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Effect of electrolysis factors on crystal orientation and morphology of electrodeposited cobalt

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Abstract

Cobalt electrodeposition was carried out using sulfate and chloride baths to investigate the effects of electrolysis factors on the crystal orientation and morphology of the deposits. The preferred orientation of Co deposited from the sulfate baths changed from (0 0 0 2) to $(1\ 1\ \bar{2}\ 0)$ plane with an increase in the deposition overpotential and the deposits showed the largest grain size with a smooth surface in the low overpotential region. On the other hand, no dependence of crystal orientation and morphology on deposition overpotential was found in chloride baths.

1. Introduction

Thin films of Co alloys, such as Co–Ni, Co–P [1, 2] and Co–Ni–P [3], have been employed as materials for magnetic recording devices. Electroplating and electroless plating are widely used for the formation of these thin alloy films. On the one hand, electroless plating has the advantage of forming a homogeneously thin film on a substrate and, in recent years, electroless Co–Ni–Re–W–P and Co–Ni–Re–P alloy films have been developed for perpendicular magnetic recording media with a higher density. On the other hand, attention has also been paid to electroplating because it is favourable for easy control of film thickness as well as high stability of the plating baths [4, 5].

It is reported that the magnetic properties of thin films depend both on the orientation and grain size of the crystals [6, 7]. Especially for the application of the Co alloy to perpendicular magnetic recoding media, it is necessary that the Co films grow along the *c*-axis of easy magnetization in the hexagonal closed packed structure [2, 8, 9]. Therefore, in order to produce magnetic films of the Co alloy system by electroplating, factors affecting the film structure should be studied from a crystallographic point of view [10].

In the present paper Co was electrodeposited from sulfate and chloride baths and the effects of plating factors on the crystal orientation and morphology of the deposited Co were discussed in terms of the overpotential for Co deposition.

2. Experimental details

2.1. *Electrolysis*

Table 1 shows the electrolysis conditions and the bath composition employed. The baths were prepared by dissolving a fixed amount of high-grade reagents in distilled and deionized water. The bath pH was adjusted to a fixed value with sulfuric acid for the sulfate bath and hydrochloric acid for the chloride bath. A beaker-type electrolytic cell was used for the electrolysis under galvanostatic conditions. The cathode was a polycrystalline Cu sheet and the anode was a Pt sheet.

Electrodeposits were dissolved from the cathode with nitric acid, and Co was quantitatively analysed by atomic absorption spectrometry. The current efficiency and the partial current density of Co were then calculated.

2.2. *Measurement of overpotential*

The cathode potential during Co deposition was measured with reference to a saturated Ag/AgCl electrode. The overpotential for Co deposition was determined from the difference between the equilibrium potential of Co calculated by Nernst's equation and the measured cathode potential. The overpotential determined in this manner includes, the overpotential for Co deposition and the resistance overpotential derived from the ohmic resistance of the electrolyte between the cathode surface and the capillary tip. The resistance overpotential was

Table 1. Electrolysis conditions

Item			Range
Bath composition	Sulfate bath	$CoSO_4 \cdot 7H_2O$ (mol dm^{-3}) pH	0.5 3, 5 [3]
	Chloride bath	$CoCl_2 \cdot 6H_2O$ (mol dm^{-3}) pH	0.5 3, 5 [3]
Operating conditions	Current density (A dm^{-2}) Temperature (°C) Coating thickness (μm) Quiescent bath Cathode Anode		0.1–30 [3] 5, 40, 80 [40] 2, 10, 20 [20] Cu (1 × 2 cm^2) Pt

[ ] : Standard conditions.

measured using the current-interruption technique. The deposition overpotential for Co deposition, which is directly related to the electrocrystallization process, was determined by subtracting the resistance overpotential from the calculated overpotential.

2.3. *Crystal orientation and surface morphology*

The crystal orientation of the deposited Co was determined using Willson and Rogers' method [11] with an X-ray diffraction intensity of the (0 0 0 2), (1 0 $\bar{1}$ 1), (1 1 $\bar{2}$ 0) and (1 0 $\bar{1}$ 0) planes. The morphology of the deposited Co was observed by scanning electron microscopy (SEM).

3. Results and discussion

3.1. *Crystal orientation of Co films electrodeposited from sulfate baths*

Figure 1 shows the effect of the plating factors such as current density, temperature and bath pH on the crystal orientation of the Co deposited from sulfate baths. Although preferred orientations of the (0 0 0 2) and (1 0 $\bar{1}$ 0) planes were observed at 0.1 and 1 A dm^{-2}, respectively, the orientation index of the (1 1 $\bar{2}$ 0) plane increased steeply with increase in current density and showed a maximum value at 10 A dm^{-2}. With further increase in current density, the orientation index of the (1 1 $\bar{2}$ 0) plane decreased without any change in the orientation indices of the other planes. Therefore, the deposited Co seemed to have an unoriented state at higher current densities. However, with increase in temperature and pH, the orientation index of the (1 1 $\bar{2}$ 0) plane decreased rapidly and the (0 0 0 2) plane became preferentially oriented. No preferred orientation of the (1 0 $\bar{1}$ 1) plane was observed over the entire range of electrolysis conditions.

The effect of overpotential on the crystal orientation of several deposited metals was reported by Pangarov [12, 13]. He calculated the relative values of the two-dimensional nucleation work on the various types of crystals and showed the overpotential-dependence of the preferred orientation on the supposition that the two-dimensional nuclei were so formed as to result in the

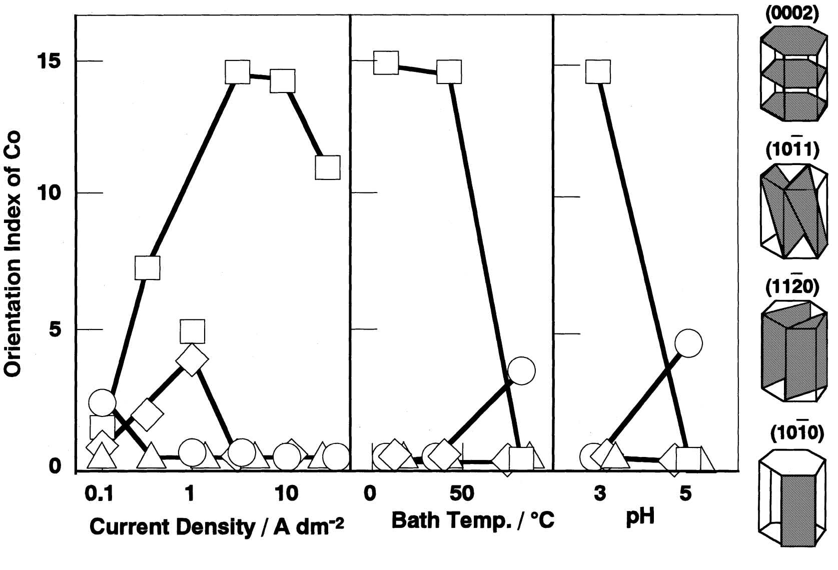


Fig. 1. Effect of plating factors on the crystal orientation index of Co electrodeposited from sulfate bath. Orientation index: (○) (0 0 0 2), (△) (1 0 $\bar{1}$ 1), (□) (1 1 $\bar{2}$ 0), (◇) (1 0 $\bar{1}$ 0).

smallest nucleation at a given crystallization overpotential.

The crystal orientation of the deposited Co is discussed with respect to the deposition overpotential. As previously mentioned, the ohmic resistance of the electrolyte was measured by the current-interruption technique in order to determine the net deposition overpotential of Co. The dependence of the ohmic resistance of the sulfate baths on the current density at 5, 40 and 80 °C is shown in Figure 2, as an example. The ohmic resistance decreased with increase in current density at all temperatures. If the bath composition is not different between the vicinity of the electrode and the bulk solution, the ohmic resistance should be independent of current density. However, the ions involved in an electrochemical reaction are depleted in the vicinity of the cathode and hence the ohmic resistance of the electrolytes increases as the electrolysis progresses. Therefore, it was suggested from Figure 2 that increasing the current density enhanced the agitation due to hydrogen evolution at the cathode surface to retard the depletion rate of the depositing ions in the vicinity of the cathode, resulting in a decrease in electrolyte ohmic resistance. Since both the current efficiency for Co deposition and the electric conductivity of the electrolytes normally decrease simultaneously with decrease in temperature, the ohmic resistance of the electrolytes at 5 °C showed the highest value and significantly depended on current density.

Figure 3 shows the relationship between crystal orientation and overpotential for Co deposition from sulfate baths, when current density, temperature and bath pH were varied. The Co deposited at a low overpotential of 0.05 V, possessed the preferentially oriented (0 0 0 2) plane. As the overpotential for Co deposition increased, the orientation index of the (0 0 0 2) plane decreased and those of the $(1\ 1\ \bar{2}\ 0)$ and $(1\ 0\ \bar{1}\ 0)$ planes correspondingly increased. With further increase in overpotential, the orientation of the $(1\ 1\ \bar{2}\ 0)$ plane only was observed.

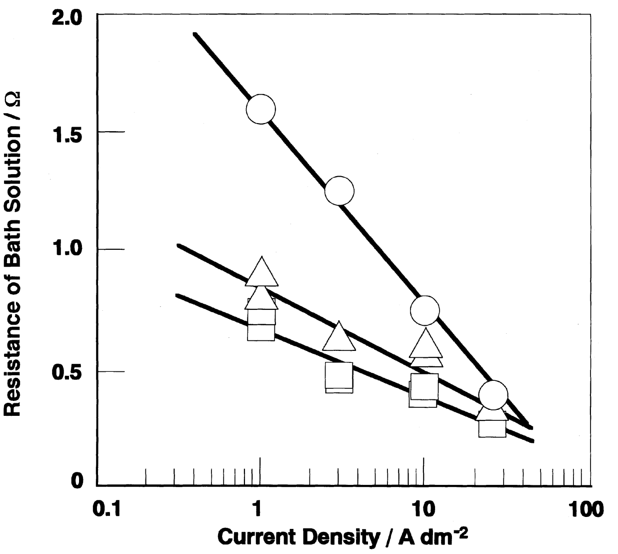


Fig. 2. Examples of resistance of bath solution during Co electrodeposition in sulfate bath. Temperature: (○) 5 °C, (△) 40 °C, (□) 80 °C.

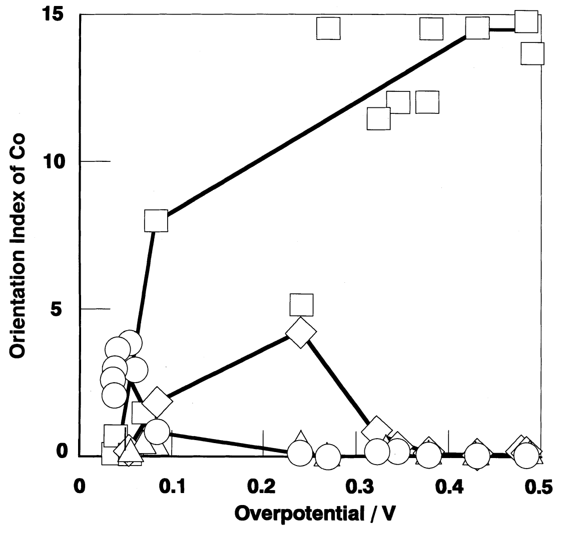


Fig. 3. Relationship between overpotential and crystal orientation index of Co electrodeposited from sulfate bath. Orientation index: (○) (0 0 0 2), (△) $(1\ 0\ \bar{1}\ 1)$, (□) $(1\ 1\ \bar{2}\ 0)$, (◇) $(1\ 0\ \bar{1}\ 0)$.

According to the mechanism proposed by Pangarov, the plane with the preferred orientation in h.c.p. Co is (0 0 0 1) at low overpotential and it is then shifted to $(1\ 0\ \bar{1}\ 1)$, $(1\ 1\ \bar{2}\ 0)$ and $(1\ 0\ \bar{1}\ 0)$ as the overpotential for Co deposition increases. The results shown in Figure 3 agree with Pangarov's prediction in the respect that the plane with a preferred orientation was (0 0 0 2) at low overpotential and that the orientation index of $(1\ 1\ \bar{2}\ 0)$ increased with increase in overpotential. However, the $(1\ 0\ \bar{1}\ 0)$ plane was not preferentially orientated at higher overpotentials but its orientation index showed a maximum value at a moderate overpotential of 0.25 V.

3.2. *Crystal orientation of Co films electrodeposited from chloride baths*

Figure 4 shows the effects of the plating factors such as current density, temperature and pH on the crystal orientation of Co deposited from chloride baths. The crystal orientation of Co was significantly different between the chloride and sulfate baths, and a preferred orientation of the $(1\ 1\ \bar{2}\ 0)$ plane was observed in the chloride baths over the entire range of electrolysis conditions.

Figure 5 shows the relationship between the crystal orientation and the deposition overpotential in the chloride baths. Regardless of the deposition overpotential, the deposited Co showed preferred orientation of the $(1\ 1\ \bar{2}\ 0)$ plane, while the $(1\ 0\ \bar{1}\ 0)$ plane was slightly oriented at potentials between 0.08 and 0.32 V. Pangarov suggested that two-dimensional nucleation could change when hydrogen was simultaneously discharged and certain foreign additives were adsorbed on the cathode [12, 13]. It is known that Cl^- affects the metal deposition by specifically adsorbing on the cathode [14].

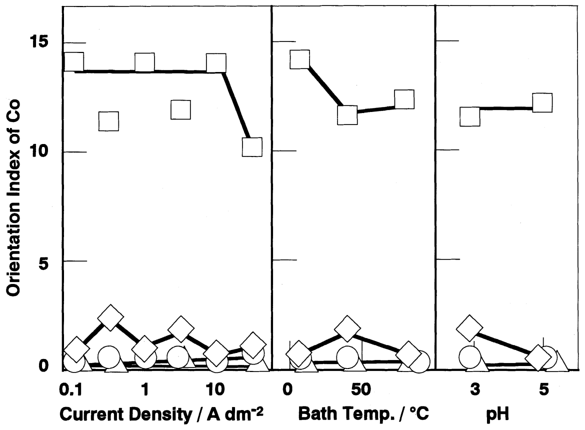


Fig. 4. Effect of plating factors on crystal orientation index of Co electrodeposited from chloride bath. Orientation index: (○) (0 0 0 2), (△) (1 0 $\bar{1}$ 1), (□) (1 1 $\bar{2}$ 0), (◇) (1 0 $\bar{1}$ 0).

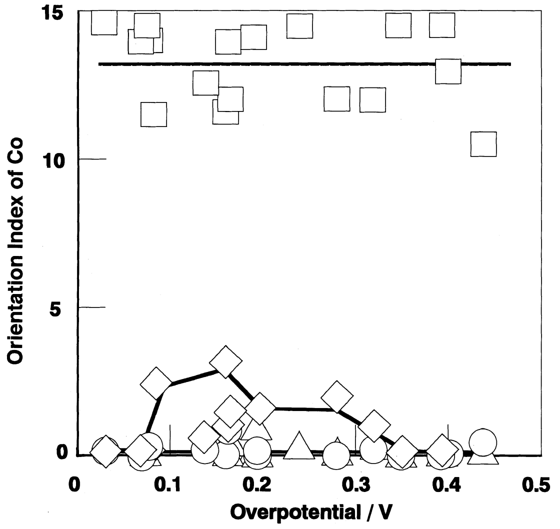


Fig. 5. Relationship between overpotential and crystal orientation index of Co electrodeposited from chloride bath. Orientation index: (○) (0 0 0 2), (△) (1 0 $\bar{1}$ 1), (□) (1 1 $\bar{2}$ 0), (◇) (1 0 $\bar{1}$ 0).

Furthermore, especially during electrodeposition of iron-group metals, it is also reported that an intermediate MOH$^-_{ad}$ (M: Fe, Ni or Co) complex was formed during the reduction of simple hydrated iron-group metal ions and Cl$^-$ changed the structure of the intermediate to the more easily reducible MCl$^-_{ad}$ [15]. Therefore, it is possible that these ionic species adsorbed on the cathode affected the nucleation and growth of the specific plane of the deposited Co.

3.3. *Effect of film thickness on the crystal orientation of Co*

Figure 6 shows the relationship between crystal orientation and film thickness of Co deposited from sulfate baths. The Co deposited at a low overpotential of 0.05 V showed the preferentially oriented plane of (0 0 0 2) and the thickness dependence of the crystal orientation was not recognized. In the deposit obtained at a moderate overpotential of 0.24 V, the orientation indices of the (1 1 $\bar{2}$ 0) and (1 0 $\bar{1}$ 0) planes were higher than those of other planes and the index of the (1 0 $\bar{1}$ 0) plane increased slightly with increase in film thickness. At the higher overpotential of 0.38 V, the orientation of the (1 1 $\bar{2}$ 0) plane was more predominant, while the orientation index of the (1 1 $\bar{2}$ 0) plane increased but that of the (1 0 $\bar{1}$ 0) plane correspondingly decreased with increase in film thickness.

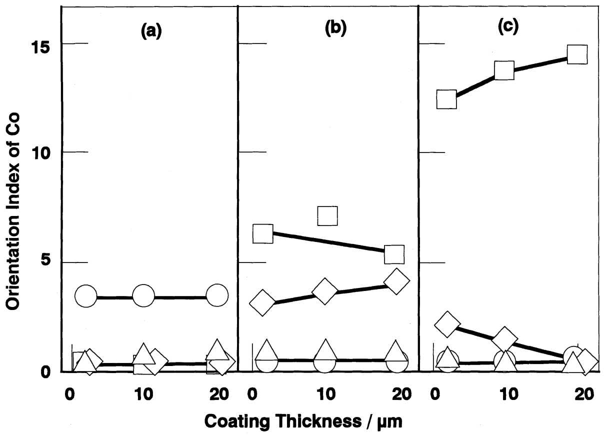


Fig. 6. Effect of coating thickness on crystal orientation index of Co electrodeposited at various overpotential in sulfate bath. Overpotential: (a) 0.05 V, (b) 0.24 V, (c) 0.38 V. Orientation index: (○) (0 0 0 2), (△) (1 0 $\bar{1}$ 1), (□) (1 1 $\bar{2}$ 0), (◇) (1 0 $\bar{1}$ 0).

Figure 7 shows the effect of film thickness on crystal orientation of Co deposited from chloride baths. Although Co was deposited with the preferred orientation of the (1 1 $\bar{2}$ 0) plane at any overpotential (Figure 5), a thickness dependence of the crystal orientation was definitely observed; that is, the Co deposited from the chloride baths grew with preferred orientation of the (0 0 0 2), (1 1 $\bar{2}$ 0) and/or (1 0 $\bar{1}$ 0) planes during the early stages of electrolysis. With increase in film thickness, the orientation indices of the (0 0 0 2) and (1 0 $\bar{1}$ 0) planes decreased and the corresponding in-

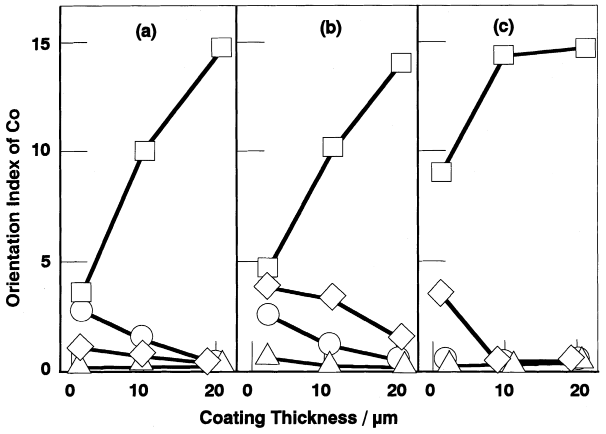


Fig. 7. Effect of coating thickness on crystal orientation index of Co electrodeposited at various overpotential in chloride bath. Overpotential: (a) 0.03 V, (b) 0.20 V, (c) 0.35 V. Orientation index: (○) (0 0 0 2), (△) (1 0 $\bar{1}$ 1), (□) (1 1 $\bar{2}$ 0), (◇) (1 0 $\bar{1}$ 0).

crease in the orientation index of (1 1 $\bar{2}$ 0) was distinctly observed.

It is well known that the structure of a deposit is strongly affected by the crystal orientation of a substrate and the deposit grows epitaxially on the substrate during the early stage of metal deposition [16]. An increase in the film thickness diminishes the effect of the substrate, and therefore, the structure of the deposit is controlled by the electrolysis conditions. In this study, a cold rolled Cu sheet with the preferred orientation of the (1 0 0) plane (orientation index 3.8) was used as the substrate. Among the preferentially oriented planes during the early stage, the (0 0 0 2) plane was not oriented at any overpotential but the preferentially oriented (1 0 $\bar{1}$ 0) and (1 1 $\bar{2}$ 0) planes were observed at moderate overpotentials in the bulk of the deposit (Figure 5). Therefore, it seemed that the preferred orientation of the (0 0 0 2) plane during the early stages of electrolysis resulted from the epitaxial growth of Co on a Cu substrate. Actually, the misfit between the (0 0 0 2)Co and (1 0 0)Cu is 12.2%, permitted epitaxial growth of Co on a Cu substrate [17]. Furthermore, it is also reported for the epitaxial growth of electrodeposited Zn and Cd (hcp) on a Cu substrate that the crystallographic relationship of (0 0 0 2)Zn and Cd//(1 0 0)Cu is satisfied between the deposits and the substrate [18].

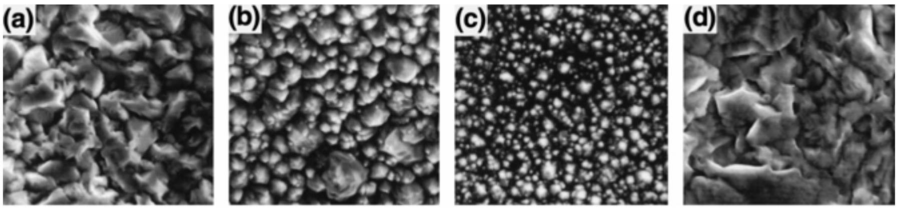
Figure 7 also indicates that the decrease in orientation index of the (1 0 $\bar{1}$ 0) plane was followed by an increase in that of the (1 1 $\bar{2}$ 0) plane with increase in film thickness. Both (1 1 $\bar{2}$ 0) and (1 0 $\bar{1}$ 0) planes are at right angles to the (0 0 0 2) basal plane of h.c.p.-Co and hence the plane with a preferred orientation might be easily altered from (1 0 $\bar{1}$ 0) to (1 1 $\bar{2}$ 0) with a slight variation in plating factors.

3.4. *Effect of plating factors on the morphology of the deposited Co*

Figure 8 shows the surface morphology and the corresponding orientation indices of the (1 1 $\bar{2}$ 0), (1 0 $\bar{1}$ 0) and (0 0 0 2) planes in Co deposited from sulfate baths. The deposition overpotentials were confirmed to conform to Tafel behaviour by measuring the partial polarization for Co deposition. That is, the concentration overpotentials were negligible in this study. Block-type structures were present in the Co deposited at 40 °C, and they became roundish and finer in size when the current density increased (a and b). At the same current density of 3 A dm^{-2}, finer particles were observed at lower temperatures (c). These changes in the morphology of the deposited Co were dependent on the deposition overpotential, and the Co deposited under slight overpotentials at 80 °C showed a smooth surface consisting of relatively large blocks (d).

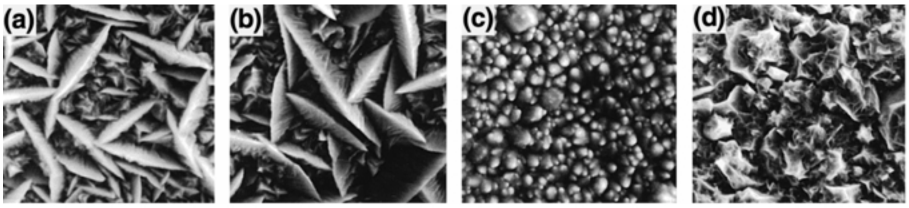
The surface morphology of the Co deposited from the chloride baths and the corresponding orientation indices are shown in Figure 9. The Co deposited at 5 °C under a significantly large overpotential was composed of relatively fine particles (c). As previously mentioned, the Co deposited from the chloride baths showed preferred orientation of the (1 1 $\bar{2}$ 0) plane over the entire range of electrolysis conditions. Therefore, it seemed that a large polarization and the preferred orientation of the (1 1 $\bar{2}$ 0) plane produced deposited Co consisting of fine particles in chloride baths as well as in sulfate baths. However, the morphology of the Co deposited at 40 and 80 °C was independent of the deposition overpotential. Large platelets appeared perpendicular to the substrate in Co deposited at 40 °C (a and b) and a small block-type structure was present in deposits obtained at 80 °C (d).

The adsorbed species such as halide ions and the intermediates have been reported to affect the morphology of the deposited Co [19]. It was shown that large platelets of deposited Co were formed by decrease in surface energy due to adsorption of halide ions and intermediates [19]. Furthermore, halide ions were suggested to produce fine crystallite when these ions inhibit the surface diffusion of ad-atoms and the growth of Co crystals [19]. Consequently, Co deposited from chloride baths showed significantly different shape and size at all temperatures, and the morphology could not be systematically explained in terms of the plating factors.



C.D. / A dm^{-2}	Temp. / °C	Overpot. / V	Orientation index (11$\bar{2}$0)	(10$\bar{1}$0)	(0002)
(a) 0.3,	40	0.08	7.8	1.7	0.4
(b) 3,	40	0.28	14.5	0.1	0
(c) 3,	5	0.48	15.0	0.1	0
(d) 3,	80	0.03	0.2	0.3	3.2

Fig. 8. Effect of plating condition on morphology of Co electrodeposited from sulfate bath.



C.D. / A dm^{-2}, Temp. / °C	Overpot. / V	Orientation index		
		$(11\bar{2}0)$	$(10\bar{1}0)$	(0002)
(a) 0.3, 40	0.08	11.5	2.5	0
(b) 3, 40	0.28	11.9	2.0	0
(c) 3, 5	0.39	14.5	0.2	0
(d) 3, 80	0.14	12.7	0.6	0

Fig. 9. Effect of plating condition on morphology of Co electrodeposited from chloride baths.

4. Conclusion

Cobalt was electrodeposited from sulfate and chloride baths to investigate the effect of plating factors on the crystal orientation and morphology of the deposited Co. The crystal orientation of Co deposited from sulfate baths depended on the deposition overpotential; that is, the (0 0 0 2) plane was preferentially oriented in the low overpotential region and the preferred orientation of $(1\ 1\ \bar{2}\ 0)$ became distinguished with increase in overpotential. However, Co deposited from chloride baths showed preferred orientation of the $(1\ 1\ \bar{2}\ 0)$ plane alone over the entire range of electrolysis conditions. Furthermore, a thickness dependence of the crystal orientation was recognized in Co deposited from chloride baths, which might be attributed to epitaxial growth of Co on a Cu substrate during the early stages of electrolysis.

The grain size of Co deposited from sulfate baths became smaller with increase in deposition overpotential, while Co deposited at low deposition overpotential showed a smoother surface with a high orientation index of the (0 0 0 2) plane. The morphology of Co deposited from chloride baths varied with changing plating conditions but was independent of the magnitude of the Co deposition overpotential.

References

1. J.H. Kefalas, *Plating* **54** (1967) 543.
2. T. Homma, Y. Kurokawa, M. Yamamoto and T. Osaka, *J. Surf. Finish. Soc. Jpn.* **44** (1993) 1099.
3. Y. Kita, T. Homma and T. Osaka, *J. Surf. Finish. Soc. Jpn.* **49** (1998) 1358.
4. F. Goto, T. Osaka, I. Koiwa, Y. Okabe, H. Matsubara, Wada and N. Shiota, *IEEE Trans. Magn.* **20** (1984) 803.
5. T. Osaka, T. Homma, K. Inoue, Y. Yamasaki and K. Namikawa, *J. Magnetics. Soc. Jpn.* **13** (1989) 85.
6. J.S. Sallo, *J. Electrochem. Soc.* **109** (1962) 1040.
7. J.S. Judge, *Plating* **53** (1966) 441.
8. J.S. Sallo and J.M. Carr, *J. Electrochem. Soc.* **109** (1962) 1040.
9. F. Sato, N. Tezuka, T. Sakurai and T. Miyazaki, *J. Magnetics. Soc. Jpn.* **17** (1993) 886.
10. S. Maruyama, H. Numata, I. Ohno and S. Haruyama, *J. Surf. Finish. Soc. Jpn.* **48** (1997) 68.
11. K.S. Willson and J.A. Rogers, *Tech. Proc. Amer. Electroplaters Soc.* **51** (1964) 92.
12. N.A. Pangarov, *Electrochim. Acta* **9** (1964) 721.
13. N.A. Pangarov, *J. Electroanal. Chem.* **9** (1965) 70.
14. T.C. Franklin, *Surf. Coat. Technol.* **30** (1987) 415.
15. M. Yasuda, I. Ohno and S. Haruyama, *J. Surf. Finish. Soc. Jpn.* **41** (1990) 312.
16. T. Watanabe, *J. Surf. Finish. Soc. Jpn.* **41** (1990) 652.
17. T. Seiyama, *Denki Kagaku* **38** (1970) 707.
18. S. Ito, Doctorial thesis, Kyushu University (1976), p. 64.
19. M. Yoshitake, K. Yamakawa and S. Yoshizawa, Proc. of 10th World Congress on Metal Finishing, Japan (1980), p. 38.