

Electroless Deposition of Nickel—phosphorus Alloy*

— on the Surface Submitted to Cathodic Pulse Current

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ABSTRACT The pulsed electroless deposition of nickel—phosphorus has thoroughly been investigated to find out the relationship of phosphorus content in deposits and deposition rate with parameters of pulse current and temperature. The accumulation of phosphite in the electroless nickel plating solution can be improved due to using pulse current. Furthermore, it was discovered that the reaction of the pure electroless nickel deposition was accelerated by the pulse current.

KEY WORDS chemical plating / nickel—phosphorus, pulsed electroless deposition

The process of electroless nickel deposition is slow and energy—inefficient. The application of pulsed current to electroless nickel had been shown by Mallory and Lloyd^[1] to increase the deposition rate a factor of several times while yielding deposits with properties similar to those of conventionally applied electroless nickel. The new process was called as pulsed electroless deposition. No further works have been found since then.

The first aim of our investigation was initiated to investigate the relationship of phosphorus content in deposits and deposition rate with parameters of pulse current and temperature. Another problem for the electroless nickel plating is the short life of the plating bath, which is attributed to the accumulation of the reaction product (phosphite) in bath solution^[2]. So, another incentive for working on pulsed electroless process is to ascertain the possibility of renewing the electroless nickel plating solution containing reduced phosphite.

1 Experimental

All Ni—P alloy deposits were obtained from a conventional electroless plating solution with the following compositions: $\text{NiSO}_4 \cdot \text{H}_2\text{O}$ (28g/L), $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ (24g/L),

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CH_3COONa (17g/L) and stabilizer (1.5mg/L) at a pH of 4.6. The plating bath temperature was thermostatically maintained at $(80 \pm 0.2)^\circ\text{C}$ except for the test for temperature effect.

To enhance the accuracy of measurement, deposition was on copper sheet with large surface area (32cm^2) exposed to the solution. For the sake of comparison, the ratio of the active surface area of samples to the volume of plating solution was kept constant for all tests.

Cathodic rectangular pulses was impressed on the samples in this study. They were generated by a multi-waveform pulse power supply. The pulse frequency applied to all tests was fixed at 1000Hz.

Subsequent to the plating, the phosphorus content in deposits and the concentrations of phosphite and hypophosphite in solution were analyzed employing conventional wet chemical analysis. The plating time in all cases was chosen as 30 min. These 30 min periods were used to provide a detectable increase in mass. The deposition rate of Ni-P alloy was on average determined from the total weight deposited for 30 min.

2 Results and Discussion

2.1 Phosphorus content in deposits

The result with respect to the effect of pulse current density on phosphorus content in deposits is shown in Fig. 1. The phosphorus content (%) decreases with increasing pulse peak current density (i_p) no matter what duty cycle (R) is adopted.

The processes of both electroless and pulsed plating are responsible to the change of phosphorus content in the mode of pulsed electroless plating. The nickel-phosphorus alloy could spontaneously be deposited in a way of electroless process when the samples were immersed in a conventional electroless nickel bath used in this study. The electroless nickel obtained in this way contains 11.4% P. On the other hand, some electrodeposition reactions of Ni-P alloy would simultaneously take place due to the action of pulse current. The fast-rate electrodeposition produced much more deposit than the electroless deposition with a slow rate in the same plating duration. As a result, the average phosphorus content in the deposit resulted from the two synchronous plating processes was mainly controlled by electrodeposition. With reference to the result of electrodeposition by direct or pulse current^[3], the increasing current density necessarily resulted in a decrease in average phosphorus content in the deposits plated under pulse current.

2.2 Changes in bath components

The consumption rate of hypophosphite and accumulation rate of phosphite in the plating baths for conventional (duty cycle $R=0\%$) and pulsed ($R = 50\%$) electroless nickel deposition processes are shown in Fig.2. The results indicate that for depositing the same amount of nickel-phosphorus alloy, less hypophosphite as reducing agent was consumed and less phosphite as reaction product was generated for pulsed than conventional process. Furthermore, the difference in the concentrations of hypophosphite and phosphite them became more great when more Ni-P alloy was deposited.

In electroless deposition of Ni-P, hypophosphite (H_2PO_3^-) is employed as the reducing agent, and partly reduced to P and partly oxidized to phosphite (H_2PO_3^-) accompanied by reduction of nickel ions and excessive hydrogen evolution^[4]. It causes an accumulation of phosphite in plating solution. However, this situation was improved by the use of pulse current (see Fig.2). The phosphite resulted from electroless plating process was probably reduced to hypophosphite under cathodic current^[5]. Consequently, less phosphite was produced in bath during plating under pulse current due to this reduction reaction occurred in solution. As a result, the accumulation rate was declined. Furthermore, the hypophosphite produced was in turn supplied for the pulsed electroless plating as a reagent.

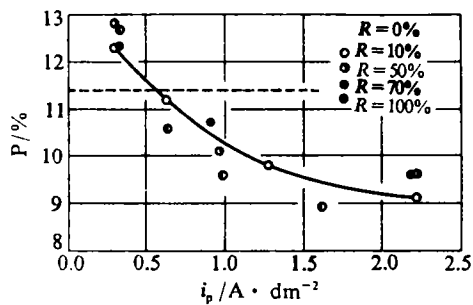


Fig.1 Phosphorus content in deposits

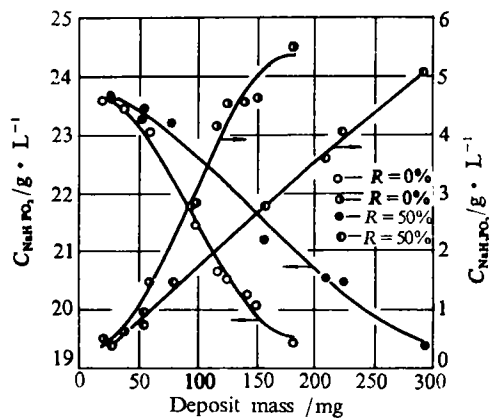


Fig.2 Dependence of the concentration of hypophosphite and phosphite in solution on the increasing deposit mass

2.3 Dependence of deposition rate on pulse parameters

Effect of peak current density on deposition rate was investigated while the duty cycle was maintained at 70%, as illustrated in Fig.3. The deposition rate of Ni-P alloy ($V_{\text{Ni-P}}$) increases with the increase of peak current density, but a plateau is reached with more hydrogen evolving on sample surface at the higher current density.

The deposition rate of the component nickel in Ni-P alloy deposit, V_{Ni} , at certain peak current density could be derived from the phosphorus content and deposition rate of Ni-P alloy, V_{Ni-P} . We define the theoretical deposition rate of total nickel, $V_{Ni(T)}$, as the sum of the deposition rates of the component nickel in electroless Ni-P alloy deposit obtained when $i_p = 0$, $V_{Ni(EN)}$, and Faraday nickel that denotes the theoretical content calculated from Faraday's law, assuming that total cathodic pulse current was consumed on nickel deposition, $V_{Ni(F)}$, that is, $V_{Ni(T)} = V_{Ni(EN)} + V_{Ni(F)}$. For the convenience of discussion below, V_{Ni} and $V_{Ni(T)}$ are also shown in Fig.3.

Study on the effect of duty cycle on the deposition rate was carried out in the same way like that on current density effect. At a constant peak current density of 1.0 A/dm², the deposition rate of Ni-P alloy, V_{Ni-P} , as a function of duty cycle is shown in Fig.4. V_{Ni} and $V_{Ni(T)}$, which are the same as above-defined, are indicated in Fig.4 as well. It can be seen that there is a great resemblance of these curves appearing in Fig.4 to that in Fig.3.

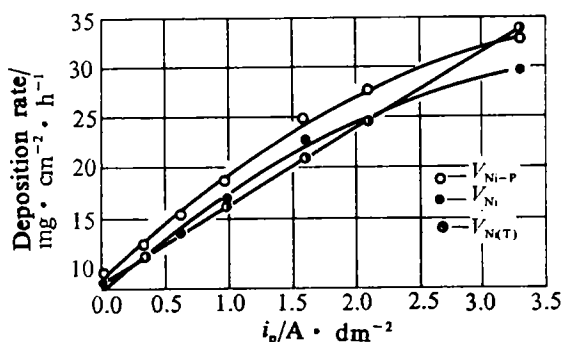


Fig. 3 Deposition rate of nickel-phosphorus alloy (V_{Ni-P}) and its component nickel (V_{Ni}) as a function of pulse peak current density at $R=70\%$

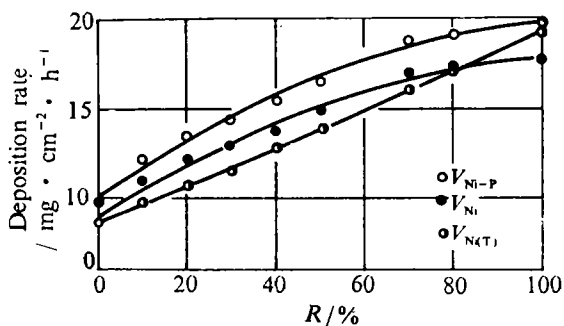


Fig. 4 Deposition rate of nickel-phosphorus alloy and its component nickel as a function of pulse peak current density at $i_p=1.0A/dm^2$

The effects of pulse peak current density (i_p) has been found to be similar to that of duty cycle (R) on deposition rate in behaviours (Figs.3 and 4). It might be due to their interrelationship through the equation $i_a = i_p \times R$ (i_a is the average pulse current density). Thus the effects of above two pulse current parameters could be considered to really reflect the effect of average pulse current density on the deposition rates.

The increase of deposition rate becomes slow and a plateau is reached at higher peak current density or duty cycle (Figs.3 and 4). The appearance of plateaus in the curves seems to be mainly due to hydrogen evolution at higher average pulse current density and consequent decreasing current efficiency for Ni-P alloy deposition reaction.

It is noteworthy in Figs.3 and 4 that over a suitable range of current density or duty cycle the real deposition rate of component nickel in the Ni-P alloy, V_{Ni} , is greater than the theoretical deposition rate of total nickel, $V_{Ni(T)}$. The result might indicate that the pulsed electroless plating process is not a simple superimposition of the pulse plating on electroless plating but that they interact each other to some extent, which is explained as follows. The value of $V_{Ni(F)}$ would definitely be larger than the deposition rate of nickel really deposited by current. This is because the Faraday nickel ($V_{Ni(F)}$) as defined previously is a theoretical value of mass calculated assuming that 100% current is consumed on the nickel deposition. Furthermore, the deposition rate of electroless nickel, $V_{Ni(EN)}$, is a measured value that was determined from sample deposited in the same plating bath without imposing pulse current. Consequently, solely possible explanation to the reason why V_{Ni} is able to exceed $V_{Ni(T)}$ is that the deposition rate of electroless nickel in the mode of pulsed electroless deposition is higher than that of electroless nickel in the conventional mode. It indicates that the process of autocatalytic electroless nickel deposition is accelerated due to the influence of pulse current. There are reasons to believe that pulse current affects the state of surface on which the electroless deposition takes place. The number of catalytic centers on the plating surface is believed to be a controlling factor for the rate of electroless nickel deposition. The fine-grained surface produced by pulse current might contain more active sites. The real mechanism remains to be proved.

2.4 Dependence of deposition rate on temperature

Variation of Ni-P alloy deposition rates with temperature in the range of from 65 to 85 °C at a pulse peak current density of 1A/dm² with a variety of duty cycle was investigated. The result is depicted in Fig.5. It indicates that the logarithmic deposition rate, $\ln(V_{Ni-P})$, has a linear relationship with the inverse of temperature, $1/T$, for conventional electroless nickel depositions ($R = 0\%$), which is identical with the previous work^[6] but non-linear for pulsed electroless nickel deposition ($R > 0\%$). At a given temperature, the deposition rate increases with the increase of duty cycle. In addi-

tion, the increment of deposition rate with dutycycle is getting smaller while temperature increases. The values of deposition rate corresponding various duty cycles tend to be close to each other at higher temperature. In other words, there is slight influence of pulse current on deposition rate at higher temperature.

The autocatalytic electroless plating is a chemical heterogeneous process by its nature. As a result, the relationship of electroless nickel reaction rate with temperature may be shown by the following equation:

$$V_{Ni-P(EN)} = K \exp(-E/RT)$$

where E is the activation energy and K is a constant. Hence, a linear relationship of the logarithmic plating rate with inverse temperature was obtained. When the pulse current is exerted the rate can approximately be considered as the sum of electroless and pulse plating processes. It can be expressed as follows:

$$V_{Ni-P} = V_{Ni-P(EN)} + V_p = K \exp(-E/RT) + V_p$$

where V_p is the electrode position rate under pulse current. V_p is referred to an electrolytic process and then essentially related to electrical parameters such as current density and duty cycle, and generally irrelative to temperature. It is obvious that the plotting of logarithmic deposition rate of pulsed electroless plating, $\ln V_{Ni-P}$, against inverse temperature, $1/T$, will not result in a linear relationship.

It is known that $V_{Ni-P(EN)}$ is getting greater with temperature, and V_p only increases with increasing duty cycle, being irrelevant to temperature. From there, it can be seen from above equation that the same increment of V_p caused by increasing duty cycle will bring about less increase of $\ln V_{Ni-P}$ due to high value of $V_{Ni-P(EN)}$ at higher temperature according to the character of exponential function. So the curves corresponding to different duty cycles are getting close each other at higher temperature.

3 Conclusions

The situation with respect to the accumulation of phosphite in the electroless nickel plating solution can be improved by using pulse current. It implies that the life of an electroless nickel bath can be prolonged.

The phosphorus content in deposits decreased and the deposition rate of Ni-P al-

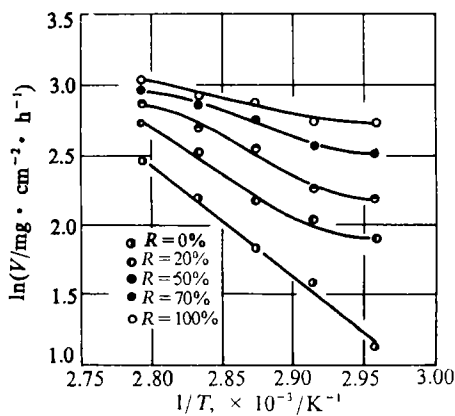


Fig. 5 Deposition rates of Ni-P alloy as a function of temperature with different duty cycles at $i_p = 1.0A/dm^2$

lloy increased in the pulsed electroless process of nickel plating when the pulse current density or duty cycle increased. Besides, it was discovered that the pulse current also promoted the reaction of the electroless nickel deposition.

For a pulsed electroless process, the logarithmic depositionrate of Ni-P alloy has a non-linear relationship with the inverse of temperature, as contrasted with a conventional electroless plating.

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阴极脉冲电流作用下的 Ni-P 合金化学镀过程

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摘要 研究了 Ni-P 合金脉冲化学镀过程, 找出了镀层 P 含量, 镀速和脉冲电流参数, 温度的关系. 由于脉冲电流的作用, 可以减缓镀液中亚磷酸盐的积累, 并且 P 的化学沉积过程也得到加速.

关键词 化学镀, Ni-P, 脉冲

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