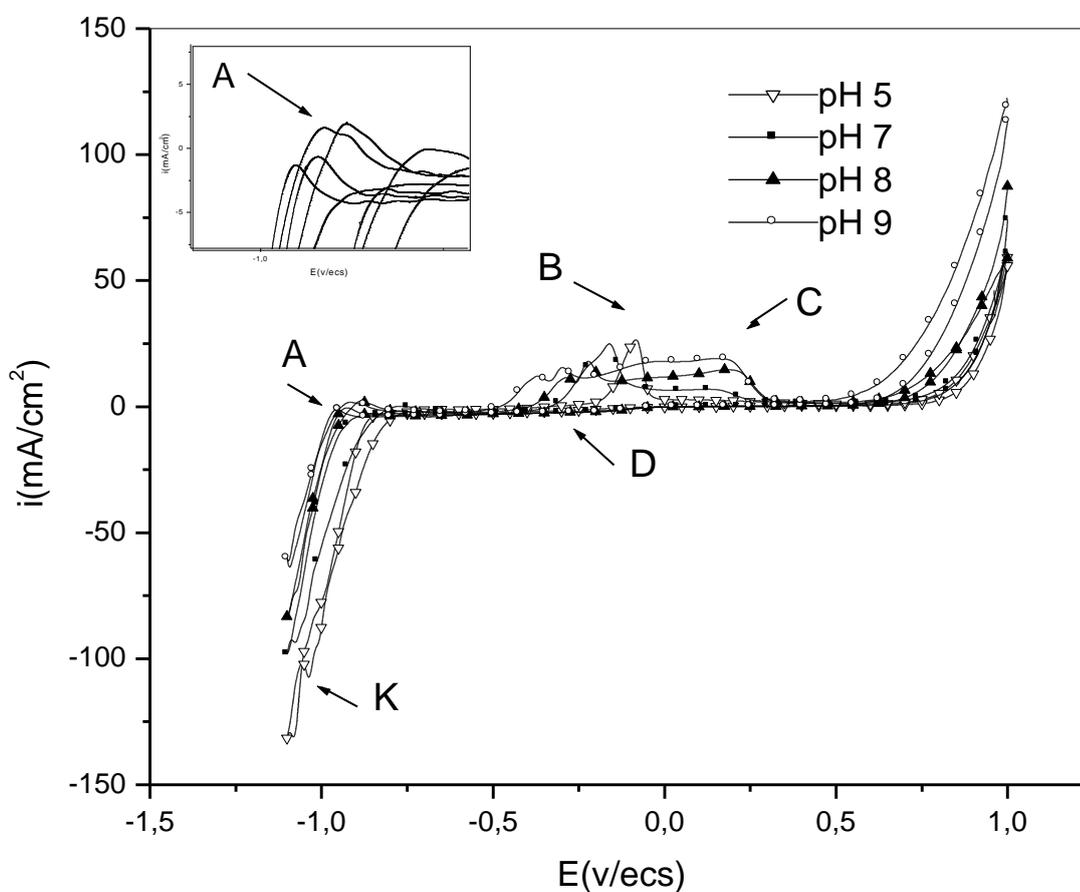
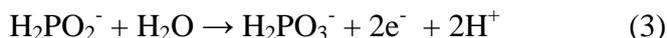


Figure 5. Cyclic voltammogram recorded on glassy carbon electrode from bath 3 (Table 1) at pH 5,7,8 and 9. Scan rate 10 mVs^{-1} .

In the anodic range (peak A), the polarization curves exhibit a maximum [22,37]. This indicates that the oxidation of hypophosphite is hindered by the adsorption of some species [22,29,39]:



The figures 6 and 7 show the evolution of the peaks intensities I_K , I_A , I_B and I_C according to the solution pH. The analysis of these figures shows that, when the pH increases, the peak intensity I_K decreases because of the inhibition of the H^+ ions reduction, and the peak intensity I_A increases, this confirms that the increase of the solution pH favors the oxidation of the hypophosphite.

The peak intensity I_B decreases, whereas the peak intensity I_C remarkably increases. Moreover, we showed previously that the increase of the pH solution acts on the structure and the copper content in the matrix. Indeed, at pH 5, the copper content is 97 wt% and has a crystalline structure: I_B (relating to the dissolution of the crystalline phase of copper-rich Cu-Ni-P alloy) \gg I_C (relating to the dissolution of the amorphous phase of Cu-Ni-P). But, at pH 9, the copper content is 17.5 wt% and the structure becomes amorphous as a result: $I_C \gg I_B$.

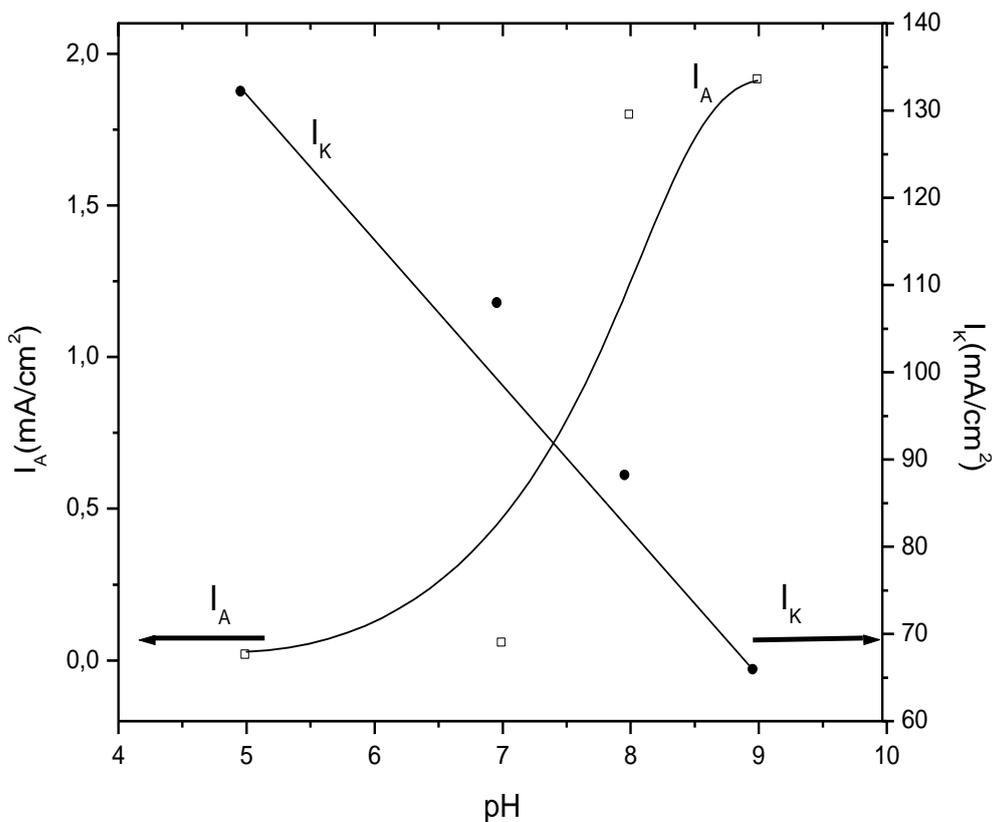


Figure 6. Deposition current, I_K , at upper cathodic limit and anodic peak current, I_A , as a function of pH solution.

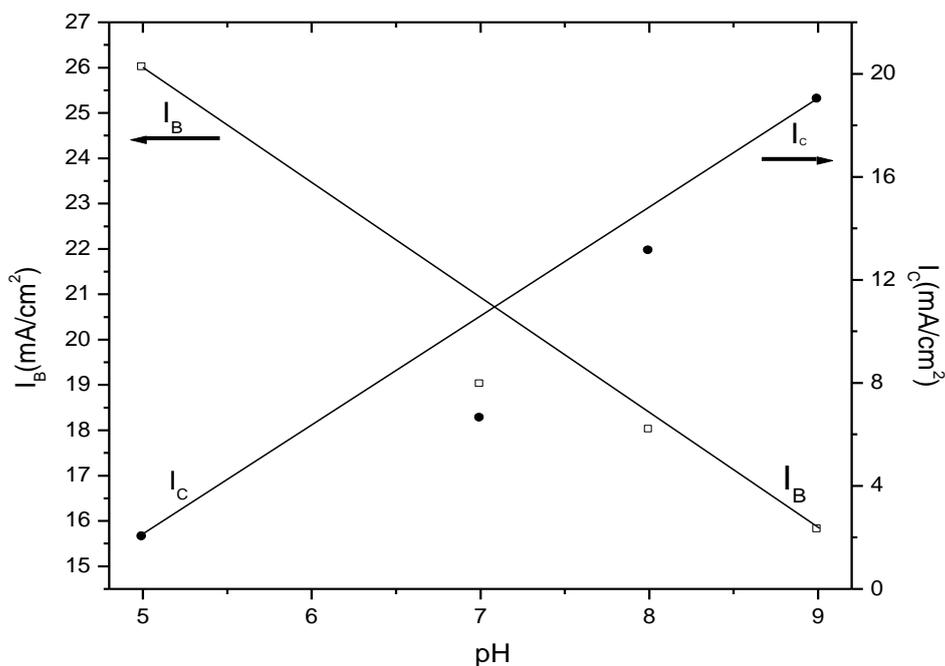


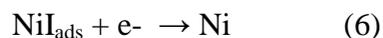
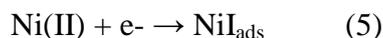
Figure 7. Evolution of the currents, I_B , the Ni–Cu–P crystalline phase and the Ni–Cu–P amorphous phase, I_C , as a function of pH solution.

3.4. Impedance behavior

The deposition potential is characterized by a net current equal to 0, resulting from two simultaneous anodic (oxidation of hypophosphite) and cathodic processes (reduction of nickel species and hypophosphite, and evolution of hydrogen). Figure 8 shows typical impedance diagrams recorded at the plating potential, for various pH values (Bath 3). At pH=8, we obtain a characteristic impedance diagram of an alloy Ni-Cu-P [30]. This diagram presents:

- In the high frequency domain, a capacitive loop appears which is related to the relaxation of the double layer capacitance whose value is $80 \mu\text{Fcm}^{-2}$, in parallel with the charge transfer resistance R_t .

- An inductive loop appears with a characteristic frequency around 5Hz. This effect is more visible when the nickel content is increased (impedance diagrams recorded at pH=9, Fig 8). A similar inductive feature is observed in the deposition of nickel and attributed to the two-step discharge of the Ni^{2+} species through the intermediate NiI_{ads} adion [37,38,40-42]:



- A capacitive loop appears in low frequency. The size of this effect increases when the content of copper increases (impedance diagrams recorded at pH=5, Fig 8). It is linked to the discharge of copper which is controlled by mass transport [22,33].

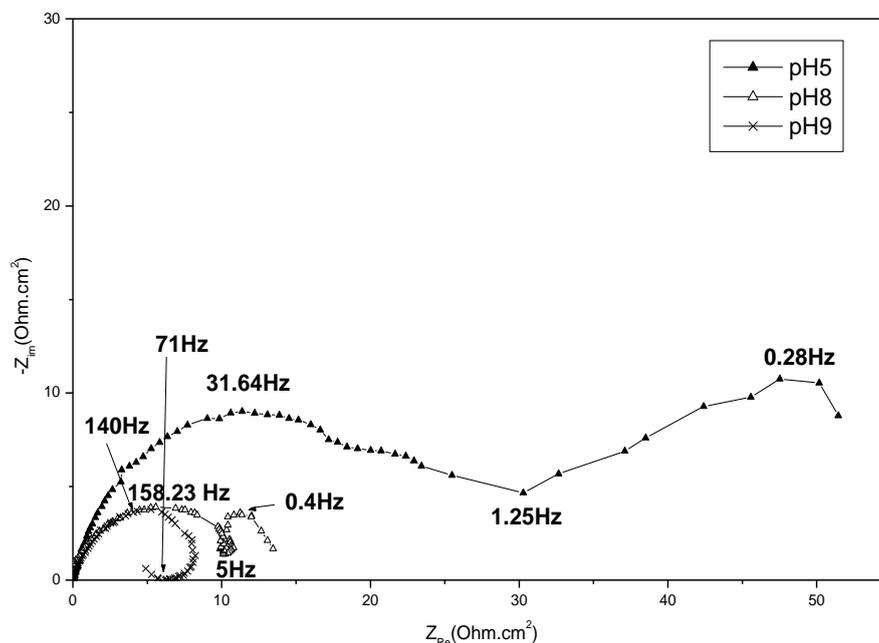


Figure 8. Electrochemical impedance plot recorded from bath 3 (Table 1) at three solutions pH ($\Omega=100$ tr/mn).

4. CONCLUSION

In this present work, we have investigated the influence of pH on electroless copper plating using hypophosphite as reducing agent. The deposit composition and the deposition rate depend strongly on the pH solution. The investigations carried out by XRD and SEM show that the pH of the solution influences the surface morphology and structure of deposits. The electrochemical investigation shows that the pH solution acts on the anodic and cathodic reactions. In addition, cyclic voltammetry confirms the evolution of the crystallinity of the alloy with pH.

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