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ELECTROLESS NI-P DEPOSITION BY USING ORGANIC SOLVENT

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ABSTRACT

Electroless nickel for electronic applications continues to grow and is clearly the most diverse market segment. The work focuses on optimizing the coating parameters of electroless nickel phosphorous (Ni-P) in organic solvent which is ethanol on a copper substrate. The maximum concentration of ethanol was 50% to be added in an aqueous solution of plating bath to dissolve the entire Ni salt, complexing agent, stabilizer and reducing agent. The effect of 50% ethanol on electroless Ni-P deposition and characterization of Ni-P coating were studied. The characterization of coating materials was conducted using X-Ray Fluorescence (XRF) and Field Emission Scanning Microscopy (FESEM) with Energy Dispersive X-Ray (EDX). The result showed that the agglomerated Ni-P deposited on coating surface become bigger when the $NiSO_4$ concentration increases at the optimum plating time of 20 minutes. The performance of deposited Ni-P in this study showed highest adhesion level when the concentration of $NiSO_4$ was 15 g/L while the thickest coating was formed at 40 minutes of 35 g/L $NiSO_4$ concentration.

Keywords: *Electroless nickel, Ni-P plating, adhesion strength, organic solvent, coating*

1.0 INTRODUCTION

Most industrial electroplating processes are performed in aqueous solutions. The electroplating of finishes, such as hard chromium, cadmium and nickel in metal finishing is today recognized as a major source of environmental pollution in every country. Therefore wet bath technologies have a promising research compared with high performance dry coating methods such as physical vapour deposition [1], plasma-assisted chemical vapour deposition, chemical vapour deposition and thermal spraying. The types of metals that can be electrodeposited from an aqueous electrolyte, however, are limited [2]. There are few problems regarding the using of water bath in conventional electroless coating. Hydrophilic particles such as SiO_2 that can be hardly co-deposited with a metal from an aqueous electrolyte can be easily co-deposited using an organic solvent [3]. Conventional electroless coating using water bath may also contain hydrogen due to liberation of hydrogen molecule, which affects their mechanical properties adversely, narrow electrochemical windows, low thermal stability and evaporation. Hydrogen inclusion is known to cause the development of high internal stresses and cracks in

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plated films. This research will explain the effect of ethanol to the Ni-P deposition on the copper substrate. In the electroless plating step, the Pd-impregnated copper is immersed in electroless nickel-phosphorus plating solution, whose major composition is water and ethanol, and Ni-P alloy film is developed. The coating form by using organic solvent may enhance layer formed at the interface between metal and substrate which plays the role of metal anchor in enhancing adhesion strength of the metal film to the substrate [4]. Electroless Ni–P composite coatings have been successfully prepared on many ceramics powders such as Al_2O_3, ZrO_2, Si_3N_4, SiC and diamond powder [5-9].

In this work, the effect of ethanol on electroless Ni-P was investigated at various concentrations of $NiSO_4$ and plating time. Morphology, chemical composition, and the thickness of deposited Ni layer was characterized by using Field-Emission Scanning Electron Microscopy (FESEM) with energy dispersive X-ray spectroscopy (EDX) and X-ray fluorescence (XRF) respectively. The coating adhesion was tested by using standard ASTM D 3359-97 tape test.

2.0 EXPERIMENTAL METHOD

Pure copper were used as a substrate for plating process with dimension of 2.5x1.5x0.15 cm. The substrate was rinsed in distilled water and cleaned by immersed it into the medium alkalinity soak for 5 minutes at temperature between 70-90°C. Then, the substrate was rinsed using distilled water again and alkaline etching by immersed it for 5 minutes in solution that contain 10g sodium pre-sulphate, 10g sodium hydroxide and 200 ml distilled water at temperature 50 °C – 60 °C and later rinsed with distilled water. Hydrosulphuric acid (H_2SO_4) was used as de-smutting solution and the immersion time was 1 minute at the room temperature. Then, the substrate was rinsed with distilled water. Lastly, substrate was soak in Palladium solution (1000 ml, 0.5 ml/L HCL and 0.1 g/L) for surface seeding with catalyst.

Electroless Ni-P deposition on Cu substrate was conducted by addition of 50% ethanol in plating solution at various plating time (10,20,30,40 and 50 minutes) and Ni concentration (15,20,30 and 35 g/L). Table 1 shows the bath composition and operating conditions of electroless deposition.

Table 1: Bath composition and operating conditions

Items	**Values**
Nickel sulfate	15 - 35 g/L
Sodium hypophosphite	23 g/L
Sodium citrate	46 g/L
Boric acid	26 g/L
pH	9 – 10
Solvent	125 ml Ethanol (99.95 vol%) + 125 ml distilled water
Temperature	40°C
Time	10 - 50 minutes

The thickness of Nickel coating was measured using X-ray Fluorescence, XRF machine (Spectro Midex). The penetration depths of x-ray allow XRF to measure the coating.

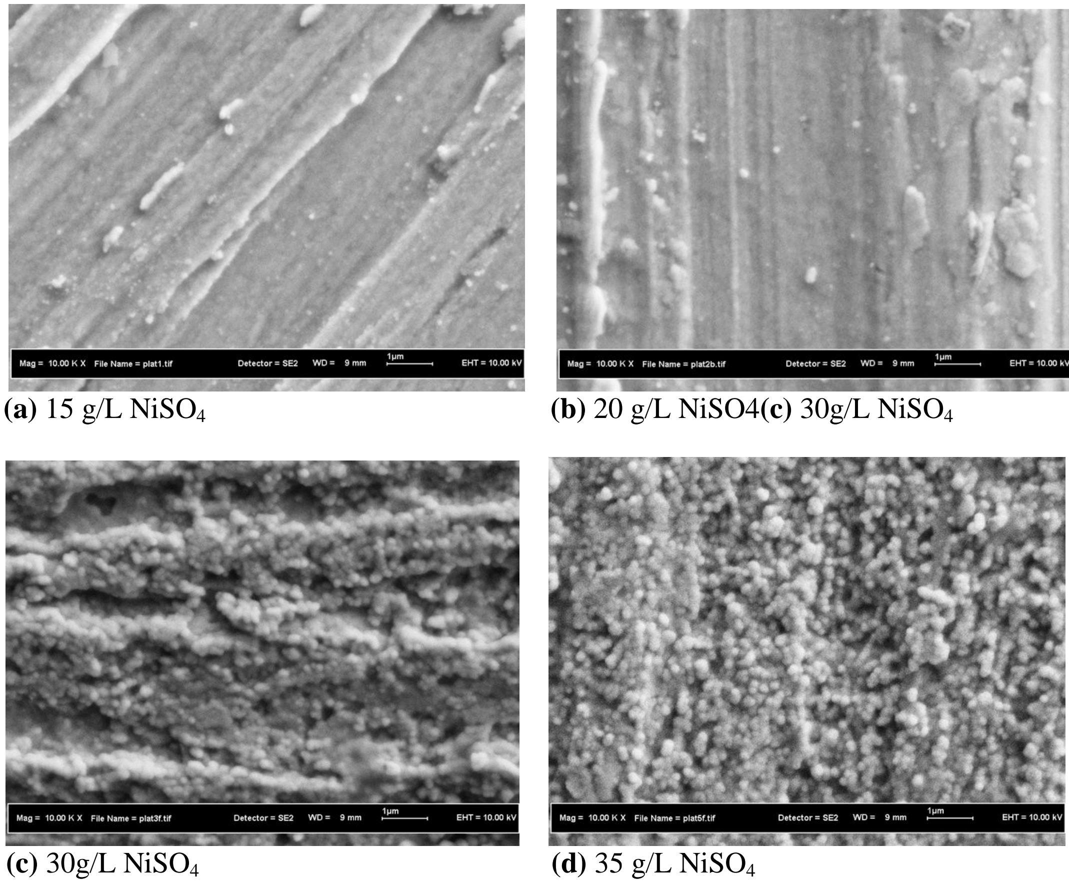
Fluorescence radiation in reflection and transmission geometry can be used to determine the mass thickness for one layer uniform films. Three points on the substrate were taken and averaged coating thicknesses were obtained from it. Field Emission Scanning Electron Microscopy (FESEM) was used to study the surface morphology of nickel coating. EDX was used to determine the chemical composition of the samples to show the evidence of existence of Nickel coating after the plating process on the substrates. Adhesion test was conducted by using the standard of ASTM D 3359-97 tape test. The test procedure are applying and removing a pressure sensitive tape over cross-cuts made on the thin film.

3.0 RESULTS AND DISCUSSION

Screening of the solubility revealed that nickel in 50% ethanol solvent showed acceptable solubility with other chemicals in the plating bath. The copper substrate which was brownish in colour turned to silvery colour after the plating processed which showed that Nickel was deposited on the substrate. Figure 1 show the microstructure obtained after 20 minutes electroless plating process with different $NiSO_4$ concentration by using FESEM micrograph. From Figure 1 (a) and (b), the surface of the film obtained at low $NiSO_4$ concentration was uniform and smooth, whereas those at high $NiSO_4$ concentration from Figure 1 (c) and (d) were less uniform, porous and rougher surface with spherical-shaped surface morphologies due to the decomposition products were adsorbed on the surface of the Ni-P films and affect the surface morphology. Result obtained in Figure 1 (c) shows spherical agglomerations particles deposited on Cu surface substrate and the film formed was gradually coalesced in dense agglomerates as shown in Figure 1 (d). Both figures show homogenous Ni-P agglomerations on the surface of substrates. Nucleation of Ni-P grain can be seen in Figure 1(c) and the grain size grown from the organic baths increased with increasing $NiSO_4$ concentration. This result indicates that the grain size Ni-P size is affected by the concentration of $NiSO_4$

Figure 2 shows plating time of 20 minutes with increasing $NiSO_4$ concentration which was the most optimum deposition time due to the consistent trends of deposition on the substrates. The Ni-P coating thickness increases with the increase of $NiSO_4$ concentration. Figure 3 shows the coating thickness increases until at 40 minutes time of plating, then the coating thickness decrease plating time of 50 minutes. The decrease of coating thickness at 50 minutes due to the instability of the plating reaction when plating duration was extended to 50 minutes. Figure 4 shows the micrograph of sample for 40 minutes plating using 35 g/L $NiSO_4$ concentration which shows the thickest coating (average thickness of 0.79 um) that was obtained from the experiment. From the micrograph observation, the coating does not have crack and pull-off.

Chemical composition of coating was analyzed by Energy Dispersive X-ray (EDX) spectrum. From Figure 5, it was conformed that Nickel (N) and Phosphorus(P) were presence on the Copper substrate (Cu) after the plating process. Furthermore, tape test was conducted according to Standard ASTM D 3359-97. In general, most coating showed very good adhesion with the adhesion level classified in the range of 3 to 5 as shown in Table 2. Concentration of $NiSO_4$ at 15 g/L showed the highest adhesion level which is above 4 for all deposition time.



(a) 15 g/L $NiSO_4$ **(b)** 20 g/L NiSO4**(c)** 30g/L $NiSO_4$

(c) 30g/L $NiSO_4$ **(d)** 35 g/L $NiSO_4$

Figure 1: FESEM microstructure of sample with various $NiSO_4$ concentrations (15-35 g/L) at 20 min plating time.

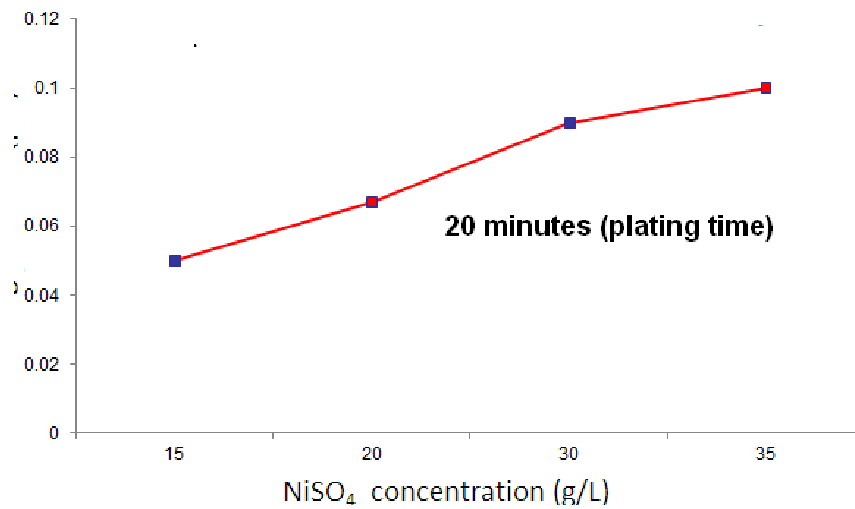


Figure 2**:** Graph of $NiSO_4$ concentration and the coating thickness at 20 min plating time.

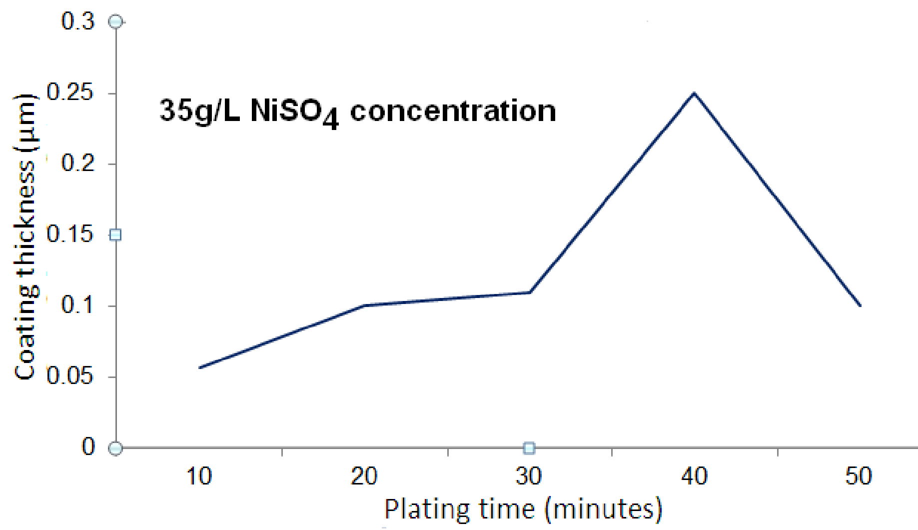


Figure 3: Graph of plating time and the coating thickness for 35 g/L $NiSO_4$

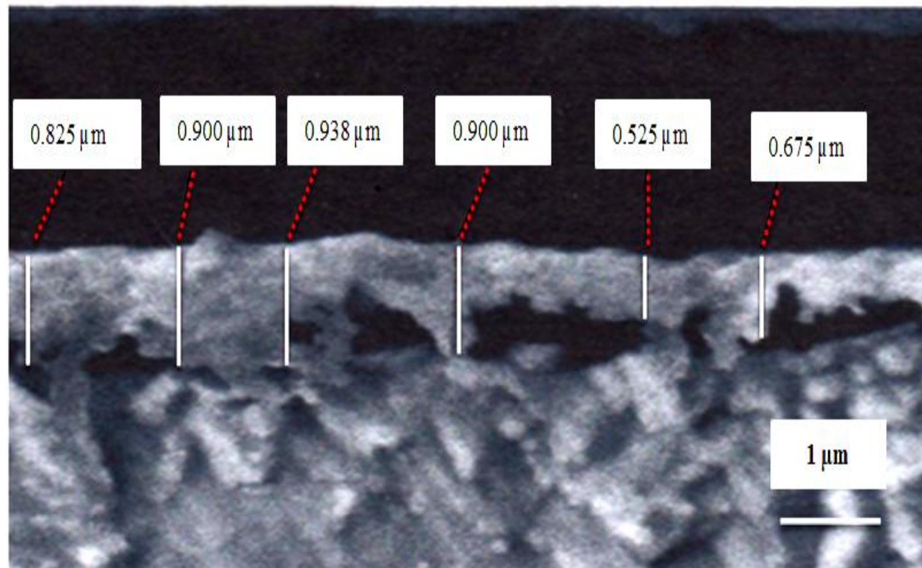


Figure 4: FESEM micrograph for **c**ross section thickness.

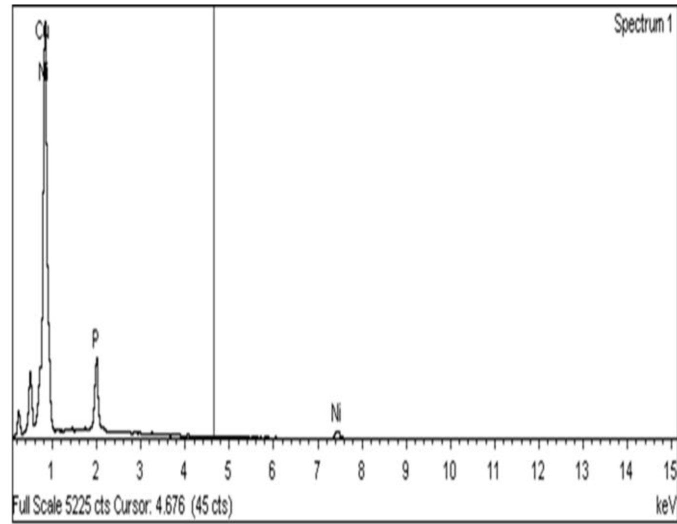


Figure 5: Chemical composition (EDX spectrum)

Table 2: Adhesion performance according to Standard ASTM D 3359-97.

$NiSO_4$ Con.(g/L)	**Time (minute)**	**Classification**
15	10	5
	20	5
	30	5
	40	4
	50	4
20	10	4
	20	3
	30	3
	40	5
	50	5
30	10	5
	20	5
	30	4
	40	3
	50	4
35	10	4
	20	5
	30	5
	40	2
	50	5

4.0 CONCLUSIONS

From the results obtained in this experiment, several conclusions can be made. It was proven in this research that 50% Ethanol can deposit the Ni-P on Cu substrate using electroless deposition. From the surface morphology observation, uniform and smooth microstructure was formed at 15 and 20 g/L of $NiSO_4$ concentration with 20 minutes of plating time. The thickest coating was formed at 35 g/L $NiSO_4$ concentration according to the coating thickness analysis and sample deposited at 15 g/L of $NiSO_4$ concentration have the best adhesion strength.

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