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# Electroless Plating through Successive Pretreatment with Aminosilane and $PdCl_2$

Takeo HAMAYA,* Yaomi KUMAGAI, Naoto KOSHIZAKI, and Tokuzo KANBE
Industrial Products Research Institute, Tsukuba, Ibaraki 305

Electroless nickel deposition on glass beads was carried out by a new plating method without using stannous chloride, which needs a successive pretreatment with aminosilane and $PdCl_2$. It was presumed that metallic palladium nuclei was formed in the initial stage and initiated the plating.

Electroless plating on nonmetallic substrates has been most commonly carried out by using $PdCl_2/SnCl_2$ catalyst system. Recently, Kumagai et al.[1)] have reported a new plating method different from its system. They found that metal could be easily deposited on mica through only immersing palladium bound substrate into plating bath. This method is characteristic of being performed without using $SnCl_2$, though it needs a successive pretreatment with aminosilane and $PdCl_2$. This method is therefore advantageous for the abbreviation of troublesome operation using poisonous $SnCl_2$ as compared with $PdCl_2/SnCl_2$ system. This is also expected to be useful for plating other nonconductive substrates, because palladium can be easily introduced from $PdCl_2$ solution on their surfaces which have been previously aminosilylated. Details of this method therefore must be studied for wide application.

Then at first, we studied the time course of electroless nickel deposition on glass beads in order to examine its reaction aspect. The reaction was examined by the following two processes. Palladium bound glass beads from $PdCl_2$ solution were immersed into plating bath (1) directly and (2) after treating them in sodium hypophosphite ($NaH_2PO_2$) aqueous solution at high temperature. Distinct difference was found between both processes; a time-lag was observed in the former, but not in the latter. In this paper, the cause of this time-lag will be discussed on the basis of X-ray photoelectron spectroscopy (XPS) analysis of palladium bound glass surface.

Glass beads were successively pretreated before chemical plating by aminosilane, $PdCl_2$ and $NaH_2PO_2$ in the following manner. Ten grams of glass beads (40-60 mesh) supplied by Gasukuro Kogyo Ltd. were reacted with γ-aminopropyltriethoxysilane (0.25%, v/v) with stirring for 2 hours at 110 °C in 6 $cm^3$ of ethanol-water (9:1) mixed solvent. Two grams of the resulting aminosilylated glass beads were treated in 10 $cm^3$ of palladium chloride aqueous acidic solution (0.0015 wt%) with stirring for 1 hour at 23 °C (beads A). One gram of beads A was treated in 10 $cm^3$ of $NaH_2PO_2$ aqueous solution (20 wt%) with stirring for 30 min at 80 °C (beads

B). Plating composition was set as follows; $NiSO_4$: 0.114 mol $dm^{-3}$, $NaH_2PO_2$: 0.037-0.186 mol $dm^{-3}$, glycine: 0.27 mol $dm^{-3}$, sodium citrate: 0.093 mol $dm^{-3}$ at pH 8. Plating was carried out by immersing 200 mg of palladium bound glass beads in 10 $cm^3$ of plating bath at 70 °C. The reaction was examined by the following two different ways; one is the process initiated by immersing beads A into the plating bath (Process 1) and the other is that initiated by beads B (Process 2). At certain time intervals, 50 µl of the solution was pipetted out and diluted 400 times. The amount of nickel bound on the surface of the beads was evaluated from the nickel ion concentration in the solution before and after deposition using atomic absorption analyzer.

Figure 1(a) shows the time course of Ni deposition for Process 1 under different $NaH_2PO_2$ concentrations. The time-lag was observed in every case. Time courses of above two processes were compared in Fig. 1(b) under the constant $NaH_2PO_2$ concentration. Nickel began to deposit about 10 minutes later from dipping of beads A, while deposition proceeded as soon as immersing of beads B at almost the same maximum rate. In other words, the time-lag observed in Process 1 disappeared in Process 2.

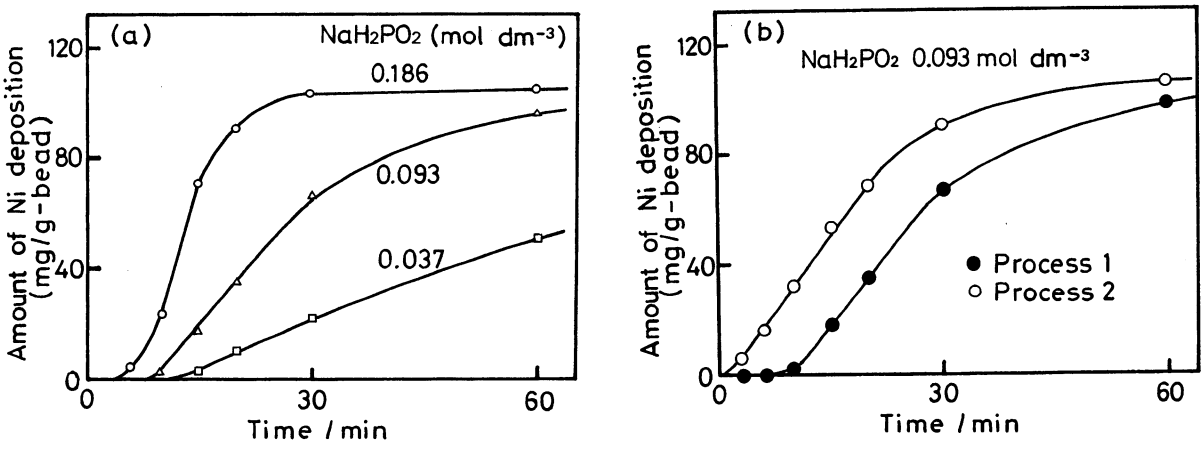


Fig. 1. Time course of nickel deposition: (a) Process 1 under the different concentration of $NaH_2PO_2$ (0.037, 0.093, 0.186 mol $dm^{-3}$). (b) Comparison between Process 1 and 2 under 0.093 mol $dm^{-3}$ of $NaH_2PO_2$.

In order to study the cause of this time-lag, the surface states of palladium bound glass beads were analyzed by XPS measurements. Palladium 3d photoelectron spectra of beads A and B are shown in Figs. 2(a) and 2(b), respectively. The doublet peaks at 343.8 and 338.4eV ($3d_{3/2}$ and $3d_{5/2}$) in Fig. 2(a) were assigned to $Pd^{2+}$ according to the results of Terasawa et al.[2] On the other hand, by $NaH_2PO_2$ treatment, new doublet peaks at 341.0 and 335.8eV appeared with diminishing $Pd^{2+}$ peak height as shown in Fig. 2(b). These new peaks are assigned to $Pd^0$ state because of a good agreement with the result of Kummer et al.[3] These results show that $Pd^{2+}$ was reduced to $Pd^0$ on the surface of glass beads by treating beads A in $NaH_2PO_2$ aqueous solution.

In order to explain the appearance of time-lag in Fig. 1, we assume the formation of metallic palladium as nuclei for our plating reaction. The chemical states of palladium bound on glass beads are $Pd^{2+}$ for beads A and $Pd^0$ for beads B as was confirmed above. $Pd^{2+}$ must be therefore reduced to $Pd^0$ to initiate reaction in Process 1. The time-lag observed might be thus period required for reducing palladium from $Pd^{2+}$ to $Pd^0$ by $NaH_2PO_2$ existing in plating bath. This is the reason why time-lag is appeared. To the contrary, in Process 2, the reaction proceeded immediately after dipping beads B into plating bath, because there exists $Pd^0$ as nuclei on their surface.

There were many arguments so far for the nucleation process in the electroless plating.[4-13]) In $PdCl_2/SnCl_2$ system, Osaka et al.[4,5]) reported the formation of colloidal particles of Pd-Sn alloy as catalytic centers and concluded that the active sites consist of a disordered Pd-Sn alloy in which the more active catalyst has the higher Pd/Sn ratio. In $PdCl_2/TiO_2$-UV light system,[8]) it has been confirmed that metallic palladium as nuclei is formed on the $TiO_2$ substrate by ellipsometry and electron diffraction. Thus the idea that the active site is metallic state palladium including Pd-Sn alloy rather than solute complex[12,13]) seems to be now accepted. Above assumption in our aminosilane/$PdCl_2$ system dose not contradict this idea.

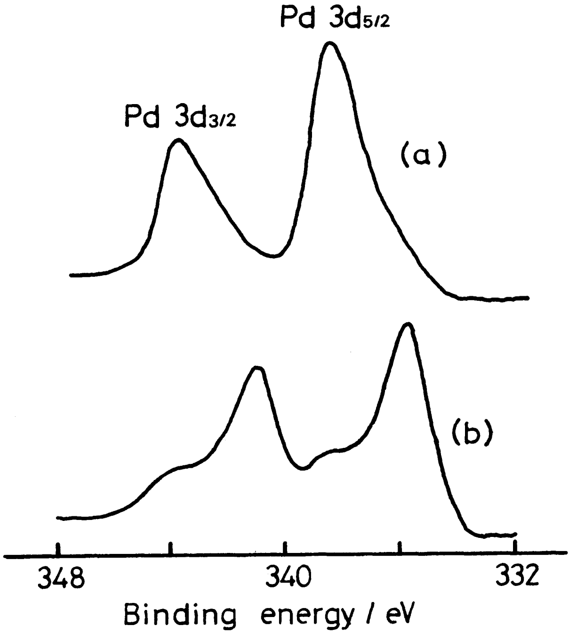
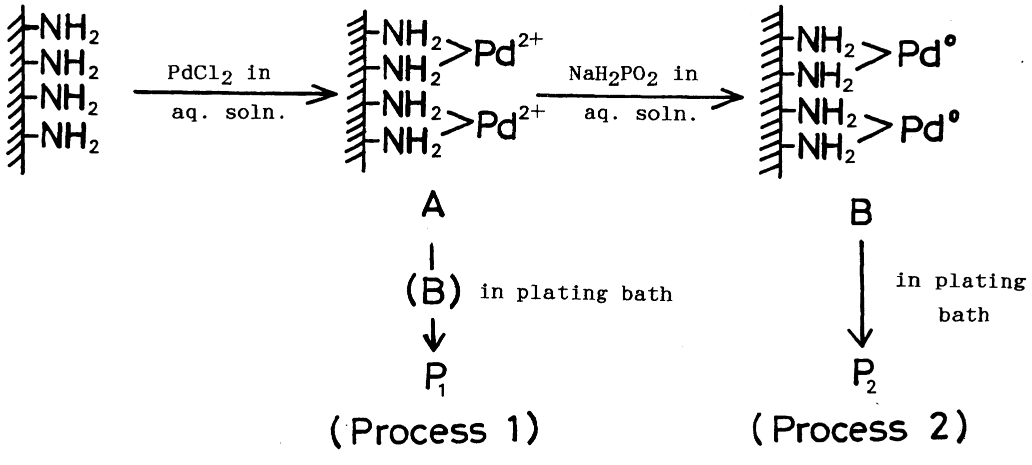


Fig. 2. Palladium 3d XPS spectra of the surface of palladium bound glass beads; (a) beads A prepared in $PdCl_2$ aqueous solution, (b) beads B prepared by treating A with $NaH_2PO_2$ aqueous solution at 80 °C. The binding energies are referenced to carbon 1s (285.0 eV).

In conclusion, reaction in Process 1 is supposed to proceed via the formation of $Pd^0$ binding product (B) like beads B as shown in the following scheme:



here, $P_1$ and $P_2$ denote the nickel deposited product.

Another interesting experimental result observed here is that palladium can be easily bound on glass beads as amine complex through aminosilane treatment. So many other amine compounds than aminosilane might be expected to be utilized as the pretreating reagent for preparing amine complex required for nucleation. Further study is now under way.

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