

Electroless Deposition of Ni-Cu-P Alloy on 304 Stainless Steel by Using Thiourea and Gelatin as Additives and Investigation of Some Properties of Deposits

N. Parvini-Ahmadi*, M. A. Khosravipour

Materials Engineering Faculty, Sahand University, Tabriz, Iran

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Abstract

In this research a layer of Ni-Cu-P was deposited on 304 stainless steels by using gelatin and thiourea as additives in a sulfate solution. In order to determine the properties of deposited layers, a microhardness tester was used for microhardness measurement, X.R.D. for microstructural analysis, and a scanning electron microscope equipped with E.D.X. for determining morphology and analyzing the deposits. The results of the experiment show that in the presence of additives in solution, deposited layers are rough, and elements such as Fe, O₂ and S enter into the layer, in the presence of thiourea and in the presence of gelatin Fe enters into the layer. The microhardness of alloyed layer without using additives is higher than the microhardness of the layer obtained in the solution containing gelatin and less than that containing thiourea. After heat treatment, the microhardness of layers increases, the reason is the formation of stable Ni₃P phase in structure.

Keywords: Electroless deposition, Ni-Cu-P, Thiourea, Gelatin

Introduction

The properties of electroless nickel alloys with phosphorus content are known. With increasing phosphorus in alloyed layer, the magnetic and wear resistance reduces while electric and corrosion resistance increases¹⁻³). Variation of phosphorus content is related to the pH, temperature, and the reducing agent⁴).

Additives have important effects on plating. The formation of a semiconductor layer using some additives in electrolytic bath reveal the importance of these additives⁵⁻⁶). Kuvang -lung Lin et al., show that with using saccharin as an additive in Ni-Cu-P alloys, stress is decreased in deposited layers because saccharin reduces grain size⁷).

In electroless process, hypophosphite is oxidized and precipitates as nickel phosphite on substrate at 80-90 °C. But at this temperature without stabilizer Ni-P layer does not deposit on substrate and decomposes the solution⁸). In the presence of stabilizer in electroless solution, the stabilizer precipitates on substrate and causes nucleation of Ni-P. The effect of heavy metal as lead acetate is known in Ni-P electroless alloys. But the toxic properties of lead restricts the use of these stabilizers.

For this purpose, some investigators have chosen thiourea instead of lead acetate⁹). Nevertheless, there is a little information about the effect of these additives on the properties of the deposited layer. In the present investigation, some properties of the deposited layers obtained from the bath containing thiourea and gelatin were studied.

Experimental procedure

In all baths for plating, 304 stainless steel was used as substrate. The baths were prepared with distilled water and analytical grade chemical materials. The samples at first were degreased in 60 g/l NaOH for 10 minutes at 60°C then deoxidized at 30% HCl for 5 minutes in ambient temperature. After these operations, they were rinsed in distilled water and finally after activation in %20HCl at 50 °C electrolessly deposited in 150 ml cells of thermostately controlled at 90°C. The composition of the solutions and condition of operation are shown in Table 1. The structure of as deposited and heat treated deposits were studied by usual continuous scanning X-Ray diffraction method with a D500 Siemens diffractometer with CuK α target. For studying of morphology, scanning electron microscope LE04401, for chemical analyzing of deposited layer the E.D.X. procedure using an Oxford 7059 and for microhardness measurement, Germanisher LLOYD-GL PX245-023 Vickers microhardness tester under a load of 50 gr. were used.

* Corresponding author

Tel.: +98-411-4245772 Fax: +98-411-4245771

E-mail address: parvini@stu.ac.ir (N. Parvini Ahmadi)

Address: Sahand University of Technology. P.O. Box 51335/1996. Tabriz, IRAN.

Result of experiment

Effect of thiourea and gelatin on deposition rate and composition of deposited layer

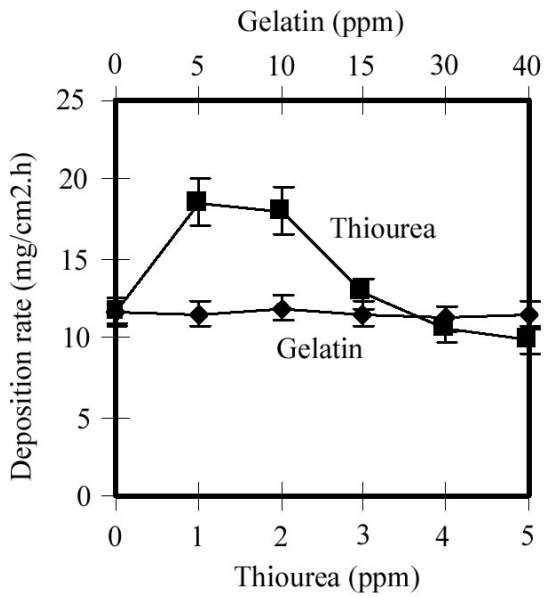


Fig. 1. Effect of thiourea and gelatin concentration on the deposition rate.

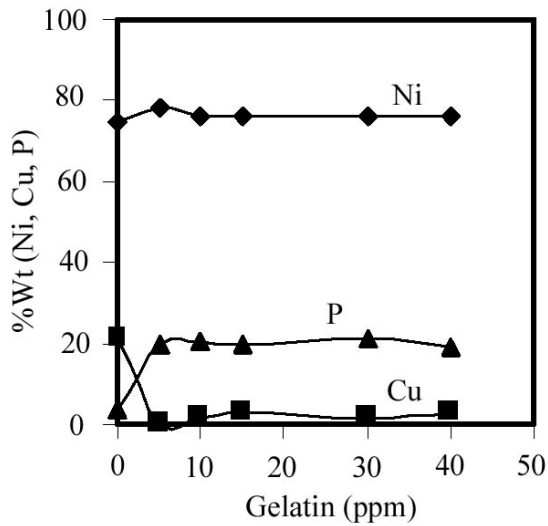


Fig. 2a. Effect of gelatin concentration on the composition of deposits.

Figure 1 represents deposition rate and Figures 2a,b, 3a,b, show percentage of elements in deposited layers in presence of gelatin or thiourea as additives in solutions, respectively. The stabilizer in the electroless nickel deposition bath stabilizes the bath by poisoning the catalytic activity of the accidentally formed nickel phosphide or metal hydroxide nuclei. It was expected that the stabilizer would also be adsorbed onto the deposit. Too much

adsorption of the stabilizer on the substrate or deposit certainly would also poison the deposition reaction⁹⁻¹⁰. As Figure 1 shows, gelatin doesn't have a major effect on deposition rate in comparison with thiourea. In solution containing thiourea, deposition rate increases up to 1ppm, then it is constant from 2 up 3 ppm, but in amounts more than 4 and 5 ppm, deposition rate decreases. As it is seen in Figure 2a. the variation of percentage of elements in deposited layer is more in solutions containing gelatin, in spite of nickel that its percentage is constant, copper percentage decreases but phosphorous percentage increases. Also a minor amount of Fe (Figure 2b) was observed in deposits (1-1.5%). It is seen that Fe as a result of oxidation, it removes from substrate and enters the solution, then from the solution it enters into the deposit. This phenomenon is well known in conversion coating.

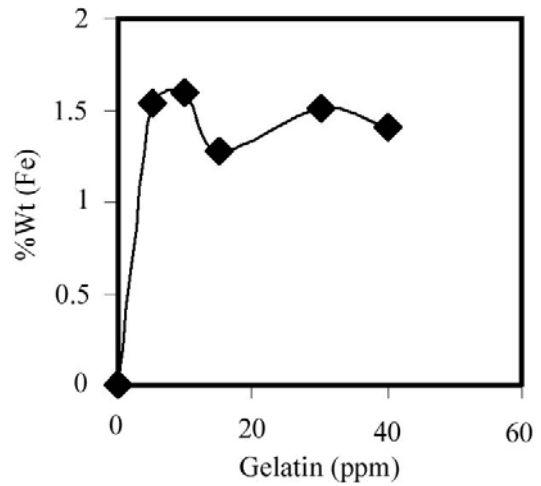


Fig. 2b. Effect of gelatin concentration on the composition of deposits.

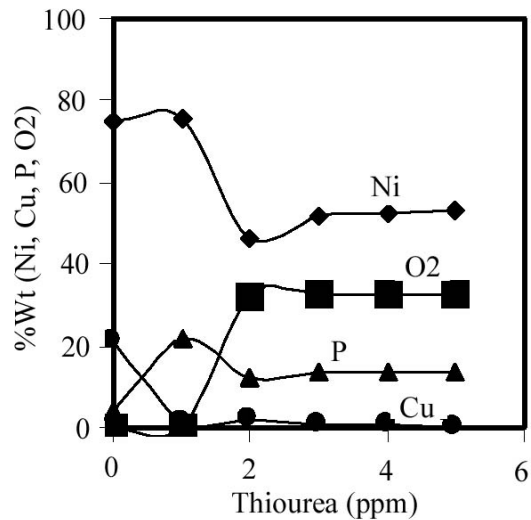


Fig.3a. Effect of thiourea concentration on the composition of deposits.

Figure 3 shows that in solutions containing thiourea, nickel and copper percent in the deposited layer decreases but the phosphorus percentage increases (Figure 3a). More variations of percentage of elements are seen from 1 to 2 ppm thiourea but with increase of thiourea in solution, the changes of nickel and phosphorus in deposited layers is negligible. On the other hand, with the increase of thiourea, the percentage of copper decreases in deposits. So, at 5 ppm thiourea copper isn't observed in the layer. Besides Ni, P and Cu, other elements such as Fe, O₂ and S were observed in deposits (Figure 3b). Sulfur enters deposits from thiourea [CS (NH₂)₂] but the presence of oxygen in deposits needs explanation. In similar reports such elements haven't been mentioned⁹⁾.

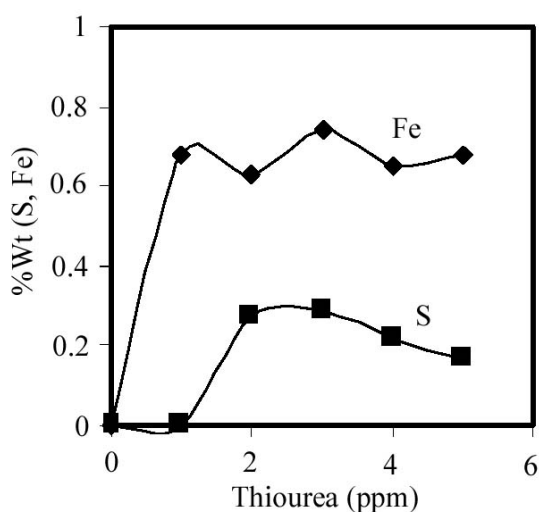


Fig. 3b. Effect of thiourea concentration on the composition of deposits.

Microstructure of deposited layers

The surface morphology of the electroless nickel deposits was investigated with SEM. Figures 4, 5 and 6 represent microstructure of deposits with thiourea, gelatin and without additives respectively. A smooth and fine microstructure is obtained in the solution without additives but in the presence of thiourea in solution, rough and spongy nodules are obtained as compared with gelatin and without additives.

Rough and spongy nodules in the presence of thiourea probably are related to high deposition rate⁹⁾ or presence of impurities such as Fe, O₂ and S in deposits. The layers obtained in the presence of gelatin have irregular nodules in spite of layers obtained from solution without additives, but don't they have spongy nodules, which are obtained from the solution containing thiourea. It is necessary to say, in deposited layers obtained from gelatin, there

are no impurities such as O₂ and S except Fe. The impurities such as O₂, S and Fe are the main reasons in of deposits obtained from solution containing thiourea being spongy.

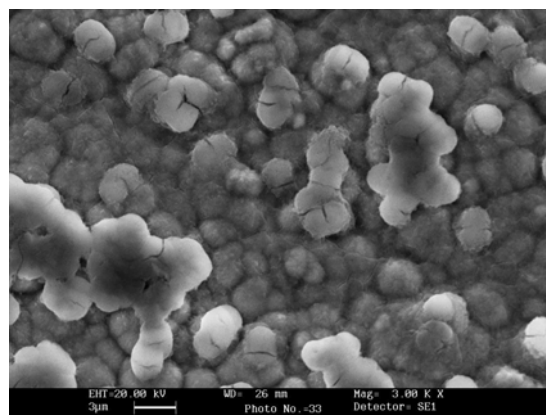


Fig. 4. The SEM morphology of deposits obtained with 2 ppm thiourea in solution.

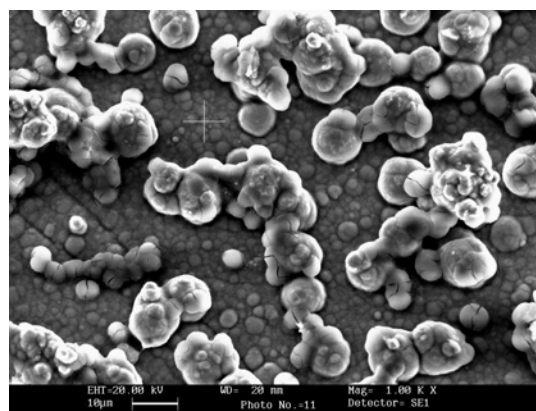


Fig. 5. The SEM morphology of deposits obtained with 10 ppm gelatin in solution.

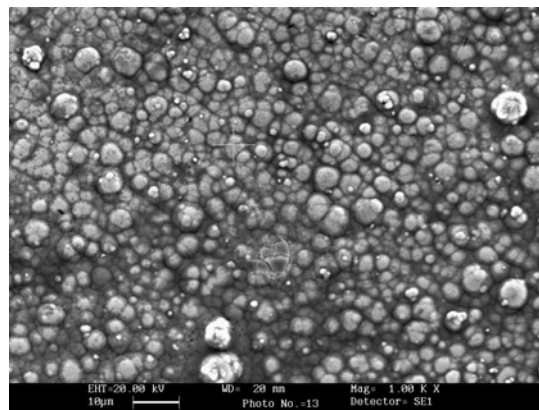


Fig. 6. The SEM morphology of deposits obtained without using additives.

Microstructure and microhardness of layers

Figure 7 represents XRD pattern of as-plated layers, a wide peak at $2\theta=44.61^\circ$ reveals (111) a plane of cubic nickel phase. In layers without additives, this peak is wide with low intensity. Therefore this structure is amorphous or microcrystalline. With increasing thiourea up to 1 ppm or gelatin up to 5 ppm, a sharp peak with high intensity was obtained at the same angle. It is obvious that, with increasing the thiourea or gelatin in the bath, the crystallinity of deposits increases. But with increasing thiourea from 1 to 5 ppm or gelatin from 5 to 40 ppm are not revealed remarkable changes in wide and intensity of the peak. The reason is related maybe to phosphorus content that with increase of thiourea or gelatin in solutions, their percentages remain constant in both cases.

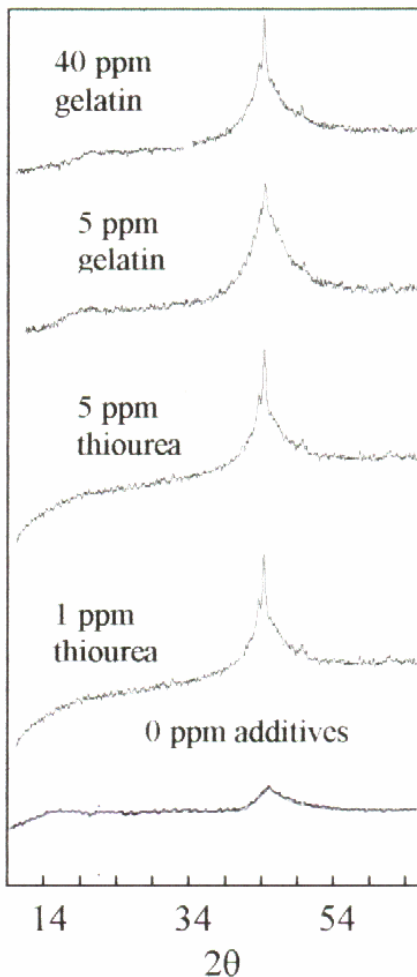


Fig. 7. XRD pattern of as-deposit layers for various gelatin and thiourea content.

Figure 8 shows XRD patterns of the same layers after heat treatment in 500°C , 1 hour, as it is seen, after heat treatment different peaks are revealed that show new phases in deposits. These peaks at $2\theta=36.32, 38.31, 41.7, 42.77, 43.62, 44.41, 45.18,$

$46.57, 48.86, 50.58, 51.98, 52.67$ are related to formation of Ni_3P crystalline phase.

Figure 9 shows that microhardness of as-deposited layers obtained from solutions containing gelatin decreases up to 5 ppm then it remains constant up 40 ppm. Decrease of microhardness is related to increase of phosphorus content from 3 to 20% and probably to the presence of 1.5% Fe in deposits. It is necessary to say that the percentage of phosphorus and Fe in deposits with various compositions of gelatin (5-40 ppm) in bath is constant. This is the main reason microhardness of deposits after 5 ppm gelatin are constant.

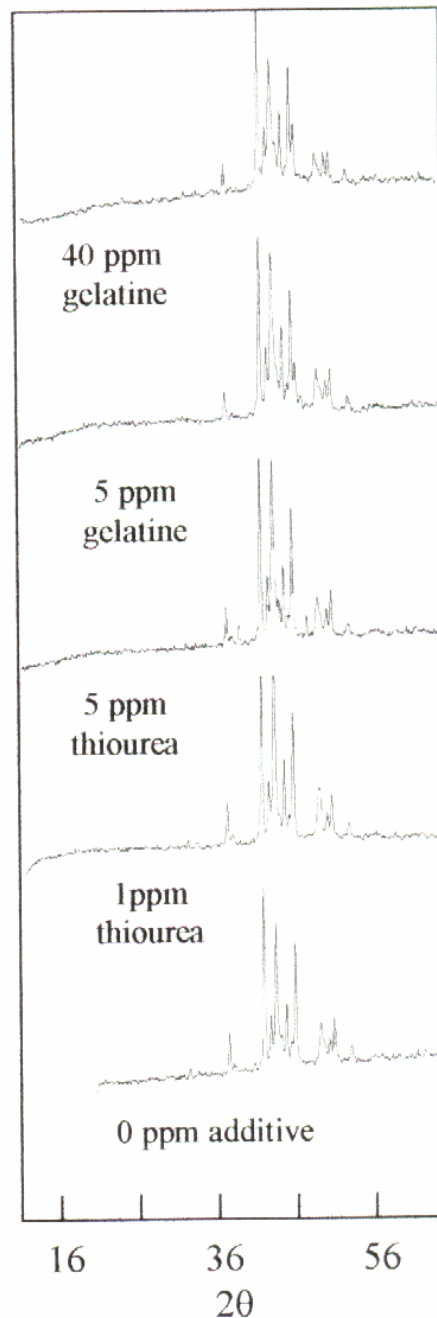


Fig. 8. XRD pattern of deposits for various gelatin and thiourea content after heat treatment.

With increasing thiourea up to 2 ppm in solution, the microhardness of deposits increases considerably (Figure 10). Increase of microhardness is related to the thickness of layer and probably to the presence of impurities such as Fe, O₂ and S that form solid solutions in deposit. But the reduction in microhardness in more amounts of thiourea from 3 to 5 ppm is related to sponging microstructure that covers the whole surface (Figure 11). After heat treatment of same samples, microhardness of layers increase as a result of formation of Ni₃P phase formation in deposits.

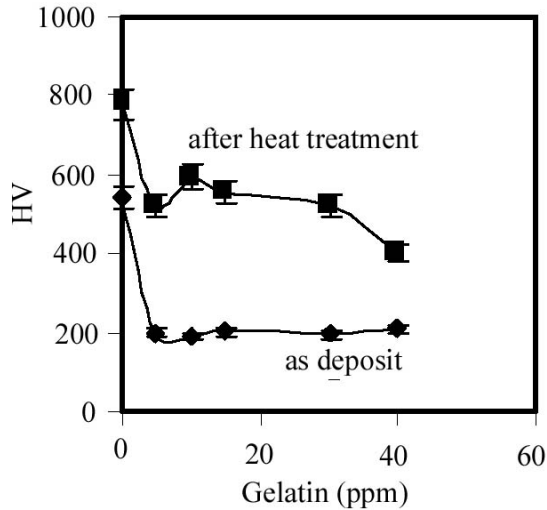


Fig. 9. Dependence of microhardness of deposits on gelatin concentration in as-deposit and after heat treatment

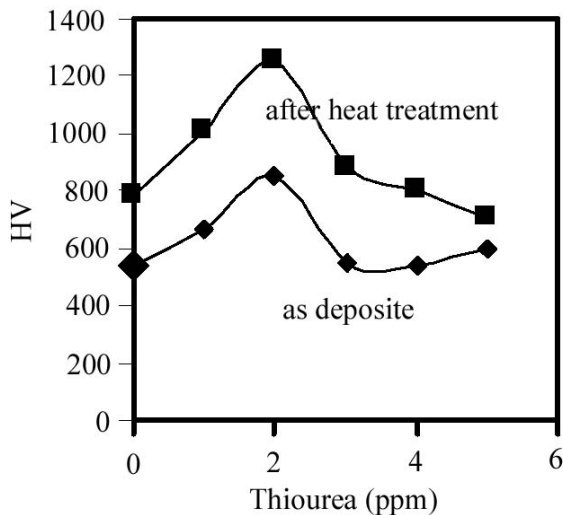


Fig. 10. The dependence of microhardness of deposits on thiourea concentration in as-deposit and after heat treatment.

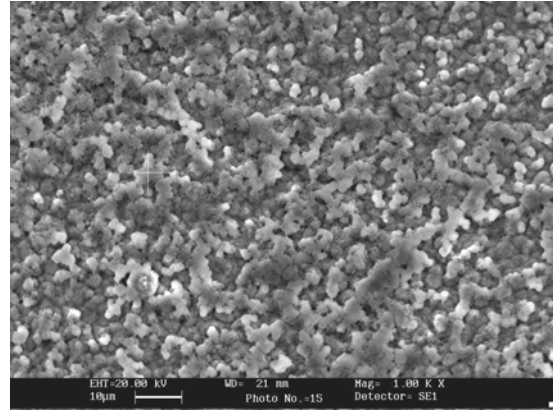


Fig. 11. The SEM morphology of deposits obtained with 5 ppm thiourea in solution.

Conclusion

Gelatin in Ni-Cu-P electroless plating has no effect on deposition rate is, but thiourea in amount of 1-2ppm increases deposition rate remarkably. Thiourea and gelatin decrease copper and increase phosphorus percentage in deposit layers. In the presence of gelatin, increase of phosphorus is more than solutions containing thiourea. On the other hand, in presence of thiourea in solution, impurities such as O₂, S, Fe and in the presence of gelatin only Fe enter into the deposited layers. Surface roughness of deposited layers in the presence of gelatin and thiourea is more than that without using additives. The microstructure of deposited layer obtained in more than 4 ppm thiourea is completely spongy.

The microhardness of as-deposit layer obtained from solution with no additives is more than deposits obtained from gelatin containing solution, but less than solutions containing thiourea.

After heat treatment, the microhardness of deposited layers increases as compared with as-deposited cases. Increase in microhardness after heat treatment is related to formation of stable Ni₃P phase.

Table 1. Chemical composition and deposition conditions for Ni-Cu-P coatings.

Composition	g/l	Baths		
		1	2	3
NiSO ₄ . 6H ₂ O	27.5	×	×	×
CuSO ₄ . 5H ₂ O	1.2	×	×	×
NaH ₂ PO ₂ .H ₂ O	30	×	×	×
CH ₃ COONa.3H ₂ O	20	×	×	×
Na ₃ C ₆ H ₅ O ₇ .2H ₂ O	55	×	×	×
CS(NH ₂) ₂ (ppm)	-	-	1-5	-
Gelatin (ppm)	-	-	-	5-40

T (°C): 90, pH: 10, t: 60 minutes

References

- [1] D. Tachev, J. Georgieva, S. Armyanov, *Electrochimica Acta*, 47(2001) ,359.
- [2] Z. Bangwei, X. Haowen, *Mater. Sci, Eng. A*, 281(2000) ,286.
- [3] M. Ishikawa, H. Enomoto, N. Mikamoto, T. Nakamura, M. Matsuoka, C. Iwakura, *Sur. Coat. Tech.*110(1998) ,121.
- [4] H. A. Sorkhabi, H. Dolati, N. Parvini Ahmadi, J. Manzoori, *App. Sur. Sci.*, 185(2002) ,155.
- [5] R.D. Mikkola, Q.T. Jiang, B. Carpenter, *Plat. Surf. Finish.* 87(2000),81.
- [6] J. Reid, S. Mayer, E. Broadbent, E. Klawuhu, K. Ashtiani, *Solid State Technol.*(2000) ,86.
- [7] K. Lung lin, Y. L C. C. Chan Huang, F. I Li, J. C. Hsu, *App. Sur. Sci.* 181(2001) ,166.
- [8] J.E.A.M. V. D. Meerakker, *J. Appl. Electrochem.* 11(1981) ,395.
- [9] K. Lung Lin, J. W. Hwang, *Mater. Chem. Phy.* 76(2002) ,204.
- [10] G.O. Mallory, J.B. Hagdu, *Electroless plating: Fundamentals and applications*, AESF, Orlando, FL, (1990) ,118.