Surfactant-mediated growth of giant magnetoresistance multilayers

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A series of experiments have been conducted to evaluate the magnetotransport properties of rf-diode-sputter-deposited giant magnetoresistive multilayers with either copper or copper-silver-gold nonferromagnetic (NFM) conducting layers. The study revealed that rf-diode-deposited multilayers utilizing Cu$_{80}$Ag$_{15}$Au$_5$ as the NFM conducting layer possess significantly superior giant magnetoresistance to otherwise identical device architectures that used pure copper as the NFM conducting layer. To explore the origin of this effect, copper and Cu$_{80}$Ag$_{15}$Au$_5$ films of varying thickness have been grown under identical deposition conditions and their surface morphology and roughness have been investigated. Atomic-force microscopy revealed significant roughness and the presence of many pinholes in thin pure-copper films. The surface roughness of the Cu$_{80}$Ag$_{15}$Au$_5$ layers was found to be much less than that of pure copper, and the alloying eliminated the formation of pinholes. Using an embedded-atom-method alloy potential, molecular-dynamics simulations have been used to investigate the role of silver and gold upon the multilayer growth process. The smoother growth surface of Cu$_{80}$Ag$_{15}$Au$_5$ was found to predominantly result from the addition of silver, which acts as a surfactant during growth. Molecular statistics estimates of atom migration energy barriers indicated that both silver and gold have significantly higher mobilities than copper atoms on a flat copper surface. However, gold was found to be incorporated in the lattice whereas silver tended to segregate (and concentrate) upon the free surface, enhancing its potency as a surfactant. The atomic-scale mechanism responsible for silver’s surface-flattening effect has been explored. We found that silver, when present at a ledge edge, reduces the Ehrlich-Schwoebel barrier for copper, promoting a step-flow growth mode. Gold was also found to reduce the Ehrlich-Schwoebel barrier, but its potency was less than that of silver due to its lower surface concentration. These observations suggest that small alloy additions can be used to manipulate the energy barriers that fundamentally control atomic assembly during vapor deposition, and provide a potentially powerful means of controlling the structure of thin films.

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I. INTRODUCTION

Metal multilayers consisting of alternating ferromagnetic (FM) and nonferromagnetic (NFM) metals sometimes exhibit large changes in their electrical resistance when a magnetic field is applied. The effect results from a change in their spin-dependent electron scattering when an applied magnetic field rotates the magnetic moment of one of the ferromagnetic layers. The giant magnetoresistance (GMR) effect has quickly become technologically important. Devices based on it are widely used as magnetic-field sensors in hard-disk-drive read heads. Related devices are being investigated for use as magnetic random-access memories (MRAM). These applications require multilayers with high GMR ratios (defined as the maximum resistance change divided by the resistance at magnetic saturation) and low magnetic-saturation fields. Both the resistance change and saturation field are sensitive to the materials used for each layer, the thickness of the layers, and the conditions used for their growth via their effect upon atomic-scale morphology and structure.

Current GMR multilayers appear not to have achieved their performance upper bound. Reducing both the roughness and chemical diffuseness of the interfaces in GMR multilayers appears to be particularly important. Even moderate interfacial roughness can result in Neel coupling and undesired electron scattering, which are both deleterious to the magnetoresistance. Extreme interfacial roughness in the NFM layer can even lead to pinholes in NFM layers. When a FM metal layer is then overdeposited, the pinhole enables a connection between the two FM layers and the formation of a strong ferromagnetic coupling. An applied magnetic field then causes no differential rotation of magnetic moments and the GMR effect is lost. Synthesizing materials with a large GMR ratio at a low saturation field therefore requires the use of materials, layer thickness, and deposition conditions that minimize interfacial roughness.

Many vapor-deposition approaches are being explored for controlling the interface morphology, including adatom-energy variations and low-voltage ion assistance. Here we use a standard growth process (rf diode deposition) to investigate the effects of adding silver and gold to a copper NFM layer in a GMR multilayer. Both the magnetotransport properties and the surface morphology are explored. Single films of both Cu and an Cu$_{80}$Ag$_{15}$Au$_5$ alloy are also grown and their surface morphology evaluated. A molecular-dynamics (MD) method is then used to investigate the atomic-assembly mechanisms during film growth for the two compositions. A dependence of interfacial roughness and pinhole formation upon the NFM layer composition is iden-
tified and correlated with the performance of the devices. The work suggests new directions for the development of improved GMR materials.

II. EXPERIMENTS

The study has focused upon the influence of the nonferromagnetic conducting-layer composition (either Cu or Cu$_{80}$Ag$_{15}$Au$_{5}$) on the GMR ratio and the saturation field of rf-diode-sputter-deposited GMR multilayers. Multilayers with either Cu or Cu$_{80}$Ag$_{15}$Au$_{5}$ NFM conducting layers as well as 100-, 500-, and 1000-Å-thick Cu and Cu$_{80}$Ag$_{15}$Au$_{5}$ single-layer films were grown at Non-volatile Electronic, Inc. (Eden Prairie, MN) using a Randex Model 2400-6J rf diode system (see Ref. 12 for details). With a target diameter of 20.32 cm, a substrate diameter of 10.00 cm, and a target-to-substrate distance of 3.81 cm, all the multilayers and the single-layer films were grown on the silicon-wafer substrates at an argon chamber pressure of 20 mTorr and a plasma power of 175 W.

The architecture and compositions of the antiferromagnetically coupled multilayers are shown in Fig. 1. The multilayers contained three repeated exchange-coupled-layer stacks. Each layer stack was a composite of two ferromagnetic layers (Ni$_{65}$Fe$_{15}$Co$_{20}$ and Co$_{95}$Fe$_{5}$) arranged so that the Co$_{95}$Fe$_{5}$ layer was at the interface with either the copper or the copper-alloy layer. This arrangement results in relatively good GMR ratios by helping to minimize the Ni and Cu interdiffusion.$^{3,5,6}$ The deposition rate for each metal target had been previously measured.$^{11}$ The layer thicknesses were therefore controlled by timing the deposition. The multilayers were grown by placing the substrate sequentially under each target. In each case a fixed NFM conducting-layer thickness of 16 Å was used. An amorphous 2000 Å Si$_3$N$_4$ film had been previously deposited on top of each wafer using a chemical-vapor-deposition method. The Si$_3$N$_4$ film
acted as an electrically insulating and diffusion inhibiting layer between the silicon wafer and the subsequently deposited metal films. The RMS roughness of the Si$_3$N$_4$ film was 2.0 Å. Si$_3$N$_4$ was preferred over SiO$_2$ because the oxygen in the latter can sometimes react with the magnetic materials and alter their coercivity.

FIG. 2. The dependence of the GMR ratio and the saturation field on the number of repeated multilayer stacks based on both Cu and Cu$_{80}$Ag$_{15}$Au$_5$ NFM conducting layers. In each case a fixed NFM conducting-layer thickness of 16 Å was used. Multilayers with the pure Cu conducting layer exhibited no giant magnetoresistance, while multilayers with the Cu$_{80}$Ag$_{15}$Au$_5$ conducting layer possessed significant GMR ratios.

III. EXPERIMENTAL RESULTS

Figure 2 shows the dependence of the GMR ratio and saturation field on the number of repeated stacks in the Cu and Cu$_{80}$Ag$_{15}$Au$_5$ conducting-layer multilayers. The results in Fig. 2 show that multilayers grown with a pure Cu conducting layer exhibited no GMR effect, whereas multilayers grown with a Cu$_{80}$Ag$_{15}$Au$_5$ conducting layer had significant GMR ratios. The saturation magnetic field of the Cu$_{80}$Ag$_{15}$Au$_5$ multilayers also increased with the number of stacks. Both the GMR ratio and the saturation fields using the Cu$_{80}$Ag$_{15}$Au$_5$ layer are reasonably well suited for magnetic-sensing applications. Many researchers have successfully used pure Cu as a conducting layer in GMR multilayers. They used a different deposition approach and the Cu layer thickness was usually greater than 20 Å. For the particular architecture and composition of the multilayer and rf-diode-deposition method investigated here, Cu thickness below 20 Å resulted in no GMR.

To explore the reasons for the loss of the GMR effect, three different thickness Cu and Cu$_{80}$Ag$_{15}$Au$_5$ single-layer films were grown under the same deposition conditions. The surface morphology of each film was then evaluated with tapping-mode atomic-force microscopy (AFM), Fig. 3. The scan size was 1 × 1 μm$^2$ and scan rate was 1 Hz for all the films. These results revealed periodic surface roughness with an asperity width that increased with the film thickness in both types of films, Fig. 3. However, the Cu films had larger asperity widths and higher surface amplitudes than their Cu$_{80}$Ag$_{15}$Au$_5$ counterparts. A top view of the films is shown in Fig. 4. Pinholes (the dark spots in the image) were present in the 100-Å-thick Cu film, Fig. 4(d). AFM measurements (Fig. 5) indicated that the average depth of the pinholes could be above 40 Å, and their diameters were approximately 800 Å. No pinholes were observed in the CuAgAu films. Figure 6 shows that the RMS roughness increased with the film thickness in both the Cu and Cu$_{80}$Ag$_{15}$Au$_5$ films, but the Cu films were always much rougher. The loss of the GMR effect in multilayers with a pure copper conducting layer is consistent with ferromagnetic layer coupling through pinholes in the NFM spacer layer.

IV. MOLECULAR DYNAMICS SIMULATIONS

The results above indicate a significant dependence of surface morphology upon the layer composition. To explore the origin of this effect, molecular-dynamics simulations of vapor deposition were conducted. Details of the method can be found in Refs. 13 and 14. For the problems of interest here, an interatomic potential that accurately describes the interaction forces between all metal atoms in the system was required. A recently developed embedded-atom-method (EAM) potential has been used for this. EAM potential incorporates the effects of local atomic environment, and has been successfully used to study a variety of surface problems in fcc metals. By normalizing the EAM functional form and generalizing the potential cutoff distance, the model has been found to realistically describe the interaction between atoms of 16 different elements.

A molecular-dynamics model of multilayer deposition was constructed by first defining the atomic coordinations of a substrate. The simulated substrate has 120 planes in the [224] direction, 12 planes in the [2 2 0] direction, and 3 planes in the [1 1 1] direction. To reduce the effects associated with the small crystal size, periodic boundary conditions were used in the x and z directions (see Fig. 7). To prevent crystal shift during adatom impact, the bottom two (111) planes were fixed. Under this condition, atoms above the fixed region were beyond their interaction range with the
atoms below the fixed region and the substrate could then be viewed as being extended indefinitely into the bulk. Due to the time-scale problem typical of molecular-dynamics simulations, an accelerated deposition rate of 4 nm/ns was employed while the substrate was held at 300 K.

Figure 7 shows the morphology of a 60-Å Cu film deposited on a Ni$_{65}$Fe$_{15}$Co$_{20}$ substrate. To amplify the flux-shadowing contribution to surface roughness, the incident flux angle was set at 45° to the copper surface. The incident atom energy was 0.15 eV, which is similar to that predicted for the rf-diode growth conditions. It can be seen that during Cu deposition, flux shadowing dominated the assembly process, which resulted in significant surface roughness and the formation of a pinhole. Figure 7(b) shows that when a
Cu$_{80}$Ag$_{15}$Au$_5$ layer was deposited, much smoother (continuous) film was achieved even at the oblique incident angle. The MD analysis indicated that by adding Ag and Au to Cu, a film can be prepared without pinhole formation, in agreement with the AFM images.

Figure 7(b) also indicates a very strong Ag surface segregation$^{17}$ even at the high deposition rate simulated. The low equilibrium solubility of Ag in Cu at 300 K suggests that even a more complete Ag segregation could be expected under the lower deposition rates encountered in real deposition.$^{18}$ Interestingly, Au atoms did not show any segregation effect, consistent with the high Au solubility and its intermetallic compound formation in Cu.$^{18}$

Figure 8 shows the simulated morphology of a GMR multilayer structure grown using Cu and Cu$_{80}$Ag$_{15}$Au$_5$ NFM conducting layers. It again shows that pinholes were formed whereas the addition of Ag and Au inhibited their formation, which resulted in smoother surface and interfaces. These results revealed that silver and perhaps gold are potent surfactants during multilayer growth. It is interesting to note that

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FIG. 4. Plan view of Cu$_{80}$Ag$_{15}$Au$_5$ and Cu films. Pinholes have been identified only in the 100-Å-thick Cu film.
silver is also able to float through the FM layers (since no significant silver concentration existed at the FM on NFM interface).

V. DISCUSSION

A growing body of experiments data \(^2\) and transport calculations \(^3\) indicate that the flattening of interfaces and reductions in interfacial mixing contribute to increased magnetoresistance in FM/NFM/FM multilayers. Improved de-minutions in interfacial mixing contribute to increased magnetic anisotropy. The barrier for hopping over an atomic terrace, the Ehrlich-Schwoebel barrier, is particularly important. In thermalized atom deposition, the only activation comes either from thermal activation provided by the background temperature or the transient heating associated with the latent heat of each adatom condensation. Smooth films require an Ehrlich-Schwoebel barrier comparable to that for hopping on a flat surface.

Using the three-dimensional EAM as a starting potential, two-dimensional molecular statics can be used to estimate the effects of Au and Ag on the activation barriers for atom migration in different pathways (see the Appendix for details). The barrier for the hopping of a Cu atom on a smooth close-packed Cu surface was found to be 0.25 eV. The corresponding energies for Ag and Au on such a copper surface were only 0.14 and 0.11 eV, respectively. If the jump-attempt frequencies are assumed identical, Ag and Au have a much higher mobility on a Cu surface than Cu atoms, Fig. 9(a). These molecular-statistics estimates also indicated that the Ehrlich-Schwoebel barrier for Cu depends on which atom type is attached to the edges of ledges. When the edge of the ledge is either Cu, Ag, or Au, the Ehrlich-Schwoebel barrier is 0.35, 0.28, or 0.33 eV, respectively, Fig. 9(b). Silver at the ledge edge reduces the Ehrlich-Schwoebel barrier for copper to approximately the barrier for hopping on a close-packed surface.

Similar molecular-statistics calculations indicated that it is energetically favorable (by 0.15 eV/atom) for a Au atom on a copper surface to exchange (and alloy) with a Cu atom, Fig. 10. They also showed that it is unfavorable (by 0.05 eV/atom) for a Ag atom on the Cu surface to exchange with a copper atom. As a result, Au is likely to be buried in Cu whereas Ag trends to segregate to the surface, which is in good agreement with the MD observations. The segregation of Ag appears beneficial since it maintains a high concentration of Ag at the surface. \(^21\) A high Ag surface concentration and a high Ag surface mobility increase the probability for Ag atoms to attach to ledge edges. This has the effect of increasing the probability for other atoms to overcome the “reduced” Ehrlich-Schwoebel barriers. This effectively minimizes flux shadowing and results in pinhole-free films and smoother surfaces. Gold atoms also reduce the Ehrlich-Schwoebel barrier, but not as significantly as the silver, and no Au concentration enhancement at the surface occurs.

Additional MD simulations were carried out to investigate the best silver concentration. The results indicated that surface roughness decreased as the Ag concentration was initially increased. However, the effects were found to have saturated at a silver concentration of about 10%. The use of small additions of elements with a low solid solubility provides a route to control barriers for atomic assembly during vapor deposition. Synergistic coupling with energetic deposition condition may provide new degrees of freedom to synthesize superior metal multilayer.

VI. SUMMARY

Radio-frequency-diode-sputter deposition has been used to grow Ni\(_{65}\)Fe\(_{15}\)Co\(_{20}\)/Co\(_{80}\)Fe\(_{5}\)/Cu or Ni\(_{65}\)Fe\(_{15}\)Co\(_{20}\)/Co\(_{80}\)Fe\(_{5}\)/Cu\(_{80}\)Ag\(_{15}\)Au\(_{5}\) multilayers. Multilayers utilizing Cu\(_{80}\)Ag\(_{15}\)Au\(_{5}\) as the nonferromagnetic conducting layer ex-
hibited significant giant magnetoresistance whereas otherwise identical device architectures that use a pure copper conducting layer fail to exhibit any magnetoresistance. The cause is the AFM-identified presence of pinholes in copper films but not in Cu$_{80}$Ag$_{15}$Au$_5$ films. Molecular-dynamics simulations revealed that silver acts as a surfactant reducing the energy barriers for atomic transport into flux-shadowed regions on the growth surface. The segregation of silver to the growth surface creates a very high silver coverage and enhancement of the surfactant effect. Molecular-statistics analyses confirmed that silver and gold atoms are very mobile and can reduce the Ehrlich-Schwoebel barriers at a copper ledge. These changes both contribute to a smoother surface.

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APPENDIX: ESTIMATES OF SURFACE KINETIC EFFECTS

1. Introduction

Kinetic effects associated with the deposition of a copper-silver-gold alloy can be studied using a two-dimensional
embedded-atom-method (EAM) model.\(^\text{26,27}\) Numerous cases can be analyzed in detail to obtain insight into the effects of the silver and gold additions to copper near its surface. The magnitudes of the specific activation energies are not significant, but the nature of the changes due to alloying are realistically indicated.

The approach begins by obtaining three-dimensional EAM models for the pure metals. These potentials are fitted to their respective equilibrium lattice spacing, cohesive energy, vacancy-formation energy, bulk modulus and average shear modulus, and cross potentials between different metals based on an analytic equation in the literature.\(^\text{27}\) The EAM parameters are then applied to a two-dimensional tightly packed plane of atoms. Relaxation is permitted only in the plane, and a two-dimensional equilibrium distance is obtained for the pure metals. Atomistic configurations (including alloying) are studied using molecular statistics. Two-dimensional alloy lattice constants are taken as an average of the two-dimensional lattice constants of the pure metals weighted by their atomic concentration. With careful use of constraints, the energy of the configuration is mapped as atomistic migration takes place to provide the requisite activation energies. With the exception of one positional component of the jumping atom, relaxation within the plane is permitted and an iterative procedure is used to minimize the energy of each configuration relative to its constraints. The energy was commonly minimized at 21 configurations to obtain the energy curve for each activation energy.

FIG. 8. (Color) Molecular-dynamics simulations of multilayer deposition showing that a pinhole was formed when pure Cu was used as the NFM conducting layer in GMR multilayer structure. The use of Ag and Au alloying promotes smoother FM on NFM interfaces and prevents formation of pinholes.
(a) Low Cu mobility and high Ag and Au mobility on Cu

(b) The Ehrlisch-Schwoebel barrier for Cu when the edge of the ledge is Cu, Ag, and Au.

FIG. 9. Alloy effects on atomic assembly. Ag and Au atoms are relatively more mobile than Cu atoms on a flat Cu surface. Ehrlich-Schwoebel barrier of Cu atoms is the lowest when the edge of the ledge is Ag rather than Cu and Au.

2. Analytic model

The energy of an atom “i” in an EAM model is the sum over neighboring atoms “j” of a two-body potential \( \phi \) an embedding energy \( F \) based on the electron density \( \rho \) at the site of atom “i”:

\[
E_i = \frac{1}{2} \sum_j \phi(r_{ij}) + F(\rho_i),
\]

where \( \rho \) is a sum of the contribution \( f \) from neighboring atoms \( j \),

\[
\rho_i = \sum_j f(r_{ij}).
\]

The analytic forms used in the present model are

\[
\phi(r) = -\phi_e \left[ 2 \left( \frac{r-r_c}{r_e-r_c} \right)^3 - 3 \left( \frac{r-r_c}{r_e-r_c} \right)^2 \right],
\]

\[
f(r) = f_e \frac{r-r_c}{r_e-r_c},
\]

\[
F(\rho) = F_e \left[ 1 - \ln \left( \frac{\rho}{\rho_e} \right) \right]^{n} \left( \frac{\rho}{\rho_e} \right)^{n},
\]

where \( r_e \) is the three-dimensional nearest-neighbor equilibrium spacing, \( r_c \) is a cutoff distance less than the second-nearest distance at which the two-body potential and the electron density function have zero value and slope, and \( \rho_e \) is the equilibrium electron density. In terms of the atomic volume \( \Omega \), the cohesive energy \( E_c \), the vacancy formation energy \( E_v \), the bulk modulus \( B \), and the Voigt average shear modulus \( G \), the parameters are given by

\[
r_e = \frac{\sqrt{2} (4 \Omega)^{1/3}}{2},
\]

\[
r_c = r_e \left[ 1 + \left( \frac{E_v}{2.5 \Omega G} \right)^{1/2} \right],
\]

\[
\phi_e = -E_v/6,
\]

\[
f_e = \frac{E_c}{12 \Omega},
\]

\[
F_e = E_v - E_c,
\]

\[
n = \sqrt{(9 \Omega B - 15 \Omega G) / (E_v - E_c) [(r_e - r_c) / (r_e + r_c)]},
\]

The two-body cross potential between type “a” and “b” is given by

\[
\phi_{ab}(r) = \frac{1}{2} \left[ \frac{f_b(r)}{f_a(r)} \phi_a(r) + \frac{f_a(r)}{f_b(r)} \phi_b(r) \right].
\]

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