

Electrodeposition of Granular Cu-Co Alloys

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Electrodeposition characteristics of Cu-Co films were studied for the formation of heterogeneous alloys for giant magnetoresistance applications. *In situ* scanning tunneling microscopy, Auger electron spectroscopy (AES), and high resolution scanning electron microscopy studies showed that rough films with a low concentration of cobalt [Cu92.5-Co7.5] (atom %) were deposited mainly due to a higher deposition rate of copper than of cobalt toward the end of the deposition process, and due to the formation of copper grains after the electrodeposition process by chemical exchange between copper ions in the solution and with the cobalt in the deposit. AES analysis revealed that the Cu-Co film is not homogeneous; the bulk of the film is richer in Co while the surface and the bottom of the film are Co-poor. X-ray diffraction showed that the electrodeposition is a topotaxial crystallization process and that the as-deposited film is composed of two phases, a solid solution of face centered cubic Cu-Co with preferred orientation of {111} planes, and a hexagonal close packed Co phase. Scanning electron microscopy micrographs and energy dispersive spectroscopy indicated the segregation of cobalt grains resulting from thermal treatments, according to the phase diagram of Cu-Co.

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One of the most exciting and startling properties exhibited by some magnetic multilayer systems is the giant magnetoresistance (GMR) effect. GMR refers to a significant change in the electrical resistance of a film or a device when an external magnetic field is applied. The GMR effect which was first discovered in magnetic multilayers¹ also exists in heterogeneous alloys with ferromagnetic granules (*i.e.*, Fe or Co) embedded in a nonmagnetic metal (*i.e.*, Cu or Ag).²

Heterogeneous alloy films are a potentially useful alternative for GMR applications, especially for magnetic sensor applications, where the sensitivity is less important than the magnitude of the response.² It is generally simpler to prepare a heterogeneous alloy film rather than a multilayer system. The heterogeneous alloy films are immiscible combinations usually prepared by physical deposition methods.^{3,4}

An alternative processing technique is electrodeposition.⁵⁻¹³ Electrodeposition has several advantages over dry processes. There are a large number of possible alloy combinations. Electrodeposition does not require vacuum technology and consequently is less expensive. It can easily be scaled up for use in large size areas, and it is capable of depositing uniform films on complex surfaces without shadowing effects often encountered in other deposition methods. The experimental systems used are much simpler than evaporation or sputtering apparatus, and electrodeposition can be a room-temperature technology. There are some drawbacks associated with the process such as the need for a conducting/semiconducting substrate, the limited number of elements that can be deposited, and the large number of variables that control this process (composition, pH, concentration, current density, temperature, agitation, etc.).

Electrodeposited binary alloys may or may not have the crystallographic structure expected from the equilibrium phase diagram formed by other methods.¹⁴ Gelchinski *et al.*¹⁵ electroplated at room temperature cobalt alloys containing the A-15 structure phase that is stable only at high temperature, according to the equilibrium phase diagram. Usually it is assumed¹⁴ that when metals are codeposited at low polarization values, the formation of solid solutions or supersaturated solid solution results. This was found to be so even when the metals are not mutually soluble in the solid state according to the bulk phase diagram. Codeposition at high polarization values was reported¹⁴ to result in two-phase alloys even for systems capable of forming continuous series of solid solutions. Thus, the formation of supersaturated two-phase Co-Cu is possible depending on the deposition conditions.

In this paper, the electrodeposition and properties of a Cu-Co alloy are described. This alloy should be a metastable phase because the Cu-Co system is immiscible under equilibrium conditions at room temperature.

Experimental

Electrodeposition.—The electrodeposition experiments were conducted on 2 cm² substrates cleaved from Si wafers, which had been previously coated by physical vapor deposition (PVD) with a copper layer (75 nm) on top of a TaN layer (30 nm). Some of the polarization measurements were performed on a platinum (Pt) sheet of 4.8 cm², in order to eliminate the reduction of an air-formed copper oxide. The substrates were pretreated before the deposition of the alloy coating by degreasing in subsequent baths of methanol and acetone, rinsed in distilled water, dipped into a concentrated H₂SO₄ solution in order to remove the surface oxide, and finally rinsed in distilled water.

The electrochemical apparatus used for the alloy deposition was EG&G (PARC) model 273 potentiostat-galvanostat. The deposition was done in a Pyrex glass cell with a standard three-electrode configuration with a platinum wire as a counter electrode and a saturated calomel reference electrode (SCE), which was positioned close to the working electrode. The following blank solution was used: 0.2 M H₃BO₃ and 0.13 M citric acid (C₆H₈O₇). Copper and cobalt ions were added to the blank solution as CuSO₄ and CoSO₄. The adjustment of pH was done by additions KOH or H₂SO₄. The deposition bath composition and the electrochemical parameters were determined by the experiments, described in the next section.

Anodic polarization measurements were conducted on a Pt substrate at room temperature ($\sim 25^{\circ}$ C) at a scan rate of 0.5 mV/s. The bath composition used for the anodic polarization consisted of 100 g/L K₂SO₄ and 20 g/L H₃BO₃. The pH of the solution was 4. The alloy coatings were deposited at room temperature. Following deposition the specimens were annealed at 450°C for 0.5, 1.5, 10, and 20 h in Ar with 7% H₂ atmosphere.

Characterization methods.—The microstructural characteristics of the granular Cu-Co films were investigated by *in situ* scanning tunneling microscopy (STM), a scanning Auger microprobe (Auger electron spectroscopy, AES), high resolution scanning electron microscopy (HRSEM), and X-ray diffraction (XRD).

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In situ STM experiments were conducted using a PicoSPM from Molecular Imaging. The tunneling tip was a platinum-iridium (9:1) wire (250 μ m thick) coated with polyethylene and etched electrochemically using a self-constructed control unit, which uses ac current.¹⁶ The etched tip radius was between 1 and 2 μ m. The tunneling scanning current was set to 0.3 nA. The experiments were performed in the same solution used for Cu-Co alloy deposition. The potentials of the specimens and the tip were controlled potentiostatically against a copper electrode as a reference electrode. The potential of the copper reference electrode in the solution was found to be 0 mV vs. SCE and remained constant throughout the experiment.

A scanning Auger microprobe (Physical Electronics PHI 590A) system was used to measure the surface composition and the depth profile of Cu and Co atoms in the Cu-Co film. The incident electron beam energy was 5 keV, the current was 2 μ A, and the scanned area of the beam was 40 × 40 μ m. Auger transitions of the elements used were C-KLL, 272; N-KLL, 390; O-KLL, 503; Cu-LMM, 918; Co-LMM-775; Si-KLL, 1619; and Ta-MNN, 1675 eV. Ar⁺ ions accelerated at 4 kV were used to sputter an area of ~2 × 2 mm. The incident angles of the Ar⁺ bombardment and that of the electron beam relative to the samples were ~60 and 30°, respectively. The approximate sputter rate was 20-100 nm/min, as estimated by a Ta₂O₅ standard. Depth profiles were obtained by measuring the peak-to-peak heights in the first derivative mode of the corresponding Auger transitions.

The composition ratio of the Cu-Co alloy was determined by energy dispersive spectroscopy (EDS), using a Pentafet EDS detector and Oxford Link ISIS Software attached to a Philips XL30 scanning electron microscope (SEM), operated at 20 kV at a working distance of 10.5 mm (penetration radius of $\sim 1 \ \mu m$ for Cu K α at 20 kV). The EDS results were obtained after calibration with a cobalt standard. HRSEM was conducted using a Leo 982 Gemini equipped with a Schottky electron source. Micrographs of Cu-Co films before and after thermal treatments were recorded at an accelerating voltage of 4 kV and a working distance of 2 mm.

The XRD system used in this study (Philips PW-3020 goniometer) included a long fine-focus copper X-ray tube ($\lambda = 0.15406$ nm), operated routinely at 40 kV and 40 mA with 1° divergent and antiscattering slits coupled with 0.2 mm receiving slits. A curved graphite monochromator ($2\alpha = 26.4^{\circ}$) preceded the detector. Diffraction patterns were acquired at steps of 0.01° 20 and 25 s/step exposure.

Results

Polarization measurements.--Preliminary experiments were conducted to find a suitable electrolyte for the deposition of Cu and Co.¹⁷ Generally, since copper is the more noble metal in the system, the concentration ratio of Co^{2+} to Cu^{2+} ions in the electrolyte has to be much higher than the ratio required in the alloy system. The standard electrode potential¹⁸ of Cu is +0.337 V (vs. standard hydrogen electrode, SHE) and that of Co is -0.277 V (SHE), which means that their deposition potentials are far apart for noncomplexed ions, making the codeposition difficult from a simple sulfate solution of Cu and Co ions. In order to bring these deposition potentials closer, a complex forming agent of citric acid is added to the Cu-Co solution.¹⁷ The solution also contains boric acid, which acts as a pH buffer agent. The concentrations of Co²⁺ and Cu²⁺ varied from 0.08 M Co²⁺ and 0.1 M Cu²⁺ in which no cobalt was detected in the film, to 0.3 M Co²⁺ and 0.15 M Cu²⁺ in which a high content of cobalt was obtained in the deposit (>42 atom %). In order to understand the influence of each component of the solution, polarization measurements were performed on a Pt substrate at a scan rate of 5 mV/s in acidic (pH 2) and neutral (pH 7) blank solutions which did not contain Co and Cu ion additions. The polarization was then repeated after the addition of each of the ions, and a combination of both. These measurements are shown in Fig. 1 at two values of pH.

р**Н=2** Current Density (mA/cm²) -0.5 -1.0 -1.5 Without Cu and Co ions +5mM Cu^{⁺†} -2.0 +0.25M Co** +0.25M Co⁺⁺ +5mM Cu -2.5 -0.5 -1.0 0.0 0.5 Potential V_{sce} b 0.0 pH=7 Current Density (mA/cm²) -0.5 -1.0 -1.5 Without Cu and Co ions - +5mM Cu^{**} -2.0 +0.25M Co** +0.25M Co⁺⁺ +5mM Cu⁺⁺ -2.5 -1.0 -0.5 0.0 0.5 Potential V_{SCF}

Figure 1. Cathodic potentiodynamic curves in the blank plating electrolyte with and without additions of 5 mM $CuSO_4$ and/or 0.25 M $CoSO_4$. Scan rate was 5 mV/s. (a) pH 2 and (b) pH 7. The substrate used was a Pt sheet. The curves are presented in a linear scale in order to elucidate the influence of the different components in the solution.

It can be seen in Fig. 1 that at the lower pH the evolution of hydrogen begins at a less negative potential than at the higher pH (Fig. 1b), as would be expected. Since copper has a high overvoltage for hydrogen evolution, a significant H₂ evolution starts only at *ca.* -0.8 V (SCE) for solutions that deposit Cu ions, and at *ca.* -0.5 V (SCE) for the other solutions at pH 2. A similar effect is noticed at pH 7 where a significant H₂ evolution starts at around -0.7 V (SCE) for the blank solution while the addition of copper ions inhibits hydrogen evolution to *ca.* -0.9 V (SCE).

When 5 mM CuSO₄ was added to the blank solution at pH 2 (Fig. 1a), the deposition of copper started at about the equilibrium value of $\sim 0 \text{ V}$ (SCE), with a diffusion-limited process of copper

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Figure 2. Potentiodynamic curves of a neutral blank electrolyte (pH 7) containing 0.125 M CuSO_4 and 0.25 M CoSO_4 . Scan rate was 5 mV/s. The substrate used was a PVD Cu platelet.

deposition at *ca.* -0.1 V (SCE) and the current started rising again with hydrogen evolution at *ca.* -0.7 V (SCE). At pH 7, the deposition of copper began at a lower potential, -0.2 V (SCE), and the current density reached a limiting value, as a result of the low concentration of copper ions in the electrolyte. Subsequently, hydrogen evolution starts as indicated by a rise in the current above -0.9 V (SCE) (Fig. 1b). From the polarization curves, it is obvious that (*i*) the copper reduction potential changes to more negative values by raising the pH, and (*ii*) the process is diffusion limited due to the low concentration of copper ions in the solution.

When 0.25 M CoSO₄ was added to the blank solution, at pH 2 the current remained very low until it rose sharply at *ca.* -0.5 V (SCE), which is close to the reduction potential of cobalt. In a solution that contained both Co and Cu ions at pH 2, the characteristics of the polarization curve were similar to those with only Cu additions, except that the current densities were somewhat lower. Blockage of the current was observed again at pH 2 after the initiation of copper deposition (*ca.* -0.2 V SCE) until a final current rise that began at -0.8 V (SCE). The final current at the high cathodic polarization would be compatible with both hydrogen evolution and cobalt deposition.

The solution chosen for Cu-Co electrodeposition was 0.25 M $CoSO_4$, 0.125 M $CuSO_4$, 0.2 M H_3BO_3 , and 0.13 M citric acid $(C_6H_8O_7)$.

While the polarization curve indicated that a high pH is favorable, the film quality was also examined as a function of the solution pH. The pH of the solution was varied between 2 and 6.5. In an acid solution (pH 2) a dark, spongy, and powdery film was obtained. As the pH was raised, a sound film was formed, which was reddish in color and more reflective. At a pH of 6.5, an optimum film was obtained. Consequently, the pH of the solution was set between 6 and 6.5.

From the polarization curve on a copper substrate in the solution that was chosen for the alloy deposition (Fig. 2), it seems that copper deposition starts at *ca.* -0.1 V (SCE) and cobalt deposition starts at *ca.* -0.4 V (SCE). These values correspond to a scan rate of 5 mV/s. The difference between the deposition potentials is small, meaning that the electrodeposition of a Cu-Co alloy is possible from



Figure 3. Anodic potentiodynamic curves at pH 6.5 of Co deposited at -1.05 V (SCE), Cu deposited at -0.5 V (SCE), and $\sim 1~\mu m$ Cu-Co alloy Cu-Co deposited at -1.2 V (SCE). Scan rate was 0.5 mV/s. The substrate used was a Pt sheet.

this solution. At the potential range of copper reduction there is a deflection in the slope of the current density *vs.* the cathodic potential. This deflection is attributed to side reactions, such as the reduction of an air-formed copper oxide, a transition of copper divalent to copper monovalent, or reduction of dissolved oxygen in the solution.

Anodic polarization curves were performed on $\sim 800 \text{ nm}$ Co, \sim 100 nm Cu, and \sim 1 μ m Cu-Co films, which were electrodeposited on a Pt substrate from a solution that contained 0.2 M H₂BO₃, 0.13 M citric acid ($C_6H_8O_7$), and the ions of either copper or cobalt at pH 6.5 (Fig. 3). Cobalt dissolution started at ca. -0.5 V (SCE) and copper dissolution at ~ 0 V (SCE). When the anodic polarization measurements of the Cu-Co film were performed at a scan rate higher than 1 mV/s, only one broad dissolution transition was observed. However, three dissolution transitions were observed at a scan rate of 0.5 mV/s. The first two transitions represent cobalt dissolution, and the third transition is attributed to copper dissolution. Gómez et al.¹³ have also examined the stripping behavior of Cu-Co alloys. Only one dissolution transition was observed which was attributed to the dissolution of a Cu-Co solid solution. The stripping analysis of Gómez et al. was performed at a higher scan rate than in our experiments, 10 mV/s vs. 0.5 mV/s. The appearance of only one transition does not necessarily mean the formation of a Cu-Co solid solution, and may be the result of convolution of two transitions.

From the anodic polarization curves one can conclude that both Co and Cu are deposited. The alloy concentration was estimated according to the integrated Cu and Co dissolution areas. The alloy concentration was 89.5% atom % Cu and 10.5% atom % Co. The cathodic current efficiency of the Cu-Co alloy deposition process was calculated by comparing the deposit weight and the calculated charge according to the Faraday law. The cathodic current efficiency was 89%.

STM.—The PVD copper on wafer substrate was first scanned in the deposition solution without polarization under an open circuit potential (OCP) of 0 V (SCE), then *in situ* electrodeposition of only copper at -0.5 V (SCE) was performed (Fig. 4). The copper layer



Figure 4. 3-D in situ STM image of a Cu layer deposited in a 0.25 M $CoSO_4$ and 0.125 M $CuSO_4$ electrolyte at -0.5 V (SCE), scanned at $5 \times 5 \mu m$. The copper layer exhibited a polycrystalline morphology, and coalescence of copper grains in clusters of 200-750 nm.

exhibited polycrystalline morphology. At the beginning of the deposition process, a fine microstructure was formed, but with increasing deposition time a rough film was formed by coalescence of copper grains in clusters of less than 100 nm and 200-750 nm (Fig. 4). When the potential was shifted to -0.92 V (SCE) (Fig. 5), in which both copper and cobalt are deposited with a higher content of copper in the film, a finer microstructure was formed, although there were still clusters of small grains of more than 1 μ m in size. This is probably due to the rough underlayer of copper. Only when the potential was shifted to -1.05 V (SCE) (Fig. 6a) did the large copper clusters disappear and the film was found to contain small grains, less than 50 nm in size. As expected, a finer microstructure was obtained by lowering the deposition potential. In addition, it seems that faceting occurred in the films, which were deposited at -0.92 and -1.05 V (SCE).



Figure 5. 3-D *in situ* STM images of a Cu-Co alloy layer deposited from a 0.25 M CoSO₄ and 0.125 M CuSO₄ electrolyte at -0.92 V (SCE), scanned at 5 × 5 μ m. A finer microstructure of Cu-Co alloy was formed with clusters of small grains of more than 1 μ m in size. Appearance of faceting occurred in the film when cobalt is incorporated in the Cu-Co alloy.



Figure 6. In situ STM images of a Cu-Co alloy layer deposited from a 0.25 M CoSO₄ and 0.125 M CuSO₄ electrolyte at -1.05 V (SCE). Threedimensional scans at (a) $5 \times 5 \mu$ m and (b) $1 \times 1 \mu$ m. A finer microstructure was obtained by lowering the deposition potential; the film contains small grains, less than 50 nm in size. Faceting still exists in the Cu-Co film.

EDS.—The composition ratio in the Cu-Co film was checked at several potentials from -0.8 to -1.2 V (SCE), and a $\sim 1 \ \mu m$ [Cu92.5-Co7.5] (atom %) film was obtained at -1.2 V (SCE). The concentration ratio of cobalt decreased with increasing film thickness, low cobalt content (7.5 atom %) was obtained in thicker films above $\sim 0.5 \ \mu m$ compared to $\sim 20 \ atom \%$ at thin films below $\sim 300 \ nm$. Films of [Cu92.5-Co7.5] (atom %) with a thickness of $\sim 1 \ \mu m$ were prepared according to the experimental description.

AES.—Auger surface composition profile analysis was performed on the as-formed Cu-Co film. Almost no cobalt was detected at the surface of the Cu-Co film. AES depth profiling was conducted to study the concentration gradients of the elements in the as-formed film. Carbon and oxygen signals rapidly decreased to a low and constant value after a few seconds of sputtering. The oxygen signal was below the quantificial limit of our AES system (~0.5%), and one cannot rule out the incorporation of cobalt hydroxide in the Cu-Co films from the AES measurements. The Auger peaks were computer differentiated and the peak-to- peak height values for Cu and Co are presented in Fig. 7. The AES data are used to show a trend rather than the precise concentration of Cu and Co since no suitable calibration was performed for the normalization of the Co peak-to-peak.



Figure 7. AES depth profile of Cu-Co film as formed. Co and Cu present opposite trends, the relative cobalt concentration was negligible at the surface and went through a peak concentration before gradually decreasing close to the copper substrate, whereas the deposition rate of copper decreased slightly during the middle stage of the electrodeposition process.

The concentration profile of Cu and Co was not uniform along the film depth. Co and Cu presented opposite trends, where the relative cobalt concentration was negligible at the surface and went through a peak concentration before gradually decreasing close to the copper substrate, whereas the deposition rate of copper decreased slightly during the middle stage of the electrodeposition process.

HRSEM.—HRSEM micrographs of Cu-Co films before and after thermal treatments are presented in Fig. 8-10. The film was rather dense at thicknesses up to \sim 300 nm. As the deposition time increased (meaning a thicker deposit), the roughness of the surface increased. Spherical particles of 0.5-1 µm in diam were found on the surface (Fig. 8). The content ratio of copper/cobalt in the film



Figure 9. HRSEM micrographs (secondary electrons) of 1500 nm electrodeposited Cu-Co alloy (top view) recorded at 4.0 kV annealed at 450°C for 90 min.

and in the particles was the same. Some of the thick specimens (>1 μ m) were cracked and spalled off after a thermal treatment, probably due to the evolution of hydrogen from the film since the electrodeposition of the Cu-Co films are accompanied by the reduction of hydrogen, which was partially trapped in the deposit.

After thermal treatments the number of the particles on top of the surfaced increased compared to the as-deposited state. The size of these particles was 2-5 μm (Fig. 9 and 10). The cobalt content in these particles was reduced (<0.5 atom %) compared to its content in the deposit (8-10 atom %). In addition, as a consequence of the annealing procedures, holes were formed (Fig. 9 and 10) indicating diffusion of cobalt away from the Cu-Co alloy, according to the EDS results.

XRD.—XRD analysis was conducted on samples before and after thermal treatment (Fig. 11 and 12). No clear evolution of a cobalt phase after thermal treatment was detected. The XRD spectrum of the 75 nm PVD copper substrate is an fcc structure with a preferred orientation of {111} planes (inset in Fig. 11). Another weak reflection at $2\theta = 41.6^{\circ}$ appeared. This reflection corresponds to an hcp cobalt phase of $(10\overline{1}0)$ planes.



Figure 8. HRSEM micrographs (secondary electrons) of 1350 nm electrodeposited Cu-Co alloy (top view) recorded at 4.0 kV. The roughness of the film increased with its thickness, and spherical particles of 0.5-1.0 μ m in diam were found on the surface.



Figure 10. HRSEM micrograph (secondary electrons) of 1500 nm electrodeposited Cu-Co alloy (top view) recorded at 4.0 kV annealed at 450°C for 10 h. Holes were formed, indicating diffusion of cobalt away from the Cu-Co alloy according to the EDS results.



Figure 11. XRD of the Cu-Co films before and after thermal treatment. Inset: XRD of a Si substrate which was deposited by 75 nm PVD copper on top of 30 nm TaN. The Cu-Co film as deposited is composed of two phases, an hcp Co phase and a solid solution of fcc rich copper Cu-Co phase with a preferred orientation of {111} planes, similar to the copper substrate.

From XRD of the Cu-Co alloy after different sequences of thermal treatments there is no indication of cobalt precipitation or evolution of a new cobalt phase (Fig. 11-12). Only one peak is observed at $2\theta = 43.7^{\circ}$, which correlates mainly to (111) face centered cubic (fcc) copper. However, there is a slight shift toward high angles for the (111) reflections with increasing annealing time (Fig. 12) and consequently a slight decrease in the d-spacing.



Figure 12. XRD of Cu-Co films before and after sequences of thermal treatments. There is no indication of evolution of a new cobalt phase, only a slight shift toward high angles for the (111) reflections with increasing annealing time.

Discussion

The results presented in this paper indicate that a high pH is favorable for the electrodeposition of Cu-Co alloys. In a solution that contained both Co and Cu ions at pH 2, the limited cathodic process between -0.1 and -0.8 V (SCE) (Fig. 1a) may indicate that the cobalt content in the alloy will be limited. At high overpotentials, more negative than -0.8 V (SCE), both cobalt and copper may be deposited together with hydrogen evolution, but the likelihood of the formation of Cu-Co solid solution will decrease due to high polarization values.¹⁴ However, at a higher pH, no blockage of the current densities occurred (Fig. 1b, 2) and the formation of a Cu-Co solid solution is possible with a higher content of cobalt in the deposit.

The anodic polarization curve indicates that both Cu and Co are deposited, although three dissolution transitions are observed. The first and third transitions are related to cobalt dissolution at ca. -0.5 V (SCE) and copper dissolution at *ca*. -0 V (SCE), respectively. The second dissolution transition may be related to dealloying of cobalt from a metastable state of Cu-Co phase which according to the XRD results exists in the Cu-Co films, or due to the formation of an overlayer of copper as found by AES studies. Shima et al.¹⁹ have studied the anodic dissolution of an ultrathin cobalt film buried beneath a copper overlayer. It was found that the cobalt underlayer can dissolve even though it is covered by a thin copper layer, and that the blocking nature of Cu overlayer was reflected in the displacement of the cobalt stripping potential to a more positive potential. The dissolution of an artificial Co/Cu structure is described by two stages: breakdown of the copper overlayer and subsequent dissolution of the buried cobalt layer. From the anodic polarization curve, it seems that in either of the two possibilities, the stripping potential of cobalt should move to more positive values. The two dissolution transitions of cobalt may indicate a nonhomogeneous Cu-Co alloy as was observed in the AES and XRD results.

According to the AES results, the bulk part of the film is richer in Co while the surface and bottom of the film are Co-poor. It was reported^{20,21} that in a vacuum environment copper segregates to the surface of Cu/Co films, in order to reduce the free surface energy. Thus, it might be that some degree of stability is established when the present films are covered by copper.

The diffusion coefficient of Co^{22} and Cu^{23} ions in aqueous solutions are 5.8×10^{-6} and 3×10^{-6} cm²/s, respectively. The higher rate of copper deposition at the first stage of the film growth may be due to the higher polarization of copper compared to cobalt, because copper is much nobler than cobalt. A possible reason for the appearance of a peak in the rate of cobalt deposition and a small decay in the copper deposition rate may be that after the electrodeposition process is started, copper deposition process becomes more diffusion limited than that of cobalt due to the higher concentration of cobalt ions in the electrolyte and a higher diffusion coefficient.

Another possible reason for the opposite trends in the deposition rate of each element is that at the beginning copper grains are formed on a copper substrate, while as the deposition process progresses the substrate changes from pure copper to the Cu-Co mixture, either as a metastable solid solution and/or as nanoclusters of cobalt inside a matrix of copper. This can lead to different growth modes. Bulk Co and Cu are considered immiscible below ~900 K.²⁴ According to Coyle *et al.*,²⁴ the Cu-Co bond energy is probably greater than 0.190 eV for the nearest neighbors and it is 0.271 and 0.190 eV for Co-Co and Cu-Cu, respectively. The deposition rate of cobalt on cobalt will be faster than cobalt on Cu and vice versa for the deposition rate of copper. The different modes of cobalt and copper deposition will be the focus of a future study. This may be also the reason for the appearance of faceting that was observed by STM. Faceting appeared in films that were deposited at -0.92 and -1.05 V (SCE) only after cobalt was incorporated into the deposit (Fig. 5, 6b). A recent in situ STM study of Cu growth on Ni(001) reports a novel model for internal faceting as a consequence of strain relief at the interface, where the lattice misfit in the Cu and Ni is 2.6%.²⁵ Such a strain relief mechanism, in principle, can occur in the Cu-Co system as well. In the fcc Cu-Co system, the lattice misfit is less than 2%.²⁶ The growth of the Cu-Co alloy may be accompanied by strain relief, resulting in the formation of faceting.

It seems from HRSEM results that the existence of a copper overlayer increases the roughness of the Cu-Co films. There may be a number of reasons for the formation of a rough film in the relatively thick layer (larger than 1 µm). As the deposition time increases, the content of Co²⁺ and Cu²⁺ ions near the cathode surface is diminished, and the overpotential reduces, there are fewer nucleation events and more grain growth with hydrogen voids in the films. Since the concentration of both metal ions is high and since copper is nobler than cobalt, its deposition rate does not change considerably, while that of cobalt reduces with increasing time. As seen in the AES studies the deposition rate of copper is higher than that of cobalt toward the end of the deposition process, and an overlayer of copper is formed on top of the alloy. This also may be the reason for the low cobalt content (7.5 atom %) in thicker films above $\sim 0.5 \,\mu m$ compared to 20 atom % at thin films (less than \sim 300 nm). In addition, according to the polarization curve of the solution containing only Co²⁺ (Fig. 1), the cobalt deposition rate remains constant until hydrogen evolution begins. Nakahara and Mahajan²⁷ claim that during cobalt deposition with hydrogen evolution, cobalt hydride or hydroxide are formed in the films. This may be the reason for a decrease in the cobalt deposition rate. Nakahara and Mahajan have examined the content of O2 and H2 in electrodeposited cobalt by using a vacuum fusion technique and mass spectrometry. They found 230 ppm H₂ and 890 ppm O₂ in the films deposited at a high pH (~5.7). According to Nakahara and Mahajan, the solubility of H₂ in cobalt is 0.041 ppm at room temperature (20°C) and its diffusivity is 1.71×10^{-11} cm²/s for fcc cobalt. Hydrogen has a high diffusivity in cobalt at room temperature and it could escape from the film very rapidly. Another option for the decrease in the deposition rate of cobalt is that when cobalt hydride/ hydroxide forms, some of the reduction current may be consumed by the reduction of these species, and hence the deposition rate of cobalt is reduced. These may be the reasons why phases of cobalt precipitates were not detected in the XRD reflections.

In addition, the OCP becomes more anodic with deposition time. This behavior is similar to the results of Bradley et al.⁹ At thickness up to \sim 300 nm the OCP remains constant *ca*. -0 mV (SCE) while at a thickness higher than 500 nm, the OCP decreases to ca. -500 mV (SCE). At least 1 min is required for the OCP to reach -100 mV (SCE). According to the polarization curve (Fig. 2) this OCP is enough for copper deposition but not for cobalt deposition. This means that at the end of the electrodeposition process copper grains may form by chemical exchange of Cu ions with the more active Co atoms in the alloy. Since the OCP is close to the equilibrium potential of copper, coarse grains of copper are deposited, as seen in the STM measurements. This also may be the reason for the particles on the surface (Fig. 7). The reason for detecting cobalt in these particles probably stems from the large penetration depth in EDS (penetration radius of $\sim 1 \ \mu m$ for Cu K α at 20 kV), due to columnar growth of copper which causes an incomplete coverage of the alloy surface⁹ and since the volume fraction of the copper grains is small compared to that in the alloy.

The deposition was conducted under a high polarization potential of -1.2 V (SCE) (current density of $\sim 8 \text{ mA/cm}^2$). Several authors^{28,29} have reported that hcp cobalt is formed by electrodeposition from solution at pH > 2.9. Thus it was expected that a two-phase structure would be formed,^{14,29} *i.e.*, hexagonal close packed (hcp) cobalt and fcc copper. However, the XRD results indicate the formation of a supersaturated solution of Cu-Co solid solution and an hcp cobalt phase. The Cu-Co alloy, which is supposed to be a metastable phase at room temperature, is a copper rich Cu-Co fcc phase with a preferred orientation of {111} planes, similar to the copper substrate (Fig. 11). This indicates a topotaxial crystallization

process. The fcc structure remains even in thick films $(1 \ \mu m)$, in which the role of the substrate (75 nm physical vapor deposited PVD copper) is negligible. The main reason for the formation of an alloy with an fcc structure is probably the high copper content in the film. A shift in the *d*-spacing of {111} copper planes from 2.088 to 2.07 Å was detected in the as-deposited films. Since the atomic volume of Co atom is smaller than that of Cu, the shift may indicate the substitution of Cu by Co atoms and the formation of a metastable phase. It may also indicate the merging of two reflections; (111) fcc Cu with (111) fcc Co.

Peter et al.³⁰ reported that the structure of a dc-plated Co rich Co-Cu alloy consisted of both hcp and fcc Co-Cu crystallites and it contained more fcc components at the solution side than at the substrate side (titanium sheet). The fraction of the fcc crystallites increased gradually during deposition from about 50 to 67%. Since both titanium and cobalt have hcp structures, the expected structure of the Co-rich alloy is hcp. According to Peter et al., 30 a possible reason for obtaining an fcc structure is the incorporation of a small amount of Cu into the deposit. In a Cu-rich film, the reverse situation may occur, where incorporation of small amount of Co into the deposit may form an hcp structure. If the $(10\overline{1}0)$ reflection was correlated to a Cu-Co alloy, the *d*-spacing would decrease. However, the *d*-spacing of the $(10\overline{1}0)$ reflection is slightly higher than the d-spacing in a pure cobalt film. Therefore one can deduce that the $(10\overline{1}0)$ reflection corresponds to a pure cobalt phase and the change in the *d*-spacing is related to a strained Co phase.

It is thus concluded that the as deposited Cu-Co film is composed of two phases, a solid solution of fcc Cu-Co phase and an hcp Co phase. The mechanism by which the Co hcp phase forms and grows is not yet known.

The formation of two phases, pure hcp phase and a rich Cu phase can result in a GMR effect in the as-deposited film without heattreatment. The magnetic properties of the Cu-Co film will be reported in a following paper.

The HRSEM and EDS results of the Cu-Co films indicate the precipitation of cobalt grains during the thermal treatments. However, from XRD of the Cu-Co alloy after different sequences of thermal treatments there is no indication of cobalt precipitation or evolution of a new cobalt phase (Fig. 11 and 12). The reflections from fcc {111} planes of copper and cobalt are at $2\theta = 43.297^{\circ}$ and $2\theta = 44.216^{\circ}$, respectively. The difference is almost 1°, which should be large enough to distinguish between the two peaks. Only one peak is observed at $2\theta = 43.7^{\circ}$, which correlates mainly to (111) fcc copper. However, there is a slight shift toward high angles for the (111) reflections with increasing annealing time (Fig. 12) and consequently a slight decrease in the *d*-spacing. The shift may indicate the progressive decomposition of Co atoms from the Cu rich matrix. The absence of an fcc cobalt reflection is probably related to the relatively low content of cobalt (7.5 atom %) and to the small grain size of cobalt (nanoscale). The annealing temperature of the Co-Cu deposit (450°C) is higher than the hcp-fcc transition temperature (422°C). Thus it is expected that the Co particles precipitate in the fcc form at 450°C and that the hcp Co phase, which was formed during the deposition process, transformed to the fcc phase. There is also a minor possibility that the fcc Co phase transformed to hcp Co while cooling down to room temperature after annealing, although the cooling process was quite rapid (15-20 min). The mechanism that inhibits the phase transformation in the Cu-Co film is not yet clear.

Conclusions

Electrodeposition from a neutral solution with a high concentration of Co and Cu ions results in a topotaxial crystallization process and a deposit [Cu92.5-Co7.5] (atom %) of two phases; a solid solution of fcc Cu-Co with preferred orientation of {111} planes and an hcp Co phase. Electrochemical analysis and AES showed that cobalt deposition is limited toward the film surface, possibly due to a higher deposition rate of copper than cobalt toward the end of the deposition process and by the formation of copper grains after the electrodeposition process by chemical exchange between the copper ions in the solution and with the cobalt in the Cu-Co film. This is the main reason for the lower cobalt content in the film, and for the rough Cu-Co films revealed by *in situ* STM and HRSEM studies.

In situ STM studies revealed that when cobalt is incorporated into the deposit, faceting develops which is believed to be due to strain relief in the growth of the metastable Cu-Co alloy. AES depth profiling analysis revealed that the Cu-Co film is not homogeneous; the bulk of the film is richer in Co while the surface and the bottom of the film are Co-poor.

SEM micrographs and EDS results indicate the precipitation of cobalt grains resulting from thermal treatments, according to the phase diagram of Cu-Co. From XRD studies there is no definite indication of evolution of an fcc cobalt phase after thermal treatments, probably due to the low content of Co (atom % 7.5) and due to its small grain size.

Both of the phases (hcp and fcc) remain stable after annealing above the hcp-fcc transition temperature.

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