

Effect of operatories parameters and elements composition of bath on the electroless copper deposition

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Abstract

The effect of operatories parameters and elements composition bath on deposition rate of electroless copper plating obtained from hypophosphite was investigated. It is found that the deposition rate increased significantly with increasing of nickel ions, acid boric and hypophosphite ions concentration and with pH value. Indeed, it is noted also that the deposition rate depend with temperature and the copper ions concentration. SEM/EDX analysis of the optimum bath showed that the deposit is generally homogeneous and presents a nodular structure and its composition contains 94.64 wt % of copper element and 5.36 wt% of nickel element. The XRD diffraction pattern of the film deposit showed that the deposit has a crystalline structure. So, the copper film with a higher (111) texture is preferred due to its higher reliability against electro-migration and lower electrical resistance.

Keywords: *Operatories parameters effect; Electroless copper plating; deposition rate; SEM/EDX; XRD.*

1. Introduction

The copper plating is 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 copper deposition 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 nano-tubes or hollow metal spheres [3,4]. Electroless copper plating as a non-electrolytic method of deposition from solution has been investigated by some researchers [1-9]. So, traditional electroless plating uses formaldehyde or its derivatives as reducing agent, two main

drawbacks: firstly, formaldehyde is mainly efficient for pH values above 11 [10, 11]. Secondly it was as hazardous to health, volatile, flammable and possibly carcinogen liquid. For these, many electroless copper solutions used non-formaldehyde reducing agents such as glyoxylic acid [12–13], hypophosphite [5, 14–16], sodium bisulfate (NaHSO_3) 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... Among them, sodium hypophosphite was especially attractive because of its low cost, good bath stability and relatively easy to control plating conditions. 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 was 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]. Therefore, high nickel contents reduce the conductivity of the deposits [25, 26]. In the present work, we investigated the effect of various parameters operators and the ions concentration of elements composition bath on the deposition rate of electroless copper deposition using hypophosphite as reducing agent.

2. Experimental procedures

All solutions used through these experiments were freshly prepared from analytical grade reagents and distilled water.

The composition and operating conditions of the plating bath are listed in Table 1. This bath contained copper and nickel sulfate as a copper and nickel ions sources, sodium hypophosphite as a reducing agent, sodium citrate as a complexing agent, and boric acid as an additive. The pH was adjusted by sodium hydroxide in the range 8.5 - 10 and the temperature was adjusted in the range $65 - 85 \pm 2^\circ\text{C}$.

The electrolysis cell was a borrosilicate glass (Pyrex[®]) cylinder closed by cap with five apertures. The investigated plate's area of the iron surface was 6 cm^2 . Prior to immersion test, the substrate was abraded using emery paper up to 1200 grade, cleaned with acetone, etched in 10 % dilute sulfuric acid, washed with distilled water, and dried finally. The deposition rate was estimated from weight gain after 30 min of immersion time.

The morphology of the deposits was examined by scanning electron microscopy, the composition estimated by EDX analysis and the crystalline structure by X-ray diffraction using a cobalt anticathode.

For the cyclic voltammetry measurements, glassy carbon as working electrode, Pt plate as the counter while a saturated calomel electrode (SCE) was used as the reference electrode. All potentials are referred with respect to this last electrode.

The polarization curves were recorded by polarization from 10 mV/SCE towards more negative direction (-1200 mV/SCE) with a sweep rate of 10 mV/s . These measurements were carried out using Potentiostat/Galvanostat/Voltalab PGZ 100 monitored by a personal computer.

Table 1. Based bath composition and operating conditions of copper electroless deposition.

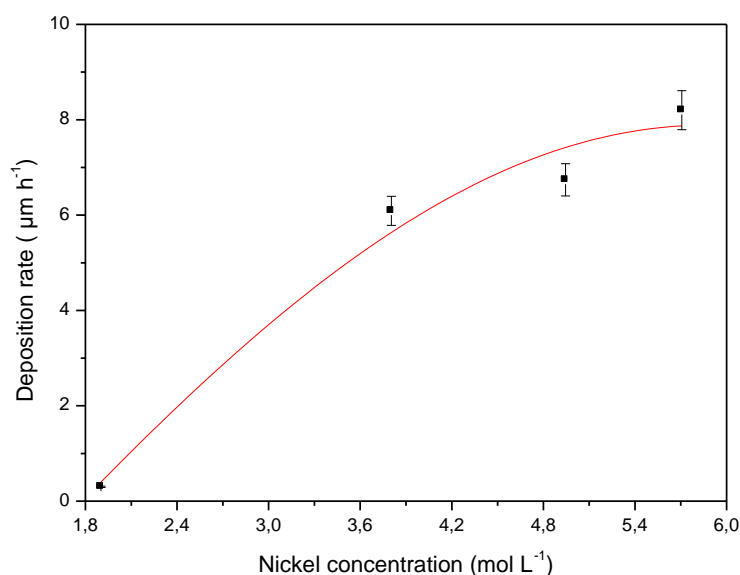
Bath composition and operating conditions	Values
NiSO ₄ ; 6H ₂ O	5.7 mM
CuSO ₄ ; 5H ₂ O	24 mM
NaH ₂ PO ₂ ; H ₂ O	0.28 M
C ₆ H ₅ Na ₃ O ₇ ; 2H ₂ O	0.1 M
H ₃ BO ₃	0.48 M
pH	9.1
T	70 °C

3. Results and discussion

3.1. Effect of bath composition element on the deposition rate

a. Effect of nickel ions concentration

Generally, the electroless copper deposition process using hypophosphite as reducing agent is more complicated than formaldehyde-based bath because copper is not a good catalyst for the oxidation of hypophosphite. For this, a small amounts nickel ions were added to the bath because it is served to catalyze the oxidation of hypophosphite enabling continuous copper deposition [27-30]. In addition, when the nickel ion concentration in the bath is low, the deposition rate of the copper plating decreases with time and finally stopped because the surface catalytic activity was not replenished. Higher nickel ion concentration causes lower solution stability and increases the nickel content in the deposit, resulting in higher deposit resistivity. Thus, it was necessary to maintain the nickel ion concentration above a critical value in the bath to sustain the deposition rate.

**Figure 1.** Effect of nickel ions concentration on deposition rate

The effect of nickel ion concentration on the deposition rate is presented in Figure 1. It is shown that the deposition rate increases remarkably nickel ions concentration. This behavior can be justified by the increase in the nickel content in the deposit improving the surface catalytic activity for the oxidation of hypophosphite such as mentioned in Figure 2. Furthermore, a lower nickel ion concentration than 38 mM, a thin layer of copper deposit was obtained and then electroless plating was stopped. Therefore, 38 mM value is the critical point of nickel ion concentration in the plating solution. In the author hand, Honma et al. [30] were reported that the optimum mole ratio between copper and nickel ions was approximately 13:1. However, it is shown that the voltammograms presented in Figure 2, 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 -900 mV/SCE , which is observed only in the presence of Ni^{2+} ions in the bath, relating to the oxidation of H_2PO_2^- ions and hydrogen atoms adsorbed to the surface of the electrode,
- Tree peaks B (at -270 mV/SCE), C (at -100 mV/SCE) and E (180 mV/SCE) relating to the dissolution of the Cu-Ni deposit.

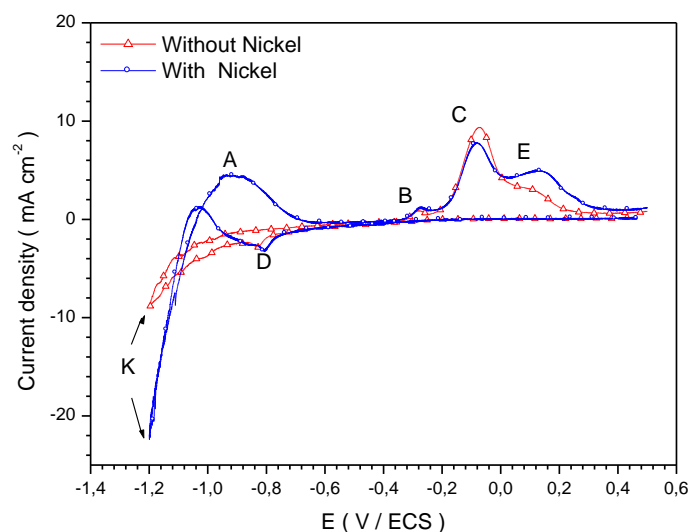


Figure 2. Cyclic voltammogram recorded on glassy carbon electrode in the absence and presence of nickel ions ($\text{pH} = 9$. Scan rate 10 mVs^{-1})

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 [31-32]. Some authors have studied the copper behavior by the cyclic voltammetric in alkaline solution, they have observed the appearance of tree anodic peaks, the first anodic peak corresponds to the oxidation of Cu to Cu_2O film formation, the second and third peaks are attributed the anodic formation of CuO/Cu(OH)_2 mixture film via the oxidation of Cu_2O film [33, 34]. Thus, the

both peaks C and E can be relating to the dissolution of the amorphous phase in the two stages. In comparison, the anodic peak A represent the hypophosphite oxidation in only observed in the presence of the Ni^{2+} ions in the electrolyte. This indicates that some Ni^{2+} ions were reduced and co-deposited with copper on the deposit then catalyzed the hypophosphite oxidation at - 950 mV/SCE

b. Effect of boric acid concentration

The effect of boric acid concentration on the deposition rate is shown in Figure 3. It is remarked that the deposition rate increases exponentially with boric acid concentration. In addition it is noted that when the concentration of boric acid is less than in 0.32 M the process of deposition was stopped in some minutes. So, the visual aspect of deposits obtained in the presence of boric acid at 1.13 M showed that the nickel content was improved than that obtained at 0.32 M.

However, a study [16] realized by cyclic voltammetry on the effect of boric acid concentration on the electroless copper plating process showed that its presence increased the hypophosphite oxidation current density and shifted the reduction potential of copper and nickel to anodic potential. It is predicted also that in alkaline solution polymeric ions of boric acid may enhance the electron transfer reaction [35-36]. Furthermore, boron has been detected by electron spectroscopy for chemical analysis (ESCA) in the nickel coating using boric acid and hypophosphite as reducing agent at pH=9 [37]. Therefore, it is speculated that a trace amount of boric acid may co-deposit with nickel as Ni-B alloy, which has lower energy state than pure nickel. Hence, the reduction potential of Ni-B alloy is higher (less negative). Then, the effect of boric acid is: (i) to improve the nickel reduction; (ii) to promote catalytic activity of nickel deposit on hypophosphite oxidation affecting its oxidation [16].

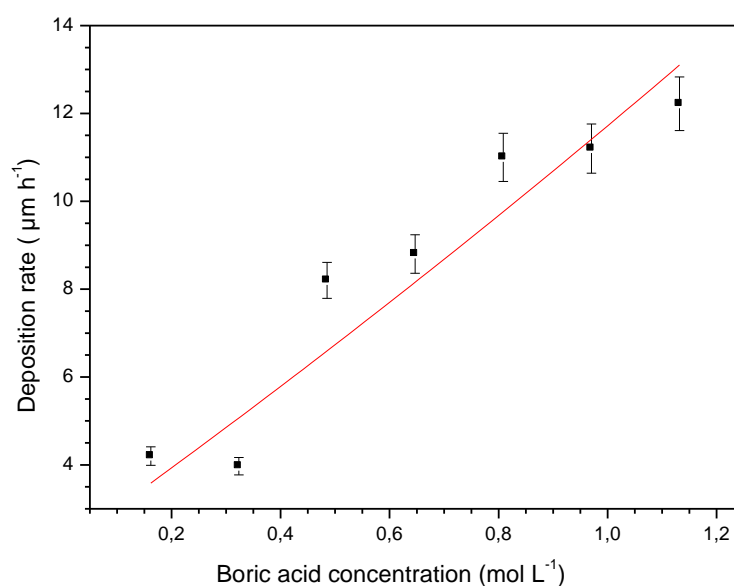


Figure 3. The effect of boric acid concentration on deposition rate

c. Effect of copper ions concentration

The effect of copper ions concentration on the deposition rate is presented in Figure 4. It can be remarked that this curve subdivides to two parts. The first, when the copper ions concentration increases from 7.5 to 32 mM, the deposition rate increases obviously from 3 to $8.8 \mu\text{m h}^{-1}$. This behavior can be justified by the increase of the free quantity of copper ions in solution. The second, when the copper ions increase from 32 to 47.5 mM, the deposition rate decreases and becomes $2 \mu\text{m h}^{-1}$. This can be explained by the increase of copper content in deposits [5] causing the reduction of nickel active sites in the surface deposit. Therefore, at 32 mM of copper ions concentration the deposition rate reaches its maximum $8.8 \mu\text{m h}^{-1}$. This result demonstrated that the copper does not catalyze the hypophosphite oxidation such as mentioned by the cyclic voltammetry study (Figure 2).

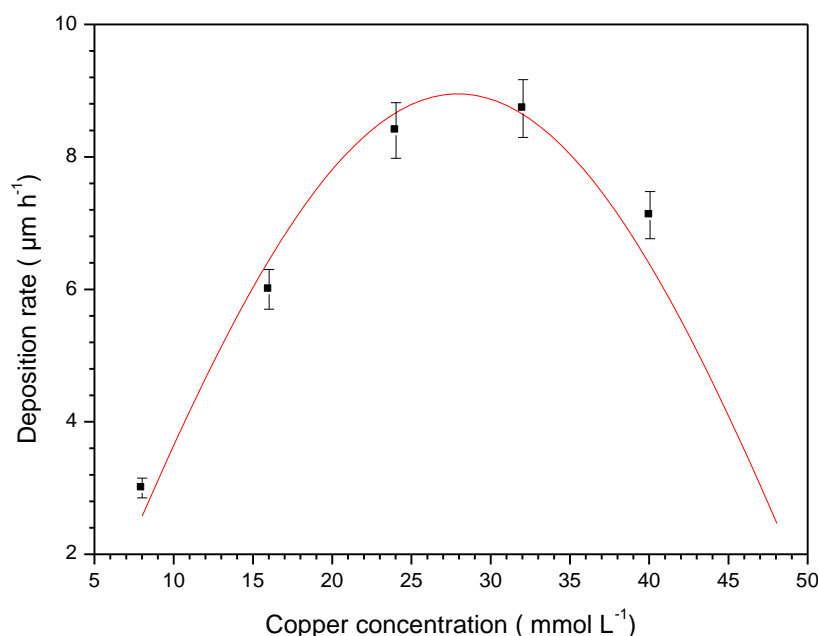


Figure 4. Effect of copper ions concentration on the deposition rate

d. Effect of citrate ions concentration

Due to the large difference on the deposit potentials of nickel and copper ions, the complexing agents were necessary for their co-deposition. Tri-sodium citrate is the most widely used as complexing agent [15, 16, 23]. Figure 5 shows the concentration effect of this agent on the deposition rate. It can be noted that the citrate ions concentration has a great effect on the deposition rate. Thus, when the citrate ions concentration increases from 0.034 to 0.17 M the deposition rate decreases from 16.3 to $2 \mu\text{m h}^{-1}$. This can be explained that the citrate ions are a good complexing agent for copper and nickel ions reducing their free quantities in the solution. Consequently, the citrate ions control the deposition rate.

Other study was realized on the copper-citrate ions distribution with the citrate ions concentration varying from 0 to 0.1 M and the total copper concentration at 0.025 M. the pH and temperature were fixed at 5 and 25 °C, respectively. It is found that when the citrate ions concentration is lower ($< 0.025\text{M}$), the free copper ions and $\text{Cu}_2\text{Cit}_2\text{H}_1$ are dominants. When the citrate is in excess ($> 0.025\text{M}$), the free copper ions are completely missing and the $[\text{Cu}_2\text{Cit}_2\text{H}_1]^{3-}$ and $[\text{Cu}_2\text{Cit}_2\text{H}_2]^{4-}$ are the dominant complexes [38].

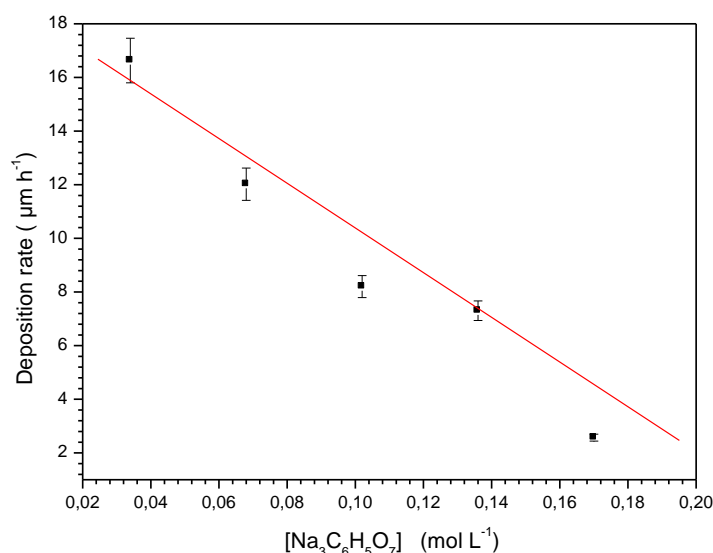


Figure 5. Effect of tri-sodium citrate ions concentrations on deposition rate.

d. Effect of hypophosphite ions concentration

The effect of the reducing agent concentration on the deposition rate is shown in Figure 6. It is observed that the deposition rate increases from 8 to 14 $\mu\text{m h}^{-1}$ with the increases of H_2PO_2^- concentration from 0.18 to 0.55 M. this can be explained by the increase in the electron result from the hypophosphite oxidation.

Other study on the hypophosphite concentration effect on the deposition rate was investigated. It is found that the deposition rate increased firstly and reached a maximum, and then decreased with hypophosphite concentration [39]. The same results were obtained in the case of electroless Co-P [40], Ni-B [41] and Fe-B [42] deposits. In addition, Shrivastava et al. [43] studied the effect of dimethylamine-borane (DMAB) concentration, as a reducing agent, on the deposition rate of a Ni-B coating. They found also a maximum of the deposition rate at a critical concentration of DMAB.

Another study was realized by cyclic voltammetry for various hypophosphite concentrations on the Ni-P deposition process. It is shown that the hypophosphite oxidation peak was observed at 0.1M of hypophosphite concentration. It is noted also that the peaks intensities I_A and I_K (at upper cathodic limit) increased linearly with hypophosphite concentration [44]. These results indicated that hypophosphite has a marked effect on the anodic and cathodic

process. Indeed, it is found that the hypophosphite enhanced the nickel discharge and eventually hydrogen evolution for Ni-Cu-P deposition [45].

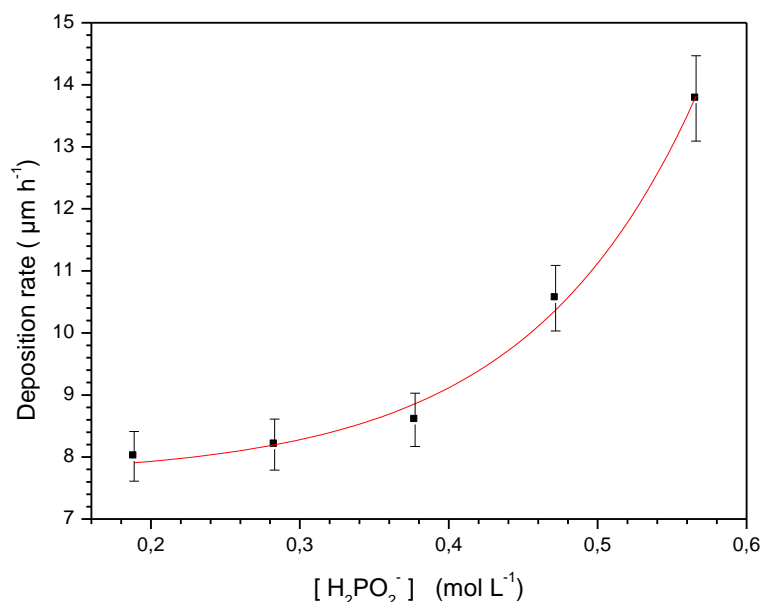


Figure 6. Effect of hypophosphite ions concentration on deposition rate

3.2. Effect of operatories parameters on the deposition rate

a. Effect of the pH of solution on the deposition rate

The pH of solution is a very important factor in the electroless deposition process. Indeed, it affects both anodic and cathodic reactions and various phenomena associated with the structure and composition of metal/solution interface. The major phenomena include; adsorption, potential zero charge, double layer structure, structure of ions species in the solution and the ionic strength of the solution. All these phenomena affect the deposition rate of electroless copper deposition [46]. The effect of the pH of solution on the deposition rate is shown in Figure 7. It is remarked that the deposition rate increases remarkably from 5 to 9 μm h⁻¹ with the increase of solution pH from 8.5 to 10. A similar evolution was observed previous studies on electroless Cu- Ni-P [5, 47] and copper [5, 32] plating. This behavior can be justified by the effect of the pH of solution on the anodic reaction [22]. In our previous studies on the electroless Ni-P deposit in ammoniacal medium [44], we showed that in the 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, the anodic oxidation of hypophosphite is the dominant factor in electroless deposition [22, 48].

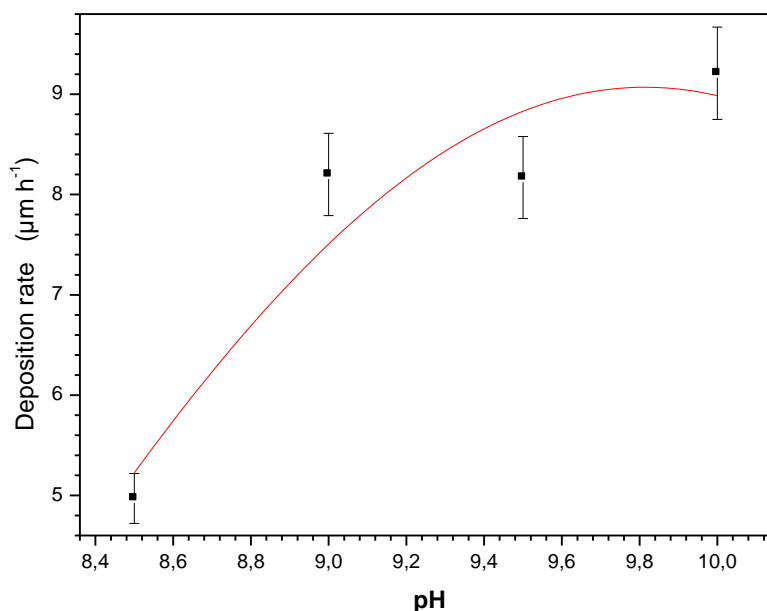


Figure 7. Effect of solution pH on deposition rate

b. Effect of the electrolyte temperature

Generally, the temperature of electrolyte affects the physical and chemical proprieties of electroless process. So, a study realized on the electroless Ni-P deposition showed that when the electrolyte temperature increases from 60 to 80 °C, the nodule size of the Ni-P layer increases, the deposit becomes more compact and the phosphorus content in the deposits improves [49]. Also, it is noted that at higher temperature, the microhardness of Ni-P deposits has higher values. This is attributed to the changes in the deposit structure and becomes more crystalline and the hardness increases [50].

The deposition rate versus reciprocal temperature is can be expressed by the Arrhenius law:

$$v_{\text{deposit}} = K \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

where v_{deposit} is the deposition rate, K is the Arrhenius pre-exponential factor, T is the absolute temperature and R is the gas constant.

The Arrhenius plot according to equation (3) is presented in Figure 8. The obtained plot is straight line and its slope gives the activation energy E_a . The calculated activation was 32 kJ mol⁻¹. This value is greater compared to this obtained for electroless copper deposition in acidic solutions which is between 20 and 25 kJ mol⁻¹ [5] and is about 6.28 kJ mol⁻¹ in the case of electroless Ni-Cu-P deposition on aluminum alloy in alkaline solution [51].

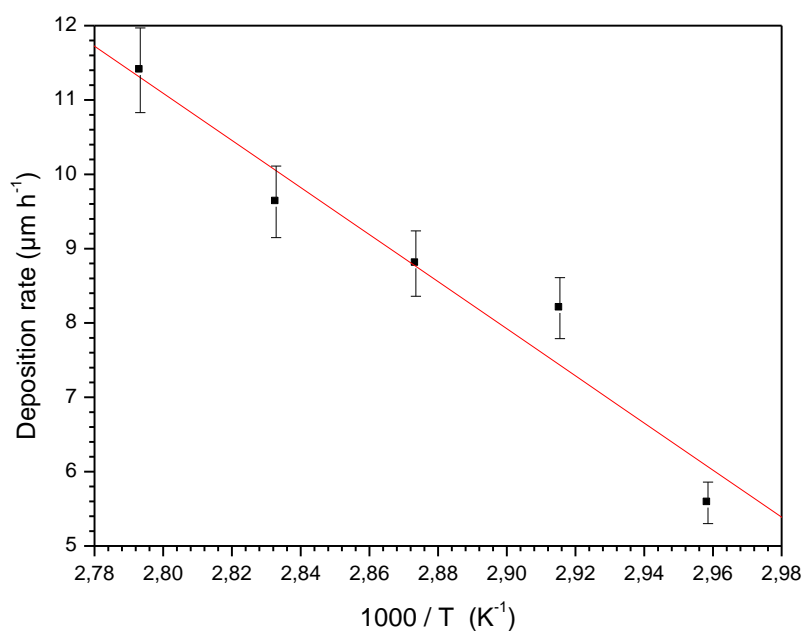


Figure 8. Effect of the electrolyte temperature on the deposition rate

3.3. Characterization of the optimum bath: Morphology, composition and structure

Figure 9 shows the SEM micrograph of the deposit obtained from the based bath condition (table 1).

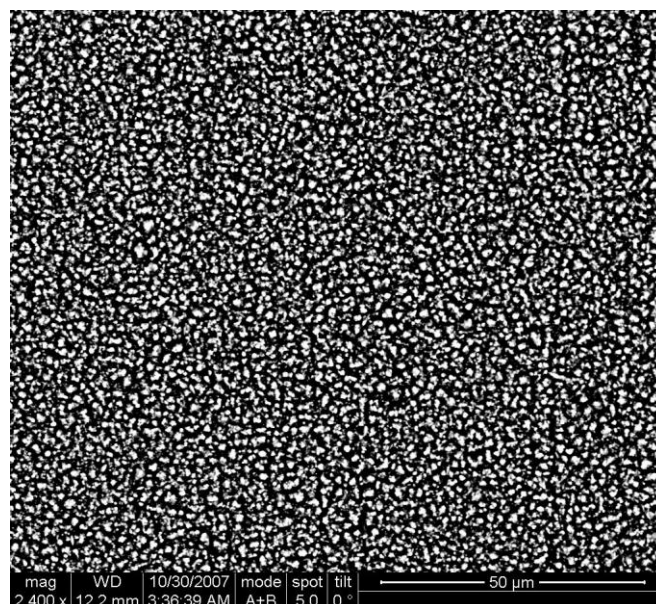


Figure 9: SEM photographs of the electroless copper deposits obtained from the based bath (94.64 wt% Cu, 5.36 wt% Ni).

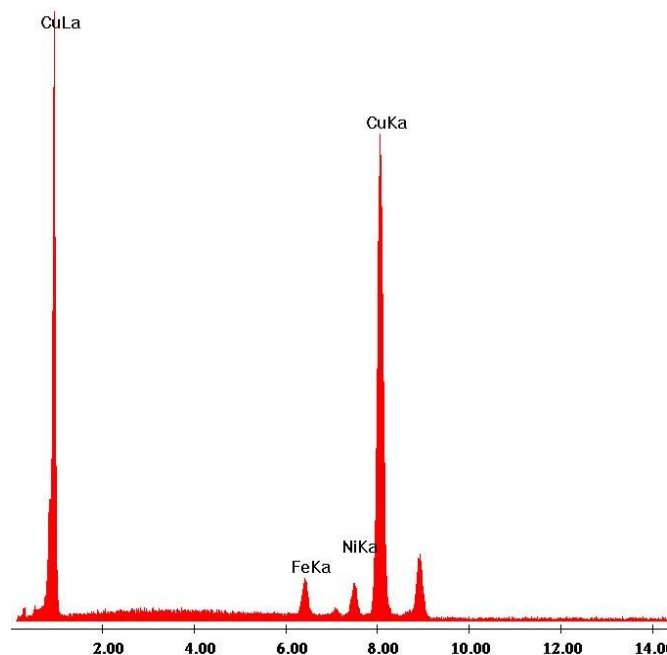


Figure 10. EDX profile for the electroless copper deposit obtained from the based bath (94.64 wt% Cu, 5.36 wt% Ni)

It noted in this case that the deposition rate value is about $8.2 \mu\text{m h}^{-1}$. From this figure, the deposit is generally homogeneous and presents a nodular structure. In addition, the EDX analysis shows that the deposit contains 94.64 wt % of copper element and 5.36 wt% of nickel element (Figure 10). The absence of phosphorus element on the deposit shows clearly that the hypophosphite oxidation reaction is not catalyzed by copper [16, 22-24] and confirms the obtained result by cyclic voltammetry.

However, the XRD diffraction pattern of the deposit film is shown in Figure 11. It is shown that this coating (pure copper (94.64Cu- 5.36 Ni) has a crystalline structure. In addition, the peaks appearing at $2\theta = 43.5, 50.7, 74.4$, and 90.3 represent (111), (200), (220) and (311) planes of copper, respectively. High Cu (111)/ Cu (200) ratio is observed in the copper deposit, indicating that the copper film manifests the preferred (111) orientation. The copper film with a higher (111) texture is preferred due to its higher reliability against electro-migration and lower electrical resistance [52]. In our previous study, we are found that these micrographs are improved by the DMF addition [32].

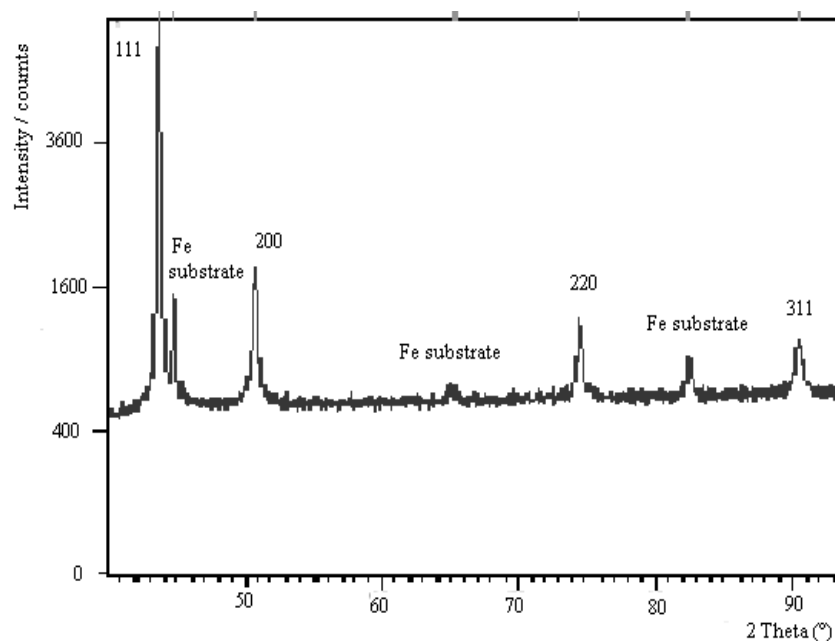


Figure 11. X- ray diffraction patterns of electroless copper deposits obtained from the based bath (94.64 wt% Cu, 5.36 wt% Ni)

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