

ELECTROCHEMICAL STUDY OF ELECTROLESS PLATING OF SILVER

Jae-Ho Lee

*Dept. of Metallurgical Engineering and Materials Science, Hong Ik University
72-1 Sangsu-dong, Mapo-gu, Seoul 121-791, Korea*

Abstract

Silver has the highest electrical conductivity of all metals and consequently this property is an attractive feature which makes it a leading candidate for use in electronic devices. The research conducted was focused primarily on the development of a process for obtaining a deposited silver-coating onto alumina, for applications related to electrical-conducting devices and, ancillary, catalysts. Alumina balls and plane substrates were utilized for the investigation. The coating process employed an aqueous ammoniacal silver-nitrate electrolytes with a formaldehyde solution as the reductant. Modifying additives—an activator which would be expected to promote good deposition-characteristics onto the (dielectric) substrate and an inhibitor which would obviate homogeneous reduction (precipitation) of silver was observed when the activator-containing silver-electrolyte reductant constituents were combined. However, the silver-electrolyte/reductant system with inhibitor could be employed (at 80°C) to achieve a viable (subject to future research optimization) coating on alumina. The influence of the processing temperature on the deposition process was delineated during the course of the research. The morphology of the deposited-silver on the alumina balls was assessed by SEM imaging. A tape-peel test was employed, with the plane substrates, to semi-quantitatively characterize the adhesion to the alumina.

Key words : *Electroless plating, Silver, Formaldehyde, Glycine, Sorbitol*

1. INTRODUCTION

Silver has the highest electrical conductivity of all metals and consequently this property has been exploited for the conducting devices from silver solder and more recently electronic packaging. There are many applications for deposition of silver onto a dielectric material. Electroless-deposition techniques are, potentially, a low-cost

processing scheme which may achieve the necessary objective. For example, electroless silver-coating onto glass is a well established silver-coating technology¹⁻³⁾. However, in its simplest practice, there is no inherent selectivity and silver deposited onto other surfaces besides the glass. In the late seventies, Diem et al. selectively coated ceramic-beads with silver for use as a catalyst⁴⁾. In their research, several reducing a-

gents and inhibitors in conjunction with a silver electrolyte, were investigated for coating porcelain beads. Hydrazine, and its derivatives, formaldehyde, and hydroxylamine were assessed as reducing-agent candidates. Carboxylic acid amino-compounds were explored as inhibitors. The aqueous silver-electrolyte was formulated from silver-nitrate salt, with ammonia serving as a complexing ligand. It was recognized that several of the organic reagents cited in this reference, are either highly toxic, or carcinogenic. The reductant and inhibitor employed in the research reported in this paper were selected so as to minimize any hazard potential. Formaldehyde and sorbitol were selected so as to minimize any hazard potential. Formaldehyde and sorbitol were selected since it is a well known metal-ion reductant, and less toxic than hydrazine. Glycine, also non-toxic was selected as the inhibitor. Sodium hydroxide was selected as the activator-for modifying the substrate surface so as to promote suitable characteristics of the deposited silver. Alumina was selected because of its potential use as a dielectric substrate in electronic devices (and as a catalyst support). The primary objective of the research was to develop a process for depositing an adherent coating of silver onto an alumina substrate. This was successfully accomplished by employing formaldehyde as the reductant and an aqueous ammoniacal silver-nitrate inhibitor-containing electrolyte, at 80°C.

2. EXPERIMENTAL PROCEDURES

2.1 Reagents

All solutions were prepared from chemicals of analytical grade and distilled water. Two types

of modifying reagents were used—an inhibitor and an activator. The coating solutions with inhibitor consisted of a reductant and the silver electrolyte. The reductant was formulated from 5ml of (37%) formaldehyde (HCHO) diluted with water to a volume of 100ml so as to provide for a 5v% formaldehyde solution. The silver precursor-electrolyte consisted of 25g of AgNO₃ dissolved in approximately 100ml of water to which 7.5g of glycine (inhibitor), 250g of NH₄OH (28w% NH₃) were added together with water to produce a total volume of 500ml. The mixed solutions with activator contained: reductant, activator and silver electrolyte. The silver electrolyte consisted of 125g of AgNO₃ dissolved in 100ml of water and 150g of NH₄OH (28w% NH₃) to which water added to produce a total volume of 500ml. The activator solution was consisted of 50g of NaOH dissolved in approximately 200ml of water to which 5g of NH₄OH (28w% NH₃) and water added to produce a total volume of 500ml. The reductant solution consisted of 100g of sorbitol (70%) and 5ml of (37%) formaldehyde diluted with water to a volume of one liter—this two-reagent reductant system had been previously employed in the coating of (non-conductive) glass substrates for mirror²⁾.

2.2 Substrates

Two types of γ -alumina were used. Balls, 3mm diameter, supplied by Sinwall, and alumina plates of dimensions 5cm × 5cm × 0.64mm (thickness), obtained from Kyocera. Coating-adhesion tests were performed on the silver-coated alumina-plate samples.

2.3 Electroless Plating Procedure

Alumina substrates were sequentially cleaned

with acetone and distilled water in an ultrasonic bath for 5 minutes to remove surface contaminants. Alumina balls were first contacted with the reductant solution in the reactor vessel. The solution was agitated by the impeller in the reactor vessel for 5 minutes in order to promote adsorption of the reductant onto the alumina surface. The silver electrolyte was then added to the reactor vessel with continuous agitation for 10 minutes. The mixed solution consisted of, i) one volume of reductant and two volumes of inhibitor-containing silver-electrolyte; and, ii) one volume of each solution for the activator-containing solution-system. After completing the above procedure, the coated alumina was cleaned with distilled water in an ultrasonic bath and then dried. Surface imaging was conducted by SEM. The electrical-conductivity response, of substrates which appeared to have been successfully coated, were evaluated with a two-probe ohmmeter (multimeter). The temperature characteristics of the deposition process were investigated at 25°C, 40°C, and 80°C. The procedure which was discovered to provide a viable silver coating was also performed on the alumina-plate sample. Subsequently, the (3M) tape-peel test was conducted to assess the adhesion of the silver to the substrate.

3. RESULTS AND DISCUSSION

3.1 Assessment of Homogeneous Reduction (Precipitation) of Silver

In the Pyrex-reactor vessel, a volume of 1ml of the reductant solution was added to 2ml of the inhibitor-containing silver electrolyte (for the mixed-system with activator, 1ml of each constit-

uent solution was utilized). The solution was allowed to stand for a period of 10 minutes to 1 hour, so as to assess the homogeneous reduction of silver in the solution. After 1 hour had elapsed there was no evidence of silver reduction for the mixed-solution system for which the inhibitor-containing electrolyte was a constituent. This established that this coating-solution system had the potential to selectively deposit silver onto the alumina substrate under suitable, yet to be determined, conditions. In contrast, it was found that for the coating-solution system with activator, silver precipitated in the solution immediately upon addition to, and subsequent mixing of, the reductant solution to the silver-electrolyte/activator mixed solution. Silver, not surprisingly, was also precipitated onto the Pyrex reactor vessel. The homogeneous reduction of silver was expected, because a similar composition mixed-solution system had been used for silver-mirror manufacturing^{2, 3}. Consequently, the mixed-solution system with activator was ultimately eliminated as a candidate coating-solution system. Fig. 1 is an SEM photomicrograph

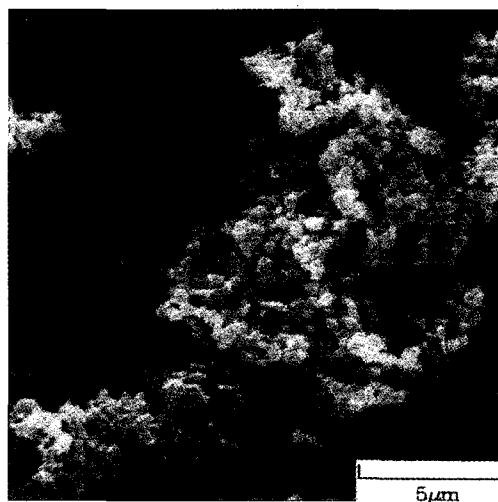


Fig. 1 Microstructure of silver precipitates

of the structure of the silver precipitates collected from the solution.

3.2 Coating of Substrates with Activator-Containing Solution System

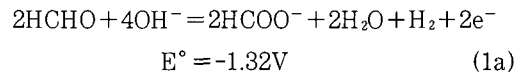
In spite of the homogeneous precipitation of silver experienced with the activator-containing solution system, the procedure for coating the alumina balls, as presented previously, was effected. Indeed, silver was precipitated onto the alumina substrate. However, unlike that which has been achieved on a glass substrate, the adhesion of silver onto the alumina was insignificant. When the balls were washed with distilled water in the ultrasonic bath, most of the deposited silver (or surface-occluded silver-precipitate) was removed.

3.3 Coating of Substrate with Inhibitor-Containing Solution System

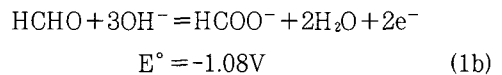
It was discovered, in a previous research effort, that an inhibitor-containing silver-coating solution system with produced satisfactory silver-coating on tungsten at ambient temperature (25°C)⁵⁾. However, when this solution system was employed with the alumina substrates of the

present research, not only was there no homogeneous precipitation in the solution, but in addition deposition of silver did not occur onto the surface of the balls. The reduction and oxidation reactions, reaction 1a/1b and 2, respectively, together with the standard reduction potentials, which describe the mechanism of the deposition process are presented below.

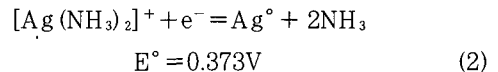
Anodic reaction (oxidation of formaldehyde)⁵⁻⁸⁾



or



Cathodic reaction (reduction of silver)^{5, 9)}



Although the potential difference between redox reactions at standard state is very high, the rates of the redox processes was imperceptible. It would appear that the controlling electrode reaction is the oxidation of formaldehyde on the alumina substrate interfacial region. Furthermore, there is high activation energy associated

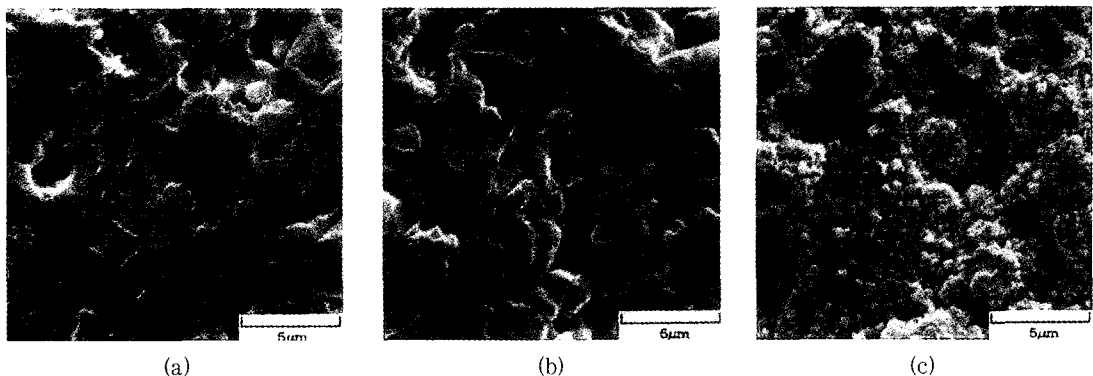


Fig. 2 Morphology of surface region of alumina balls subjected to treatment inhibitor containing coating solution: (a) 25°C (b) 40°C (c) 80°C

with this electrode process⁹). Thus, it was expected that an increase in temperature would have a significant effect on the rate. Consequently, processing temperatures of 40 and 80 °C were subsequently employed. However, silver deposition could only be observed at 80 °C. Moreover, some homogeneous precipitation of silver also occurred in the solution. An SEM photomicrograph, showing the morphology of surface region of the alumina balls, is presented in Fig. 2 for the three processing-temperatures investigated. The alumina plate sample was subsequently subjected to the treatment as for the alumina balls processed at 80 °C. The adhesion of silver to this alumina plate substrate was evaluated by the (3M) tape peel test. Only the loosely adhering silver was detached. The continuous silver-deposit on the surface remained intact.

4. CONCLUSION

The important conclusions derived from the research conducted are enumerated below.

1) Based on semi-quantitative assessments of coating adhesion and electrical conductivity, satisfactory silver-coating of alumina was achieved at 80 °C, with an aqueous silver-coating solution system consisting of an inhibitor (glycine) containing silver electrolyte and a formaldehyde reductant. The concentrations of the constituents of this two part coating solution are as listed in Table 1. The mixed solution system contained one volume of reductant to two volumes of the inhibitor containing silver electrolyte.

2) Further research will be required to achieve an optimal system based on the system described in 1 above.

3) Silver was homogeneously precipitated from the silver coating solution system which incorporated an activator. The mixed solution system consisted of equal volumes of the three solutions (electrolyte) with constituent concentrations as listed in Table 2. Although silver was also deposited onto alumina balls there was no significant adhesion to the substrate.

ACKNOWLEDGEMENT

Author gratefully acknowledges the financial support of the Korean Ministry of Education Research Fund for Advanced Materials in 1996.

REFERENCES

1. Workens, US Patent 4135006, 1979
2. H. Bahls, US Patent 4102702, 1978
3. J. I. Duffy, Electroless and other nonelectrolytic plating techniques—recent development, (Noyes, 1980), 5-11
4. Diem et al., US Patent 4126582, 1978
5. J. H. Lee and G. P. Martins, "Non-electrolytic deposition of silver onto tungsten powder particles", EPD Congress 1997, TMS 217-225
6. F. Van Den Meerakker, "On the mechanism of electroless plating. I. Oxidation of formaldehyde at different electrode surfaces", *J. of Applied Electrochem.*, 11 (1981), 387-393
7. P. Bindra and J. Roldran, "Mechanisms of electroless metal plating II. Formaldehyde oxidation", *J. of Electrochem. Soc.*, 132 (1985), 2581-2589
8. H. Kim, "Trends in electroless plating" (KINI-TI technical report 90, 1994)
9. J. Dean, *Lange's Handbook of Chemistry*, 13th ed, (McGraw Hill, 1985), 6-5