Electroless Deposition of Palladium Using Hypophosphite as a Reducing Agent

By S.S. Djokić

Electroless deposition of flat and shiny coatings and powders of Pd-P alloy from an alkaline solution containing $PdCl_2$ as a source of Pd(II) ions and hypophosphite as a reducing agent was investigated. The results showed that the rate of deposition increased as temperature increased. On the other hand, an increase in pH led to a decrease in the rate of palladium deposition. Deposited Pd-P films and powders exhibited an amorphous structure. According to the DSC analysis, recrystallization of these materials was observed at a temperature of about 290 °C. In the recrystallized sample, phases such as Pd_6P and elemental palladium were identified.

Electroless deposition of palladium is used in electronics industries for the production of barrier layers, conductive films, corrosion-resistant non-porous deposits, for increasing the surface hardness of components, etc.[1]

Various solutions for electroless plating of palladium have been used in practice. Usually, electroless plating of palladium is carried out in alkaline solutions using hydrazine[2] or hypophosphite[3-5] as reducing agents of Pd^{+2} ions.

The first solution for electroless deposition of palladium with hypophosphite was described by Pearlstein and Weightman.[4] They reported that the rate of deposition increased as temperature and palladium chloride concentration increased. Increasing the concentration of NH_4Cl resulted in a marked decrease in the deposition rate. This result was attributed to more effective complexing of Pd(II) ions with ammonia ligands, because the stability of solution increased with an increase in ammonium chloride concentration.

An investigation of electroless deposition of palladium with hypophosphite, and various additives, such as ethylenediamine, ammonium chloride, lead sulfide and sodium thiosulfate, led to the conclusion that the rate of deposition and the stability of the solution were highest in the presence of sodium thiosulfate (1.5×10^{-4} to 1.8×10^{-4} mol/L).[5]

In this study, electroless deposition of palladium from the Pearlstein and Weightman solution[4] was investigated. Attempts have been made to investigate the effect of pH and temperature on the rate of palladium deposition. Recrystallization and thermal behavior of electroless deposited palladium films and powders were also investigated.

Experimental Procedure

Electroless deposition of palladium was carried out using the following solution: 2 g/L $PdCl_2 \cdot 2H_2O$, 27 g/L NH_4Cl, 10 g/L $NaH_2PO_2 \cdot 2H_2O$ and 160 mL/L NH_4OH (28%). A copper foil with an apparent surface area of 10 cm^2 was used as a substrate for electroless deposition of palladium. Clean Cu substrates were activated in an acidic solution containing 2 g/L $PdCl_2 \cdot 2H_2O$ and 50 mL/L HCl (36.5%). Activated copper specimens were immersed in the solution and electroless deposition of palladium was carried out at different temperatures (from 50 to 70 °C) for one hr. The effect of pH on deposition rate was investigated by an addition of 2.0 M NaOH solution at constant temperature (70 °C). The deposits obtained were analyzed using X-ray diffraction (XRD), electron dispersive spectroscopy (EDS), scanning electron microscopy (SEM) and differential scanning calorimetry (DSC).

Results & Discussion

The effect of temperature on the rate of electroless deposition of palladium, in terms of an Arrhenius plot, is shown in Fig. 1. As can be seen, there is a linear relationship between the rate of palladium deposition and 1/T. It should be noted that

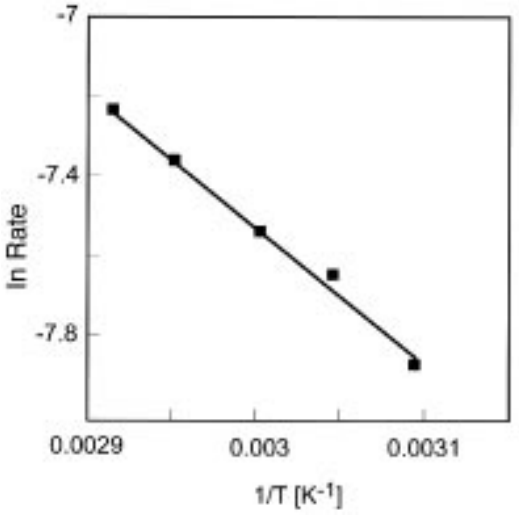

Fig. 1—Plot of ln(Rate) vs. 1/T for electroless deposition of palladium with hypophosphite; pH 9.6.

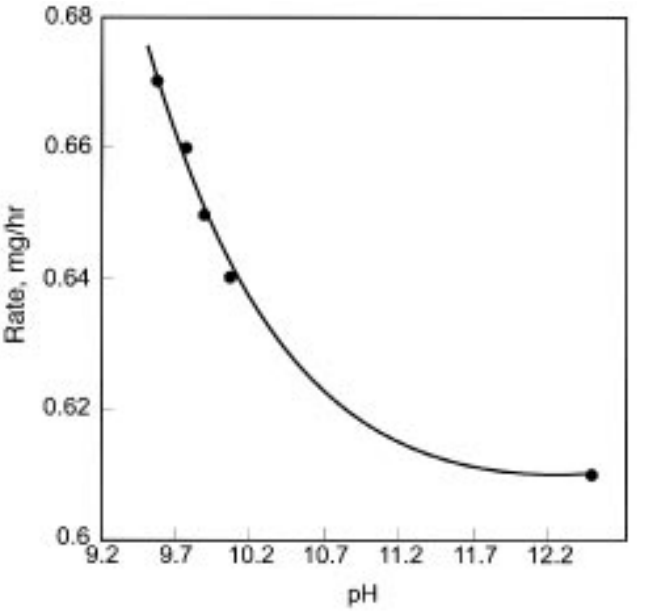

Fig. 2—Effect of pH on rate of palladium deposition at 70 °C.

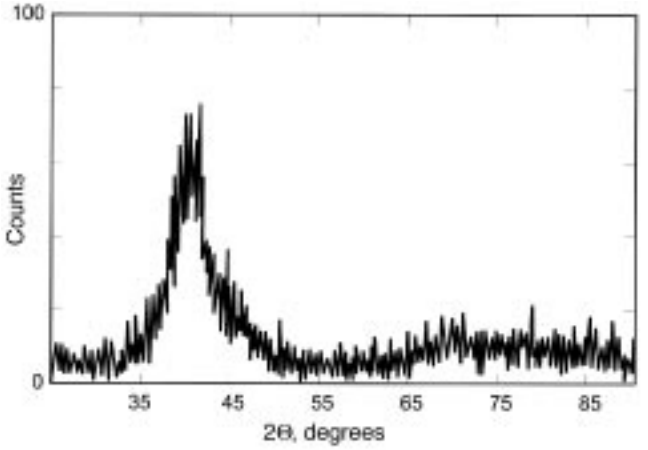

Fig. 3—XRD pattern of as-deposited palladium at 70 °C.

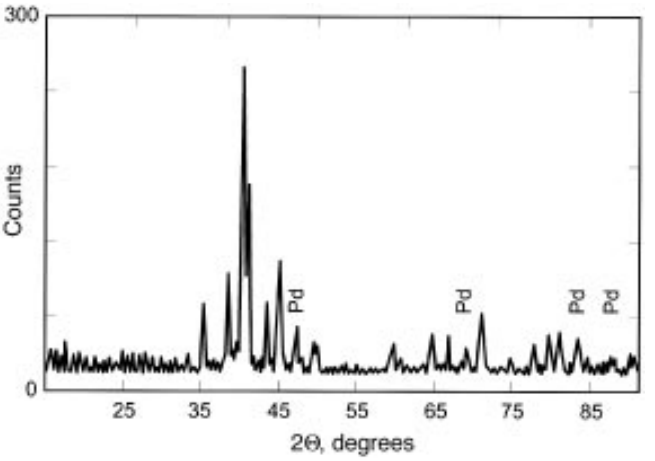

Fig. 4—XRD pattern of electroless palladium heat-treated at 400 °C for 4 hr in argon atmosphere.

the original rate units shown in Fig. 1 are ln (g/min). Activation energy, Ea, was determined from this plot and found to be about 28.09 kJ/mol K. This value is in good agreement with the calculated value for the activation energy from Pearlstein's data,[4] which had a value of about 33 kJ/mol K.

The effect of pH was also investigated. Increasing pH from 9.5 to 12.4, at 70 °C led to a decrease in the deposition rate. This is illustrated in Fig. 2.

Characterization of Electroless Palladium Films

Plated palladium films were smooth and shiny in appearance. A typical XRD pattern of electroless palladium is shown in Fig. 3. The pattern exhibits a broad peak suggesting an amorphous structure of electroless Pd films. The shape of this broad peak is similar to those reported for electroless nickel with hypophosphite[6] or electrodeposited Co or Ni films from a solution containing H_3PO_3 as a source of phosphorus.[7] The EDS analysis found that the deposited palladium films contained about 3.5 percent phosphorus. It is obvious, according to these data, that phosphorus is an amorphizing element in electroless Pd-P films, as in electroless Ni-P films or in electrodeposited Ni-P and Co-P coatings.

Heat treatment of deposited Pd-P films leads to their recrystallization. The XRD pattern of the heat-treated Pd-P films at 400 °C for four hr under argon atmosphere is shown in Fig. 4. The heat-treated samples of Pd-P exhibited a clear, crystalline structure. The phases identified included Pd_6P and pure Pd. The minor amount of elemental palladium in the recrystallized sample was identified for 2Θ 46.659 deg, 68.080 deg and 82.090 deg. The average crystallite size of pure palladium was estimated at about 59 nm. The major phase in the recrystallized sample was Pd_6P (all other peaks in the pattern in Fig. 4), with an average crystallite size of about 49 nm.

To find the recrystallization temperature, electroless Pd-P films were examined by DSC. A typical DSC curve for electroless Pd-P films is shown in Fig. 5 (curve 1), where it clearly exhibits an exothermic peak with a maximum at about 290 °C. This exothermic peak is related to the recrystallization of electroless Pd-P films and formation of phases mentioned above. The energy of the exothermic peak was estimated at about 28 J/g. It should be noted that this peak was not observed by DSC analysis of heat-treated samples. Figure 5 (curve 2) shows the DSC curve of heat-treated electroless Pd-P material at 400 °C under an argon atmosphere for four hr.

It was observed in this study that an increase in either plating temperature or hypophosphite concentration leads to bath destabilization. Under these conditions, fine Pd-P particles were formed in the bulk solution; the reduction of Pd(II) ions remaining in solution was completed in 10 min. A SEM micrograph of deposited Pd powders is shown in Fig. 6. It should be noted that all other analyses (XRD, EDS and DSC) found the same results as those reported for flat, shiny Pd-P films. These results suggest that the electroless deposi-

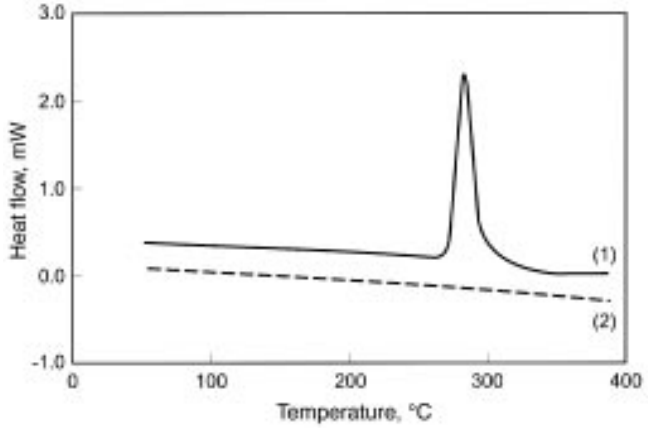

Fig. 5—(1) DSC curve of electroless Pd-P films (heat rate 10 °C/min, Ar atmosphere); (2) DSC curve of electroless Pd-P films heat-treated at 400 °C for 4 hr in Ar atmosphere (heat rate 10 °C/min).

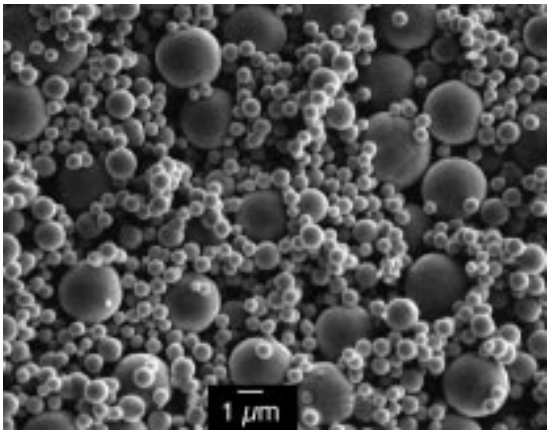

Fig. 6—SEM micrograph of Pd-P powder produced in the bulk solution.

tion of palladium films at the Pd-activated Cu surfaces and precipitation of Pd-P powders in the bulk solution proceed by the same mechanism.

Conclusions

Electroless deposition of palladium using hypophosphite as a reducing agent leads to the formation of smooth and shiny films with an amorphous structure. Recrystallization of these films was observed at about 290 °C. Consequently, heat treatment of these films at 400 °C leads to the formation of crystalline structure. Deposition rate increases as temperature increases. On the other hand, increasing pH leads to a decrease in the deposition rate. At temperatures above 70 °C, the solution for electroless deposition of palladium decomposed spontaneously, producing Pd-P powder with the same structure as deposited smooth and shiny films on the flat surface.

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