ATOMIC SCALE STRUCTURE OF SPUTTERED METAL MULTILAYERS

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Abstract—A combined theoretical and experimental approach has been used to study nanoscale CoFe/Cu/CoFe multilayer films grown by sputter deposition. Such films have applications in sensors that utilize the giant magnetoresistance effect, for example, read heads in high-density information storage devices. Atomistic simulations based on a molecular dynamics approach and an alloy form of the embedded atom method have been developed to accurately model the sputter deposition of the CoFe/Cu/CoFe multilayers. The simulations show that relatively flat interfaces are formed because of the energetic deposition conditions. However, significant intermixing at the CoFe-on-Cu interface, but not at the Cu-on-CoFe interface, was observed. An abnormal Fe depletion zone is also revealed at the CoFe-on-Cu interface. A three-dimensional atom probe method has been used for a nanoscale chemical analysis of the films. It provided direct verification of the simulations. The simulations have then been used to understand the mechanism responsible for the formation of the intermixing defects observed in the multilayers. A novel deposition technique is proposed which reduces both interfacial mixing and Fe depletion by controlling the incident adatom energies.

Keywords: Magnetoresistive effects; Multilayers; Surfaces & interfaces; Atom probe; Molecular dynamics

1. INTRODUCTION

When ferromagnetic layers (such as CoFe) are separated by a non-magnetic spacer layer (such as Cu) of an appropriate thickness (for example, approximately 2 nm), their magnetic moments will align antiferromagnetically in a zero magnetic field [1]. Spin-dependent conduction electron scattering [2, 3] then results in a relatively high electrical resistance. If a sufficiently large magnetic field is applied to reverse the magnetic moment of one of the ferromagnetic layers, a ferromagnetically aligned sandwich can be created. This alignment reduces the spin-dependent conduction electron scattering, and causes a decrease in the electrical resistance of the film—an effect known as giant magnetoresistance (GMR) [2, 3]. The GMR effect was first observed in vapor deposited Fe/Cr/Fe sandwiches in 1988 [4]. Since then, many other material systems have been shown to exhibit the effect, including the Co/Cu/Co [5, 6], NiFe(Co)/Cu/NiFe(Co) [7, 8], and NiCo/Cu/NiCo systems [9]. The significant technological importance of GMR materials as magnetic field sensors arises from their very high sensitivity to an external magnetic field when fabricated as submicron devices. Because of this, GMR multilayers are now widely used as read-head sensors in hard disk drives, and are also being actively explored for a new form of magnetic random access memory [10].

GMR materials have been synthesized using numerous vapor deposition techniques including sputter-deposition [7], ion beam deposition [11], and molecular beam epitaxy [4]. These studies have shown that the magnetotransport properties are highly sensitive to the method and conditions of growth. Experiments have indicated that a significant decrease in the GMR ratio occurs when the average spacing between the ferromagnetic layers is changed, even by as little as one monolayer [5]. High-quality GMR multilayers must therefore have a precisely controlled spacing.
layer thickness. In addition, if the layers are comparably rough in amplitude and wavelength to the spacer layer thickness, Néel coupling occurs and it becomes more difficult to reverse the magnetic moment of the layers. Furthermore, the alloying of one layer by the metal atoms of another causes an increase in spin independent scattering [12] and a loss of local magnetic alignment [13]. Relatively smooth, unmixed interfaces therefore appear desirable [7, 14]. The intrinsic properties of the material system are also important, together with other nanoscale structural features, including interfacial impurities [15], texture [16], any buffer layer material [17], the presence of surfactants during growth [18], the grain size/morphology of each layer, various lattice defects (vacancies, voids, dislocations and twins) [19], and perhaps residual stress. Of these, the atomic scale perfection across the multilayer interfaces appears to most critically affect the GMR properties [20].

Although the importance of these various effects is clear, the very small scale of the defects have made it difficult to make a direct link between a given effect and the change in magnetic properties. Results obtained from different investigations are often contradictory. In experimental studies of Fe/Cr/Fe multilayers, for instance, Petroff et al. found that increasing the interfacial roughness and the interfacial mixing both increased the GMR ratio [21], while Belien et al. indicated that a lower interfacial roughness and reduced interfacial mixing result in a higher GMR ratio [22]. The contradictory nature of these results most likely arises because the atomic scale structures of the deposited films are not well understood. In the present work, atomistic simulations based on the molecular dynamics (MD) approach have been used to investigate growth mechanisms and their control in order to create improved interfaces. This has been combined with direct atomic-scale characterization of sputter-deposited layers using the three-dimensional atom probe (3DAP), which has allowed experimental verification of the results of the simulation.

2. ATOMIC SIMULATION OF ATOMIC STRUCTURE

Many factors contribute to the structure of a vapor-deposited multilayer film, including layer composition, growth temperature and deposition energy. To explore the effects of these factors within a computer model, a highly predictive atomistic simulation method must be used. The method must not only produce reliable results, but must also not require pre-existing knowledge of the film growth mechanisms. In our work, a MD approach is used to provide an accurate description of the way in which atoms in the vapor phase arrive at a substrate surface and then subsequently rearrange themselves.

In a MD simulation, the transition of atoms from vapor to a solid surface and the subsequent surface reconstruction is simulated by tracking the positions of atoms using Newton’s equations of motion. This correctly identifies the detailed atomic structures of a deposited film, and reveals many of the mechanisms active throughout the deposition process. However, the accuracy of the simulation depends upon the fidelity of the interatomic potentials used to calculate the interatomic forces. The embedded atom method (EAM) potential initially developed by Daw and Baskes [23] has provided a good potential format for the metal atoms that are used in the GMR multilayers. The EAM potential assumes that the crystal energy is the sum of a pairwise potential and an energy required to embed an atom into a local medium with a given electron density. Because this embedding energy depends on the local “crowding” (atom density), EAM accounts for the local environment dependence of the potential, and therefore has been successfully used to solve a variety of problems involving surface structures and defect states. The potentials used in the present work are listed in Appendix A.

Initial Ni$_{80}$Fe$_{20}$ substrate crystals with a lateral size of 120 (224) planes in the $x$ direction and 16 (220) planes in the $z$ direction were used in the MD simulations (see Fig. 1). Periodic boundary conditions were used to extend the lateral dimensions of thin films. The growth was simulated by injecting adatoms to the top $xz$ surface from random starting positions far above at a frequency that gives rise to the desired deposition rate. To account correctly for the relaxation of crystal size under the influence of the internal stress between different layers, a Lagrangian form of Newton’s equations of motion [24] was used to solve for the evolution of atomic structures. To prevent the
crystal shift during energetic impacts, the bottom region of the substrate was fixed. Damping forces were applied to the atoms in a subsurface region to adjust the atom velocities so that a near constant temperature was maintained in this region. During deposition, this isothermal region was advanced upwards in a way that left several free monolayers at the surface. A 5.8 nm Co$_{90}$Fe$_{10}$/1.5 nm Cu/4.0 nm Co$_{90}$Fe$_{10}$ multilayer unit was simulated using an adatom energy of 3.0 eV, a normal adatom incident angle, a substrate temperature of 300 K, and a deposition rate of 1 nm/ns. The multilayer stack employs similar temperature of 300 K, and a deposition rate of 1 nm/ns. The multilayer in the growth direction, as shown in Fig. 2, with solid, dashed and bold lines, respectively. To quantify the atomic distributions near the interfaces, a composition vs depth profile is needed. To calculate this, a small box was defined and placed at the bottom of the layers. The atomic fraction of Cu, Co and Fe in the box was calculated by dividing the number of atoms of each species by the total number of atoms in the box. Composition–depth profiles were mapped out (by continuously moving the box across the multilayer in the growth direction), as shown in Fig. 2. The thickness of the box was chosen to be about one atomic layer (0.2 nm), and the lateral dimension of the box was such that it contained a total number of atoms per sample of $N \approx 100$. If the mean composition in the box satisfies a binomial distribution, then the standard deviation for any calculated composition $C$ is [27]

$$\sigma = \sqrt{\frac{C(1-C)}{N}} \quad (1)$$

The (1σ) error bar is therefore 5.0% at $C = 50$ at.%. For the composition range of 5–10 at.%, this error bar is further reduced to between 2.2 and 3%. Calculated composition profiles for Co, Cu and Fe are shown in Fig. 2 with solid, dashed and bold lines, respectively. The statistical fluctuations are clearly visible, for example in the Fe profile within the CoFe layer.

The composition–depth profiles of Fig. 2 give a quantitative measure of the chemical sharpness of the interfaces. Consistent with Fig. 1, Fig. 2 indicates that the Cu-on-CoFe interface is much sharper than the CoFe-on-Cu interface. If measured between 10 and 90% Cu, the interfacial widths are about 0.33 and 1.44 nm for the Cu-on-CoFe and the CoFe-on-Cu interfaces, respectively. To further explore the distribution of various species (especially the ferromagnetic atoms) across the interfaces, the Co/Fe ratio was calculated along the growth direction. The results of this calculation, which provide a good indication of the relative Co and Fe distributions across interfaces, are included in Fig. 2 as a shaded region. Compared to a nominal Co/Fe ratio of 9, Fig. 2 shows a region of abnormally higher Co/Fe ratio at the CoFe-on-Cu interface indicative of Fe depletion near this interface. However, there are fewer Co and Fe atoms in this region than within the body of the CoFe layer, so that the errors on the Co/Fe ratio are larger. We have therefore applied a two-sample $t$-test to determine the significance of the observed variation in the Co/Fe ratio. This test is used to determine at what confidence level the difference between the means of two distributions is statistically significant. Since it is reasonable to assume that a variation in the Co/Fe ratio may exist in the plane of the layers, three separate composition profiles were measured at three different lateral regions as shown in Fig. 1. Each profile
was divided into three intervals: the Cu-on-CoFe interface, the CoFe-on-Cu interface and a CoFe region that has the average data of the upper and lower CoFe layers. Mean and variance values for the Co/Fe ratio were calculated for each interval in each profile. Two-sample T-tests were then performed to determine the level of confidence at which a significant difference in means could be stated. Table 1 shows the results comparing the CoFe-on-Cu and the Cu-on-CoFe interfaces to the CoFe layer. All three profiles shown in Table 1 indicate a higher Co/Fe ratio at the CoFe-on-Cu interface than in the bulk CoFe, with two profiles showing this difference at a significant confidence level of >90%. When combining all data profiles, we find that this difference is significant at the 97% confidence level. The difference between the Cu-on-CoFe interface and the bulk CoFe is not obvious as two profiles show a lower Co/Fe ratio at the Cu-on-CoFe interface than the bulk CoFe, while the other one shows the reverse. An additional conclusion that can be drawn from the combined MD data calculation is that the Co/Fe ratio at the CoFe-on-Cu interface is higher than that at the Cu-on-CoFe interface at a confidence level of 98%.

3. EXPERIMENTAL MEASUREMENT OF ATOMIC STRUCTURE

Experimental characterization of the physical and chemical nature of interfaces in nanoscale multilayers is a challenging task, due to the very fine scale of any roughness or intermixing sufficient to generate changes in magnetic properties. What is required is a technique which has ultra-high spatial resolution in all three dimensions. Transmission electron microscopy (TEM) [28], traditionally used to study these materials, cannot in most cases chemically identify single atoms and can only provide average structure information through the specimen thickness. To overcome this problem, a 3DAP technique [27, 29] has been used that enables the three-dimensional atomic distributions in a sample to be reconstructed.

The basic concept of the 3DAP experiment is shown in Fig. 3. The sample consists of a needle with an end radius of 50–100 nm, which is held at cryogenic temperature in an ultra-high vacuum system. Under an applied electric field, pulsed field evaporation is used to ionize the atoms on the sample surface and evaporate them one by one. The evaporated ions are accelerated in a radial direction by the electric field until they impact on a time- and position-sensitive detector. This allows both the impact position and the flight time of the ion to be measured. The 3DAP acts as a point projection microscope, allowing the original position of each atom on the specimen surface to be deduced, whilst the flight time is used to determine the chemical identity of the ions. As more and more atoms are removed from the sample, sample material is gradually eroded away, and the third dimension of the measured image is built up from the sequence of ion detection. The 3DAP technique has a depth resolution of a single atomic layer and sub-nanometer lateral resolution, the latter being poorer because of small aberrations in the trajectories of the ions in the near-surface region. To obtain atomic-layer resolution for the interfaces, a new technique has been developed so that the sample can be prepared with the interfaces normal to the sample axis and the region of interest positioned within 100 nm of the needle apex [30, 31]. This new development enables a 3DAP analysis of atomic features across the interfaces of GMR multilayers. To prepare 3DAP samples, small posts (approximately 4 µm square and 100 µm long) are fabricated on a standard (001) silicon substrate. TEM results have indicated that growth of multilayers on posts of this size does not significantly affect the morphology of the layers [32].

The multilayer structure investigated by 3DAP consisted of a basic structure as follows: 5.0 nm Ni₈₁Fe₁₉/4.0 nm Co₀₉Fe₀₁/3.0 nm Cu/4.0 nm Co₀₉Fe₁₀ (layer thicknesses are nominal). To induce a <111> texture in the layers during growth, a seed layer was first deposited on the Si wafer. Ten repeats of the multilayer structure were then deposited on the seed layer, followed by a 50 nm Ni₈₁Fe₁₉ cap to protect the structure during subsequent sample preparation procedures. The deposition was carried out using DC magnetron sputtering at a base pressure of about 1×10⁻⁶ Pa. The 3DAP analysis was performed in an energy-compensated optical position-sensitive atom probe, with an ultra-high vacuum of about 5×10⁻⁹ Pa, a pulse fraction of 15% and a pulse repetition rate of 1500 Hz. The specimen temperature was held at 70–80 K during field-ion imaging and atom probe analyses.

Table 1. MD simulated composition distribution: mean Co/Fe ratio <r>, its standard deviation σ, confidence level C, for the CoFe-on-Cu interface to differ from the bulk CoFe, and confidence level C for the Cu-on-CoFe interface to differ from the bulk CoFe

<table>
<thead>
<tr>
<th>Region</th>
<th>&lt;r&gt;</th>
<th>σ</th>
<th>σ</th>
<th>&lt;r&gt;</th>
<th>σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Region 1</td>
<td>13.80</td>
<td>12.30</td>
<td>12.57</td>
<td>3.79</td>
<td>10.00</td>
</tr>
<tr>
<td>Region 2</td>
<td>9.63</td>
<td>2.97</td>
<td>8.67</td>
<td>2.08</td>
<td>9.85</td>
</tr>
<tr>
<td>Region 3</td>
<td>9.27</td>
<td>3.00</td>
<td>8.30</td>
<td>0.74</td>
<td>11.45</td>
</tr>
<tr>
<td>CoFe-on-Cu interface</td>
<td>Confidence level, C</td>
<td>93%</td>
<td>&gt;99%</td>
<td>21%</td>
<td>75%</td>
</tr>
</tbody>
</table>
A 3DAP reconstruction of a section of the stack is shown in Fig. 4. As in Fig. 1, the Ni, Fe, Co and Cu atoms are marked green, yellow, blue and red, respectively. The Cu layer thickness was found to be thinner than the nominal thickness. A remarkable similarity is found between the simulated image in Fig. 1 and the experimental image in Fig. 4. For instance, the roughness (amplitude and wavelength) for both the Cu-on-CoFe interface and the CoFe-on-Cu interface seen in Fig. 4 are very close to those in Fig. 1. As in the simulated image, the Cu-on-CoFe interface in Fig. 4 is relatively sharp while the CoFe-on-Cu interface is diffuse, and the Cu atoms are mixed in the CoFe layer. This experimental observation verifies that Cu mixing in the subsequent CoFe layer is much more significant than in the CoFe layer deposited previously.

To quantify the 3DAP data, the same sampling method described above was used to analyze the variation of Co, Cu, and Fe concentration along the growth direction. To highlight the statistical variations of the data, measurements were performed for various regions on several samples. The results of the composition profiles for two of the samples are shown in Figs 5(a) and (b), respectively. Again, a remarkable
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Fig. 5. Composition vs thickness profiles for the 3DAP measured NiCo/Cu/NiCo multilayer.

Fig. 5. Composition vs thickness profiles for the 3DAP measured NiCo/Cu/NiCo multilayer.

Similarity is found between the simulated results in Fig. 2 and the experimental results in Fig. 5. It can be seen from both Figs 2 and 5 that the Cu, Co, and Fe composition profiles are asymmetric across the two interfaces on either side of the Cu layer. The compositions undergo a sharp transition across the Cu-on-CoFe interface, but the transition across the CoFe-on-Cu interface is much more diffuse. Quantitatively, Fig. 5(a) shows interfacial widths of about 0.3 and 0.95 nm, respectively, for the Cu-on-CoFe and the CoFe-on-Cu interfaces, and Fig. 5(b) shows interfacial widths of about 0.5 and 1.2 nm, respectively, for the Cu-on-CoFe and the CoFe-on-Cu interfaces. These result in estimates of mean width and standard deviation of 0.4 ± 0.14 and 1.08 ± 0.18 nm, respectively for the Cu-on-CoFe and the CoFe-on-Cu interfaces.

Similar to the calculation for the MD profiles, a determination of the significance of the variation in Co/Fe ratio over the profiles calculated from the 3DAP data was performed using two-sample T tests. The results obtained from five 3DAP composition profiles (including the two shown in Fig. 5) that encompass different regions of the multilayer are listed in Table 2. It can be seen from Table 2 that all five profiles indicate a higher Co/Fe ratio at the CoFe-on-Cu interface than in the CoFe bulk, with three of the profiles showing a confidence level of above 90% for this difference. When combining all 3DAP data profiles, we found that the difference is significant at a confidence level of 99%. Additionally, Table 2 suggests a lower Co/Fe ratio at the Cu-on-CoFe interface than in the CoFe bulk. We also found from the analyses of all 3DAP data that the Co/Fe ratio at the CoFe-on-Cu interface is higher than that at the Cu-on-CoFe interface at a confidence level of 93%.

4. MECHANISMS FOR FORMATION OF INTERFACE IMPERFECTIONS

Elementary thermodynamic arguments indicate that a material A cannot wet the surface of a material B if B wets A. When wetting does not occur, flat interfaces are difficult to form in nanoscale multilayers because of the tendency for the nonwetting layer to grow by an island mechanism. As a result, GMR multilayers with all interfaces flat cannot be obtained under kinetically unconstrained (thermal equilibrium) growth conditions. Previous MD simulations have indicated that the use of energetic (several eV) adatom impact induces atomic jumps, resulting in a flattening of the surface asperities present during deposition by island growth [25]. This promotes flatter interfaces, and appears to account for the observation that multilayers grown by magnetron sputtering [7] and ion beam deposition processes [11] (where adatoms have an average impact energy of ~3 eV or above) often have superior GMR properties to those grown by a low impact energy molecular beam epitaxy method [4].

However, energetic adatom impacts can cause other phenomena to occur, in particular atomic mixing. Figs 1, 2, 4 and 5 indicate that in sputter deposited CoFe/Cu/CoFe multilayers, the Cu-on-CoFe interface is relatively sharp, while the CoFe-on-CoFe interface is quite diffuse. MD analyses of metal multilayer growth by energetic atom deposition have indicated that this interfacial mixing can occur by an impact induced exchange event [25]. In this process, the energetic adatom penetrates the surface sufficiently so that it is embedded in the substrate and ejects a substrate atom onto the surface. The exchange probability is lower on a flat surface than on a rough surface, and increases with increasing impact energy. The question raised within the present work is why there should be an asymmetry in the intermixing. In order to address this question, the MD method was used to calculate the exchange probabilities during a large number of random impacts by 10 eV Cu, Co and Fe atoms on flat (111) surfaces of fcc Cu and Co crystals. Because the intent is to determine the relative exchange probabilities among different species, a high energy of 10 eV was chosen for study so that significant exchanges can be observed on the ideally flat surface. The results indicate that Co and Fe atoms impacting on a Cu surface have an exchange probability of 82 and 54%, respectively, while Cu atoms of similar energy impacting on a Co surface have an
exchange probability of only 6%. The higher exchange probability between Co adatoms and Cu surface atoms therefore leads to a diffuse CoFe-on-Cu interface. Conversely, because Cu adatoms are less likely to exchange with Co or Fe surface atoms, the Cu-on-CoFe interface is relatively sharp (unmixed).

Since the melting point of Cu is lower than that of Co or Fe, it might be expected that incident atoms of whatever type would be more likely to exchange with surface Cu atoms than with surface Co or Fe atoms. However, a further driving force for thermal diffusion induced exchange would be provided by any tendency for surface segregation. To investigate this further, Cu and Co crystals with a (111) surface were simulated. A monolayer of Cu, Co, or Fe was placed either on the surface or one monolayer below the surface of these crystals. After relaxing the crystals by energy minimization based on a conjugate gradient method, the average energy change \( \Delta E \) associated with moving atoms from subsurface to surface lattice positions was calculated. The values of \( \Delta E \) for Cu segregation to the surface of Co, Co segregation to the surface of Cu, Fe segregation to the surface of Cu, and Fe segregation to the surface of Co are \(-0.22, 0.19, 0.00,\) and \(-0.20\) eV per atom, respectively. It can be seen that Cu and Fe both tend to segregate to the surface of Co (both processes reduce the energy).

Both the atomistic simulation and the 3DAP data above indicate that in the \( \text{Co}_{10}\text{Fe}_{80}/\text{Cu}/\text{Co}_{10}\text{Fe}_{10} \) multilayer, the Fe concentration is lower than the nominal value at the CoFe-on-Cu interface. While it is unclear if this Fe depletion has any effect on the GMR properties, several mechanisms have been identified that could be the cause of this effect. During deposition of the CoFe layer on top of a given Cu plane, a deposited Co atom exchanges more frequently with a Cu atom in that plane than a deposited Fe adatom. As a result, the fraction of deposited Co atoms that will occupy that plane will be greater than in the bulk of the CoFe layer. A relatively Fe depleted (with respect to Co) region is then created at the CoFe-on-Cu interface. In addition, Fe tends to segregate to the surface of Co. A continuous Fe migration to the surface of the CoFe layer through thermally activated diffusion would also result in a Fe depleted zone at the CoFe-on-Cu interface and a Fe enhancement at the Cu-on-CoFe interface. At the high deposition rate (or the short time scale) simulated, thermally activated diffusion is negligible. However, any thermally activated diffusion that can exist at the realistic low deposition rate should be reflected by the 3DAP data. Evidence for the Fe enhancement is less strong than for the Fe depletion described previously. This is because both impact induced exchange and thermal diffusion induced exchange cause the Fe depletion at the CoFe-on-Cu interface, but only the thermal diffusion can cause the Fe enhancement at the Cu-on-CoFe interface. It is likely that insufficient bulk diffusion exists during room temperature sputter deposition for Fe surface segregation to occur, and the Fe depletion effect seen at the CoFe-on-Cu interface is believed to be mainly caused by the higher probability of impact induced exchanges with Cu surface atoms.

5. GROWTH PROCESS IMPROVEMENT

MD simulations provide compelling evidence that increasing the adatom energy flattens interfaces, but induces interlayer mixing at interfaces when a high tendency exists for the underlying material to segregate to the surface of the material being deposited. While lowering the adatom energy can sharpen the chemical boundary of the interface, it is accompanied by increased interfacial roughness. As a result, better GMR properties are obtained from materials grown with an intermediate adatom energy [7, 11]. Detailed analyses of the asymmetric interfacial structures and their formation mechanisms indicate that the use of different adatom energies to deposit the Cu and the CoFe layers may be more beneficial than the use of a single "optimum" energy for deposition of all layers. In particular, the use of a lower adatom energy for

### Table 2. 3DAP measured composition distribution: mean CoFe ratio \( \langle r \rangle \), its standard deviation \( \sigma \), confidence level \( C_1 \) for the CoFe-on-Cu interface to differ from the bulk CoFe, and confidence level \( C_2 \) for the Cu-on-CoFe interface to differ from the bulk CoFe

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \langle r \rangle )</th>
<th>( \sigma )</th>
<th>( \langle r \rangle )</th>
<th>( \sigma )</th>
<th>( \langle r \rangle )</th>
<th>( \sigma )</th>
<th>( \langle r \rangle )</th>
<th>( \sigma )</th>
<th>( \langle r \rangle )</th>
<th>( \sigma )</th>
</tr>
</thead>
<tbody>
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<td>Sample 1</td>
<td>11.30</td>
<td>0.93</td>
<td>17.72</td>
<td>10.50</td>
<td>10.10</td>
<td>2.05</td>
<td>12.55</td>
<td>6.97</td>
<td>17.40</td>
<td>9.53</td>
</tr>
<tr>
<td>Sample 3</td>
<td>6.55</td>
<td>2.14</td>
<td>5.37</td>
<td>2.16</td>
<td>6.16</td>
<td>4.24</td>
<td>6.72</td>
<td>2.42</td>
<td>5.37</td>
<td>5.70</td>
</tr>
<tr>
<td>Sample 4</td>
<td>Confidence level, ( C_1 )</td>
<td>93%</td>
<td>92%</td>
<td>81%</td>
<td>59%</td>
<td>98%</td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>Sample 5</td>
<td>Confidence level, ( C_2 )</td>
<td>89%</td>
<td>&gt;99%</td>
<td>74%</td>
<td>94%</td>
<td>78%</td>
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</table>
deposition of the CoFe layer on Cu than for the Cu on CoFe layer (interlayer energy modulation) can effectively sharpen the CoFe-on-Cu interface. This strategy has been experimentally implemented and found to improve the GMR ratio [33]. Even better results may be possible by modulating the energy during deposition of each layer (intralayer energy modulation). To investigate this idea, a simulation was conducted where the first few monolayers of Cu (or CoFe) were deposited on CoFe (or Cu) using a low adatom energy to avoid impact induced mixing. After the interface was well buried below the surface, higher adatom energy was used to flatten the surface. The result of simulating the growth of the 5.8 nm Co$_{90}$Fe$_{10}$/1.5 nm Cu/4.0 nm Co$_{90}$Fe$_{10}$ multilayer on a 1 nm Ni$_{80}$Fe$_{20}$ substrate using this modulated energy scheme is shown in Fig. 6. It can be seen that compared to the result shown in Fig. 1, the interlayer mixing is greatly reduced while the interfacial roughness remains almost unchanged. A composition depth profile was also calculated, and is shown in Fig. 7. The interfaces are seen to be very sharp, and the Fe depletion at the CoFe-on-Cu interface due to the exchange mechanism is also removed. The interfacial widths are about 0.33 and 0.24 nm, respectively, for the Cu-on-CoFe and the CoFe-on-Cu interfaces. The two interfaces on either side of the Cu layer are hence much narrower and more symmetric.

An intralayer energy modulated deposition has not been tested experimentally. This is because current sputter deposition and ion beam deposition systems are not designed for an independent control of adatom energy within the range required for the energy modulation. Nevertheless, the perspective provided by the combination of simulation and experiment immediately leads to a direction for modifying the deposition parameters to improve multilayer properties.

6. CONCLUSIONS

An integrated approach combining atomistic simulations and three-dimensional atom probe experiments has been developed to study atomic scale structures of nanoscale metal multilayers. The application of this approach to the sputter deposition of nanoscale CoFe/Cu/CoFe multilayers revealed the following:

1. Energetic adatom impact with the growth surface can cause exchange between the adatom and underlying atoms. The exchange probability is much higher when the underlying material is Cu rather than Co and Fe. Consequently, the Cu-on-CoFe interface is much sharper than the CoFe-on-Cu interface, and Cu mixing in the subsequently deposited CoFe layer is much more significant than in the pre-deposited CoFe layer.

2. During deposition of the CoFe layer on Cu, the Co adatoms exchange more frequently with underlying Cu atoms than the Fe adatoms. As a result, a relatively Fe depleted (with respect to Co) region is created at the CoFe-on-Cu interface.

3. Adatom energy is a key parameter for the deposition of GMR multilayers. Low adatom energies reduce the exchange probability and hence the interlayer mixing. However, high adatom energies are essential to flatten the surface. An interlayer modulated energy deposition can produce lower combination of interfacial roughness and interlayer mixing than a single “optimum” energy deposition. An intralayer modulated energy depo-
sition was predicted to have a further potential to reduce the interfacial roughness and interlayer mixing and to remove the Fe depletion zone at CoFe-on-Cu interfaces.

The limitations of past experimental techniques for the direct analysis of atomic scale microstructural features combined with a limited understanding of atomic assembly processes have been responsible for a slow convergence upon the ideal processes for synthesizing GMR multilayers. The emergence of a reliable combination of computer modeling and atomic level experiments provides an integrated approach to the design of these (and potentially many other) nanostructured materials. It permits not only the identification of atomic scale structure, but also the prediction of compositions and processing routes needed to achieve desired properties. This combined approach may be critical to the successful synthesis of many of the complex devices of future interest.

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REFERENCES


APPENDIX A

EAM potentials developed for atoms of a single element generally cannot be applied to alloys. The potential cut-off distances fitted for individual elements are often not consistent. By normalizing the EAM potentials and introducing an EAM alloy potential database, the EAM potentials and their cut-off distance [34]. This generalized EAM potential has been extended to enable calculations of alloys with any combination of 16 metals (Cu, Ag, Au, Ni, Pd, Pt, Al, Pb, Fe, Mo, Ta, W, Mg, Co, Ti, and Zr). These potentials are well fitted to basic material properties such as lattice constants, elastic constants, bulk moduli, vacancy formation energies, sublimation energies, and heats of solution. The use of molecular dynamics for the simulation of GMR multilayer assembly from alloy vapors reported here has now become possible due to the recent development of this potential database.

The derivation of integrated EAM potentials for a variety of elements and their alloys has been described in detail previously [34], and hence only the results are listed here. In EAM, the total energy $E$ of the crystal can be expressed as
Alloy EAM potentials can be constructed from elemental EAM potentials if the potentials are normalized [35] and unified cutoff functions are used. To fit such an EAM potential set, the generalized pair potentials were chosen to have the form

$$E = \frac{1}{2} \sum_{i,j,i \neq j} \phi_{ij}(r_{ij}) + \sum_i F_i(r_i) \tag{A1}$$

where $\phi_{ij}$ represents the pair energy between atoms $i$ and $j$ separated by $r_{ij}$, and $F_i$ stands for the embedding energy to embed an atom $i$ into a local site with electron density $\rho_r$. $\rho_r$ can be calculated using

$$\rho_r = \sum_{i,j,i \neq j} f_i(r_{ij}) \tag{A2}$$

with $f_i(r_{ij})$ the electron density at the site of atom $i$ arising from atom $j$ at a distance $r_{ij}$ away.

Alloy EAM potentials can be constructed from elemental EAM potentials if the potentials are normalized [35] and unified cutoff functions are used. To fit such an EAM potential set, the generalized pair potentials were chosen to have the form

$$\phi(r) = A \exp \left[ -\alpha \left( \frac{r}{r_c} \right)^{\nu} \right] \frac{1}{1 + \left( \frac{r}{r_c - \kappa} \right)^{20}} - B \exp \left[ -\beta \left( \frac{r}{r_c} \right)^{\nu} \right] \frac{1}{1 + \left( \frac{r}{r_c - \lambda} \right)^{20}} \tag{A3}$$

where $r_e$ is the equilibrium spacing between nearest neighbors, $A$, $B$, $\alpha$, $\beta$, $\kappa$, $\lambda$ are four adjustable parameters, and $\kappa$, $\lambda$ are two additional parameters for the cut off [35].

The electron density function is taken with the
same form as the attractive term in the pair potential with the same values of $\beta$, and $\lambda$, i.e.,

$$f(r) = \frac{f_e \exp\left(-\beta \left(\frac{r}{r_e} - 1\right)\right)}{1 + \left(\frac{r}{r_e}\right)^2}$$  \hspace{1cm} (A4)$$

Using the alloy model [35], the pair potential between different species $a$ and $b$ is constructed as

$$\phi^{ab}(r) = \frac{1}{2} \left( \frac{F_i(r)}{f_i(r)} \phi^{ei}(r) + \frac{F_i(r)}{f_i(r)} \phi^{be}(r) \right)$$  \hspace{1cm} (A5)$$

To have embedding energy functions that can work well over a wide range of electron density, we have used three equations to separately fit to different electron density ranges, $\rho < \rho_o, \rho_o \leq \rho < \rho_n$, and $\rho_o \leq \rho$. By using $\rho_o = 0.85 \rho_e$ and $\rho_n = 1.15 \rho_e$ where $\rho_e$ is the equilibrium electron density, we can ensure that all equilibrium properties can be fitted in the electron density range $\rho_o \leq \rho < \rho_n$. For a smooth variation of the embedding energy, these equations are required to match values and slopes at their junctions. These equations are listed as follows:

$$F(\rho) = \sum_{i=0}^{3} F_i \left( \frac{\rho}{\rho_o} - 1 \right)^i, \rho < \rho_o, \rho_o = 0.85 \rho_e$$  \hspace{1cm} (A6)$$

$$F(\rho) = \sum_{i=0}^{3} F_i \left( \frac{\rho}{\rho_o} - 1 \right)^i, \rho_o \leq \rho < \rho_n, \rho_n = 1.15 \rho_e$$  \hspace{1cm} (A7)$$

$$F(\rho) = F_e \left[ 1 - \ln \left( \frac{\rho}{\rho_e} \right)^\eta \right] \left( \frac{\rho}{\rho_e} \right)^\rho, \rho \leq \rho_e$$  \hspace{1cm} (A8)$$

With this model, the parameters needed to define all the 16 metals are listed in Table A1.