The low energy ion assisted control of interfacial structure: ion incident angle effects

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Abstract

It is difficult to maintain smooth unmixed interfaces during the vapor deposition of giant magnetoresistive multilayers, especially as the number of layers is increased. Recent atomistic modeling of normal incident angle ion impacts with model Ni/Cu/Ni multilayer surfaces have indicated that low energy (3 eV) inert gas ion bombardment significantly reduced the roughness of Cu on Ni interfaces without causing interlayer mixing. Higher ion energies (12 eV or above) were necessary to achieve similar smoothing of the Ni on Cu interface, but this was accompanied by extensive mixing between the surface Ni atoms and the underlying Cu atoms by an impact ion induced exchange mechanism. Here, molecular dynamics simulations have been used to explore the effect of varying the incident ion angle during 12 eV Ar$^+$ and Xe$^+$ ion bombardment of a model Ni on Cu surface. The results indicate that increasing the incident ion angle up to 70° reduced the probability of intermixing while retaining most of the surface flattening effect seen in the previous study. A low combination of interfacial roughness and intermixing was obtained for an incident ion angle of approximately 60°. The heavier Xe$^+$ ions were found to transfer more momentum to the surface atoms than the lighter Ar$^+$ ions, and resulted in significantly more mixing at all angles of incidence. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Multilayer structures with atomically sharp interfaces can exhibit technologically useful properties not possessed by their component materials alone. For instance, giant magnetoresistance (GMR) is observed when thin electrically conductive metal layers (such as Cu) are sandwiched between pairs of low coercivity ferromagnetic (e.g., permalloy) layers [1–3]. The effect can be observed as a large (5–50%) change in resistance to the propagation of a small electric current through the layers when a magnetic field is applied. It occurs because of a change in spin dependent electron scattering when the relative orientation of the magnetic moments in the ferromagnetic layers is changed [4–6]. These GMR materials are the basis for a number of magnetoelectronic devices including non-volatile magnetic random access memory and the read head sensor in hard disk drives [7–9].
Both experimental and theoretical studies have indicated that the properties of GMR multilayers are sensitive to the atomic scale structure of the devices. Because the thickness of each layer is small (typically around 20 Å for the conductive layer [1] and 60 Å for the magnetic layer [10]), the best GMR properties are obtained when the roughness of interfaces and the chemical mixing between layers are both minimized [11,12]. A thermodynamics analysis indicated that the use of high substrate temperature and low deposition rate cannot result in nanoscale multilayers with all their interfaces flat [13]. To avoid intermixing of the layers by thermally induced diffusion, GMR films are usually composed of materials pairs with large miscibility gaps, and are deposited at low (near ambient) temperatures [14]. Experiments have shown that the interfacial roughness and interlayer mixing are then very sensitive to the incident adatom energy [15–18]. The best performance GMR films are obtained using vapor deposition approaches such as plasma or ion beam sputtering that result in moderate incident metal atom energies of a few electron volts [15–18].

Molecular dynamics (MD) simulations of the vapor deposition of model Ni/Cu/Ni multilayers have indicated that increasing the incident adatom energy lowers the interfacial roughness by primary knock-on of atoms attached to surface asperities [19]. However this can also be accompanied by interlayer intermixing by an impact induced atomic exchange mechanism. MD results have shown that the optimum (smallest) combination of interfacial roughness and intermixing occurs at an intermediate incident energy of around 1–3 eV [19]. Similar simulations have indicated that the shadowing associated with a high adatom incident angle results in an increase in both interfacial roughness and intermixing [20]. Substrate rotation can reduce the shadowing (and hence the interfacial roughness) under low energy and oblique angle deposition conditions [20]. Analyses of the simulations have also led to the proposition of a modulated energy deposition strategy for minimizing the interface roughness and mixing [19,20]. In this approach, low (~0.1 eV) incident energies are used to deposit the first few monolayers of a new material layer (thereby limiting intermixing) and higher energies (e.g., 5 eV) are used for the remainder of the layer to ensure its flatness. The simulations indicated that multilayers with flat interfaces and almost no intermixing could be grown over a wide range of incident angles with or without substrate rotation using this approach [20].

During the growth of thin films, it is well known that the growth surface almost always becomes rougher as film thickness increases. The use of inert gas ion assistance to reduce surface roughness then becomes attractive. Because modulated energy deposition and ion beam assisted deposition (using either Ar⁺ or Xe⁺ ions) can both be easily implemented in an ion beam deposition system, interest has grown in designing ion beam deposition processes for GMR multilayer structures [21]. The implementation of an ion beam assisted deposition scheme requires knowledge of ion impact effects on the interfacial structures of multilayer surfaces. A recent MD simulation of ion assisted multilayer growth indicated that interface flattening without intermixing could be achieved using a modulated low energy ion assistance strategy [22]. A follow up MD study more systematically explored the mechanisms by which normal incident inert gas ion impacts affected surface morphology [13,23]. Simulations of normal incident angle Ar⁺ and Xe⁺ impacts with the model surfaces like those encountered during the [1 1 1] growth of Ni/Cu/Ni multilayers indicated that ion energies in the 4–9 eV range could be used to flatten Cu asperities on Cu as well as Ni asperities on Ni surfaces [23]. Because the flattening of Cu asperities on a Ni surface occurred at ion energies below 3 eV while mixing between the surface Cu atoms and the underlying Ni atoms only became significant at ion energies above 9 eV, normal incident angle ion assistance in the 3–6 eV range appears to be a robust approach to control Cu asperities on Ni surfaces. However, similar ion assistance strategies resulted in extensive mixing when Ni was deposited on an underlying Cu surface, even at the lowest (~12 eV) ion energy that needed to flatten the Ni on Cu surface. The resulting asymmetrical interfacial structures accompanying a permalloy/copper/permalloy deposition sequence have been recently observed using three dimensional (3D) atom probe techniques [24].
Ion impact induced flattening and mixing are a direct consequence of the transfer of momentum from an incident ion to atoms near the impact point on the surface. The effects are therefore likely to depend upon the angle of ion impact. Here, the MD approach used in earlier studies has been extended to investigate the effect of incident ion angle for 12 eV Ar+ and Xe+ impacts with Ni asperities on a (111) Cu surface.

2. Computation method

Details of the MD model for studying inert gas ion impacts with a metal surface have been described in earlier papers [13,23]. Briefly, a Cu–Ni alloy embedded atom method potential developed by Foiles [25] was used to calculate the forces between metal atoms, and a universal potential [26] was used to define the interactions between inert gas ions and metal atoms. The initial crystal before ion impacts is illustrated in Fig. 1. The lower part of the crystal (lightly shaded) is copper. It contains 72 (2 2 4) planes in the x direction, 8 (1 1 1) planes in the y direction, and 42 (2 2 0) planes in the z direction. An array of nickel pyramids (darkly shaded) was constructed on the copper surface to mimic the “rough” nickel islands nucleated on an underlying copper crystal. During the simulations, a periodic boundary condition was used in the x and z directions, and the atoms in the two monolayers at the bottom (y) surface were fixed at their equilibrium positions [13,23]. The atoms located three monolayers below the copper surface were constrained at a substrate temperature of 300 K [13,23]. Ions with a kinetic energy of 12 eV and an incident angle, $\theta$, were injected towards the top (y) surface at 2 ions/ps from random locations far above. To uniquely define a 3D direction with a single angle, the incident direction was constrained in the $x$–$y$ plane (see Fig. 1). The surface evolution was then tracked by solving for the trajectories of both the atoms and the impacting ions using Newton’s equations of motion.

3. Surface roughness

3.1. Atomic configurations

Simulations of Ar+ and Xe+ ion impacts with a model rough Ni on Cu surface were conducted for a range of ion incident angles. Selected atomic configurations following 1500 Ar+ and Xe+ ion impacts (corresponding to a fluence of ~0.5 ions/Å²) are shown in Figs. 2 and 3, respectively. Fig.

![Diagram](image-url)  
**Fig. 1.** Crystal geometry used for the simulation.
Fig. 2. Evolution of Ni islands on underlying Cu during 12 eV Ar⁺ ion impacts.

2(a)–(c) indicates that most of the pyramidal Ni islands were reduced to monolayers following 12 eV Ar⁺ ion impacts at incident angles ranging from 0° to 70°. However, Fig. 2(d) shows that none of the non-planar Ni clusters were fully reduced when 12 eV Ar⁺ ion impacts had an impact angle of 85° and beyond. Hence, while 12 eV Ar⁺ ion impacts could be used to flatten the Ni on Cu surface over a wide ion angle range between 0° and 70°, the flattening effect quickly diminished as the
ion angle increased above 70°. It is also interesting to note that the Ni monolayer islands formed during the low angle (0–15°) ion impacts were smaller than those formed during higher angle (such as 70°) impacts. This arose because the lateral momentum of obliquely incident ions promoted a lateral migration of the surface atoms and the connection of adjacent islands.

The effects of Xe⁺ ion impacts were quite similar to those of Ar⁺ ion impacts. Fig. 3(a)–(c) shows that all of the non-planar Ni islands were flattened after 12 eV Xe⁺ ion impacts at ion angles between

Fig. 3. Evolution of Ni islands on underlying Cu during 12 eV Xe⁺ ion impacts.
0° and 70°. Fig. 3(d) indicates that all of the Ni islands remained non-planar following 12 eV Xe⁺ ion impacts above an ion angle of 85°. The small Ni monolayer islands seen at low Xe⁺ incident angles (Fig. 3(a) and (b)) were again observed to coalesce into large monolayer islands at a high Xe⁺ incident angle (Fig. 3(c)). This suggests that oblique low energy ion assistance may also be a potent means for controlling the grain size of polycrystalline films.

3.2. Functional dependences

For the Ni on Cu surface studied here, a normalized surface roughness is defined as the fraction of nickel atoms remaining more than one monolayer above the copper surface. Impacts may cause the underlying copper atoms to be ejected onto the surface, resulting in the formation of vacancies and related surface roughness. Since the probability for the atoms to be ejected to the second monolayers above the copper crystal is small, the vacancy caused surface roughness will not affect the normalized roughness parameter. Under this condition, the normalized roughness parameter measures the extent by which three dimensional surface asperities become planar configurations. The roughness parameter was calculated and the results are plotted in Fig. 4. It can be seen that the surface roughness was relatively independent of the ion incident angle over a 0–75° range, but then started to rapidly increase as the angle was increased above 75°. This indicates that the flattening effect observed earlier for normal ion incidence [23] is retained over a wide range of ion angles.

4. Interlayer mixing

4.1. Atomic configurations

Fig. 2(a) and (b) indicates that at low (0–15°) incident angles, 12 eV Ar⁺ impacts both ejected the underlying Cu atoms onto the surface (creating vacancies in the Cu layer) and cause surface Ni atoms to be exchanged with underlying Cu atoms. It can be seen that both mechanisms contributed to a significant interlayer mixing following ion irradiation. Increasing the Ar⁺ ion incident angle resulted in a decrease in mixing. Beyond an Ar⁺ ion incident angle of 70°, no mixing could be observed (Fig. 2(c) and (d)). A similar mixing phenomenon was also found after 12 eV Xe⁺ impacts (Fig. 3). The extent of mixing caused by the Xe⁺ impacts was significantly higher than that caused by Ar⁺ impacts, especially at near normal (0°) incident angles.

![Fig. 4. Surface roughness as a function of ion incident angle.](image-url)
4.2. Functional dependences

A normalized mixing parameter was defined as the fraction of the Ni surface atoms that were exchanged into the underlying Cu crystal after 1500 ion bombardments. This mixing parameter was calculated for various ion incident angles, and the results are shown in Fig. 5 for both ions. It can be seen that the functional dependence of mixing upon the ion angle is similar for both Ar$^+$ and Xe$^+$ impacts. The mixing probability initially decreased as the ion angle was increased from normal incidence to about 5°. The mixing probability then increased with ion angle until it reached a local maximum at about 15°. Thereafter, the mixing probability rapidly decreased with ion incident angle. At ion angles above 50° for argon and 80° for xenon, mixing was essentially negligible. Xe$^+$ ion impacts resulted in significantly more mixing over the entire ion incident angle range.

5. Discussion

Simulations of 12 eV ion impacts indicate that Ar$^+$ and Xe$^+$ ions had similar effects on surface smoothing. Flattening of the Ni on Cu surface is possible over a wide range of impact angle between 0° and 75° with either ions. However, the flattening effect quickly disappeared as the incident angle was raised above 75°. It has been shown that adatoms impacting a flat surface at oblique incident angles can be reflected almost elastically, with almost no energy transferred to the surface during such a reflection event [27]. To explore the energy transfer during off-normal incident angle ion impacts, the average energy transferred to the surface per ion impact was calculated (from the energy difference of the incident and reflected ions) for the 1500 ion impacts with the Ni on Cu surface. The results of this calculation are shown in Fig. 6 (using symbols and solid lines). It can be seen in Fig. 6 that the transferred energy decreased rapidly with ion incident angle, and that the heavier Xe$^+$ ions transferred more of their energy than Ar$^+$ ions (especially at lower ion angles). For instance, an Ar$^+$ ion transferred about 8 eV while a Xe$^+$ ion transferred about 10 eV at the normal incidence, whereas the Ar$^+$ and Xe$^+$ ions transferred only about 1 eV at an incident angle of 75°.

This behavior can be qualitatively described by a simple two-particle collision model shown in Fig. 7. Suppose that an ion with a mass $m$ collides with a part of the surface with a mass of $M$ during the impact at an incident angle of $\theta$. The total ion energy before impact, $E$, can be partitioned into...
two parts \(E \cos(\theta)^2\) and \(E \sin(\theta)^2\), related to the momentum components in the vertical and horizontal directions respectively. Because the energy transfer to the surface results mainly from the vertical momentum component, the energy transfer due to the horizontal momentum component can be ignored, at least to a first order approximation. If the surface material in the zone of interaction (with mass \(M\)) is initially stationary, then the energy transfer due to the vertical momentum is simply \(\Delta E = \left(4mM/(m+M)^3\right)E\cos(\theta)^2\). By fitting to MD results, \(M/m\) was obtained to be 3.82 for \(\text{Ar}^+\) ion and 1.95 for \(\text{Xe}^+\) ion. The fitted curves are shown as the dash lines in Fig. 6. Despite of the approximations that \(M\) is independent of the incident angle and the lateral momentum transfer is ignored, the “two-particle” collision model captures the trend seen in the MD results. Because the atomic mass \(m\) for \(\text{Ar}^+\) and \(\text{Xe}^+\) ions is 40 and 129 amu respectively, the “two-particle” collision model predicted that metal masses \(M\) of 153 and 252 amu interacted with \(\text{Ar}^+\) and \(\text{Xe}^+\) ions relatively weakly.
spectively. As the atomic masses for Cu and Ni atoms are 64 and 59 amu respectively, the Ar⁺ ion impact appear to have interacted with about two surface atoms while the heavier Xe⁺ ions interacted with about five surface atoms. The significant transferred energy is an indication of strong impacts between the ions and surface islands, and accounts for the flattening observed at the ion angles below 75°. As the ion angle was increased above 80°, it can be seen that the transferred energy quickly dropped to zero and the elastic reflection of ions became dominant, resulting in a loss of flattening.

Mixing at first decreased as the ion incident angle was raised from 0° to about 5° (Fig. 5). The mixing then increased with ion angle until it reached a local maximum at 15°. Thereafter, mixing continuously decreased as the ion angle was increased from 15° to 90°. To more clearly study this, time lapse results were examined. Single Ni atoms were placed on the surface of a Cu crystal. Head-on collisions between 12 eV Xe⁺ ions and the Ni atoms were then simulated. Snapshots of the crystal as well as a 2D projection of the two (2 2 0) atomic monolayers near the impact plane are shown in Fig. 8(a)–(d) as a function of time. For clarity, only part of the crystal is displayed. To better observe the trajectory of individual atoms, some atoms in the projection are marked with (●), (■), and (○) symbols. Fig. 8(a) shows four 12 eV Xe⁺ ion impacts with four Ni atoms at four incident angles, 0°, 5°, 15°, and 60°. In the 2D projection, the incident directions are marked with dash lines. The three Ni atoms that were impacted

Fig. 8. Atomic exchange processes during ion impacts at different ion incident angles.
at angles of 0°, 5°, and 15° are seen in Fig. 8(b) to have all penetrated into the underlying Cu crystal within 0.3 ps of impacts initiation. However, when a Ni atom was impacted by an ion at 60°, it was observed to migrate on the Cu surface by a small lateral distance in the direction of ion incidence. Observation of the 2D projection indicates that during normal incident ion impact, Ni penetration occurred when the atom marked by (●) was pushed toward the interior of the lattice. On the other hand, the lateral momentum of the incident ions at the 5° and 15° incident angles was transferred to the Ni atoms, which in turn was transferred to the (●) atoms. As a result, less downward movement was seen for the (●) atoms. Because the incident line that went through the center of the Ni atom was above the center of the nearest Cu atom (see Fig. 8(a)), no Ni penetration occurred at the 60° ion incident angle.

At 0.5 ps (Fig. 8(c)) the lateral momentum acquired by the (●) atoms during the 5° and 15° ion impacts had transferred to the (○) atoms. This resulted in the (○) atoms being ejected onto the surface, the (●) atoms taking the original sites of the (○) atoms, and the Ni atoms occupying the original sites of the (●) atoms, etc. For a normal ion incidence, the (●) atom started to bounce back, but the exchange had not been accomplished by this time. At a later time of 1.0 ps (Fig. 8(d)) the (●) atom had then bounced back sufficiently to allow the (○) atom to be ejected onto the surface. During this process, the (○) atom occupied the original site of the Ni atom, the Ni atom took the original site of the (●) atom, and the (●) atom came to rest in the original (○) atom site.

From the analysis described above, it can be seen that at an intermediate ion incident angle (such as 15°), the probability of atomic exchange is high because the incident line points to a low energy lattice channel (between the (●) and (■) atoms in Fig. 8(a)) and the lateral momentum transfer facilitates the subsequent atomic jumps in a direction of the exchange. The exchange probability may be reduced at near normal ion incidence because either less lateral momentum is available or the incident line may align with a harder lattice direction (such as pointing to the center of the (■) atom in Fig. 8(a)) which inhibits the lattice penetration and the subsequent atomic exchange. The exchange probability continuously decreases as ion angle increases above 15° because of a gradual transition of Ni penetration into the Cu lattice to Ni migration on the Cu surface. This is consistent with the finding in Fig. 5 that mixing was a maximum at an ion angle of about 15°, and then continuously decreased to zero at 90°. It is also consistent with the finding in Fig. 6 that the ion transferred energy decreased with ion angle. Because Xe+ transferred more energy and interacted with more surface atoms than Ar+, the extent of mixing formed during Xe+ impacts is expected to be higher than that formed during Ar+ impacts.

To design a low energy ion assisted deposition process for a multilayer material system, the effects of material properties upon roughness and mixing must be understood. Detailed analysis indicated that as the cohesive energy of the atoms forming the non-planar islands is increased or the cohesive energy of the underlying atoms is decreased, the ion energy required to flatten the non-planar structure is increased. For instance, the cohesive energies of copper and nickel are 3.54 and 4.45 eV respectively [25]. The ion energy required to flatten copper on copper and the copper on nickel surfaces is significantly lower than that required to flatten the nickel on nickel and the nickel on copper surfaces [23]. During deposition of either copper or nickel, the ion energy for multilayer surface flattening is lower if the subsurface material is nickel rather than copper [23].

This cohesive energy effects can be easily understood. The cohesive energy of the overlying atoms is related to the energy required to break their bonds with the non-planar configuration, and the cohesive energy of the underlying atoms contributes to the energy that can be reduced by forming the bonds with the underlying surface. The combination of the cohesive energies of atoms in the overlying and underlying crystals then measures the energy change ΔE associated with the flattening. The energy difference between a non-planar and a planar surface cluster composed of ten atoms has been used to quantify the energy change during the flattening [23]. The values of ΔE and surface roughness following ion impacts have also been calculated for the eight different surfaces.
in the Cu–Ni and the Ag–Au systems [23]. Based upon these calculations, the $\Delta E$ dependence of the surface roughness after 1500 Ar ion impacts at normal incidence was obtained, and the results are shown in Fig. 9. It can be seen from Fig. 9 that for most surfaces, flattening reduces the energy. This is because flattening always results in extra bond formation. The Ni on Cu surface is an exception. The flattening of the Ni on Cu surface would require some of the nickel–nickel bonds to be broken up to form the copper–nickel bonds. Because the binding energy between nickel–nickel atoms is much lower (larger negative value) than that between nickel–copper atoms, the energy reduction due to the extra bond formation cannot compensate the energy increase due to the change of the bond types. As a result, the flattening of the nickel on copper surface is associated with an energy increase. Generally, lower cohesive energy atoms on a higher cohesive energy surface, such as the Cu on Ni and the Ag on Au, are seen to have the largest energy decreases during the flattening. Fig. 9 indicates that in general, high surface roughness occurs in the material systems with high $\Delta E$. One exception to this is the Ni on Ni surface which has a large negative values of $\Delta E$, but has an abnormally high surface roughness after ion impacts. It was found that the strongly bonded Ni cluster is associated with a big energy barrier during the rough to flat transition [23]. Consequently, the Ni on Ni surface remained rough after the ion impacts.

During ion impact, mixing could occur only when an ion or a surface atom penetrated an underlying lattice and caused the ejection of an underlying atom onto the surface. As a result, ion induced mixing is sensitive to the species of the underlying atoms, but is less dependent on the surface atoms. Generally, ion penetration is more likely to occur when the cohesive energy of the underlying surface is lower. Because the binding between copper atoms is much weaker than that between nickel atoms, mixing is much more significant when the underlying material is copper rather than nickel.

It is interesting to note that ion impact induced flattening was retained over a wide ion angle range (from $0^\circ$ to $75^\circ$) while ion impact induced mixing was not significant at oblique ion incident angles $>60^\circ$. This observation suggests that the use of ion assistance at a relatively high ion incident angle, $60^\circ < \theta < 75^\circ$, can induce flattening without mixing during the deposition of a strongly bonded (high surface energy) material on a more weakly
bonded (lower surface energy) material. This observation may be of significance for ongoing efforts to grow GMR spin valves and multilayers.

6. Conclusions

MD simulations have been used to quantify the incident angle effects of 12 eV Ar\(^+\) and Xe\(^+\) ion impacts with the Ni on Cu surface during the Ni/Cu/Ni multilayer deposition. The simulations have indicated that:

1. Increasing the ion incident angle from 0\(^\circ\) to 75\(^\circ\) retains most of the flattening effect observed at a normal ion incident angle. The flattening effect quickly disappears as the ion angle is increased above 75\(^\circ\).
2. Mixing can be reduced by increasing the ion incident angle. Flattening with minimal mixing can be achieved using ion incident angles between 65\(^\circ\) and 75\(^\circ\).
3. High angle ion impacts promote the lateral migration of surface islands and lead to their coalescence.
4. At 12 eV, Ar\(^+\) and Xe\(^+\) ions have a similar flattening effect, but the Xe\(^+\) ions induce more significant mixing.
5. The energy transferred to the surface per ion impact decreases with ion incident angle. The heavier Xe\(^+\) ions transfer more energy than Ar\(^+\) ions.
6. Surface roughness is reduced when the cohesive energy of the overlying atoms is decreased and the cohesive energy of the underlying atoms is increased. Mixing is reduced when the cohesive energy of the underlying atoms is increased.

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