Electroless Nickel Plating for Nanofabrication in Optics

T. Kobayashi,^a J. Ishibashi,^a S. Mononobe,^c M. Ohtsu,^{c,d} and H. Honma^{b,*,z}

^aGraduate School and ^bFaculty of Engineering, Kanto Gakuin University, Kanazawa-ku, Yokohama-shi, Kanagawa 236-0032, Japan ^cKanagawa Academy of Science and Technology, Takatsu-ku, Kawasaki-shi, Kanagawa 213-0012, Japan ^dInterdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Midori-ku, Yokohama-shi, Kanagawa 226-0027, Japan

The electroless plating method has played an important role as an indispensable metallization technology for miniaturization of electronic components. This investigation discusses selective metallization on the fine area (nanometer size) by electroless plating. The experimental purpose is to fabricate a probe which is used for scanning near-field optical microscopy. The probe (cone angle 20° , probe size 4 µm) is comprised of an optical fiber covered with a metal film except for an aperture at the apex of the fiber. Nickel-plated probes with an aperture of 100 nm were fabricated by optimization of the plating conditions (dissolved oxygen concentration, bath temperature, and bath pH) and the addition of a catalytic poison into the plating bath. © 2000 The Electrochemical Society. S0013-4651(98)10-118-0. All rights reserved.

Manuscript submitted October 29, 1998; revised manuscript received September 8, 1999.

Miniaturization and high efficiency of electronic devices depend heavily on advances in semiconductor-processing technologies. Currently, the semiconductor devices are scaled down to 0.25/0.18 μ m as a design rule. Consequently, fine processing technology will enter into the nanosize fabrication stage in the near future. At present, thin-film formation by dry processes and pattern formation by lithographic techniques are applied widely. Application of electroless plating for fine wiring formation on semiconductor devices has been studied.¹⁻³ In this paper, we discuss the preparation of the fiber probe for a near-field optical microscope as a nanofabrication technique using electroless plating.

Resolution of an optical microscope is restricted by the wavelength of the incident light. According to the theory of the diffraction limit of Abbe, the limit of resolution is about 60% of the incident wavelength. However, the resolution of the optical microscope can be improved by detecting the evanescent field occurring at the vicinity of the surface of the object. Scanning near-field optical microscopy (SNOM) is realized based on this fact.^{4,5} The resolution of SNOM depends on the size of the opening at the probe tip, which detects the evanescent field. When an optical fiber with a nanosized tip is used as the probe, the main factor determining the resolution of the SNOM imaging is the apex size of the probe. The sharp edges of the fiber must be coated with metal except for the apex region to suppress scattering and generation of low-spatial-frequency components of the near field. Vacuum deposition techniques, such as evaporation or sputtering, have been reported as methods for coating the fiber probe.^{6,7} After the fiber is vacuum-coated with chromium and gold, the coating must be removed from the apex region. Conventionally, the fiber is dipped in an acrylic resin solution. When the fiber is withdrawn from the resin solution, a submicrometer apex region of the sharpened core is exposed, which is then etched by KI-I2 solution. These procedures for probe-tip preparation are very complicated, however, and reproducibility is low. As a more efficient and simpler alternative, the applicability of electroless nickel plating for preparation of fine aperture on the protruded fiber is examined in this report.

Experimental

Protruded probe preparation method⁸.—Optical fibers with 125 μ m diameter cladding and 2 μ m diam core, doped with GeO₂, were used. These fibers were sharpened by immersing them in an etching solution containing NH₄F (40 wt %), HF (50 wt %), and H₂O. We denote the volume ratio of etching solution as X, 1:1, which corresponds to the order of NH₄F, HF, and H₂O, respectively.

In this study, two types of etching processes were performed as shown in Fig. 1. For sharpening the core, the fibers were etched in a

^z E-mail: honma@kanto-gakuin.ac.jp

ter could be reduced to 100, 50, and 25 μm by an etching solution with a composition ratio of 1.7:1:1. Figure 2 shows SEM micrographs of the sharpened fiber probe with a magnified view of the apex region. The radius of curvature is less than 5 nm and the cone angle is 20°. In this way, controlling the shape of the apex of the sharpened core can be achieved with high reproducibility. All treatments were performed at 25°C.

solution with a composition ratio of 10:1:1 for 90 min. Clad diame-

Electroless nickel plating process.—The sharpened fiber probes with flattened apex were coated with nickel by electroless plating. Pretreatment processes are shown in Table I. The basic bath composition and operating conditions of the electroless nickel plating bath are shown in Table II. The impurity in the electroless plating solu-



^{*} Electrochemical Society Active Member.



Figure 2. SEM micrographs of fine probe for SNOM.

tion could have influenced the deposition at the probe surface. To avoid this, the plating solution was filtrated through the membrane filter with a pore size of $0.2 \ \mu m$.

The deposition morphology on the fine apex areas were observed by scanning electron microscopy (SEM). Dissolved oxygen concentration in the plating bath was measured under the plating condition using a dissolved oxygen (DO) meter (UD-1 type, Central Science Co., Ltd., resolution 0.01 ppm).

Results and Discussion

Influence of the DO concentration in plating solution.-It is a well-known fact that the deposition behavior on a small substrate area is influenced by the DO concentration in the plating bath.⁹⁻¹¹ The DO effect has been explained with a mixed potential theory.¹²⁻¹⁴ Accordingly, we have examined the effect of DO in our plating solution. We have seen that when DO exceeds over 3 ppm, the entire area of protruded probe was not plated at all. This is because DO in the plating solution concentrates at the probe by nonlinear diffusion. Therefore, reduction of oxygen occurs preferentially and the nickel deposition reaction is suppressed. Nickel was deposited on the probe tip by introducing nitrogen gas in the bath before plating (DO 0.7 ppm) or by continuously purging with nitrogen during plating (DO 0.1 ppm) as shown in Fig. 3. The deposition configurations might have been delicately influenced by the several depositionrelated factors at the protruded points of the probe, such as the differences of DO level, dynamics at the reaction interface, concentration of reaction species, etc.



Table II. Bath composition and plating conditions.

$\begin{array}{l} \text{NiSO}_4 \cdot 6\text{H}_2\text{O} \\ \text{CH}_3\text{COONH}_4 \\ \text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O} \end{array}$	0.10 M 0.40 M 0.20 M
Temperature	50°C
pH	5.0



Figure 3. Effect of dissolved oxygen concentration on deposition configuration.

These are many differences between our observations and previously reported results,¹⁰ which revealed that oxygen reduction did not inhibit metal deposition from an electroless nickel bath without any stabilizers. It is supposed that the oxygen is reduced only at the apex area of fiber below the order of submicron for electroless nickel plating. Moreover, the condition of nonlinear diffusion for DO is accelerated in this condition, since only three fiber probes are immersed into the 100 mL of plating bath. Thus, a lot of factors are involved to interpret these differences. Therefore, analysis of the electrochemical activity in this extremely small area is necessary to clarify these contradicting phenomena.

From these observations, DO was adjusted at 0.7 ppm by purging with nitrogen gas before plating to avoid the stirring effect and plating was performed for 15 min under the static condition in subsequent experiments.

Influence of the clad diameter.—We have studied the behavior of nickel deposition by using the fibers with different sizes of clad



Figure 4. Influence of clad diameter on deposition configuration.

Journal of The Electrochemical Society, **147** (3) 1046-1049 (2000) S0013-4651(98)10-118-0 CCC: \$7.00 © The Electrochemical Society, Inc.



Figure 5. Relationship between plating time and deposition configuration.



Figure 6. Relationship between bath pH and deposition configuration.

diameters, since reaction species and oxygen are concentrated by nonlinear diffusion at the protruded area. Figure 4 shows the dependence of plating on the clad diameter. Nickel coating was complete on the protruded area of the fiber probe with a clad diameter of 100 μ m. However, no nickel deposition was observed up to a length of 1 μ m from the apex at the protruded area for a 50 μ m diam fiber. Nickel deposition at the protruded area did not occur at all with a clad diameter of 25 μ m. These differences in deposition can be explained by the mixed-potential theory.¹²⁻¹⁴ From these results we can conclude that when the clad diameter of the probe is greater than 100 μ m, DO does not influence nickel deposition. However, the partial anodic current needed for oxygen reduction increases with the decrease in clad diameter. Therefore, the reduction of oxygen and the oxidation of reducing agent occur preferentially and nickel reduction is terminated.

From these results, we adjusted the DO to 0.1 ppm and 100 μ m diameter of fiber was selected. Figure 5 shows the relationship between the plating time and deposition configuration. Ideal deposition configuration was obtained corresponding to 15 min. However, nickel gradually reached the apex area and all apex area was completely covered within 30 min.

Influence of pH and temperature of the plating solution.—The deposition morphology at the protruded area is greatly influenced by the condition of the plating solution. Accordingly, we studied the bath pH dependence of the deposition morphology at the probe tip at 50°C for 30 min. As shown in Fig. 6, nickel was not deposited at the apex of the protruded area below pH 4.5. On the other hand, thickness of deposition gradually increased with increasing pH. Ideal deposition for our purpose was achieved at the pH range 5-5.5.

Plating bath temperature is also a key factor for the deposition morphology at the protrusion area. Therefore, the bath temperature and pH dependence were investigated. As shown in Fig. 7, the ideal deposition morphology was obtained between the pH range 4.5-6 and temperature range 45-55°. Nickel was not deposited at the apex area below the bold line, nickel completely covered the apex area above the line.

Thus, the process window for our aimed shape is very narrow and reproducibility is low. These deposition differences can be attributed to various factors like chemical adsorption of reaction species, charge transfer, electrical double layer, adsorption and desorption of the



Figure 7. Dependence of pH and temperature on deposition configuration.



Figure 8. Effect of addition of catalytic poison on deposition configuration.

reducing agent, etc. These deposition-related factors at the vicinity of the protruded reaction site are greatly different from the bulk.

Effect of addition of inhibitors.—Our target is to shield the fiber by electroless nickel deposition except the apex region. To ensure controlability and reproducibility of the process, the effects of different catalytic poisons were evaluated. Lead (Pb) and 2-mercaptobenzo-thiazole (2-MBT) were selected as catalytic poisons. Effects of addition of lead are shown in Fig. 8. Appearance of the nickel deposit on the probe was not influenced by the addition of Pb below 0.01 ppm. Nickel deposition was inhibited only at the apex area when the amount of Pb was raised to 0.1 ppm. The plating reaction is completely inhibited at the protruded area by the addition of Pb over

0.5 ppm in the plating bath. Nickel was deposited on the fiber except the apex area by the addition of 1 ppm of 2 MBT. This configuration is ideal for our proposed purpose.

Thus, we confirmed that the addition of inhibitors in the plating bath which was reported elsewhere is an effective method for controlling the deposition condition even at the extremely fine area such as the apex of the fiber probe.

Conclusion

Preparation of the optical fiber probe for SNOM was studied as an application of electroless plating to coat a minute area. The following conclusions were reached

1. Nickel deposition occurred at the protruded area of the probe when the dissolved oxygen in the plating solution was lowered to 0.1 ppm.

2. Nickel deposition at the protruded area depends on the plating reaction area. The deposition morphology on the protruded point was greatly affected by the clad diameter of the fiber probe.

3. Shielding the fiber with electroless nickel, except the apex area, can be accomplished by the addition of a suitable catalytic poison into the plating solution.

Kanto Gakuin University assisted in meeting the publication costs of this article.

References

- V. M. Dubin, Y. Shacham-Diamand, B. Zhao, P. K. Vasudev, and C. H. Ting, J. Electrochem. Soc., 144, 898 (1997).
- 2. H. Watanabe and H. Honma, J. Electrochem. Soc., 144, 471 (1997).
- 3. S. Abe, T. Fujinami, T. Aono, and H. Honma, Hyomen Gijutsu, 48, 433 (1997).
- S. Jiang, N. Tomita, H. Ohsawa, and M. Ohtsu, Jpn. J. Appl. Phys., 30, 2107 (1991).
- S. Jiang, H. Ohsawa, K. Yamada, T. Pangaribuan, M. Ohtsu, K. Imai, and A. Ikai, Jpn. J. Appl. Phys., 31, 2282 (1992).
- 6. R. Uma Maheswari, S. Mononobe, and M. Ohtsu, Appl. Opt., 35, 6740 (1996).
- 7. S. Mononobe, M. Naya, T. Saiki, and M. Ohtsu, Appl. Opt., 36, 1496 (1997).
- 8. S. Mononobe and M. Ohtsu, J. Lightwave Technol., 14, 2231 (1996).
- 9. J. W. M. Jacobs and J. M. G. Rikken, J. Electrochem. Soc., 135, 2822 (1988).
- 10. A. M. T. van der Putten and J. W. G. de Bakker, J. Electrochem. Soc., 140, 2221
- (1993).
 11. A. M. T. van der Putten and J. W. G. de Bakker, J. Electrochem. Soc., 140, 2229 (1993).
- 12. M. Paunovic, Plating, 55, 1161 (1968).
- 13. P. Bindra and J. Tweedie, J. Electrochem. Soc., 130, 1112 (1983).
- 14. P. Bindra and J. Roldan, J. Electrochem. Soc., 132, 2581 (1985).