Low-energy ion-assisted control of interfacial structures in metallic multilayers

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Abstract

A molecular dynamics method has been used to simulate the argon ion-assisted deposition of Cu/Co/Cu multilayers and to explore ion beam assistance strategies that can be used during or after the growth of each layer to control interfacial structures. A low-argon ion energy of 5–10 eV was found to minimize a combination of interfacial roughness and interlayer mixing (alloying) during the ion-assisted deposition of multilayers. However, complete flattening with simultaneous ion assistance could not be achieved without some mixing between the layers when a constant ion energy approach was used. It was found that multilayers with lower interfacial roughness and intermixing could be grown either by modulating the ion energy during the growth of each metal layer or by utilizing ion assistance only after the completion of each layers deposition. In these latter approaches, relatively high-energy ions could be used since the interface is buried and less susceptible to intermixing. The interlayer mixing dependence upon the thickness of the over layer has been determined as a function of ion energy.

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1. Introduction

Metallic thin-film multilayers can possess high strength and hardness \([1–5]\) and sometimes exhibit unusual electron transport properties such as giant magnetoresistance \([6,7]\), which is utilized for magnetic field sensing \([8]\) and other spin-based devices \([9]\). Metal superlattice structures also have tunable high reflectivity that has led to their use in X-ray, soft X-ray, and extreme ultraviolet (EUV) telescopes for solar physics and astronomical research \([10–12]\). These applications utilize multilayers that are composed of many metal layers ranging from a few monolayers to several nanometers in thickness.

The roughness and degree of intermixing at the interfaces between the metal layers in multilayer films can greatly affect their properties \([13–15]\). While the role of interface structures upon the magnetotransport \([6,7,13–15]\) and optical properties \([10,11]\) of thin films has been extensively studied, the mechanisms that control interfacial roughness and intermixing during multilayer growth have only recently begun to be addressed. Several experimental studies have sought to understand the kinetic and thermodynamic factors controlling the growth of thin films and multilayers by changing the growth temperature or using plasma-based methods to increase adatom mobility \([10,16–18]\). The best metal superlattices are usually grown at relatively low homologous temperatures to avoid interdiffusion across interfaces. However, these conditions can result in the formation of rough interfaces and other defects \([19]\).

Ion beams \([17]\) and plasmas \([10,20]\) are widely used to induce inert gas ion impacts with growth surfaces. This results in local energy transfer to surface atoms and enhanced surface atom mobility and enables use of a low
epitaxial growth temperature to avoid interlayer diffusion in the subsurface region [21–23]. However, conventional ion beam-assisted deposition processes utilize high-energy ion fluxes in the 50 eV to 5 keV range during metal deposition. While these have been successfully used to create flat surfaces on thick monolithic films [21,22], these ion energies exceed the damage threshold energy for multilayers with nanoscopic layer thicknesses and result in significant interlayer mixing [24,25].

Molecular dynamics (MD) simulations have been used to explore the atomic assembly mechanisms during the vapor deposition of metallic multilayers [26–29]. The structures predicted by these accelerated deposition rate simulations are surprisingly similar to those observed by three-dimensional atomic probe techniques [30]. The predicted misfit dislocation structures are also similar to those observed by high-resolution transmission electron microscopy [31,32]. Recent simulations of ion interactions with a model Co-on-Cu bilayer system indicate that low (5–10 eV) energy impacts can be highly effective at flattening small (10 atoms) cobalt clusters on (1 1 1) copper surfaces without inducing interfacial alloying [24,33,34]. They also reveal that appropriate combinations of ion species (mass), ion energy, ion fluence, and ion incident angle can be used to selectively activate either atom recoil, atomic exchange, or direct jumping mechanisms to flatten surface asperities [24,33]. These studies further indicate that nearly perfect multilayer structures can be vapor deposited using ion assistance if the ion energy is maintained between the critical energies for flattening and intermixing. These energies and the energy gap depend on the ion incident angle and ion mass. The widest critical energy gap is achieved for an ion incident angle around 50° from surface normal (which avoids easy atom penetration in crystal channeling directions) using an ion mass comparable to that of the metals [33].

There are many ways, in which a low-energy ion assistance method could be used to control the assembly of a metal multilayer thin film. In the example above, constant energy ion bombardment was used simultaneously with the deposition process. However, the ion energy could also be varied (modulated) during the metals deposition, or the ion bombardment could be applied only after each metal layer had been deposited (sequential assistance). Here, we utilize MD simulations to investigate these three ion assistance approaches for controlling the interfacial structures of a model Cu/Co/Cu trilayer system. Several near-optimal processes for the growth of metallic superlattices with chemically sharp, planar interfaces are identified.

2. Simulation methodology

2.1. Molecular dynamics simulation

In MD simulations, a computational crystal is created by assigning the positions of atoms to an assembly of lattice sites. An interatomic potential is then used to calculate the forces between atoms, and Newton’s equations of motion are used to calculate the velocities and positions of all atoms. This approach dynamically solves for atom vibration around the occupied lattice sites. It also naturally incorporates the energy barriers for the various jump paths and correctly simulates the thermally activated jumps of the vibrating surface atoms from one local energy minimum site to another. The various hyperthermal impact effects can also be accurately represented by Newton’s equations of motion. Hence, MD captures all of the complicated atomic assembly phenomena described above.

The model system analyzed consisted of a Cu substrate made up of 72 (2 2 4) planes in the x direction, eight (1 1 1) planes in the y (growth) direction, and 42 (2 5 0) planes in the z direction. To minimize the effect of the small crystal size, periodic boundary conditions were used in both the x and z directions so that the simulated surface was extended infinitely in these two directions. A free boundary condition was used for the y surface. To avoid a crystal shift due to the ion impacts with the top surface, the coordinates of the atoms in the bottom two (1 1 1) Cu layers were fixed during simulation. The crystal was kept at a constant film temperature of 300 K by applying damping forces to a region below the surface [35].

The numerical scheme of MD simulations requires the use of short time step (10−15 s) to solve for the dynamics of lattice vibration. As a result, MD can only simulate a very short (10−9–10−8 s) process. High ion/adatom fluxes must be used in order to simulate a sufficient number of ion/adatom impacts within the available computational time. Deposition and ion assistance were simulated by injecting metal and argon ion atoms toward the surface at an angle, θ, to the [1 1 1] direction in the (1 1 0) plane. The incident particles were assigned an incident energy, $E_i$. First, a cobalt and then a copper layer were deposited onto an initially flat (1 1 1) copper surface. For all simulations, a fixed deposition rate of 1 nm/ns and an adatom energy of 0.5 eV were used. Ion/adatom flux ratios of two and four were used for simulations of simultaneous and modulated energy ion assistance schemes, respectively. An ion fluence of 0.5 ions/Å² was used to assess sequential ion assistance schemes. Under these high rates of ion/adatom impacts, the time for the thermal diffusion of atoms on a free surface was significantly shortened. Nonetheless, the simulated conditions were carefully chosen to ensure that the time interval between ion or adatom arrival was at least 0.15 ps or above. This time interval allows the impact-induced surface reconstructions to be realistically captured and should allow the effects of assisting ions to be accurately predicted [24,33]. The study was restricted to argon ion effects since it is the most commonly used inert gas in ion-assisted vapor deposition experiments. The magnitude of ion assistance effects are dependent upon the ion mass and are described in the previous study [24].
2.2. Interatomic potentials

MD simulations yield reliable results only when high fidelity interatomic potentials are used to calculate the interatomic forces. For closely packed metals such as Cu and Co studied here, the embedded atom method (EAM) potential initially proposed by Baskes and Daw [36] meets this requirement [30,35]. The EAM potentials developed for elemental metals cannot be directly used to study alloys [37]. Alloy interactions are important and must be incorporated. Here, we use an alloy EAM model that incorporates interactions between Cu and Co atoms [30,37].

In previous simulations of low-energy inert gas bombardment of a metal surface [24,33], interactions between inert gas ions and metal atoms were found to be well represented by a universal pair potential derived from experimental ion bombardment data [38]. This universal pair potential was used here to calculate the ion–ion and ion–metal interactions.

3. Simultaneous ion assistance with metal flux deposition

In conventional ion beam assistance methods, continuous inert gas ion irradiation of the growth surface accompanies metal deposition [21]. Numerous simulations of a Cu/Co/Cu trilayer structure deposition with argon ion assistance were conducted with ion incident energies between 0 and 30 eV and different ion incidence angles. Details of the atomic reassembly mechanisms using simultaneous ion assistance can be found in previous papers [24,33]. Fig. 1 shows examples of the atomic structures obtained using selected ion energies between 0 and 20 eV, a fixed ion/metal ratio of two, and a normal ion incident angle. In the figure, copper, cobalt, and argon atoms are marked by white, gray, and black spheres, respectively. The simulations reveal a strong dependence of the atomic scale structure upon the incident ion energy. When there is no ion assistance, Fig. 1(a), the cobalt adatom surface mobility is insufficient to reconstruct the surface. As a result, a rough cobalt surface is formed, and when this is subsequently buried by the copper layer, it becomes a rough Cu-on-Co interface. When the adatom energy was close to 0 eV, very little intermixing between layers was observed, consistent with earlier studies [24]. When the ion energy was increased to 8 eV, Fig. 1(b), the cobalt film surface and resultant interface roughness were both reduced. The previous study has shown that this reduction arises because the assisting ions are able to transfer sufficient momentum to surface cluster adatoms enabling them to migrate and find ledge/edge sites that are one or two monolayers below the cluster peak [24]. For ion energies below 10 eV, this process leads to a significant flattening of the interface without activating much interdiffusion. However, if the ion energy is raised too high, Fig. 1(c), the interface becomes heavily intermixed as it is flattened. Thus, there exists an optimum ion energy near

![Fig. 1. Atomic structures of a Cu/Co/Cu trilayer grown using simultaneous metal deposition and argon ion assistance. The substrate temperature was 300 K and ion/metal flux ratio was two. Assisting argon ion energies were: (a) 0 eV (no ion assistance), (b) 8 eV, and (c) 20 eV. The ions were introduced in the \( \bar{1}\bar{1}\bar{1} \) direction.](image-url)
8 eV that minimizes a combination of surface roughness and interfacial intermixing. This optimum energy is also a function of ion species and ion/atom flux ratio [24,33].

A root-mean-square (RMS) deviation parameter can be used to quantify the roughness of the trilayer structure, and the number of cobalt atoms mixed into the underlying copper layer at a Co-on-Cu interface can be used to quantify intermixing. The RMS roughness and mixing as a function of ion energy for simultaneous ion assistance is shown in Fig. 2 as solid circles. Open circles and solid squares are results for the modulated energy and sequential ion assistance schemes discussed in next section. The results in Fig. 2(a) indicate that the roughness is significantly decreased as assisting ion energy is increased. For instance, the RMS roughness was approximately 6.3 Å without ion assistance but decreased to 4.5 Å using 10 eV argon ion assistance. Although ion energies above 10 eV further decrease the RMS roughness, Fig. 2(b) indicates that this is accompanied by significant interlayer mixing using a simultaneous assistance approach.

Fig. 2. (a) RMS roughness and (b) number of cobalt atoms mixed into the underlying copper layer as a function of argon ion energy. The ions were introduced in the [1 1 1] direction.

Ion incidence angle effect was further investigated (not shown here) and indicated that both roughness and mixing parameter dependencies on ion energies are rather insensitive to ion incident angle for angles lower than 50°. However, the roughness or mixing increases or decreases very rapidly once the ion angle exceeds 50°, which is consistent with previous study of ion incident angle in ion-assisted deposition [33]. Further analysis indicates that the lowest combination of roughness and mixing occurs at an ion energy of 10 eV and ion incident angle of 50°.

The amplitude of the interfacial roughness and width of intermixing at an interface are critical properties of a multilayer. To explore this further, the copper composition was calculated as a function of film thickness for multilayers deposited using different ion energies and a fixed ion/metal ratio of two, Fig. 3. The results indicate that the Co-on-Cu interface grown using 20 eV argon ion assistance much more diffuses than that grown with 8 eV or without any ion assistance. This mixing has been shown elsewhere [24] to occur by a high-energy ion impact-induced exchange mechanism. It can also be seen that the Cu-on-Co interfaces grown using either no assistance or with 20 eV ion assistance more diffuse than those obtained at 8 eV ion assistance. The diffuse Cu-on-Co interface formed using 20 eV ion assistance is again the result of an atomic exchange mechanism [24], whereas the apparent diffuse Cu-on-Co interface achieved without ion assistance is a manifestation of the rough interface (see Fig. 1(a)).

4. Other ion assistance schemes

4.1. Effects of interface depth

It has been shown that quite chemically sharp, almost flat interfaces can be fabricated using an optimized ion energy simultaneous ion-assisted deposition scheme.
However, the optimum ion energy is sensitive to underlying/overlying materials. Both Figs. 1 and 3 indicate that the mixing and roughness of the Cu-on-Co and Co-on-Cu interfaces are different when the same growth conditions are used. This arises because the energy barriers for cobalt migration over terrace edges and the atomic exchange of copper adatoms with underlying cobalt atoms are higher than those for copper atom migration as well as the exchange of a cobalt adatom with an underlying copper atom. Universal ion energy is therefore a compromise for the two materials and a better structure would be obtained using different energies for the two layers.

We also recognize that high-energy ion-induced mixing occurs only when an interface is near to the surface where ion impacts occur. The momentum transfer process is unable to drive the exchange processes more than a few monolayers below the surface. The degree of mixing can therefore be reduced by using the high-energy ion assistance only after the interface has been buried deeply by deposition of the next material layer. As the interface becomes more deeply buried, it is reasonable to expect that more energetic ions could be used for surface flattening without incurring a higher probability of mixing. To explore this, a series of structures were created by depositing cobalt in different thicknesses on a copper substrate. Ion impacts were then introduced and the intermixing probability examined.

The contour map of interlayer mixing probability as a function of ion energy and interface depth is shown in Fig. 4, which shows that increasing the interface depth significantly reduces interfacial mixing. It can also be seen that the use of ion energy in the “optimized energy region” for simultaneous ion assistance (8 eV) requires only one monolayer of coverage to avoid mixing. As the ion energy is increased to 20 eV, the intermixing probability at the interface drops from around 12%, to 5% and then 2% for one monolayer, two monolayers or three monolayers of interface coverage. Almost no mixing was found for four and five monolayers of coverage at a 20 eV ion energy. If the ion energy is further increased to 30 eV, four monolayer coverage still results in only a 4% mixing probability and five atomic layers result in almost no mixing for a 30 eV ion energy.

4.2. Modulated energy ion assistance

As discussed above, once a complete coverage of the underlying material by four or five atomic layers of new material has been achieved, the subsequent use of higher energy ion impacts to more effectively flatten the layer is much less likely to cause intermixing. It might then be possible to use a modulated ion energy scheme to promote flatness without inducing interlayer mixing. In such an approach, the first few atomic layers of a new material layer would be deposited with a very low-energy (or no) ion assistance, and then the remaining layer deposition would be completed using higher energy assistance.

Simulations were performed to explore this modulated energy ion assistance strategy for the deposition of a cobalt layer on a copper substrate. The first five atomic layers of cobalt were deposited without ion assistance, Fig. 5(a). The remainder of the cobalt layer was then deposited with ion assistance using various ion energies and a fixed ion/metal ratio of four. Figs. 5(b)–(d) show typical structures obtained using 6, 15, and 20 eV argon ion energies. When the first half cobalt layer is deposited without ion assistance, there is essentially no intermixing at the interface. However, the surface roughness is high due to the lack of surface atom migration. Fig. 5(b)–(d) indicate that the surface roughness is progressively decreased as the assisting ion energy is increased while the interlayer mixing remains relatively low. Very flat surfaces and interfaces are obtained using ion energies of around 20 eV. The roughness and interlayer mixing resulting from this modulated energy ion assistance method are summarized in Fig. 2 with open circles. The surface roughness progressively decreases with increasing the ion energy while interlayer mixing remains low. The minimum combination of mixing and roughness were achieved at an argon ion energy of around 20 eV for the Co-on-Cu interface.

The modulated ion assistance technique was also used to deposit copper layers on the bilayer structure shown in Fig. 5(d). Again, the first five atomic copper layers were deposited on the cobalt surface without ion assistance, Fig. 6(a). The remainder of the copper layer was then deposited with ion assistance at an ion energy of 20 eV and an ion/metal ratio of four, Fig. 6(b). It can be seen that the modulated energy ion assistance scheme resulted in multilayers with chemically sharp, physically flat interfaces.

4.3. Sequential ion assistance

The maximum ion energy that can be used in a modulated ion energy assistance scheme is limited by the
distance between surface and interface at the onset of ion assistance. The highest ion energy (greatest smoothing rate) can be used once a layer has been fully deposited. A sequential ion assistance approach was therefore explored in which a complete metal layer was first deposited without (or with very low energy) ion assistance, and then relatively high-energy ion impacts were used to flatten the metal surface after the metal layer was deposited. The interfacial roughness and intermixing results for the sequential ion beam assistance scheme are also summarized in Fig. 2 with solid squares. It can be seen that the mixing was always very low and the RMS roughness was decreased (to as low as 2.9 Å) as the ion energy was increased to 30 eV. The combination of roughness and mixing continued to decrease as the ion energy was increased to 30 eV.

A complete Cu/Co/Cu trilayer was grown using the sequential deposition scheme with an ion energy of 30 eV, Fig. 7. Fig. 7(a) shows the cobalt layer deposited on copper without ion assistance. The surface was
then irradiated with ions at an ion energy of 30 eV to an ion fluence of 0.5 ions/Å², Fig. 7(b). This process was very effective at smoothing the surface. A copper layer was deposited onto this smoothed cobalt layer without ion assistance, Fig. 7(c). Finally, the copper surface was irradiated with ions at an ion energy of 30 eV to an ion fluence of 0.5 ions/Å², Fig. 7(d). The results show that the sequential ion assistance scheme resulted in a multilayer structure with planar interfaces and little interfacial mixing even when a moderately high ion energy of 30 eV was used.

Examination of the three ion assistance approaches, Fig. 2, also indicates that at the same assisting ion energy, the simultaneous ion beam assistance approach usually resulted in slightly lower surface roughness values but was accompanied by the highest probability of interfacial mixing. The sequential ion beam assistance in all but the 30 eV case resulted in the smallest flattening effect, and the least interfacial mixing. Additional simulations (not shown) indicated that for all three ion assistance schemes, the roughness increased as the ion energy was increased above 30 eV due to the resputtering of the surface atoms. The effect of ion incident angle was also examined for the modulated energy and sequential ion assistance schemes. These simulations indicated very similar effects to those reported for the simultaneous ion assistance approach described above.

5. Discussion

The results discussed above indicate that optimum ion energy (to achieve the lowest combination of interfacial roughness and mixing) in a Cu/Co/Cu multilayer structure depends on the ion assistance method. For example, the optimized argon ion energy for simultaneous assistance is around 8 eV, whereas for modulated energy or sequential ion assistance, it is either 20 eV or more than 30 eV, respectively. This difference arises in part because the size of asperities that must be smoothed is different for the three ion assistance methods. During simultaneous ion assistance, the assisting ions arrive simultaneously with the metal atoms and therefore continuously reduce the small surface asperities that are nucleated during layer growth. As a result, relatively low-energy (8 eV) ions are effective at flattening the surface. When the assisting ions are only applied after a certain layer thickness has been deposited, as in both modulated energy and sequential ion assistance processes, the average size of the surface asperities already became much larger, as shown in Figs. 5(a) and 7(a). For a fixed
ion fluence, higher energy ions are then needed to flatten the more well-developed roughness. This is the primary explanation of the best flattening performance of the simultaneous ion assistance method in the low-energy region of Fig. 2.

It is important to recognize that even using a modulated ion energy or sequential ion-assistance scheme, mixing still occurs when high ion energies are used. The highest ion energy that does not result in significant intermixing depends on the distance between the surface and the underlying interface as summarized in Fig. 4, which is in the form of mixing fraction contours on an ion energy-interface depth map. The map provides a convenient means identifying the selection of an ion energy and layer thickness to achieve a desired level of mixing. For example, use of an argon ion energy of 10 eV can be used in simultaneous ion assistance schemes to flatten a surface without causing significant mixing. If the smallest energy that can be used is 20 eV, then four monolayers of cobalt must be deposited before ion assistance is applied and a modulated or sequential assistance approach is preferred.

Finally, we note that both simultaneous and sequential ion assistance techniques have been widely used for vapor deposition processing. The techniques can be differentiated by the method used to create the assisting ion flux [21,39]. One approach utilizes ion beam gun technology and has been combined with which can be used in many ion beam deposition [40–42], magnetron deposition [43] and evaporation techniques [25]. The assisting ion beam can be used either for simultaneous or sequential ion assistance. In order to focus ion beam on a substrate, ion gun approaches normally require the use of a relatively high ion energy >50 eV. The ion incident angle is easily varied by gun placement. This ion energy range is well suited for sequential ion assistance provided the layers of multilayers are more than five monolayers in thickness. Electrostatic deceleration schemes near the substrate in principle provide a means to reduce the ion energy into the range best suited for simultaneous or modulated ion assistance.

The second approach utilizes plasmas located near the substrate to provide an assistance. Examples include high-pressure RF diode and magnetron sputtering techniques [44–47]. These methods utilize a negative bias voltage applied to the substrate to attract ions from plasma to the growth surface. They are usually used for simultaneous or sequential ion assistance. Since the plasma is also used to create the vapor flux to be deposited, the ion energies can be high, but collisions with background gas atoms in high-pressure processes can reduce their energy into the range of interest for simultaneous assistance. Modulated ion assistance appears to be more difficult to implement using this approach. A sequel paper reports a comprehensive experimental study of the low-energy (<30 eV) ion-assisted growth of thin films using a biased target ion beam deposition [48].

6. Conclusion

An MD method has been used to explore low-energy argon ion-assisted deposition approaches for the fabrication of Cu/Co multilayers. The study indicates that:

1. During continuous ion assistance, the ion energy significantly affects the interfacial structure of multilayer structures. High-ion energies promote migration of surface atoms over Ehrlich–Schwoebel barriers and promote flattening of the film surface. However, during multilayer growth they can also result in interlayer mixing by an atom exchange process. A narrow “optimal” ion energy range (5–10 eV) exists for fabricating high structural quality interfaces using simultaneous metal deposition and ion assistance.

2. A modulated energy ion assisting method (which uses low ion energy or no assisting ions to deposit the first few atomic layers of each new material layer and higher ion energies for the remainder of that layer) is found to result in a lower combination of interfacial roughness and interfacial mixing than the simultaneous ion assistance approach.

3. A sequential assistance method, which deposits a complete metal layer with very low-energy (or no) assisting ions, followed by high-energy ion surface modification of the fully deposited metal layer, can result in very high-quality interfacial structures and may be more easily implemented using ion beam deposition approaches.

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References
