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Development of the Ni-P Electroless Plating by Photon Energy

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Abstract

Conventional electroless plating is the subsequent deposition of metal without using energy except heating. However, electroless plating is almost universally used because it offers good mechanical properties of surface and high resistance to corrosion as well as it is an economical way of deposition. This work is focused on decreasing the consumed energy when heating by using photon energy (UV radiation) instead, as an assistant source. Furthermore, the effect of UV exploiting on the Ni-P electroless plating compared to heating only was studied. The best temperature and the pH of the deposition bath to obtain a better and stable thickness of Ni-P alloy coating were investigated in this paper. The compositions of deposition bath were about 21.2, 24, 28, 2.2 g/L and 0.8 ppm for $NiSO_4.6H_2O$, $NaH_2PO_2.H_2O$, C_3H_6O, and CH_4N_2S, respectively. The experiments were conducted with heating only by changing the temperature from 25 to 80 °C and heating with expositing UV radiation. In addition, the pHs of the baths were ranged from 3.5 to 8. The thickness of deposit layer was obtained by using a sensitive balance and permascope apparatus. The concentrations of $NiSO_4.6H_2O$ were measured by spectrophotometer. The composition of deposited layer was conducted by XRD. The resulted thicknesses were the combination of Ni-P which were increased rapidly with increasing time of deposition, as well, the temperature of bath and pH of solution in present or without UV light. The thickness of Ni-P alloy in presence UV light was increasing at low acidic and alkaline medium (pH up to 6). The novel technique using UV energy was enhancing the depositing of Ni-P alloy without and with heating. The resulted Ni-P layer was uniform, stable for above seven years and has good mechanical properties on both sides of the samples.

Keywords: Electroless plating; UV radiation; Ni-P layer; temperature; pH.

1. Introduction

Electroless plating is a process to produce thin metallic coatings on objects without the application of external current. The advantages of this process over electroplating are the possibility to produce coatings on insulating materials, and to produce uniform thickness coatings on geometrically complex surfaces. The first description of electroless plating was that of Von Liebig involving the reduction of silver salts by reducing aldehydes [1]. Modern electroless plating began in 1946 with the rediscovery by Brenner and Riddell, that hypophosphite could bring about nickel deposition [2]. First electroless nickel solution capable of the wide use on plastics was introduced in 1966; As aforementioned, the electroless plating process was achieved to improve the mechanical properties of the metal namely hardness, corrosion resistance, and wear resistance. Hiratsuka et al. have studied the effect of the Ni-P electroless plating on the wear properties of the metals [3]. The rate of deposition of electroless Ni–P coating is found to be a function of concentration of thiourea, succinic acid and lead acetate additives. Thiourea accelerates the rate of deposition up to (0.8 ppm) and started to inhibit at a concentration of 1 ppm [4-6]. Mild steel was electroless coated with nickel–phosphorus alloy from a bath containing sodium hypophosphite and glycin–citrate complexing agents, the effect of coat-

ing time on phosphorus content, thickness, structure and hardness of the deposits were also analyzed [7].
Limited literatures have been reported how the effect of UV on the electroless plating process and most of them was dealing with the polymer substrates. On the other hand, it has also been reported that the electroless plating rate of nickel was suppressed by UV irradiation onto the substrate removed from the sensitizer solution [8]. Additionally, the UV irradiation was used in an electroless plating solution of nickel, where it was suppressed the plating rate significantly [9]. It is expected that these techniques will be applied to make metal film patterns on printed circuits. The effect of UV irradiation on nickel plating during the electroless plating process was investigated. Both enhancement of the plating rate and the quite opposite effect, suppression, were obtained. Either enhancement or suppression can be caused by selecting the step at which the UV light is irradiated on the substrate. By using these effects, a pattern can be made on nickel film without the etching technique. This technique is similar to the so-called Etchingless technique used to make semiconductors [9]. Lee and Horiuchi have studied the effected electron beam lithography of electroless nickel plating on patterned catalytic surfaces [10], Nickel–phosphorus (Ni–P) alloy thin films with high-resolution features were created on patterned palladium (Pd) catalytic surfaces by electroless plating [10]. In another work, a research worked on the fabrication and selective metallization of high aspect ratio curing SU-8 polymer microstructures on a silicon substrate using UV lithography technology and selective electroless plating method was reported [11]. Electroless plating of metal films on both the top and sidewall surfaces of microstructures was achieved while the silicon substrate was not coated [11]. The surface modification was realized through attaching Au colloidal film to amine group, which forms a seed layer on cured SU-8 polymer for electroless plating of copper after the polymer surfaces were exposed under large UV irradiation. Their experiments demonstrated that UV exposure dosage and illumination direction are two of the most dominant parameters in the selective electroless plating process. The approach can also be easily adapted to electroplating other metals with different electroless plating baths in theory [12-14]. Recently, Singh et al. were purposed that the experiments have been performed in different lighting conditions like dark, ambient and varying intensity UV-VIS light. Also, the nickel depositions have been done in different periods of time from a very small period from 30 sec to 4 min, this is to observe the effect on the initial stage of depositions as well as for prolonged deposition. Alkaline bath (pH $\sim$7.5) was selected for EN-deposition and other experimental conditions were kept same for all the experiments [15]. In this study, the affected parameters (temperature, pH, and deposition time) in case using photonic energy for electroless plating alloy from Ni-P were investigated. The deposited layers were characterized by scanning electron microscope (SEM) and X-ray diffractometer (XRD).

2. Material and Methods

2.1. Materials

The chemicals were used in experiments of electroless plating were Nickel Sulphate Hexahydrate ($NiSO_4.6H_2O$, Aldrish), Sodium hypophosphite monohydrate ($NaH_2PO_2.H_2O$, Aldrish), Thiourea S-$C(NH_2)_2$, Aldrish), Lactic acid ($C_3H_6O_3$, Aldrish) and Propionic acid ($C_3H_6O_2$, Aldrish).

2.2. Sample Preparation

The raw materials and chemical composition used for experimental work are shown in the Table 2.1. The electroless deposition bath was containing of Nickel sulphate hexahydrate as a nickel source.
Sodium hypophosphite was used as the reducing agent, which also serves as a Phosphorus source in the coating. Lactic acid and Propionic acid were used as the complex agents to control the rate of release of free metal ions for the reduction reaction. Thiourea was used as additives in the plating bath. Among them, Thiourea was added as complex agents in order to avoid spontaneous a decomposition of the bath.
The substrate used for plating were iron specimen which produced by Libyan Iron & Steel Co., with special specification. The chemical compositions of steel metallic piece were included on Fe, C, Si, Mn, P, S and Al with 99.402, 0.095, 0.22, 0.207, 0.014, 0.001 and 0.061 respectively. The substrates were prepared with 12 cm^2 surface area and 1 mm thickness. The cleaning was done using diluted nitric acid; this step is used to activate the surface for the precipitation process. The substrate was washed many times by deionized water and lastly acetone, finally it dried well and weighted.

Table 2.1: Raw Material for the Bath [4]

Chemical	Formula	Concentration g/L
Nickel Sulphate Hexahydrate	$NiSO_4.6H_2O$	21.2
Sodium hypophosphite monohydrate	$NaH_2PO_2.H_2O$	24
Thiourea	$SC(NH_2)_2$	0.0008
Lactic acid	$C_3H_6O_3$	28
Propionic acid	$C_3H_6O_2$	2.2

Table 2.2: Operating Conditions

PH	3.5-8
Temperature	25-80 °C
Duration	30-120 min

2.3. Measurements and Characterization

In this work, in order to investigate, how change in various parameters (temperature, pH, and deposition time) when using photonic energy for electroless plating alloy from Ni-P, they will affect the deposition. The samples obtained were characterized by SEM, XRD, techniques. The operation parameters of electroless Ni-P deposition bath are shown in Table 2.2.

The instrument as UV exposure box (Radio Spares, model No.556-238) used to exposure the UV light on the baths. Spectrophotometer (8700 SERIES UNICAM UV/V spectrophotometer), Permascope (D211D type D211D NO.03112864), Scanning electron microscope, sensitive level balance and X-ray diffraction (XRD), were used to investigate the composition of deposition layers. The thickness of the coat was measured using Permascope apparatus; furthermore, the Spectrophotometer has been used to measure the concentration of the green nickel sulphate hexahydrate before and after precipitation process.

3. Results and Discussion

The measurements of concentration of $NiSO_4.6H_2O$ in the deposition baths were estimated by using the UV-Vis spectrophotometer apparatus. The maximum wavelength (λmax) of $NiSO_4.6H_2O$ is at 405 nm. The calibration curve of the $NiSO_4.6H_2O$ was from Beer's Law at (λmax=405) as the following Equation:

$$Absorbance\,(A_i) = S \times C_i \qquad (3.1)$$

where: Ai: absorbance (%), S: slope of the curve and Ci: concentration,(g/l). In our case; the concentration was calculated from the following calibration equation: Ai = 0.295 Ci with a good fitting ratio (R^2= 0.995).

Furthermore, Figure 3.1 was presented the best samples which gave a uniform layer of deposition on the substrate. The deposition conditions were conducted at 80 °C and at pH equal to 6.5, in the case of exposing UV light and without exposing. The deposition layer was appeared in silver-green colour, and the deposition was covered almost the surface of the substrate. The morphology of the deposit coating was analyzed by using SEM; Figure 3.2 shows the cross section of deposit layer, the coating has a good adhesion to the substrate with a few cracks and holes were observed.

Figure 3.1: The shape of the sample after plating at T=80°C, pH=6.5: (a) No light, (b) Light.

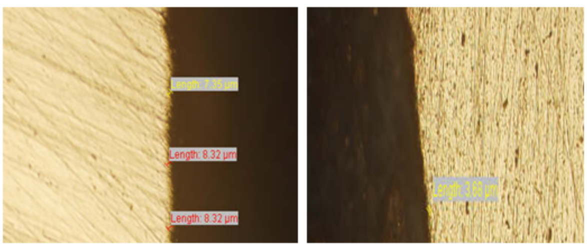

Figure 3.2: SEM of cross section view of an electroless plating coating at temperature=80 °C and pH at 4.5

The effect of temperature on plating thickness was investigated, where, the thickness of nickel deposition increased rapidly with increasing the temperature in case of present light or without light. Some of the experiments were conducted at 25 °C; the nickel deposition rate without exposing light was less than with exposing light. The light causes increasing of the temperature and reaction rate (increase the ion mobility) in the bath of deposition, and then increased the plating thickness. The results were presented in Figure 3.3 which agreed with Baldwin and Such [16].

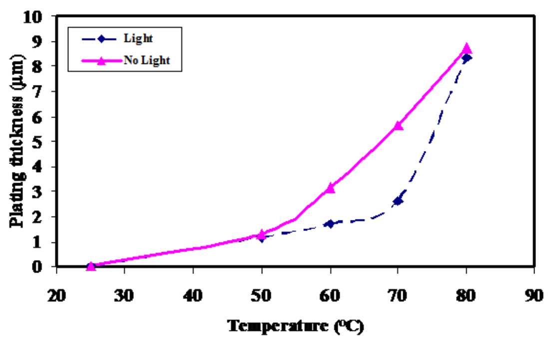

Figure 3.3: Effect of Temperature on plating thickness at pH=4.5 for 30 min.

On the other hand, the time effects on plating thickness were another factor which examined in our work and several researches. The thickness of deposit layer increase fast with increasing time in both cases as shown in Figure 3.4, this is due to enhance the oxidization/reduction reactions and increase the deposition of Ni-P alloy [4, 17].

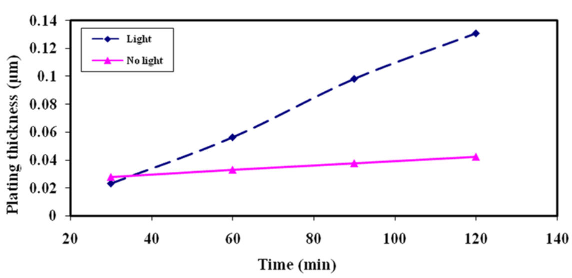

Figure 3.4: Effect of time on plating thickness at pH=4.5 and temperature = 25°C.

The Effect of deposition bath's pH on plating thickness was illustrated in Figure 3.5, the study was presented the effect of pH with a range from 3.5 to 8 values, under fixed conditions at 80 °C and for 60 min. It can be seen in Figure 3.5 that the thicknesses of nickel deposition increase rapidly with increasing pH value in presence light or without light. From the experimental observation, it can be concluded that the thickness of deposit Ni-P alloy increases in the less acidic medium due to the mechanism of reaction which activates the reaction occurrence and plating in the medium. At pH greater than 6, the plating thickness in the existence of light is more than that without light. This can be owed to light increases the reaction mechanism in the less acidic and alkaline medium. Using the without light these matches with the results of Mallory G. [18]. This conclusion is confirmed by Nakamichi et al, where the light increases the plating in the alkaline medium and deceases the plating in the acidic [9]. Moreover, the plating depends on the light wavelength.

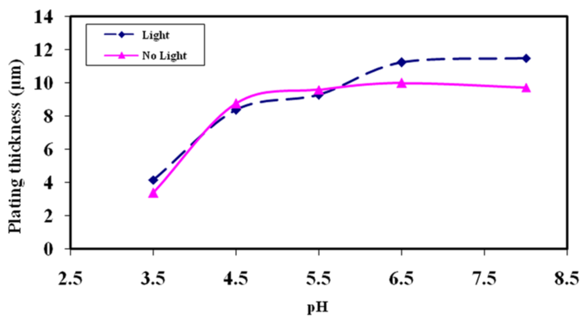

Figure 3.5: Effect of pH on the plating thicknesses at 80 °C for 60 min.

Figure3.6 shows the comparison between the experimental data of presence light and without light at pH equals to 4.5, the comparison results were showed that the effect of light is enhancement of plating thickness at condition of low time (for 30 min) and low temperature (at 25°C). This might be attributed that light increases the temperature of reaction bath leading to reaction's occurrence and plating at room temperature. On the other hand, the effect light is suppression of plating thickness at increase time or increase temperature. This is because light together with heating hinders plating in the more acidic medium. Therefore the influence of plating with heating is more obvious when increasing time and temperature at pH equals to 4.5, the reason due to the reaction mechanism in solution.

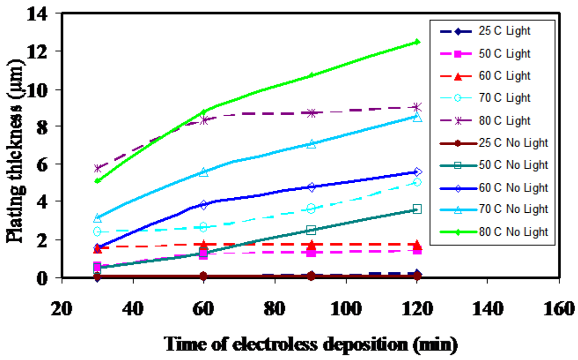

Figure 3.6: Effect of Light and without light on plating thickness at pH=4.5.

From Figure 3.7 shows the comparison at pH (6.5) or change in concentration of the bath the samples were appeared enhancement of plating thickness. The effect of UV irradiation on nickel plating during the electroless plating process was investigated. Both enhancement of the plating rate and the quite opposite effect, suppression, were obtained. Either enhancement or suppression can be caused by selecting the step of solution preparation and sample. This confirmed by Nakamichi et al, [9] where the plating rate depended on the composition of the solution. In alkaline solution, enhancement appeared, but suppression appeared in acid solution. The word enhancement indicates that the rate of plating in the irradiated region appeared to be much greater than that in the non irradiated region. The word suppression indicates that the plating rate appeared to be suppressed by UV irradiation. The effect light on plating thickness affected by the wavelength of UV radiation and pH (acidic and alkaline) of solution and surface activation and the distance between the lamp and the cup of plating and conditions plating.

The effect of $NiSO_4.6H_2O$ concentration on plating thickness is depicted in Figure 3.7 which that indicates the plating thickness increase with the increase concentration from 19.2 g/l to 22.2 g/l then decreasing at 23.2 g/l. The reason due to the reaction mechanism because the solutions consist of many compounds which help with takes place reaction of reduction and oxidation and deposited Ni-P alloy. The main substance is Sodium hypophosphite monohydrate ($NaH_2PO_2.H_2O$), which bounded the plating thickness because it is the reducing agent then the nickel reduction was taken place and deposited on the steel piece. Also, the oxidation reaction hypophosphite and phosphorous deposited on Nickel was taken place to obtain the Ni-P alloy. Therefore the concentration of hypophosphite related to concentration of nickel sulphate hexahydrate. In the presence light of maximum concentration is 22 g/l and pH (6.5) or maximum concentration at without light was 21.2 g/l. The effect of the light on plating thickness is greater in the presence of light. This is due to the effect of concentration on the reaction mechanism or the effect of the light on deposition rate.

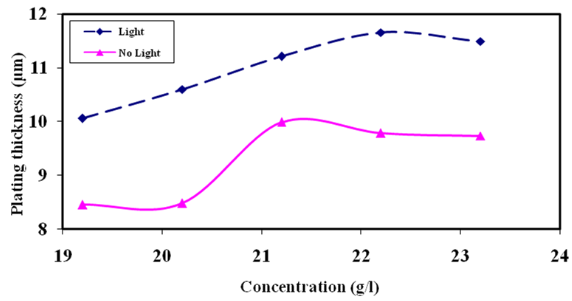

Figure 3.7: Effect of change concentration Nickel sulphate hexahydrate ($NiSO_4.6H_2O$) on plating thickness at (T=80 °C,t=60 min,pH=6.5).

Additionally, the results of the XRD for the best deposit samples were presented in this paper. XRD reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials. XRD is the best analysis instrument can show the composition of the prepared coating layer. The results were shown the significant conclusions about the formed electroless layer with and without invoking the UV light. Thus, pH value of 6.5 is the best value to obtain well crystallinity layer with and without using light as can be observed from Figure 3.8 and Figure 3.9. Besides, using different pH values were badly affected on the crystallinity of the layer. As well, the optimum plating time in case of using UV and without exposing light was 60min. As aforementioned, the broadness of the obtained peak refers to the grain size of the produced grains; broad beak denotes to the small grain size and vice versa. A typical reason for that can be stated as: with increasing the plating time the grains split into smaller ones due to the high internal energy due to the chemical activity of the metals and the corresponding used temperatures. In case of using light, also the temperature has an effect on the grain size. In the normal case (i.e. without using the light), the grain size is sensitive to time more than temperature. An interesting note can be observed by comparing the planar spacings of the obtained peaks and the standard pure nickel peaks. In case of invoking the light, the planer spacings are relatively closer to standard nickel that means the amount of phosphorous metal in the coated layer is small. In other words, utilizing the light enhances the purity of the obtained layer. It is noteworthy mentioning that, the mechanical and electrical properties mainly depend on the purity of the layer.

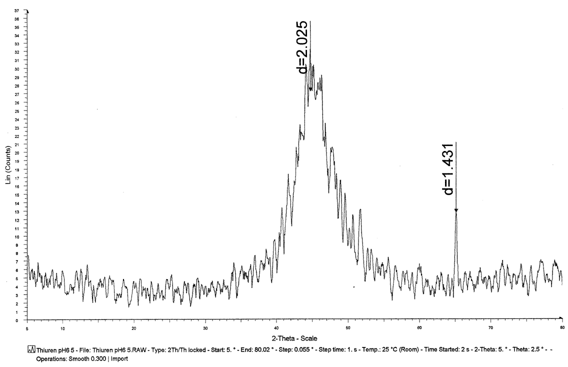

Figure 3.8: X-ray diffraction pattern of electroless Ni-P coatings obtained using light at Temp. = 80°C, for 60 min and pH =6.5 (Conc ($NiSO_4.6H_2O$=21.2g/l)).

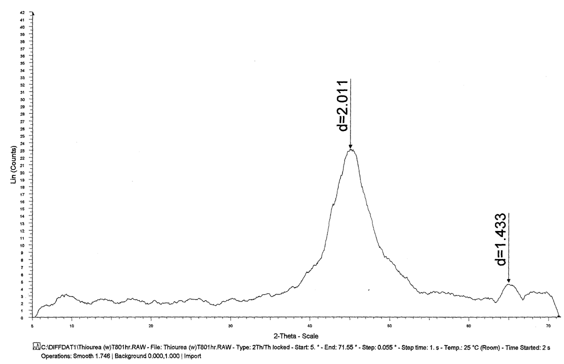

Figure 3.9: X-ray diffraction pattern of electroless Ni-P coatings obtained without using light at Temp. = 80°C, for 60 min and pH =6.5 (Conc ($NiSO_4.6H_2O$=21.2g/l)).

4. Conclusion

The deposited thickness of Ni-P increased rapidly with increasing the time, the temperature as well pH of solution in present light or without light. Ni-P deposit layer is good, stable and uniform on over both sides of the surface. The affect of light on electroless deposition is clear at room temperature (i.e 25 °C) and pH=4.5 compared with no light because the light causes increasing in the temperature and rate of reaction in deposition bath, then the thickness is increased. The plating at without using light and pH=4.5 value in more acidic medium, the best deposited thickness compared with the deposited thickness of layer in presence light at temperature 50, 60, 70 and 80°C, so the light in this medium was slightly affected on the deposition rate. The thickness of Ni-P alloy deposition at presence light is increasing in the low acidic and alkaline medium at pH up to 6 values. The reason due to that the reaction mechanism affected on the rate of reaction in the medium. The measurement of thickness by Permascope apparatus indicated to uniformity of plating layer.

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