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Influence of the Complexing Agents on the Thickness Uniformity of Electroless Nickel Plating in Deep-Recessed Trenches

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Electroless plating has been extensively applied to electronic devices because it provides superior throwing power and uniform film formation for complicated geometries. In this study, the formation of the conductive layer in the deep-recessed trenches using electroless Ni-B plating was investigated. Uniformity of plating films was greatly influenced by the selection of the complexing agent. Superior uniformity of Ni films in deep-recessed trenches was obtained by the electroless plating bath containing DL-malic acid. On the other hand, Ni films from a bath containing glycine were not uniformly deposited and no deposition was obtained at the bottom of deep-recessed trenches. Dependence on a selected complexing agent to the initial plating reaction was investigated by the electrochemical analysis. It is confirmed that the induction time before initiation of deposition was influenced by the complexing agent, and adsorbed Pd catalyst in the trenches was dissolved during the induction time and Ni films are not uniformly deposited by the dissolution of adsorbed Pd in the trenches if the plating bath shows the long induction time. © 2004 The Electrochemical Society. [DOI: 10.1149/1.1784211] All rights reserved.

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Electroplating and electroless plating are actively applied to the formation of metal films for high-density electronic components. In particular, electroless plating is applied to the fabrication of microcomponents on nonconductors such as silicon, ceramics, glass, and resin substrates because the metals can be uniformly formed on the nonconductive substrates.¹⁻⁶ Among electroless plating methods, Ni-B plating features good solderability and electric conductivity.⁷

In this study, applicability of electroless Ni-B plating using dimethylamine-borane (DMAB) as a reducing agent to achieve uniform nickel deposition on the ceramics comprising deep trenches was investigated.

Experimental

Electroless nickel plating.—Ceramics $(1 \times 2 \text{ cm})$ with trenches of aspect ratios of 1, 3, 5, and 7 were used as samples. Figure 1 shows a cross-sectional view of the sample ceramics.

The electroless plating bath was composed of nickel sulfate as a metal source and DMAB as a reducing agent. As the pattern is formed on the actual devices, an organic resist is necessary. Therefore, the electroless nickel plating bath should be operated at moderate conditions to avoid damage to the organic resist. The pH of the plating bath was adjusted to 6.0 using H_2SO_4 and NaOH. The temperature was maintained at 60°C. The basic plating bath composition and operating conditions are shown in Table I. Deposition thickness uniformity was evaluated using electroless nickel plating baths containing glycine, DL-malic acid, lactic acid, ethylenediamine, or acetic acid as a complexing agent.

After degreasing and acid treatment, Pd catalysts were deposited on the sample with sensitizing and activation, and then followed by the deposition of nickel. The pretreatment process is shown in Table II.

Evaluation of deposition thickness uniformity.—After the electroless nickel plating, the samples were embedde in epoxy resin and cross-sectional views of trenches were observed by an optical microscope.

Figure 2 shows the cross-sectional image of deposited Ni-B films in the trenches. Thickness of Ni-B films was measured at each few points around the aperture and the bottom area. The uniformity of Ni-B film thickness in the trenches was calculated from $\{(B_1 + B_2 + B_3)/3\}/\{(A_1 + A_2 + A_3 + A_4)/4\} \times 100.$

Reactivity of electroless nickel plating.-The reactivity of elec-

troless Ni-B plating was evaluated from partial polarization curves. Electrochemical measurement was performed with potentiostat (Hokuto Denko, HZ3000). The partial anodic polarization behavior was measured using the nickel bath without nickel sulfate. The partial cathodic polarization behavior was measured using the nickel bath without DMAB.



Figure 1. Trench patterned ceramics and the cross-sectional view of the sample ceramics.

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Table I. The basic plating bath composition and operating conditions.

Component	Concentration (mol/dm ³)
$NiSO_4 \cdot 6H_2O$	0.1
Complexing agent	0.3-1.0
DMAB	0.05
H ₂ SO ₄ and NaOH	Adjust pH to 6.0

A standard three-electrode configuration was employed with one side of the nickel rod as a working electrode, an Ag/AgCl/3M KCl electrode (E = 0.222 V vs. NHE at 25°C) as a reference electrode, and a Pt plate as a counter electrode. The linear sweep voltammograms were measured at a sweep rate of 10 mV/s, and were scanned first to the negative and then to the positive direction. The pH of the plating bath was adjusted to 6.0 with dilute H₂SO₄ and NaOH. The pH buffer solution was not used to confirm the clear influence of a complexing agent.

The nickel disk electrode was used for the measurement of the electrode potential around the aperture of the trenches. A nickel rod was buried in PTFE, and the exposed top surface was used as a disk electrode. The potential of the bottom area was measured using a trench-bottom electrode with trenches having an aspect ratio of 10. The trench-bottom electrode was designed for these experiments. Figure 3 shows the pattern diagrams of these electrodes.

*Immersion potential and mixed potential*⁸.—Immersion potential and mixed potential at the aperture part and the bottom area were measured to elucidate the initial plating reaction using a disk electrode and the trench-bottom electrode. To avoid the influence of evolved hydrogen gas due to the electroless plating reaction, the working electrode was placed upward under the counter electrode.

Analysis of the electrode reaction during the induction period.—The quartz crystal microbalance (QCM) method was used to analyze a reaction mechanism during the initial plating reaction. QCM were measured with an electrochemical quartz crystal microbalance by an ALS/CHI model 400 (ALS/CH Instruments).

Results and Discussion

Influence of various complexing agents to the thickness uniformity.—Concentration of the chemical ion species in the plating solution, pH, and temperature are the important factors governing the thickness uniformity of the deposition. It is believed that the thickness uniformity is greatly affected by the complexing agent in the plating solution.

Uniformity of Ni-B plating film thickness in the trenches was evaluated using various kinds of complexing agents. No dependence on the complexing agent was noticed and uniform deposits were formed on the trenches of a aspect ratio of 1. However, significant differences of the thickness uniformity, in the trenches using aspect ratios above 3 were confirmed between the complexing agents. Figure 4 shows the cross-sectional views of deposited nickel films in the case of glycine bath, no Ni-B film deposits were observed in the





Conformality (%) =
$$\frac{(B_1+B_2+B_3)/3}{(A_1+A_2+A_3+A_4)/4} \times 100$$

Figure 2. Uniformity calculation of the Ni deposit in the trench.

bottom region of the trenches above aspect ratio 3. On the other hand, as shown in Fig. 5, Ni-B films were deposited even at the bottom of aspect ratio of 7 using DL-malic acid as a complexing agent.

Comparison of deposition uniformity in the trenches was measured using glycine, DL-malic acid, acetic acid, lactic acid, or ethylenediamin as a complexing agent in the electroless Ni solution.

Deposition uniformity in the trenches at aspect ratio of 7 was about 27% from the acetic acid bath, and about 75% from the lactic acid bath, and about 33% from the ethylenediamine bath. The DLmalic acid bath showed the highest thickness uniformity (82%) among these complexing agents.

In this way, remarkable differences of thickness uniformity were indicated among of the complexing agents in the plating bath.



Figure 3. Schematic diagrams of the electrodes used.



Figure 4. Ni-B films in the trenches of aspect ratio 1 to 7 by the glycine bath.

*Partial anodic polarization curve*⁹.—To elucidate the reactivity of the electroless Ni-B plating in the trenches, the electrochemical technique was employed.

The partial anodic polarization curve was measured using glycine and DL-malic acid bath which showed the most typical differences in the thickness uniformity.

As shown in Fig. 6, when the disk electrode which assumed the aperture part of the trench was used for the measurement, the oxidation peak based on the DMAB of the glycine bath was smaller than that of the DL-malic acid bath. Note, however, that the oxidation peaks of DMAB decreased using the trench-bottom electrode. This may be due to the retardation of the ion diffusion at the bottom of the trenches. The peak potential of the DL-malic acid bath was not significantly changed, while the oxidation curve of DMAB of the glycine bath was greatly shifted in the noble direction. Therefore, it was confirmed that plating rate of glycine bath was greatly suppressed at the bottom of the trenches.

*Electrochemical analysis by the mixed potential*⁸.—The mixed potential was calculated by the partial anodic polarization and the partial cathodic polarization. Figure 7 and 8 show the results. As shown in Fig. 7, the mixed potential and the exchange current densities of the aperture and the bottom area of the trenches were almost the same using DL-malic acid bath. Therefore, plating progressed at approximately the same rate on the aperture part and the bottom of the trenches.

On the other hand, as shown in Fig. 8, mixed potential at the bottom of the glycine bath shifted to the noble direction, and the exchange current value was greatly decreased.

Thus, the plating rate of the glycine bath at the bottom decreased remarkably. These electrochemical measurements indicated that the deposition behavior in the trenches corresponded to each of the electroless Ni-B plating conditions.



Figure 6. Partial anodic polarization curves with DL-malic acid and glycine bath.



Figure 7. Mixed potential curves with DL-malic acid bath.



Figure 5. Ni-B films in the trenches of aspect ratio 1 to 7 by the DL-malic acid bath.



Figure 8. Mixed potential curves with glycine bath.



Figure 9. Immersion potential curves with DL-malic acid bath.

Immersion potential and induction time.—The time dependence of deposition potential was measured using nickel disk and trenchbottom electrodes as a working electrode.

Figure 9 and 10 show the immersion potential of nickel electrodes under the each condition. As shown in Fig. 9, the induction time was about the same on the disk and the trench-bottom electrodes from the DL-malic acid bath. Consequently, the plating reaction initiates simultaneously on the aperture and the bottom parts of trench by the DL-malic acid bath.

On the other hand, the induction time was extended at the trenchbottom electrode from the glycine bath, as shown in Fig. 10.

It is assumed that the adsorbed Pd catalyst on the bottom area dissolves into the glycine bath during the induction time. The density of the catalyst decreases and catalytic reaction will be suppressed. Consequently, plating rate at the bottom is retarded by the glycine bath.

Analysis of the electrode reaction in the induction time.—The quartz crystal which deposited Pd nuclei by sensitizing and activation was immersed in the solution containing complexing agents, and the change of resonance frequency was measured. The result is shown in Fig. 11 by DL-malic acid and glycine baths.

In the solution containing DL-malic acid, the frequency changed gradually. On the other hand, in the solution containing glycine, the frequency rapidly changed in the dissolving direction, compared with the case of the solution containing DL-malic acid. This phenomenon is due to the dissolution of Pd catalysts from the quartz crystal.

From the result of Fig. 10, the induction time of the glycine bath was about 7 min at the trench-bottom electrode. Therefore, before



Figure 10. Immersion potential curves with glycine bath.



Figure 11. Change of resonance frequency.

the plating reaction, Pd may have dissolved from the bottom area of the trenches during the induction time, terminating the deposition reaction.

Conclusion

Thickness uniformity of deposits by the electroless nickel plating was examined using the trench wall construction of high aspect ratios and the following conclusions were obtained.

Uniformity of the plated films thickness was greatly influenced by the complexing agents.

Ni film thickness obtained from a glycine bath was not uniform. No deposition was observed at the bottom of the deep-recessed trenches.

Superior uniformity of Ni film thickness was obtained by the plating bath containing DL-malic acid as a complexing agent.

The induction time at the bottom of the trench was influenced by the complexing agents.

Glycine bath showed longer induction time than DL-malic acid bath. Pd catalyst might be dissolved during the induction time, causing less deposition at the bottom of the trench in the glycine bath.

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