*Journal of the Korean Electrochemical Society*
*Vol. 3, No. 4, 2000, 196-199*

# Characteristics of Micro-hardness and Corrosion of Electroless Nickel-Phosphorus Plating depending on Heat Treatment

Seung-Jun Jung and Soo-Gil Park†

*Dept. of Industrial Chemical Engineering, Chungbuk National University*

(Received April 7, 2000 : Accepted July 13, 2000)

**Abstract :** Electroless plating is the desirable surface treatment method which is being widely used to all kinds of material such as requiring corrosion resistance, wear resistance and conductivity, especially plating of nonconductive material. Electroless nickel deposit has particular characteristics including non-magnetic property, amorphous structure, wear resistance, corrosion protection and thermal stability. In this study, electroless nickel plating was studied with an change in hardness and corrosion resistance of electroless nickel-phosphorus deposit depending on heat treatment. The highest hardness value was obtained by heat treatment at 500°C Corrosion resistance of deposit, which had been heated at 300°C, was excellent when it was immersed in 1 M $H_2SO_4$ solution for 60 hrs.

**초 록 :** 무전해 도금은 내식성, 내구성, 전도성 특별히 비전도성 물질의 도금이 요구되는 모든 재료에 폭 넓게 사용되는 우수한 표면 처리 방법이다. 무전해 니켈 도금은 비자성, 무정형 구조, 내구성, 내식성 그리고 열적 안정성 등의 많은 장점을 갖는다. 본 연구에서는 무전해 니켈 도금의 열처리에 따른 무전해 니켈-인 도금의 경도와 내식성의 변화를 연구하였다. 가장 높은 경도 값은 500°C 열처리에서 얻어졌다. 300°C에서 열처리한 도금의 내식성이 60시간 동안 1 몰의 황산 수용액에서 테스트 한 결과 가장 우수하였다.

**Key words :** Electroless plating, Nickel, Hardness, Corrosion resistance

## 1. Introduction

Electroless plating is one of the most widely used methods as a general surface treatment. Electroless plating has the ability of coating on non-conductive surface such as plastics, ceramics as well as metals. Also, electroless plated nickel is a popular barrier material because of its particular characteristics including non-magnetic property, amorphous structure, wear resistance, corrosion protection and thermal stability.[1,2] Therefore, electroless nickel plating has attracted interests for application in many electronics industry because of its excellent solderability and conductivity. In addition, the capability of acting as the suitable diffusion barrier between conductor metals, such as Al and Cu, and solders are essential in electronic packaging in order to sustain a long period of service.[3,4] The electroless plating method has been developed by so many related technologies since Brenner and Riddle had used in 1944.[5] Nickel-phosphorous alloys that are produced from electroless nickel plating are well known for their physical and mechanical properties and magnetic effects. The properties are strongly dependent on the content of phosphorous in nickel deposit and heat-treatment.[6] Among these characteristics, the most remarkable one is that electroless nickel plating generates coatings with uniform thickness as the thickness becoming thick due to the nickel plating show an amorphous structure, which doesn't show crystalline. Recently, electroless nickel deposits have been extensively used in the electronic industry because that metalization technique of the fine patterns by electroless plating is required in place of electrodeposition as high-density printed circuit boards (PCB) become indispensable with the miniaturization of electronic components.[7,8)

The purpose of the present work is to find the optimum condition of the electroless nickel plating on copper substrate. So, we studied that electroless nickel plating was conducted with varying bath composition and plating condition. In addition, the effects of heat treatment on structure, hardness, corrosion resistance of electroless nickel deposits was also investigated.

## 2. Experimental

### 2.1. Condition and process of deposition

The Electroless Ni-P was deposited on copper substrate. All solution were prepared from chemicals of analytical grade and distilled water. Nickel sulfate($NiSO_4$°§$6H_2O$) was used as metal source, sodium hypophosphite used as a reducing agent. Sodium acetate ($NaC_2H_3O_2$°§$H_2O$) was used as complexing reagents acting as forming nickel complexes, preventing excess free nickel ion concentration and nickel phosphite precipitation. After making electroless nickel solution, we adjusted pH value of solution using sulfuric acid and ammonia solution. The process of electroless nickel plating is shown in figure 1. The specimen were pretreated with

†E-mail: sgpark@cbucc.chungbuk.ac.kr

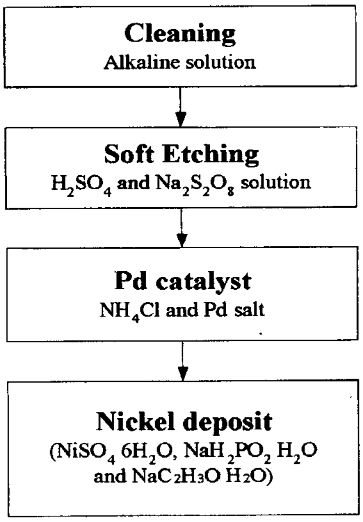


**Fig. 1. Flow chart of Electroless Ni-P plating process.**

alkaline degreasing, soft etching and palladium catalyst treatment in order before plating. The activated copper substrate was immersed in Ni-P deposition solution at 80°C with stirring for 30 minutes. After deposition, we investigated a change of microstructure and hardness of the specimen which ere heat treated in Ar atmosphere in the range of 200~600°C for 1 hour and measured the weight loss of the specimen when the specimen were immersed in 1 M $H_2SO_4$ solution at intervals of 12 hours during 60 hours.

### 2.2. Measurement of thickness and physical property of deposition

The characteristics of Electroless Ni-P deposits were analyzed with scanning electron microscope (SEM), X-ray diffractometer (XRD). We used CMI (coating measurement instrument) to measure the thickness of nickel deposits. The heat treatment was conducted in Argon atmosphere on 200, 300, 400, 500, 600°C for 1 hour and then hardness were measured by Micro-Vickers Hardness Tester with loading 50 g. We got the mean of measurement that was pointed on 3 points.

## 3. Results and Discussion

### 3.1. Effect of composition of nickel solution on the nickel deposit

The deposition rate was observed to decide proper ratio of nickel source and reducing agent. The concentration of nickel and reducing agent were both varied from 0.1 to 0.4 M. The thickness of nickel deposited specimens was measured by CMI.

The pre-experiment showed the relation of deposition rate on concentration of nickel and reducing agent. When the ratio is 1 : 1, the thickness of nickel is relatively constant as 6 $\mu m$. In spite of decrease of nickel salt and reducing agent, all of the solution of 1 : 1 ratio brought up stables thickness. When the ratio is 1 : 2, the thickness of nickel is the highest, 8.4 $\mu m$. Then, in order to investigate the effect of stabilizer

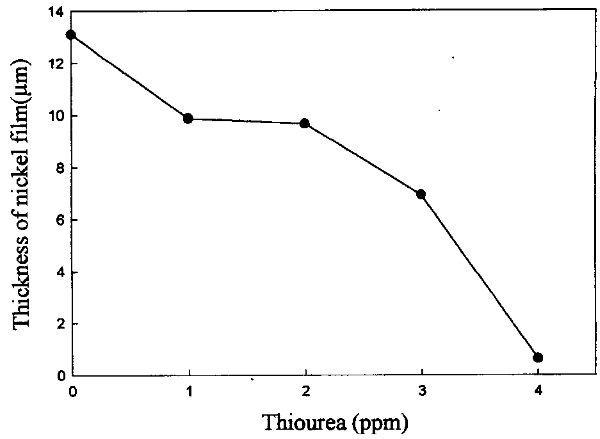


**Fig. 2. Thickness variation of nickel film with concentration of thiourea.**

on the nickel solution, we selected the ratio of 1 : 2 due to the highest thickness.

### 3.2. Effect of thiourea concentration on nickel solution

We observed the thickness of nickel deposits changing the content of thiourea to investigate the effect of adding thiourea. Sodium acetate is used as complexing reagents, which concentration was 0.1 M. The deposition rate was observed with varying the concentration of thiourea, from 1 to 4 ppm. The figure 2 shows the effect of stabilizer concentration on deposition rate. Nickel deposition continuously carried out 3 times in same nickel bath. There is no remarkable decrease from 1 to 2 ppm. But thickness of deposit was dramatically decreased when thiourea concentration was from 3 to 4 ppm. From this result, We got the proper concentration of thiourea is 1~2 ppm. We conducted the following experiment on using 1 ppm concentration of thiourea.

### 3.3. Effect of heat-treatment temperature on hardness, structure and surface of nickel deposit

To evaluate physical property such as hardness and corrosion resistance of electroless nickel deposits, we observed the characteristic of nickel deposits which were heated at 200, 300, 400, 500, 600°C in Ar atmosphere for 1 hour.

1) Change of hardness by heat-treatment

The hardness of copper substrate is about 140 Hv before nickel plating. When concentration of thiourea was 1 ppm, figure 3 shows the effect of heat-treatment on hardness of nickel deposits using Micro-Vickers hardness tester. The result shows the hardness were increased with heating temperature up to 500°C. Over 500°C, hardness decreased the hardness was higher than other one. The value of hardness increased slowly up to 500°C and decreased a little bit over 500°C. We investigated by XRD, SEM in order to figure out this result.

2) Change of crystalline by heat-treatment

The figure 4 shows the XRD analysis to find out a change of deposits in nickel layers by heat-treatment. In general, deposits have been found to have nickel (111) orientation at around 44.5°. The several small peaks were found 40° to 50°

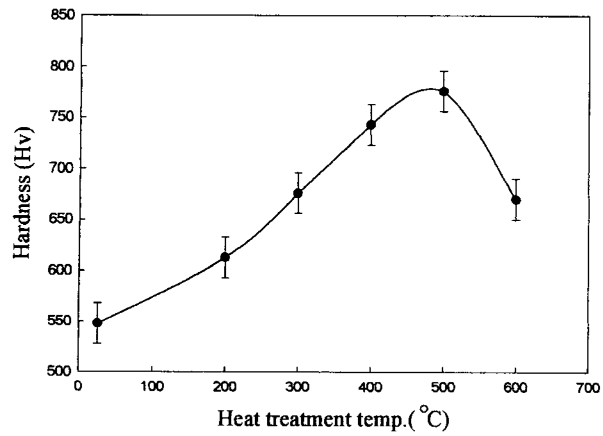


**Fig. 3. Effect of heat treating temperature on hardness of electroless nickel deposits. (hardness of copper substrate : 140 Hv)**

at 600°C. These peaks were regarded as $Ni_3P$ compound caused by co-deposit of phosphorous. From XRD result, it was estimated at the Ni-P deposit and $Ni_3P$ compound crystallized in range of 400~500°C. If heat-treatment temperature was higher increases, the more peaks of $Ni_3P$ compound may be appeared in the nickel deposits.

3) Change of surface morphology with heat-treatment

The figure 5 shows change of boundary of grain by heat-treatment. From the result of SEM image, we confirmed conventional shape of electroless nickel surface. There is no remarkable change in the image of SEM. However, boundary of grain of nickel decreased with heat treatment upto 400°C and again increased with heat treatment.

We could observed by SEM mapping that the particle of surface heated at 300, 400°C were relatively more dense than other heated at 500, 600°C that was produced $Ni_3P$ compound.

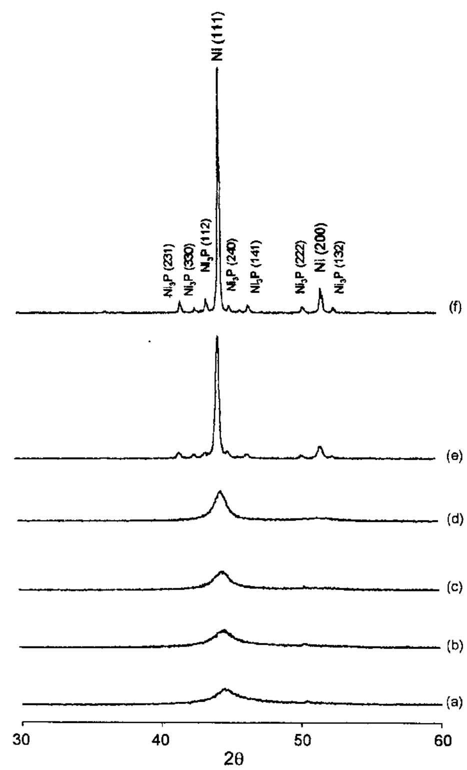


**Fig. 4. X-ray diffraction of deposits for heating temperature. (a)As deposited, (b) 200°C, (c) 300°C, (d) 400 °C, (e) 500°C, (f) 600°C**

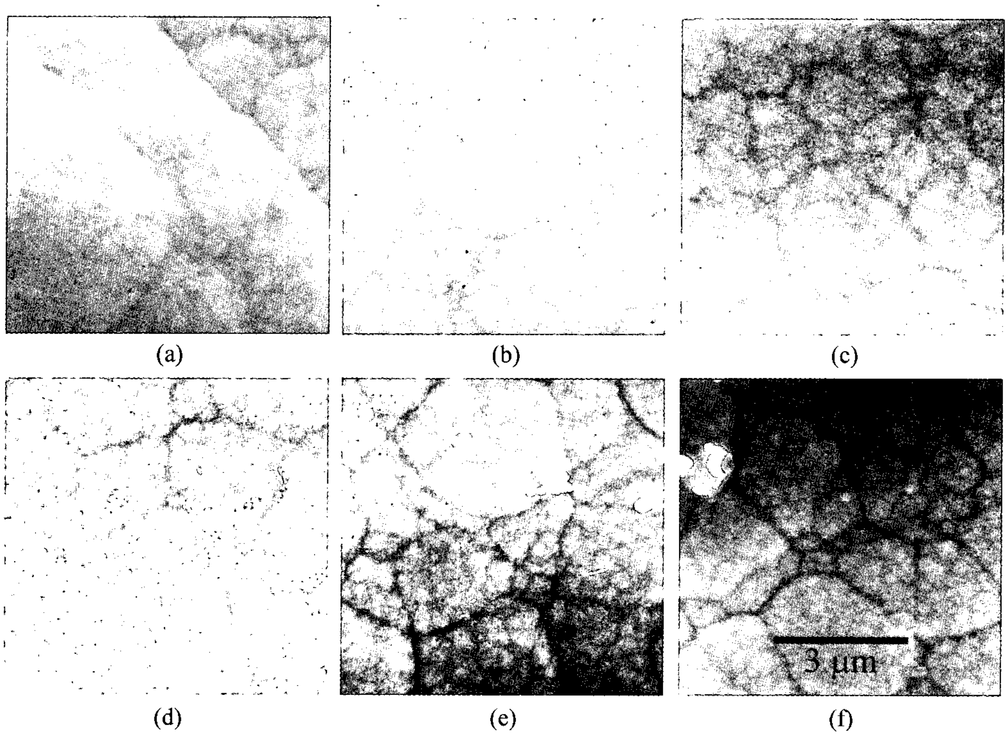


**Fig. 5. SEM of electroless nickel plating surface after heat treatment. (a) As deposited, (b) 200°C, (c) 300°C, (d) 400°C, (e) 500°C, (f) 600°C**

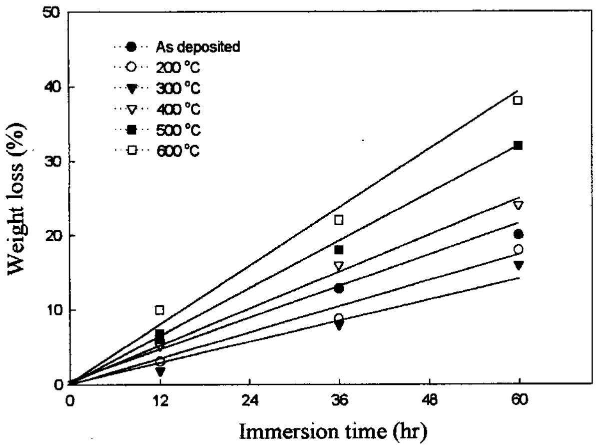


**Fig. 6. Weight loss of electroless nickel film at 1 M $H_2SO_4$ solution.**

### 3.4. Change of corrosion resistance after heat-treatment

The figure 6 shows change of corrosion resistance after heat-treatment. After the specimens who were heat-treated at different temperature was immersed in 1 M $H_2SO_4$ solution at intervals of 12 hrs for 60 hrs. We evaluated corrosion resistance by calculating the weight loss. The deposits were heated under 300°C where $Ni_3P$ compound wasn't occurred enhanced the corrosion resistance than those were heated up to 400°C where $Ni_3P$ compound was appeared. The deposits were heated under 200, 300°C enhanced more better corrosion resistance than one was not heat-treatment.

## 4. Conclusion

1) when the ratio of nickel salt and reducing agent was 1:2, the optimum of concentration of thiourea was 1~2 ppm

2) The hardness of nickel deposit under heat-treatment has tendency of increase with temperature. The highest hardness of nickel deposit was about 780 Hv at 500°C.

3)From XRD result, it was estimated that the Ni-P deposit and $Ni_3P$ compound was generated on range from 400°C to 500°C.

4) The corrosion resistance according to heat-treatment on electroless nickel deposits was more enhanced to heated at 300°C in comparison with those heated up 600°C

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