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Electroless nickel-phosphorus plating on copper plate by palladium activation technique

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GRAPHICAL ABSTRACT

Iron plate after being treated with palladium activator and KFJ-20 bath

ABSTRACT

Electroless plating is an autocatalytic method which is not require electrical current for deposition to occur. The deposition occurs by the supply of electrons with the presence of reducing agent that contains sodium hypophosphite (SHP). The electroless Ni-P deposited on copper plates which are passive metal and need to be pretreated by a suitable activator. Thus, this research investigates the operation condition of a palladium activator and Ni-P bath on copper plates. Deposition of nickel uses KFJ-20 bath which is one of the best formulations from Uyemura (M) Sdn. Bhd. KAT-450 activator that contains palladium is used to activate the plate before nickel plating takes place. The electroless plating process begins with cleaning, soft-etching, acid dipping, activation and deposition of Ni-P. Besides copper, Ni-P was also deposited onto iron plates to differentiate the effectiveness of palladium as an activator. The best deposition condition was found to be on iron plates with 3 mins dipping time in activator, 20 mins deposition time and bath temperature at 90 °C. Deposition of nickel onto iron was also done without activator and the best deposition time is at 40 mins with bath temperature at 90 °C. Meanwhile, the copper plate shows all negative results which indicate that palladium activation was failed to deposit nickel onto it. The roughness of the surface depends on the concentration of palladium on the KAT-450 activator and deposition time.

Keywords: electroless nickel, nickel-phosphorus, sodium hypophosphite, KFJ-20 bath, KAT-450 activator

1. INTRODUCTION

Electroless (EN) process is also known as autocatalytic method which includes chemical reduction of metallic ions in the aqueous solution. The thin film deposition can be carried out through the oxidation of a chemical compound (reducing agent) that is present in the solution itself [1]. The function of reducing agent is to supply an internal current and the most common reducing agent used in EN process is sodium hypophosphate (SHP) [2]. EN helps to improve the physical state of the surface material for copper or other metals such as high hardness, excellent corrosion and wear resistance, thickness uniformity and good lubricity. The equations below are the of deposition reaction that involve anodic and cathodic reactions [3,4].

Anodic reaction

$$H_2PO_2^- + H_2O \rightarrow H_2PO_3^- + 2H^+ + 2e^- \qquad (1)$$

Cathodic reactions

$$H_2PO_2^- + 2H^+ + e^- \rightarrow P + 2H_2O \qquad (2)$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad (3)$$

$$Ni^{2+} + 2e^- \rightarrow Ni \qquad (4)$$

This project is proposed by Uyemura (Malaysia) Sdn. Bhd. (UMM) that specializes in electro and electroless plating chemicals and treatment chemicals. The main raw ingredients of UMM are nickel sulfate and SHP. The project focuses on using one of the best products of UMM which are Nimuden KFJ-20 and KAT-450. KFJ-20 bath is an EN product that can deposit nickel on copper substrates while KAT-450 is an activator that contains palladium. The presence of SHP in KFJ-20 bath supplies electron necessary to the EN process. Phosphorus content is also supplied by these hypophosphite components. The whole process for EN plating involves pretreatment process, activation and deposition of nickel.

The untreated copper surface has low performance requirement and therefore deposition of nickel cannot occur. To overcome this problem, a suitable pre-treatment process is chosen with an appropriate activation technique. The presence of phosphorus and nickel content in KFJ-20 bath influence the plating process. The study of electroless nickel-phosphorus (Ni-P) plating is important as it is for improving the surface performance. The pre-treatment process, bath composition and operation condition can improve the performance of copper plate to obtain better coating properties.

2. EXPERIMENTAL

The experiment was divided into three main stages. The first stage focused on the pre-treatment of the copper surface. In addition, the second stage was deposition of palladium in KAT-450 onto the copper surface. The last stage was the deposition of nickel from KFJ-20 onto the copper surface. Figure 1 shows the electroless Ni-P deposition process. The first step in pre-treatment is cleaning with cleaner C-4000T at 62°C for 1.5 min. After 1.5 min, the copper plate was rinsed with deionized (DI) water and dried using a metal dryer. The plate was weighed to get the initial mass and the cleaning process was continued using cleaner C-4000T for the rest 1.5 min. The copper plate was dipped into soft etching bath, pre-dip bath and acid-dipping bath for 1 min each. The last step in pre-treatment was activation technique where the copper plate was placed inside the KAT-450 activator. The copper plate was rinsed with DI water for every step respectively. Then, the copper plate was immersed into KFJ-20 bath solution at optimum condition. Deposition time and temperature are the parameters that were being optimized.

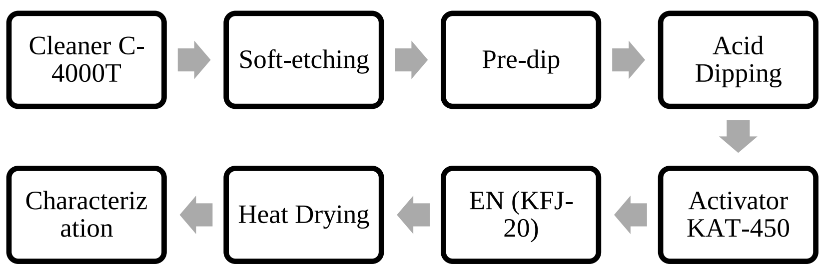

Figure 1 Electroless Ni-P deposition process.

3. RESULTS AND DISCUSSION

3.1 Effect of KAT-450 Activator Dipping Time on Plating

As the palladium activation time increases, the number of palladium nanoparticles also increases on the deposited layer. The surface morphology of copper substrate is shown by FESEM. It was reported that the nanoparticles in nanometer size were formed and dispersed on the copper substrate [5]. Figure 2 shows the graph of activator dipping time versus deposition speed. The weight of copper is decrease after being plated because KAT-450 activator that contain palladium is failed to deposit nickel from KFJ-20 bath. Figure 4.1 shows the graph of activator dipping time versus deposition speed. Weight of nickel deposited on the copper plate and deposition speed shows all negative results. The deposition of nickel onto copper increase from 120 sec to 150 sec. The optimum dipping time of the activator is 3 min.

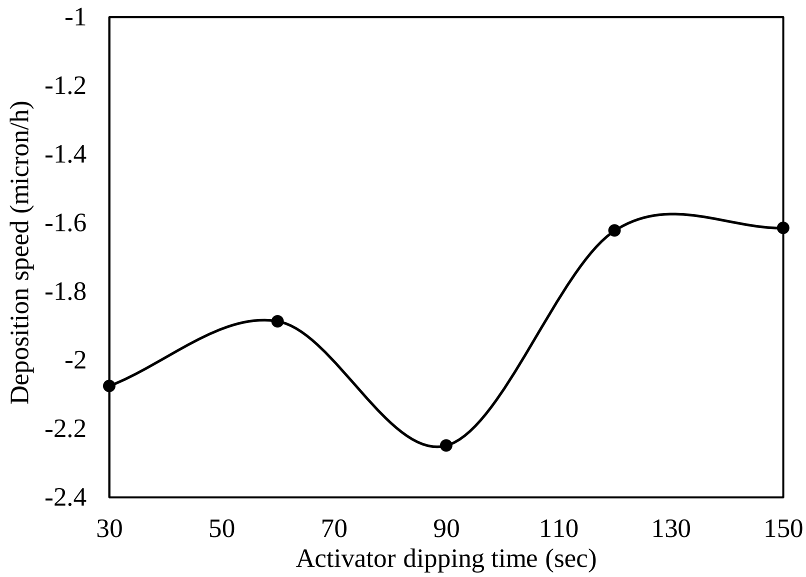

Figure 2 Graph of activator dipping time versus deposition speed.

3.2 Effect of KFJ-20 Bath Temperature on Plating

Another important parameter on EN plating is temperature. The study of the effect of temperature on nickel coating found that when the temperature was below 50°C, there no apparent reactions occur. When the temperature reaches above 90°C, the bath composition becomes unstable and the fiber breaks down easily [6]. The deposition time and pH for each set of experiment is same. Figure 3 show the graph of bath temperature versus deposition time. For the optimization of KFJ-20 bath temperature on copper plate using KAT-450 activator, the weight of nickel deposited on plate decrease as the temperature increase. The best value temperature for nickel deposition with KAT-450 activator is at range 80˚C to 85˚C. Meanwhile, for the optimization of bath temperature without KAT-450 activator, the value of deposition speed decline rapidly at 90˚C. Both experiments were tested on copper plate.

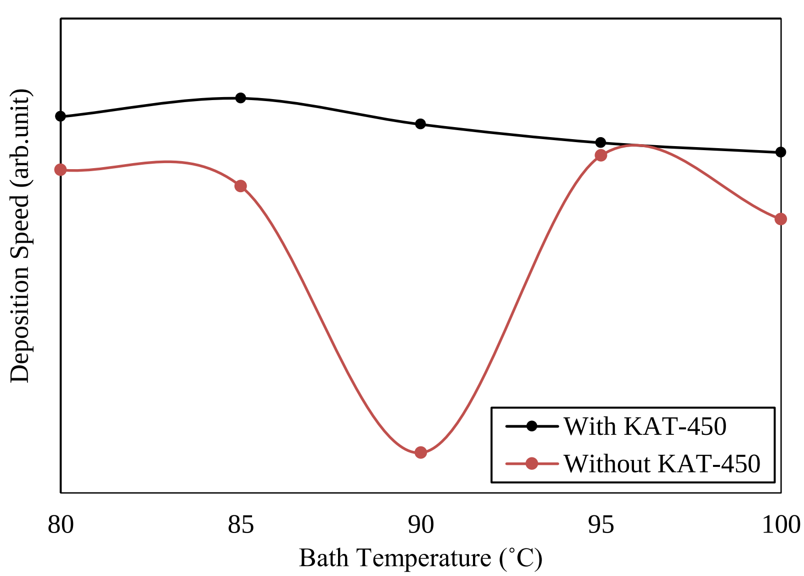

Figure 3 Graph of bath temperature versus deposition speed.

3.3 Effect of KFJ-20 Bath Deposition Time on Plating

In EN plating, deposition time of plating is one of the important parameters that can change the deposition speed of the substrate. For the optimization on deposition time, it was tested on both copper and iron plate. The nickel deposition increases as the deposition time increase on both experiment for copper plate, with and without using KAT-450 activator. Figure 4 shows the graph of deposition time versus deposition speed for copper plate. For copper that using KAT-450, the graph increase from 30 mins to 60 mins. However, the nickel deposition seems begins to stable and decrease when deposition time reach 60 mins and above. Thus, the best deposition time for copper without KAT-450 is at range 20 min to 40 min and the deposition speed slowly drop after 40 mins.

Figure 5 shows the graph of deposition time versus deposition speed for iron plate. For iron plate that using activator, the deposition of nickel increases as the deposition time increase. The graph line is more stable compared to iron plate without using KAT-450. Meanwhile, for the iron plate without using activator, the deposition of nickel increases as the deposition time increase until at 40 mins and it decrease after reached 50 mins. The best deposition time for iron plate that using activator is at range 20 min to 30 min while for iron plate without using activator is at range 20 min to 40 min.

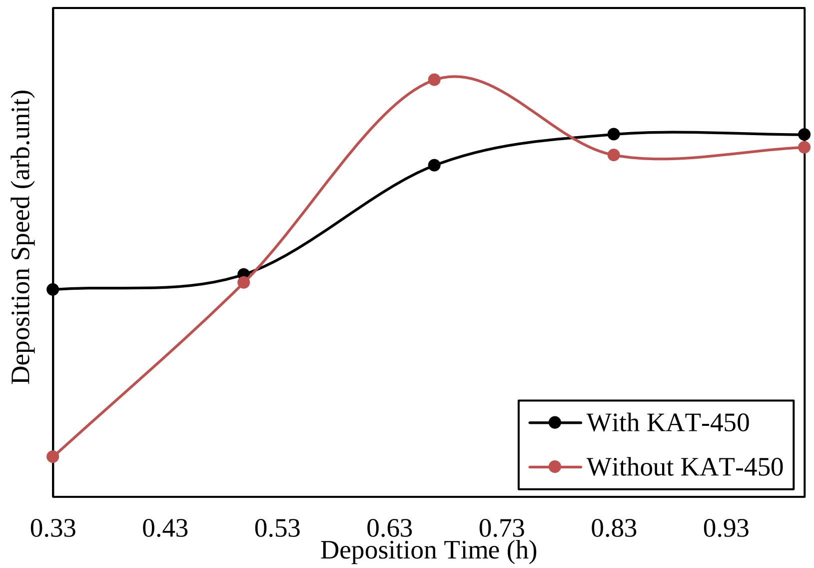

Figure 4 Graph of deposition time versus deposition speed of copper plate.

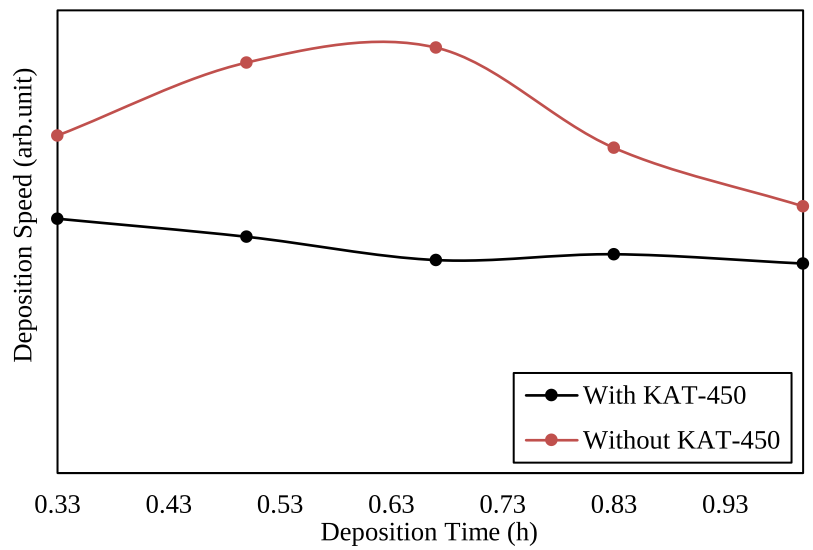

Figure 5 Graph of deposition time versus deposition speed of iron plate.

3.4 Analysis of Palladium Concentration in KAT-450

The calibration curve for palladium are constructed by plotting graph of absorbance versus concentration. A linear regression by the least square method is then applied. The value of the determination coefficient showed excellent linearity of the calibration curve which is R^2 equal to 0.09998. Table 1 shows the concentration and absorbance for diluted standard solution of palladium. Figure 6 shows a graph of absorbance versus concentration. From the graph, unknown concentration of palladium in the KAT-450 activator can be determined. The concentration of palladium in 100 mL of KAT-450 is 8.120 mg/L with 0.095 absorbance. After 2× of dilution, the concentration of palladium is 6.244 mg/L with 0.073 absorbance. After 10× of dilution, the concentration is 0.531 mg/L and the absorbance is 0.006. In every EN plating process, the amount of activator that being used is 100 mL. The usage of activator might be not suitable because it was recycled for every 5 processes. The same activator has been used to activate 5 plates without being change. Thus, the concentration of palladium in the activator might change. The surface uniformity of nickel is better than palladium but the phosphorus content in both Ni-P layer are almost identical [7].

Table 1 Concentration and absorbance of calibration standard

Solution	Concentration (ppm)	Absorbance
Blank	0	0
Calibration standard 1	1.303	0.015
Calibration standard 2	2.169	0.025
Calibration standard 3	3.006	0.035
Calibration standard 4	3.877	0.045
Calibration standard 5	4.939	0.058

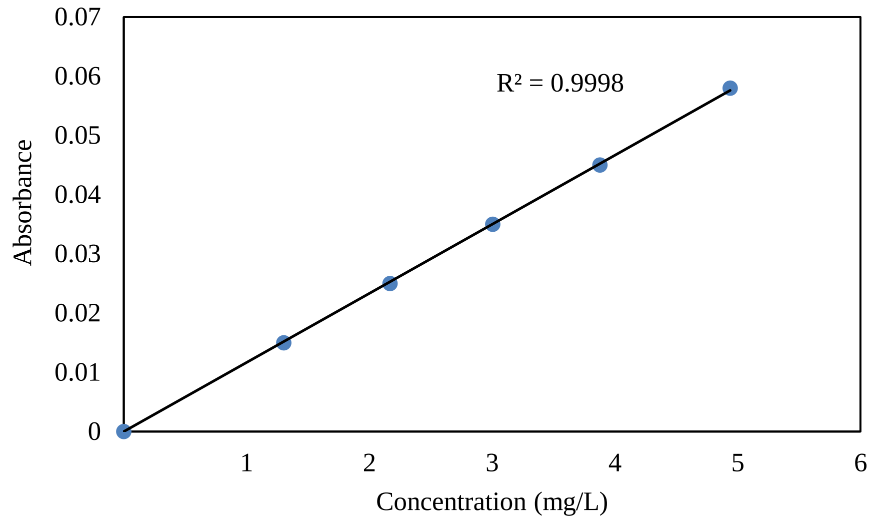

Figure 6 Graph of Absorbance versus Concentration.

3.5 Surface Morphologies of Plating by FESEM

Figure 7 shows the surface morphologies of electroless Ni-P plating at 2000 magnification. It shows the morphology of copper with KAT-450, copper without KAT-450, iron with KAT-450 and iron without KAT-450. Figure 7(a) and (b) illustrate that the surface of both copper plate is rough as KFJ-20 bath failed to deposit nickel on it. Deposition of nickel onto copper failed due to the palladium activator. During activation technique, the palladium from KAT-450 failed to replace most of the copper atom on the surface which make the copper is still more noble than nickel. Some of the palladium deposited onto the copper surface and it formed Pd-Cu interlayer (residue). The copper atom and palladium atom is removed from the copper plate while Pd-Cu interlayer remained [8]. Meanwhile, the surface of iron plate is a bit smooth because the deposition of palladium and deposition of nickel is success on it. In Figure 7(d), the deposition of Ni-P seems only cover certain part of the iron surface compared to Figure 7(c).

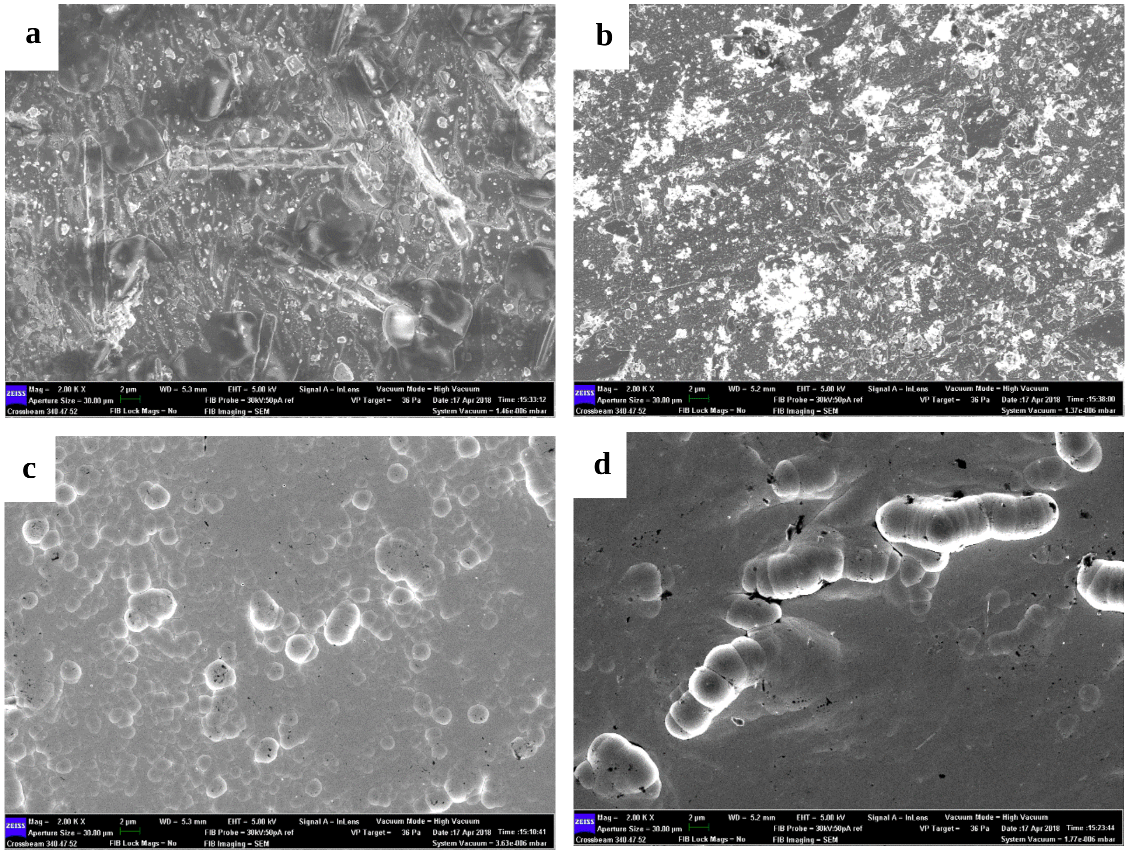

Figure 7 Surface morphologies of electroless Ni-P plating at 2000 magnification: (a) copper with KAT-450, (b) copper without KAT-450, (c) iron with KAT-450 and (d) iron without KAT-450.

Figure 8 shows the close-up surface morphologies of copper and iron plate with magnification of 15000. The surface morphology of Ni-P deposit on copper plate in Figure 8(a) showed a crack (forming valleys) with discontinuous structure. Cracks was predominated along the surface of copper which means that the deposition was irregular or even absent. Figure 8(b) showed coarse grain crystal structure because the deposition of Ni-P was also irregular as the activation step does not applied on it. it Surface morphologies for iron plate showed the spherical nodular structure as shown in Figure 8(c) and (d).

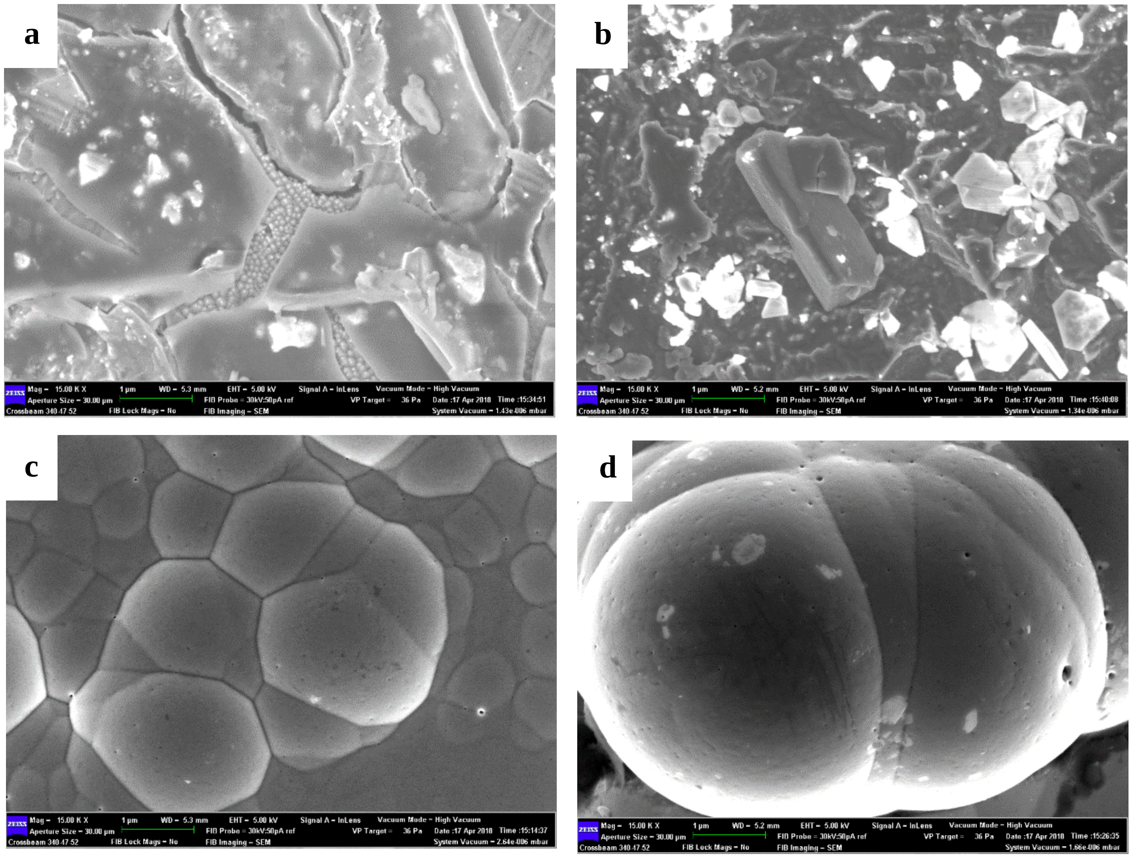

Figure 8 Surface morphologies of electroless Ni-P plating at 15000 magnifications: (a) copper with KAT-450, (b) copper without KAT-450, (c) iron with KAT-450 and (d) iron without KAT-450.

4. CONCLUSION

In this experiment, the focus is to deposit electroless Ni-P plating on copper plates by using a palladium activation technique. The operating parameters including dipping time of KAT-450 activator, temperature, and deposition time of electroless Ni-P were investigated. The electroless Ni-P bath or KFJ-20 bath solution was also prepared according to the optimum condition. The copper plates were optimized at different temperatures and deposition times of bath solution. The best value for temperature for copper plate is at range 80˚C to 85˚C and for deposition time is between 20 min to 30 min. Besides copper, iron plate also used to compare the effectiveness of palladium, deposition speed and surface morphologies. Deposition speed of copper plates shows all negative results which indicate that deposition of palladium and deposition of nickel onto copper plate failed. Surface morphology for copper showed cracks and a discontinuous structure. Meanwhile, deposition speed of iron plate shows all positive results and the best deposition condition was found at 20 mins and 90˚C. Surface morphology for iron is smooth compared to copper and it illustrates a spherical nodular structure. The activation technique affects the properties and surface morphologies of the materials. As the conclusion, the properties of copper plate can be improved continuously by suitable surface treatment process and activation technique during electroless Ni-P plating.

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