- 9. N. Ibl, "Advances in Electrochemistry and Electrochemical Engineering," Vol. 2, C. W. Tobias, Editor, Chap. 3, Interscience Publishers, Inc., New York (1962)
- M. Loshkarev, A. Ozerov, and N. Kudriavtzev, Zhur. Prikl. Khim (USSR), 22, 294 (1949).
 N. Ibl, Y. Barrada, and G. Trumpler, Helv. Chim. Acta, Difference of the second secon
- **37,** 583 (1954).
- 12. N. Ibl and R. H. Müller, Z. Electrochem., 59, 671 (1955).
- 13. A. Tvarusko and L. S. Watkins, This Journal, 118, 248 (1971).
- 14. Y. Awakura and Y. Kondo, ibid., 123, 1184 (1976).
- 15. F. R. McLarnon, R. H. Müller, and C. W. Tobias, ibid., 122, 59 (1975).
- Y. Fukunaka, K. Denpo, M. Iwata, K. Maruoka, and Y. Kondo, *ibid.*, **130**, 2492 (1983).
- 17. C. R. Wilke, M. Eisenberg, and C. W. Tobias, ibid., 100, 513 (1953).
- 18. J. Newman, "Electrochemical Systems," Prentice-Hall, Inc., Englewood Cliffs, NJ (1973).
- 19. A. Calusaru, "Electrodeposition of Metal Powder," Elsevier Scientific Publishing Co., New York (1979).

Magnetic Anisotropy of Electrodeposited Cobalt on Alumite Substrate

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ABSTRACT

Magnetic anisotropy of electrodeposited cobalt film on porous alumite can be modulated by controlling the pH of the solution and the pulsed current density. The microstructure of the thin Co film depends on the interfacial pH. Hexagonal [00.2] preferred orientation is obtained when the interfacial pH is higher than six and approaching the solubility limit of Co(OH)₂. High interfacial pH can be obtained by operating above the limiting current density. Different microstructures are obtained by modulating the interfacial pH through the applied current density and the solution pH. Anisotropy fields as high as 3600 Oe are obtained for high aspect ratios when the hexagonal [00.2] preferred orientation structure is obtained.

The microstructure of cobalt film obtained by electrodeposition was shown to depend on the pH of the plating solution (1, 2). Goddard and Wright (3) investigated the structure of single-crystal films of cobalt grown epitaxially by electrodeposition onto electropolished copper substrates and observed that for pH > 2.4, only a fcc cobalt was deposited, whereas from solution with pH < 2.9, a hcp cobalt was produced. In the pH range of 2.4-2.9, the deposits consisted of varying proportions of fcc and hcp phases. Wright (4) and Gaigher and van der Berg (5) also reported on the influence of pH on the fcc \Leftrightarrow hcp phase transition during the early stages of cobalt electrodeposition. Nakahara and Mahajan (6) showed that at low pH (~1.6), the microstructure of plated Co consisted of highly faulted fcc regions and at high pH (~5.7), a hcp phase was observed, and the density of faults was greatly reduced. A martensitical transformation mechanism was proposed (6). Recently, Croll (7) plated Co from a simple $CoSO_4$ bath, with or without boric acid, and an abrupt transition in the preferred orientation (P.O.) is observed to occur in the pH range of 4-6.5. The c-axis orientation in this region changes from in-plane to predominantly vertical to the film plane, along with corresponding changes in magnetic properties.

From the previous experimental results regarding the phase transition of plated Co films, it is concluded that the cited pH range for the Co[00.2] preferred orientation is inconsistent and scattered because the formation of OHions or the consumption of H⁺ ions at the cathode can significantly change the interfacial pH from the bulk pH. The following reactions can occur simultaneously with Co deposition

$$\mathbf{H}^{+} + e \leftrightarrow \frac{1}{2} \mathbf{H}_{2}$$
 [1]

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in an acidic solution, or

$$H_2O + e \leftrightarrow OH^- + \frac{1}{2}H_2$$
 [2]

in an alkaline bath. Consequently, the pH at the interface can be higher than its bulk value. It is desired to establish a higher pH environment to induce certain preferred orientation; however, the pH should also be kept below the solubility limit where the nonmagnetic hydroxide forms. The hydrolysis constant for Co(OH)₂ has been reported to be 2.5×10^{-16} (8), and the critical pH for hydroxide formation can be estimated for a particular local cobalt concentration. The interfacial pH, controlled by the applied current density, can affect the resultant microstructure. The magnetic properties of plated Co film can therefore be modulated through different plating operations.

In this communication, we report the following studies. First, the effect of pH on the Co preferred orientation is studied in a well-agitated bath where the concentration difference between bulk and interface is minimized. In the second part, a porous alumite film was used as a substrate to grow Co metal within each micropore. The goal is to establish the role of interfacial pH in governing the preferred orientation.

Experimental

Co films were electrodeposited on flat brass substrates from different solutions. The bath pH was carefully adjusted by NaOH or H₂SO₄. An x-ray diffractometer with high resolution was used to characterize the preferred orientation of each sample. A commercially available alumite membrane (Anotec Separations LTD) was sealed on one side with conducting silver paint (Ernest F. Fullam, Incorporated) and served as a substrate for pulse plating on the other side. Based on the anodization technique, the alumite substrate was formed into a hexagonally distributed porous structure with a pore axis vertical to the substrate plane. The porosity was determined by SEM as approximately 64%. The pore diameter is 2000Å and the substrate thickness is 50 μ m which allows the formation of different lengths of metal deposit. A SEM micrograph along with a schematic sketch of the porous substrate are illustrated in Fig. 1. The electrolyte for the plating bath contains 50 g/liter CoSO₄ · 7H₂O and 25 g/liter H₃BO₃. Pulse plating technique was applied using different current magnitudes and pulse widths by a PAR Model 173 potentiostat/galvanostat and a PAR Model 175 universal programmer. Various periods of electrodeposition were used to obtain different film thicknesses.

The magnetic properties of materials were determined from the saturated hysteresis loops measured by a vibrating sample magnetometer (EG&G PAR Model 155) in both in-plane and vertical-to-the-film plane configurations. To estimate the magnetic anisotropy field, the in-plane loop in the case of Co films deposited on the alumite substrate is taken as the hard-axis direction, and the standard procedure is adopted to measure the anisotropy field H_k which is determined by extending the tangent of the initial magnetization to the interpolation of the saturation magnetization.

Results and Discussion

The phase transition for a series of Co films electrodeposited from different pH baths was examined by a thin film diffractometer. A summary of the integrated intensity of each phase is given in Fig. 2 which clearly shows that the pH significantly affects the microstructure of the plated Co films. The integrated intensity for Co[00.2] changes abruptly from 62 to 1323 (in arbitrary unit) while the bath pH narrowly changes from 5.53 to 5.97. The values for the Co[10.0] peak drop, however, from 579 to 145 in this small range. It is concluded that in order to produce crystallographic preferred orientation parallel to [00.2] with stronger magnetic anisotropy, the pH of electrolyte has to be greater than 6.0, quite close to the solubility limit of Co(OH)₂. In a recent work by Chen (9), perpendicular Co thin film was electrodeposited through forming isolated acicular particles whose long axis is in the direction of the hexagonal c-axis. In that process, the solution pH was kept near the precipitation point of Co(OH)₂ (i.e., between pH 6-7), where a morphological stability for cellular growth could take place. Along with that cellular or columnar



Fig. 1. SEM picture of porous alumite (a) along with schematic sketch of the hexagonal arrays of pores (b).



Fig. 2. Integrated intensity (in arbitrary unit) from XRD for phases in electrodeposited Co films from different baths.

growth, an interparticle separation exists due to the presence of the nonmagnetic Co(OH)₂ precipitate.

In our investigations, when a porous anodized alumite substrate is used, the metal deposit inside the film is guaranteed to be rod-like with a high aspect ratio. Figure 3 shows the correlation between the anisotropy field H_k and the aspect ratio for electrodeposited Co films on porous alumite substrates. For all the samples, the anisotropy field increases as the film thickness and the corresponding aspect ratio increases. For an applied current density of 50 mA/cm², which is under the calculated limiting current of 79 mA/cm², there is no H₂ coevolution and the interfacial pH should be close to the bulk pH. Under this situation, the anisotropy field is always higher for samples obtained from a pH = 6 bath than those from a pH = 3 bath, as different crystalline structures are formed from these two baths. Hexagonal [00.2] preferred orientation structure is formed from higher pH baths. However, in Fig. 3, the H_k of the pH = 3 group increased as well to within the H_k for pH = 6 when a current density of 100 mA/cm², higher than the limiting current density, was applied. Beyond the limiting current density, hydrogen evolution occurred and the interfacial pH changed to a higher value, under which the formation of [00.2] orientation of hcp is preferred.



Fig. 3. Anisotropy field H_k vs. aspect ratio for electrodeposited Co on porous Al_2O_3 : applied current $i_{ov} = 50 \text{ mA/cm}^2$ for \bigcirc , \square ; 100 mA/cm² for \times .

In the porous alumite film, it is possible to electrochemically grow Co from the bottom of the micropores where no convection flow occurs and the depletion of H⁺ is significant under high applied current densities. The interfacial concentration of each reacting species and the limiting current under different pulse plating conditions have been calculated (10) as the operating criteria. For iron-group electrodeposition in a regular sulfate bath, hydrogen evolves before the metal layer is laid down and the interfacial pH, in the absence of the boric acid, rises to a higher value. In our experiments, boric acid was added to the sulfate bath to induce metal deposition before H₂ evolution. The role of boric acid in Watts-type bath was assumed to act as a buffer to control the interfacial pH at a low value (11-13). Recent investigations show that in fact, boric acid is a homogeneous catalyst for the reduction of metal ions (14, 15) as it lowers the overvoltage for metal deposition. This leads us to believe that in Watts-type or sulfate baths with boric acid, hydrogen is not evolved at low current densities and the pH at the metal-solution interface does not change during the cathodic process. Under higher current densities, hydrogen can evolve and the pH would increase at the interface (15). Thus, the OH⁻ generation or H⁺ consumption along with H₂ evolution are advantageously used to adjust the interfacial pH. This modulated interfacial pH may help establish preferred orientation and induce a strong magnetocrystalline anisotropy.

Conclusion

The magnetic anisotropy of Co films, plated from either an agitated bath or a stagnant bath inside porous alumite film, shows a strong pH dependency. Experimentally determined by a series of plated films from different pHbaths where the pH difference between the bulk and the interface is minimized, the transition to Co[00.2] happens abruptly at pH 6.0. In a Watts bath, where the overpotential for the metal deposition is reduced by the presence of boric acid, the interfacial pH can be manipulated by the magnitude of applied current density. By plating with either higher or lower current densities than the limiting current, the microstructure of the Co deposit can be changed and the anisotropy field is modulated accordingly.

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REFERENCES

- 1. H. Kersten, Physics, 2, 274 (1932).
- Yu. M. Polukarov, Russ. J. Phys. Chem., 34, 68 (1960).
 J. Goddard and J. G. Wright, Br. J. Appl. Phys., 15, 807 (1964).
- 4. J. G. Wright, Thin Solid Films, 22, 197 (1974).
- 5. H. L. Gaigher and N. G. van der Berg, Electrochim Acta, 21, 45 (1976).
- 6. S. Nakahara and S. Mahajan, This Journal, 127, 283 (1980).
- I. M. Croll, IEEE Trans. Mag., MAG-23(1), 59 (1987).
 L. B. Harris, This Journal, 120, 1035 (1973).
 T. Chen, U.S. Pat., 4,405,677 (1983).

- T. J. Cheng, J. Jorné, and J.-S. Gau, In preparation.
 A. Brenner, "Electrodeposition of Alloys," Academic Press, Inc., New York (1963).
- 12. A. Saraby-Reintjes and M. Fleishmann, Electrochim.
- Acta, 29, 557 (1984).
 13. F. A. Lowenheim, "Modern Electroplating," John Wiley & Sons, Inc., New York (1974).
 14. J. P. Hoare, *This Journal*, 133, 2491 (1986).
 15. J. B. Hoare, *ibid* 214, 210 (1997).
- 15. J. P. Hoare, ibid., 134, 3102 (1987).

Pd⁺²/Poly(acrylic acid) Thin Films as Catalysts for Electroless Copper Deposition: Mechanism of Catalyst Formation

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ABSTRACT

The mechanism involved in the initiation of electroless copper deposition onto dielectric substrates using Pd+2/ poly(acrylic acid) thin films is described. Dielectric substrates are catalyzed by dip-coating in aqueous poly(acrylic acid) to deposit a 50-300 nm thick film of the polymer on the surface; the coated substrate is then immersed in aqueous $PdSO_4$. It is shown that uptake of palladium in the poly(acrylic acid) film occurs by H⁺/Pd⁺² ion exchange. The active catalyst is identified by x-ray photoelectron spectroscopy as zerovalent palladium, formed when the Pd+2-exchanged polymer film is immersed in an electroless copper deposition bath.

Electroless deposition is a well-known chemical process for preparing metallic coatings, particularly of nickel and copper. Electroless deposition occurs by a redox process, where the cation of the metal to be deposited is chemically reduced. For electroless deposition of copper, the typical reducing agent is basic formaldehyde, which reduces the EDTA complex of Cu⁺² to Cu⁰ according to the reaction shown in Eq. [1] (1, 2)

 $Cu(EDTA)^{-2} + 2H_2CO + 4 OH^{-1}$

 \rightarrow Cu + 2HCOO⁻ + 2H₂O + H₂ + EDTA⁻⁴ [1]

The redox process of electroless deposition generally occurs only on appropriate catalytic surfaces, which must include the deposited metal to enable deposition of thick films. A noncatalytic substrate, such as a polymer dielectric or a ceramic, must be treated with a noble metal catalyst before it can be metallized via an electroless process.

One of the more important recent applications for electroless deposition of copper involves fabrication of high density printed circuit boards (PCBs) (3). Fabrication of PCBs via electroless copper deposition currently requires treatment of the PCB substrate (typically a glass-fiber/ epoxy composite) with a catalyst that consists of a colloidal suspension of palladium particles (4-8). The suspension is prepared by mixing acidic aqueous solutions of SnCl₂ and $PdCl_2$, inducing a redox reaction whereby Sn^{+2} is oxidized to Sn⁺⁴ and Pd⁺² is reduced to Pd⁰. The particle size of the palladium colloid thus formed is \sim 1-2 nm. Growth beyond that point is limited by the spontaneous formation of a tin chloride shell around each Pd particle (9, 10). Catalysis of PCBs toward electroless copper deposition is accomplished by dip-coating the PCB substrate in the colloidal suspension, depositing the palladium particles on the surface. Before electroless copper deposition can begin, however, the tin chloride shell must be removed, since this