Strong mass effect on ion-beam mixing in metal bilayers: A ballistic picture

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Molecular dynamics simulations have been used to study the mechanism of ion beam mixing in metal bilayers. We are able to explain the ion induced low-temperature phase stability, atomic mixing and melting behavior of bilayers using only a simple ballistic picture up to 10 keV ion energies. The atomic mass ratio of the overlayer and the substrate constituents seems to be a key quantity in understanding atomic mixing. This picture explains in a simple way ion beam mixing in a overwhelming number of miscible and immiscible bilayer systems up to high ion energies. Remarkably the existing experimental data follow the same trend as the simulated values. The critical bilayer mass ratio of $\delta < 0.33$ is required for the occurrence of a thermal spike (local melting) with a lifetime of $\tau > 0.3$ ps at low-energy ion irradiation (1 keV) due to a ballistic mechanism. These findings might be important in understanding the mechanism of ion induced phase evolution in solids and could improve the controlled fabrication of metal nanostructures.

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There is a great interest in the manipulation and nanoscale fabrication of ordered layered structures in a controllable manner in the last decades. This requires the fundamental understanding of the mechanism of atomic transport processes and phase evolution in solids even far-from-equilibrium since during nanoscale engineering the occurence of nonequilibrium solid phases is highly probable.[1] Ion beam mixing (IM) has been established as a powerful method for synthesizing nanoscale objects.[2,3] IM has also been introduced as a nanofabrication route to gain nanocomposite structures, based on a self-assembly phenomenon under irradiation.[3] In certain metal bilayer systems IM randomize the initially sharp interface leading to amorphization.[4–6] In many bilayers no considerable IM occurs[7,8] such as Ag/Fe in which a very poor mixing efficiency is observed.[9] As an explanation for the ion induced phase stability (instability) of interfaces, the thermal spike (TS) model is widely accepted in the last two decades[8,10] which predicts the dependence of the mixing efficiency on thermodynamic quantities such as heat of mixing.

Recently though we observed the presence of TS but failed to find any effect of heat of mixing on IM.[11,12] It is also known that the TS model has a limited applicability for systems with positive heat of mixing as well as for systems having a mean atomic number $Z < 20$.[9] Thus, accepting the importance of the TS during the phase evolution of the irradiated sample[10,13] we propose to understand its effect on IM as a purely ballistic phenomenon.[12]

In the present Letter we would like to show using molecular dynamics (MD) simulations that the atomic mass ratio has a dramatic effect on IM in various metal bilayers. Up to 10 keV Ar^+ ion bombardment no or weak IM occurs above the atomic mass ratio of $\delta = m_{overl}/m_{bulk} > 0.33$ while considerable IM occurs if $\delta < 0.33$, where m_{overl} and m_{bulk} are the atomic masses in the overlayer and in the substrate (bulk). We will demonstrate that a large number of measured mixing efficiencies follow the same trend as the simulated IM. These results challange the widely accepted thermal spike model.

Classical constant volume molecular dynamics simulations were used to simulate the ion-solid interaction using the PARCAS code.[14] Periodic boundary conditions are used parallel to the (111) planes. The computer animations can be seen on our web page.[15] Here we only shortly summarize the most important aspects. Its detailed description is given in recent communications.[11,16] We irradiate a series of (111) bilayers (Al/Pt, Ti/Pt, Al/Ag, Cu/Pt, Cu/Au, Al/Cu, Ni/Ag, Ag/Au, Ti/Co, Ag/Ni, Cu/Ni) with 1 keV Ar^+ ions. In certain bilayers (Al/Pt, Ti/Pt, Al/Cu, Ni/Ag, Ti/Co) we increase the irradiation energy up to 10 keV in order to show that the mass effect persists up to higher ion energies. For practical reasons we choose a grazing angle of incidence (the initial velocity direction of the impacting atom was 7 degrees with respect to the (111) surface of the crystal) although we are interested, not in the sputtering conditions or in surface morphology development in this article. Due to the small impacting angle the energy deposition is concentrated 4–8 monolayers (MLs) below the (111) free surface up to 10 keV ion energy hence we could minimize the depth size of our simulation cells for saving CPU time. Although the impact angle (Θ) could affect atomic mixing, however, we find that the mean range of atomic displacements is not sensitive to the variation of Θ if the depth coordinate of the interface is placed in the range of the penetration depth. Hence the applied restriction on Θ does not affect significantly the final conclusions. To obtain a representative statistics, the impact position of the incoming ion is varied randomly within a 5×5 Å^2 area completing 10 simulations for each system.

We used a tight binding many body potential given by Cleri and Rosato (CR),[17] to describe interatomic interactions. We have chosen those bilayers for which atomic potentials are available. This type of a potential gives a very good description of lattice vacancies, including migration properties and a reasonable description of solid surfaces and melting.[17] To construct AB heteronuclear interactions the geometrical mean of the elemental energy constants and the harmonic mean for the screening length are taken as in Ref. 19. It appears that the estimated AB potential describes the relaxation behavior of various (111) bilayers adequately. We get stable, atomically sharp interface structures in a wide

temperature range below the melting temperatures. The reliability of the AB cross-potential as a mean of the elemental potentials is tested in the cases of CuAu and CuAg, where an optimized CR potential is available for the alloy phases.[18] We find no considerable changes in the physical properties or in the equilibrium structure. Although this does not prove the reliability of other cross-potentials, it suggests that the estimated potentials are very close to the optimized one and should be suitable for describing the ballistic properties of IM which is the primary goal of the present report.

The construction of the interface systems is given elsewhere.[12] We only shortly summarize that the interfaces have (111) orientation and the close packed directions are parallel. The thickness of the upper layer is 4–8 monolayers (ML), while the bulk is constructed from 36 MLs in those samples subjected to 1 keV irradiation. These samples includes roughly 45 000 atoms. At a higher irradiation energy we put a thicker overlayer with 8–16 MLs and a substrate with 90 MLs (550 000 atoms). The interfacial systems are created as follows: the overlayer is put by hand on the (111) substrate (bulk) and various structures are probed and are put together randomly. Finally that one is selected which has the smallest misfit strain prior to the relaxation run. The remaining misfit is properly minimized during the relaxation process so that the overlayer and the substrate layers keep their original crystal structure and we get an atomically sharp interface.

We calculate the number of mixed atoms (N_{mix}) and the simulated mixing efficiency $\xi_{IM}^{\mathrm{sim}}=\langle R^2\rangle/6n_0E_{D_N}$, where $\langle R^2\rangle, n_0$ and E_{D_N}, are the calculated mean square atomic displacement through the interface per atom, the atomic density in the upper layer and the deposited nuclear energy. We exclude from $\langle R^2\rangle$ atomic displacements which do not lead to broadening at the interface (self-atomic mixing) because the experimental ξ_{IM} is calculated from broadening at the interface.[8,10] Further calculational details are given in Ref. 20.

We investigate the influence of the atomic mass ratio on ion beam mixing. We ion bombarded various bilayer systems with different atomic mass ratios and find that below a threshold ratio ($\delta<0.33$) the magnitude of intermixing (N_{mix}) is enhanced abruptly. The results are summarized in Figs 1 and 2. In Fig. 1 we plot the simulated N_{mix} vs δ and the experimental ξ_{IM} vs δ in Fig. 2 collected from Refs. 7,8. In the inset, Fig. 2, we also give the simulated ξ_{IM} vs δ for bilayers for which high energy (up to 10 keV) simulations are available and also for the other bilayers for which ξ_{IM}^{sim} is calculated at 1 keV ion energy. In Fig. 2 we see that the increase in ξ_{IM} occurs between $\delta\approx 1/3$ and $1/2$ which is rather similar to the inset, Fig. 1. In Fig. 2 the experimental mixing efficiency values are obtained as follows:[7] $\xi_{IM}\approx Dt/\Phi F_D$, where Dt is the diffusion length, Φ is the fluence and F_D is the deposited energy at the interface. Although there is some scatter in the data at around $\delta\approx 1/3$, ξ_{IM} increases heavily in accordance with the N_{mix} values shown in Fig. 1. Although the experimental ξ_{IM} values in Fig. 2 are obtained at high energies, however, they can be compared with our ξ_{IM}^{sim} values since IM occurs primarily in the subcascade region, where the energy is in the range we applied.[20] Above 10 keV ion energy collisional cascades split into subcascades with a deposited energy density similar to that occurs at lower ion energies.[20]

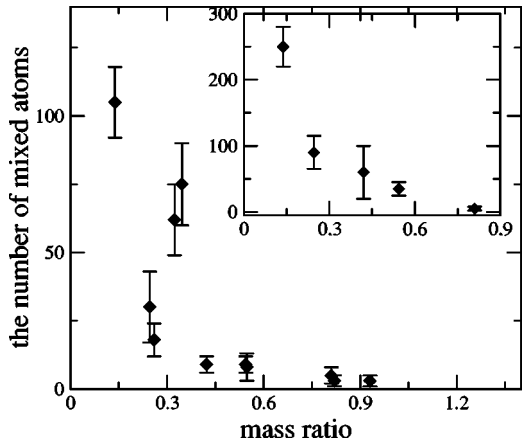

FIG. 1. The number of intermixed atoms (N_{mix}, interfacial mixing) at various atomic mass ratio (δ) in various metal bilayers obtained at 1 keV Ar^+ irradiation. Note the threshold $\delta\approx 0.33$ value below which the bilayers exhibit an ion-beam mixing "catastrophe" and above which only cascade mixing occurs. The data points correspond from left to right to the bilayers Al/Pt (0.14), Al/Ag (0.24), Ti/Pt (0.25), Cu/Au (0.32), Cu/Pt (0.33), Al/Cu (0.42), Ni/Ag (0.54), Au/Ag (1.83), Ti/Co (0.81), Cu/Ni (1.08) and Ag/Ni (1.82), respectively (the atomic mass ratios are given in the parantheses). In those case where $\delta>1$ we use $1/\delta$, because we find that N_{mix} in AB and BA systems are nearly equal. The error bars denote standard deviations. *Inset*: The number of mixed atoms is also shown for higher energies for Al/Pt (6 keV), Ti/Pt (8 keV), Al/Cu (10 keV), Ni/Ag (9 keV) and for Ti/Co (10 keV) as a function of the mass ratio.

In particular, in Al/Pt we find a strong amorphization and broadening at the interface which is in accordance with measurements.[6,12,21] In Cu/Pt and in Cu/Au the phase stability of the interface is also very weak in accordance with

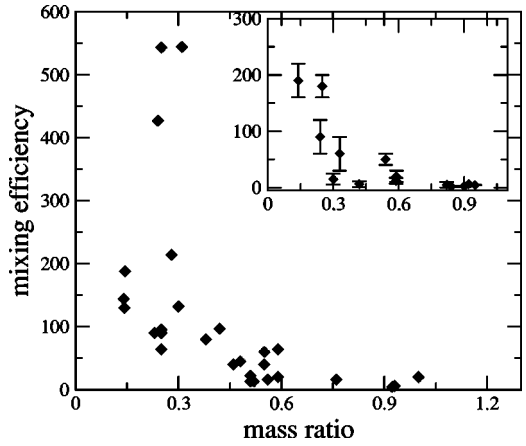

FIG. 2. The low-temperature experimental mixing efficiency ($Å^5/eV$) as a function of the atomic mass ratio (δ). The values are taken from Refs. 7,8. In those cases where $\delta>1$ we use instead $1/\delta$ because we find that there is no serious difference in mixing between AB and BA bilayers. *Inset*: The calculated (simulated) ξ_{IM} ($Å^5/eV$) vs δ.

ion irradiation experiments.[21] In Cu/Au 1 MeV ion bombardment results in strong broadening.[8,21] In bilayers Al/Ag and in Au/Ag we find a relatively weak interfacial mixing ($N_{\mathrm{mix}}<30$), however, ξ_{IM}^{sim} is large ($\xi_{IM}^{\mathrm{sim}}\approx 300\pm 120$ in Al/Ag, $\xi_{IM}^{\mathrm{sim}}\approx 115\pm 45$ in Au/Ag). A large measured value of $\xi_{IM}^{\mathrm{exp}}\approx 265$ is found in Au/Ag[7] and this data point is plotted at $1/\delta=0.55$ in Fig. 2. Interestingly the atomic mobility is relatively large in these systems while the gross number of mixed atoms (N_{mix}) is small. We attribute this "anomalous" behavior of Au/Ag to the tendency of crater formation in Au.[10] It has been shown, recently, that crater formation enhances mass transport hence atomic mobility between the interface and the free surface.[16]

For bilayers with $\delta>0.33$ starting with Al/Cu ($\delta=0.42$) we got a weak interfacial mixing in accordance with the MD[22,23] and experimental studies.[7] The strong mass effect can be understood as the ballistic mechanism plays an essential role in IM and may stem from an increased backscattering of light overlayer atoms from the heavy substrate.[12] Moreover the density of the collisional cascades depends on the bilayer mass ratio.[12] It should also be stressed that in pure elements or even in metal alloys we find a much weaker IM and shorter TS[15,16] due to the strong (re)ordering forces. In order to elucidate the relative roles of ballistics and TS in the interfacial mixing we examined the prototypical bilayer Ni/Ag ($\delta\approx 0.54$) and found a very weak interfacial mixing at 1 keV bombardment and no occurrence of a real TS period. The energetic atoms (recoils, hot atoms[12]) dissappear at less than 0.3 ps, which is typically the end of the cascade period. This system is relatively well studied theoretically[22] at 10 keV ion energy and being a typical example of a segregating system which has a high positive heat of mixing in the liquid.[22] At 9 keV we find a real thermal spike which persists up to 3 ps. The number of mixed atoms (N_{mix}) is, however, much smaller then in Al/Pt or in Ti/Pt (inset, Fig. 1). Therefore, although there is an increase in N_{mix}, the trend remains the same: the effect of the mass ratio is also robust at higher energies. We attribute, however, the weak IM in Ni/Ag not to the positive heat of mixing, but to the weak mass effect in this system ($0.33<\delta\approx 0.54$). In Ti/Co we find no TS up to 10 keV as well as IM is very weak in this system ($\delta\approx 0.82$). It should be emphasized that the similar situation is true for all the bilayer samples which have $\delta>0.33$ (Fig. 1). This observation clearly indicates a robust mass effect when $\delta<0.33$, hence a kinematic and ballistic picture seems to be sufficient for describing IM in bilayer systems. In those systems, where TS does not occur, cascade mixing is the only IM effect.

In order to show the effect of mass ratio on the density of the collisional casacades the trajectories of energetic (hot) atoms are shown with positions projected to the *xz*-plane [perpendicular to the (111) surface] in Figs. 3 and 4. In the case of Ti/Pt we get a dense collision cascade, the recoils (hot atoms) are concentrated within a smaller region due to couple of reflections while in Ti/Co the high energy particles are scattered in a larger volume hence the deposited energy spreads over a larger irradiated region. Therefore if the mass ratio $\delta>0.33$, the cooling of the cascade is ultrafast due to the low concentration of the recoils (hot atoms). Indeed, we

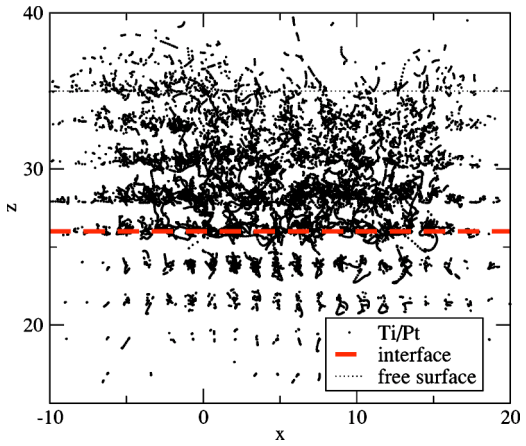

FIG. 3. The *xz* atomic positions of the energetic atoms at 1 keV ion energy collected up to 4 ps in Ti/Pt. The z-coordinate is the depth position. The dashed line denotes the interface.

found that the average atomic concentration of the hot atoms in the irradiated zone ($V\approx 1000$ Å^3) is around 10^{22} atom/cm^3 for $\delta>0.33$ and 4×10^{22} atom/cm^3 for $\delta<0.33$. These values should also be compared with the average atomic concentration of $5-8\times 10^{22}$ atom/cm^3 in metals. If the mass ratio drops below 0.33, the hot particles are still present in the TS. One can see that for $\delta<0.33$ the peak hot atom concentration is close to the atomic concentration. In these systems we no longer have a simple liquid ensemble, it is rather a superheated system.[12]

Qualitatively we explain the observed strong mass effect as follows: In elastic collisions of the recoils (energetic light particles from the overlayer) with the heavier substrate atoms the kinetic energy of the moving atoms is partly transferred to the heavier atoms, which, however, might not be kicked out of their positions because of the large mass difference. The colliding heavy partner of the recoil becomes vibrationally excited, which means that its rms amplitude of thermal vibrations becomes equal to about 50% of the interatomic distance. That is basically the Lindeman's criterion for lattice instability during melting: a crystal melts when the

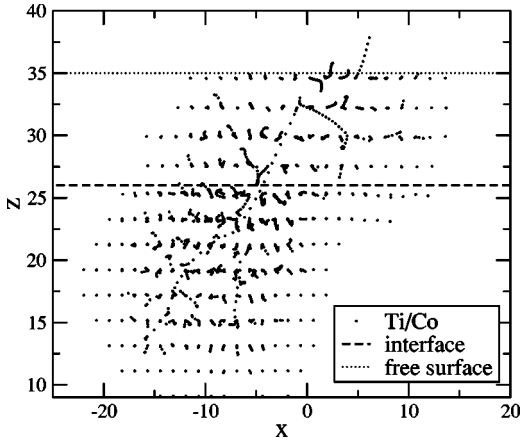

FIG. 4. The *xz* positions of the energetic atoms at 1 keV ion energy collected up to 0.3 ps in Ti/Co. The *z*-coordinate is the depth position. The dashed line denotes the interface.

rms thermal displacement of atoms from their equilibrium positions become large enough to invade their nearest-neighbor spaces.[5] For such thermal displacements, the thermal expansion would far exceed the critical value for shear instability (the Born criterion, the lost of at least one of the shear moduli) leading to mechanical instability.[5] The neighborhood of this hot heavy atom is heated up and local melting occurs (TS). When the mass of a recoil and the colliding partner is comparable the target atom might be displaced from its original position leaving a vacant site. In this case the slowing down of the recoil in the bulk does not result in local melting because the kinetic energy of the recoil spreads over a too large volume.

The important question remained to be answered what is the reason of the critical mass ratio of $\delta \approx 0.33$? We do believe that the threshold value is due to the emergence of a strong backscattering of the recoiling light atoms at the interface. Below this value hence the energy deposition becomes extremely effective at the interface through energy transfer to the standing heavy atoms. The backscattering effect at the interface results in the confinement of the light recoils in the overlayer which leads to superheating. This is the primary reason of the high concentration of hot atoms in these bilayers (see Figs. 3). The interfacial backscattering phenomenon can be attributed partly to the mass difference and also to other effects such as the difference in the cohesive energies in the substrate and in the overlayer.[12]

In summary, we have shown that intermixing in metal bilayers strongly depends on the relative masses of the constituents under the effect of ion irradiation. There exists a threshold mass ratio value below which the interface system is unstable against ion bombardment. We propose to understand ion beam mixing as a ballistic process. The observed strong mass effect in heterophases might be an important topic in preparation of thin films and multilayers.

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