Low energy ion assisted control of interfacial structure: Ion fluence effects

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Multilayered thin films consisting of high electrical conductivity copper layers sandwiched between pairs of low coercivity ferromagnetic alloys can exhibit giant magnetoresistance. The magnitude of the magnetoresistance increases with the structural and chemical perfection of the interfaces. Recent atomistic modeling and experimental observations have shown that nickel and cobalt atoms in the ferromagnetic layer readily exchange with underlying copper atoms during the deposition of the ferromagnetic layer upon the copper spacer. This results in mixing at the ferromagnetic metal on copper interface. Low energy (1–20 eV) inert gas ions can be used during deposition to flatten the surface of layers, in some cases without causing interlayer mixing. Here we use the molecular dynamics simulation method to investigate the effects of the assisting ion fluence upon the surface roughness and interlayer mixing of a model Ni/Cu/Ni multilayer system. The results reveal that the surface roughness initially drops rapidly with ion fluence and then approaches a limiting roughness that is dependent upon the surface type, the ion energy, and the ion mass. For a Cu on Ni surface irradiated by 2.0 eV Xe\(^{+}\) ions, the flattening transition occurs at a fluence of about 0.2 ions/Å\(^2\) (corresponding to an ion-to-metal deposition flux ratio of about 5). The same transition was seen at a similar fluence for a Ni on Cu surface, but at a higher Xe\(^{+}\) ion energy of 14.0 eV. Threshold energies for flattening and mixing were identified for various surfaces. The probabilities of both flattening and mixing were found to increase with ion fluence and ion energy. Because the threshold energy for mixing was lower than that for smoothing, significant interfacial mixing was only seen during ion assisted flattening of the Ni on Cu interface. Simple models have been developed to establish the functional dependence of interfacial structural parameters upon the assisting ion fluence. © 2000 American Institute of Physics. [S0021-8979(00)06022-9]

I. INTRODUCTION

Magnetic metal multilayers are the basis for several new magnetoelectronic devices.\(^1\) For instance, films composed of thin (~60 Å) ferromagnetic metals (such as Ni\(_{80}\)Fe\(_{20}\) or Co) sandwiching a thin (~20 Å) electrically conductive (e.g., Cu) metal layer can exhibit a large change in electrical resistance when a magnetic field is applied.\(^2–5\) This giant magnetoresistive (GMR) effect results from a change in electron spin dependent electron scattering due to a shift in the alignment of the magnetic moment of one of the magnetic layers.\(^6–8\) The effect can be sensed when a small electrical current is propagated either in the plane (CIP) or perpendicular to the plane (CPP) of the multilayers.\(^1\) A few repeats of the basic sandwich structure are used in CIP GMR multilayers to create spin valves.\(^9\) These structures have been used to build a new generation of read heads for magnetic hard drives, which is responsible for much of the recent increase in hard drive capacity.\(^1.9.10\) Several groups are attempting to use many repeats of the sandwich structure in a CPP architecture as a potential route to the creation of nonvolatile magnetic random access memory.\(^1\) The performance of either device is improved by increasing the GMR ratio (defined as the maximum resistance change divided by the resistance at magnetic saturation), lowering the saturation magnetic field, and increasing the thermal stability. These performance parameters depend upon the material system and the conditions used for growth. The best magnetoresistive performance for a particular material system is achieved when the interfacial roughness and the interlayer chemical mixing are minimized during growth by vapor deposition.\(^11.12\)

Interfacial roughness in multilayers grown under kinetically limited diffusion conditions is determined by the surface roughness of each layer at the start of the next layer’s overgrowth. This is controlled by a combination of thermodynamic and kinetic factors. A simple thermodynamic argument (Fig. 1) can be used to analyze the growth of an A/B/A multilayer (where B is deposited on A and vice versa). In Fig. 1(a), B atoms completely wet an A surface. This requires that the A and B surface energies, \(\gamma_A\) and \(\gamma_B\), as well as the B/A interface energy \(\gamma_{AB}\), satisfy the relation: \(\gamma_B + \gamma_{AB} < \gamma_A\). In the absence of kinetic constraints, atoms of B will then attach to ledges and epitaxially cover the A surface. However, under this condition, A atoms cannot completely wet a B surface since \(\gamma_A + \gamma_{AB} < \gamma_B + 2\gamma_{AB} > \gamma_B\). As Fig. 1(b) indicates, this promotes stable islands of A on a B surface because a nonzero angle \(\theta\) can be defined from

\[
\cos(\theta) = \frac{\gamma_B - \gamma_{AB}}{\gamma_A} \leq 1 - \frac{2\gamma_{AB}}{\gamma_A} < 1.
\]

This thermodynamic argument can also be understood atom-
isotactically. For the case discussed in Fig. 1, the bond energy between $A-A$ atoms is higher than that between $B-B$ atoms because bond energy scales with surface energy. If $A$ and $B$ atoms are of the same size, then $B$ wets $A$ because the more strongly bound $A$ atoms can pull $B$ atoms onto their surface [Fig. 1(a)]. This promotes $B$ layer growth by step flow across the surface, and the development of a smooth $B$ surface. However, $A$ will not then wet $B$ because it is energetically unfavorable for the relatively weakly bound $B$ atoms to break the strongly bound $A$ clusters [Fig. 1(b)].

The analyses above indicate that during the deposition of $A/B/A$ multilayers with little kinetic constraints, only one of the layers can nucleate and grow by the step flow growth mechanism. As a result, the potential for an asymmetric interfacial roughness always exists in nanoscale multilayered systems, especially when the surface energy difference is large. Significant stress driven surface roughness can also occur in systems where there is an atomic size difference, even when bond strength considerations favor step flow growth. Increasing the opportunity for atomic reassembly toward equilibrium by raising the substrate temperature or decreasing the deposition rate cannot then improve the smoothness of both the $A$ on $B$ and $B$ on $A$ interfaces in nanoscale multilayers. Such a strategy has not enhanced the performance of vapor deposited GMR films.

However, the use of hyperthermal adatoms can reduce the roughness of the $A$ on $B$ surface by breaking $A-A$ bonds in the $A$ islands and providing an opportunity for the $A$ atoms to attach to the $B$ surface. This is not the thermodynamically favored condition, but when this is done under thermally constrained diffusion conditions, the resulting $A-B$ bonds do not break to reform islands of $A$. This appears to be one reason why some energetic sputter deposition processes have produced better GMR films than those grown by molecular beam epitaxy where the atoms have low energies during impact with surface.

Sputter deposition experiments have indicated that both the interfacial roughness and the interlayer mixing are sensitive to the adatom energy used for the deposition. The lowest interfacial roughness and intermixing usually occur at an intermediate atom impact energy in the 1–3 eV range. Atomistic simulations have revealed the fundamental mechanisms of these incident energy effects. They indicated that increasing the incident energy reduced surface roughness because the energetic adatom impacts break strongly bound surface asperities, resulting in local nonequilibrium flat configurations. However, high incident atom energy also promotes interlayer mixing by an atomic exchange mechanism. These atomistic simulations have enabled an effective exploration of many deposition conditions that have not been addressed experimentally, including adatom incident angle and substrate rotation. The work has led to a proposal for the use of a modulated energy deposition strategy to improve both roughness and mixing during GMR multilayer deposition.

Ion assistance provides a second approach to controlling the interfaces of nanoscale multilayered systems. In this approach energetic inert gas ion impacts are used to break atomic scale clusters and to smooth a surface grown under conditions where thermal diffusion is limited. Atomistic simulations have again been used to explore the effects of inert gas ion assistance during multilayer deposition. The results indicated that low energy (<20 eV) ion impacts can effectively reduce the surface roughness, and provided the energy is sufficiently low, no mixing would occur. They also indicated the existence of two threshold energies above which there exists a high probability of either smoothing or mixing. Obviously, the extent of the smoothing or the intermixing is likely to depend upon the ion fluence.

Here, a molecular dynamics simulation approach has been used to investigate the effects of ion fluence on surface smoothing and interfacial intermixing. To bypass complexities associated with the variable surface roughness of each layer during a simulation of vapor deposition, we examine the effects of individual ion impacts with a model rough surface using the methodology developed in Ref. 23. For consistent comparisons with the previous work, we analyze model Ni/Cu/Ni multilayers with a (111) surface.

II. COMPUTATION METHOD

The molecular dynamics model for simulating the effects of inert gas ion impacts during multilayer deposition has been described in an earlier article. Examples of the computational crystals prior to the impacts are shown as parts (a) in Figs. 2 and 3. Cu and Ni crystals containing

![Diagram of growth modes at the interfaces between strongly bound A and weakly bound B atoms.](image)

**FIG. 1.** Growth modes at the interfaces between strongly bound $A$ and weakly bound $B$ atoms. In (a) step flow growth of $B$ is promoted. It results in the lowest surface energy configuration. In (b) the strong bonds between the $A$ atoms encourage the growth of $A$ islands and formation of a rougher surface.
72(224) planes in the x direction, eight (111) planes in the y direction, and 42(220) planes in the z direction were generated at the equilibrium lattice sites to represent a previously deposited layer. Arrays of either Cu or Ni pyramids were then created on top of these crystals to simulate a defined rough surface. The four possible materials scenarios corresponding to Cu on Cu, Cu on Ni, Ni on Cu, and Ni on Ni were all considered. To minimize the effects of small crystal size, periodic boundary conditions were used in the x and z directions and a fixed boundary condition was used for the two monolayers of atoms at the bottom y surface. This effectively extended the crystal scales both in the lateral and in the vertical dimensions. By using a temperature control algorithm, the three monolayers of atoms above the fixed region were kept at a fixed substrate temperature of 300 K. Inert gas ions with a given incident energy E were injected at a normal incident angle to the top y surface from random locations far above. A Cu–Ni alloy embedded atom method potential developed by Foiles was used to calculate the force between metal atoms and a universal pair potential was used to define the interaction between inert gas ions and metal atoms. The surface reconstruction following ion impacts was determined by solving the trajectories of both the metal atoms and the impacting ions using Newton’s equations of motion. To enable the system to relax between ion impacts, a low ion injection frequency of 2 ions/ps was used. Surface structures were analyzed at different ion fluences.

III. EFFECTS OF ION FLUENCE ON SURFACE ROUGHNESS

A. Atomic configurations

For the four surfaces (i.e., Cu on Cu, Cu on Ni, Ni on Cu, and Ni on Ni), simulations were carried out for both Ar\(^+\) and Xe\(^+\) ion impacts at various ion energies from 0.1 to 20 eV. The threshold energies for the flattening of these four surface have been determined, and are tabulated in Table I.

![Table I. Threshold energy (eV) of flattening for various surfaces and ions.](#)

<table>
<thead>
<tr>
<th>Impact ion</th>
<th>Cu on Cu</th>
<th>Cu on Ni</th>
<th>Ni on Cu</th>
<th>Ni on Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar(^+)</td>
<td>4</td>
<td>2</td>
<td>14</td>
<td>8</td>
</tr>
<tr>
<td>Xe(^+)</td>
<td>3</td>
<td>1</td>
<td>12</td>
<td>6</td>
</tr>
</tbody>
</table>

*See Ref. 23.

Selected atomic configurations for the Cu on Ni and the Ni on Cu surfaces are shown in Figs. 2 and 3 as a function of Ar\(^+\) and Xe\(^+\) ion fluences. The results for the Cu on Ni surface shown in Fig. 2 were obtained at an ion energy of 2 eV, while the results for the Ni on Cu surface shown in Fig. 3 were obtained at a much higher ion energy of 14 eV.

This is because the threshold energy for flattening of rough Ni surfaces is much higher than that for flattening of rough Cu surfaces (Table I). Figures 2 and 3 clearly show that the extent of the flattening due to the ion assistance depended...
upon ion fluence (or ion metal flux ratio during deposition). The surface roughness generally decreased as the ion fluence increased. Xe$^+$ ion impacts produced a more significant flattening effect at a given ion fluence.

**B. Functional dependence**

The surface roughness of the crystals studied here can be quantified by the fraction of atoms remaining above the first (bottom) monolayer of the islands.$^{23}$ This normalized surface roughness value was calculated as a function of ion fluence at several selected ion energies for both Ar$^+$ and Xe$^+$ ion impacts. The results for the Cu on Cu, Cu on Ni, Ni on Cu, and Ni on Ni systems are shown in Figs. 4–7 using filled and unfilled squares and circles (the curves in these figures were obtained using a continuum model described below). Results using higher ion energies are shown for the Ni islands. This choice complied with the threshold energies for the flattening of the different surfaces (Table I). Figures 4–7 indicate that while impacts with different surfaces by different ions were associated with different threshold ion energies of flattening, the surface roughness dependence upon the ion fluence at an energy above the threshold energy is quite similar for different cases. The 1 eV Ar$^+$ ion impacts with the Ni on Ni surface shown in Fig. 7 indicates that when the ion energy was below the threshold energy of flattening, the surface roughness remained at unity regardless of the ion fluence. For ion energies above the threshold, the surface roughness was seen to decrease with ion fluence and ion energy. It appeared that most of the surface roughness reduction was achieved as the ion fluence was increased to between 0.2 and 0.3 ions/Å$^2$; the roughness reduction with further fluence increase became relatively minor. At sufficiently high ion energies, the surface roughness approached zero with increasing ion fluence. Examination of Figs. 4–7 shows that at a given ion energy and ion fluence, Xe$^+$ ion impacts resulted in a lower roughness for all the surfaces.

**IV. EFFECTS OF ION FLUENCE ON INTERLAYER MIXING**

**A. Atomic configurations**

Figure 2 indicates that at a low ion energy of 2 eV, no mixing of the Cu island atoms with the underlying Ni atoms...
TABLE II. Threshold energy (eV) of mixing for various surfaces and ions.\(^a\)

<table>
<thead>
<tr>
<th>Impact ion</th>
<th>Cu on Cu</th>
<th>Cu on Ni</th>
<th>Ni on Cu</th>
<th>Ni on Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar(^+)</td>
<td>9</td>
<td>15</td>
<td>9</td>
<td>15</td>
</tr>
<tr>
<td>Xe(^+)</td>
<td>5</td>
<td>10</td>
<td>5</td>
<td>10</td>
</tr>
</tbody>
</table>

\(^a\)See Ref. 23.

occurred at any fluence during either the Ar\(^+\) or Xe\(^+\) ion impacts. The earlier study\(^{23}\) identified a material and ion specific threshold energy for mixing. These threshold energies are tabulated in Table II for different surfaces. It can be seen from Table II that in fact, no mixing occurs for the Cu on Ni surface until the ion energy is above 10 eV. However, Fig. 3 indicates that at the 14 eV ion energy necessary to flatten the Ni on Cu surface, significant mixing between the surface Ni atoms and the underlying Cu atoms occurred. The degree of mixing was higher for Xe\(^+\) ion impacts than for Ar\(^+\) ion impacts, and increased with ion fluence. These are all consistent with Table II that the threshold energy for mixing on the Ni on Cu surface is 9 eV for Ar\(^+\) ion impacts and 5 eV for Xe\(^+\) ion impacts.

**B. Functional dependence**

The extent of mixing can be quantified by the probability of atomic exchange during the ion impacts. Since the ion energy required for surface flattening exceeded the threshold energy of mixing only for the Ni on Cu surface, the mixing probability of surface atoms on this surface was calculated. The calculated data points at some selected ion energies for both Ar\(^+\) and Xe\(^+\) ion impacts are displayed in Fig. 8 as a function of ion fluence using filled and unfilled squares and circles (the curves were again obtained from a continuum model described below). It can be seen that mixing increased almost linearly with ion fluence. At a relatively low ion energy of 6 eV, both Ar\(^+\) and Xe\(^+\) impacts caused little mixing. At a higher energy of 14 eV, significant mixing occurred. At this energy Xe\(^+\) ions caused much more mixing than Ar\(^+\) ions.

**V. DISCUSSION**

Figures 4–8 indicate that the surface type, the ion species, and the ion energy all affect the functional dependence of the normalized surface roughness \(R\) and mixing \(M\) upon the ion fluence \(F\). An increasingly higher ion energy is required to flatten the Cu on Ni, the Cu on Cu, the Ni on Ni, and the Ni on Cu surfaces. By studying the energy contour over facets of various pyramids on the fcc surfaces and examining the trajectories of adatoms deposited on these facets using molecular dynamics, Halstead and DePristo have found that the surface morphology during growth is predominantly determined by the ratio of the diatomic binding energy to the bulk cohesive energy of the depositing species.\(^{26}\) Our work on the assisting ion energy effects indicated that the threshold ion energy of flattening decreased as ion mass was increased or the (net) energy change associated with the “rough to flat” cluster transition was decreased.\(^{23}\) More significant mixing was observed when the surface atoms were strongly bound (e.g., Ni) and the underlying atoms were weakly bound (e.g., Cu) than vice versa.\(^{23}\)

To evaluate the contributions of different atomic mechanisms to the results of Figs. 4–8, simple models were developed to predict surface roughness and mixing parameter as a function of ion fluence. To simplify the calculation of surface flattening, it was assumed that a nonplanar atom in a given surface asperity would become a planar atom during an ion impact when it is within a flattening distance \(r_0\) from the impact site. The flattening distance \(r_0\) is dependent upon the ion energy. For example, \(r_0 = 0\) at an ion energy below the threshold energy of flattening because even a head-on collision will not cause the flattening. In general, \(r_0\) increases as ion energy is increased. Suppose that the ion fluence during a short time interval \(t\) to \(t+\text{d}t\) is \(\text{d}F\), then the probability for a particular nonplanar atom to be flattened scales with \(\text{d}F\cdot \pi r_0^2\). Because the surface roughness is essentially the fraction of the nonplanar atoms, then the change of surface roughness \(\text{d}R\) caused by \(\text{d}F\) during random ion irradiation can be written as the fraction of flattened atoms

\[
\text{d}R = -R \pi r_0^2 \text{d}F. \tag{1}
\]

Integration of Eq. (1) yields a dependence of the roughness upon ion fluence

\[
R = \exp(-\pi r_0^2 F). \tag{2}
\]

Equation (2) can be used for constant energy ion impacts where island configurations remain constant. Figures 2 and 3 indicate that islands generally grow during ion irradiation. As the surface islands became bigger, the threshold energy of flattening increased. As a result, an ion energy can be above the threshold energy of flattening at the start of ion impacts, but can fall below it when the size of all the islands exceed a critical value \(S\). To develop a simplified model to account for this, it was assumed that all surface asperities can be divided into two types: type one with size below \(S\), and type two with
size above \( S \). Type one asperities can be flattened, and their average flattening distance is assumed to be \( r_0 \). Type two asperities cannot be flattened. The overall surface roughness can then be expressed as \( R = R_1 + R_2 \), where \( R_1 \) and \( R_2 \) correspond to the fractions of nonplanar atoms in type one and type two surface asperities, respectively. By fitting to the energy dependent saturation surface \( R \) and Ni on Cu.

Nonetheless, it is clear that rough surfaces can be flattened to metal flux ratio of 5. In general, it will depend upon the statistics of random ion impact sites. For the present extreme case where all the 120 deposited metal atoms formed the pyramids, this ion fluence corresponded roughly to an ion to metal flux ratio of 5. In general, it will depend upon the propensity for roughing, which in turn depends upon material system, substrate temperature, and metal atoms flux. Nonetheless, it is clear that rough surfaces can be flattened using an appropriate low energy ion fluence.

To explore the effects of ion fluence upon mixing parameter at the Ni on Cu surface, we considered a surface monolayer that contains \( N_{Ni} \) Ni atoms and \( N_{Cu} \) Cu atoms, and has a total area of \( S \). If the total number of atoms on this monolayer is \( N_0 = N_{Ni} + N_{Cu} \), then the number of ions impacting with Ni atoms during an ion fluence of \( dF \) can be approximated by

\[
\frac{dN}{N_0} = \frac{N_{Ni}}{N_0} \cdot S dF = \frac{N_{Ni0}(1 - M)}{N_0} \cdot S dF,
\]

where \( N_{Ni0} \) is number of Ni surface atoms before ion impacts, and the mixing parameter \( M \) can be viewed as the fraction of exchanged (mixed Ni) atoms. Each ion impacting a Ni atom has a probability \( p \) for the exchange between the Ni atom and an underlying Cu atom. Obviously, \( p \) increases as ion energy is increased. The change of mixing \( dM \) due to \( dF \), can then be approximated by

\[
dM = p \cdot \frac{dN}{N_{Ni0}} = \frac{(1 - M)}{N_0} \cdot S dF,
\]

Integration of Eq. (10) yields an expression for the mixing parameter:
For the crystals used here, \(S\) atoms and underlying \(B\) ties and the threshold energies for breaking asperities. The corresponded to an ion to metal flux ratio of 5.

This decreased with ion fluence and approached zero. The flattening dependence upon ion fluence was determined as a function of ion fluence for \(\text{Ar}^+\) and \(\text{Xe}^+\) ions. The results here indicated that at a given ion energy, \(\text{Xe}^+\) ions have a lower threshold energy for mixing than \(\text{Ar}^+\) ions. The results here indicated that at a given ion energy, \(\text{Xe}^+\) ions caused much higher degrees of mixing at various ion fluences, especially when the ion energy is high.

VI. CONCLUSIONS

Molecular dynamics simulations of the \(\text{Ar}^+\) and \(\text{Xe}^+\) ion impacts with various rough surfaces formed during the Ni/Cu multilayer growth indicated that:

At low ion energies, surface roughness was independent of ion fluence. At high ion energies, the surface roughness decreased with ion fluence and approached zero.

For ion energies below 20 eV, most of the flattening was achieved when the ion fluence had reached 0.2 ions/Å². This corresponded to an ion to metal flux ratio of 5.

The flattening dependence upon ion fluence was determined by the probability of ion impact with surface asperities and the threshold energies for breaking asperities. The threshold energy increased in going from Cu on Ni, Cu on Cu, Ni on Ni, to Ni on Cu surfaces.

The ion fluence dependence of mixing between surface \(B\) atoms and underlying \(A\) atoms was mainly dependent upon the probability of ion impact with surface \(B\) atoms and the subsequent exchange probability. The mixing probability was much higher when the underlying crystal was Cu rather than Ni.

Heavier \(\text{Xe}^+\) ions produced more smoothing and mixing because of their more efficient momentum transfer to the metal atoms per impact.

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12 W. H. Butler (private communication).