Does the thermal-spike affect low-energy ion-induced interfacial mixing?

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Molecular dynamics simulations have been used to obtain the three-dimensional distribution of interfacial mixing and cascade defects in Ti/Pt multilayer system due to single 1 keV Ar⁺ impact at grazing angle of incidence. The Ti/Pt system was chosen because of its relatively high heat of mixing in the binary alloy and therefore a suitable candidate for testing the effect of heat of mixing on ion-beam mixing. However, the calculated mixing profile is not sensitive to the heat of mixing. Therefore the thermal spike model of mixing is not fully supported under these irradiation conditions. Instead we found that the majority of mixing occurs after the thermal spike during the relaxation process. These conclusions are supported by liquid, vacancy as well as adatom analysis. The interfacial mixing is in various aspects anomalous in this system: the time evolution of mixing is leading to a phase delay for Ti mixing, and Pt exhibits an unexpected double peaked mixing evolution. The reasons to these effects are discussed.

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I. INTRODUCTION

With the appearance of nanotechnology the importance of thin films increased considerably. Either during making thin films by any kind of various sputtering processes or in thin film analysis (various kinds of sputter depth profiling techniques) the thin film system is subjected to low energy ion bombardment. For this reason the study of the effects of the low energy ion irradiation of thin film structures is of high importance.

One of the effects of ion bombardment is interfacial ion beam mixing. This term is used for that process when an originally sharp interface (IF) between pure A and B materials gets broader due to ion bombardment. The ion mixing (IM) phenomenon is known for a long time [1]. The majority of our knowledge refers to cases when the interface to be mixed is relatively deep in the matrix (that is, far from the free surface) and consequently the ion energy applied is in the range of 100 keV [2].

Several theoretical approaches and techniques have also been developed and a rather coherent picture seems to have emerged [1,2]. Though there is no principal difference between the low and high energy ion mixing still the previous experimental and theoretical techniques cannot be directly applied for the low energy case. The most important difference between the high and low energy ion mixing is that (i) the latter occurs close to the free surface and (ii) its extent is obviously much less than that of high energy mixing.

With the increasing computation speed MD simulations have become a standard tool to study the low energy ion beam surface interaction, and interface mixing as well. MD simulation of IM has been the subject of several studies in the last decades [1]. IM in multilayer system has also been investigated by several groups using MD [1,4,6,7]. A common feature of these studies is that only a single ion impact has been considered during the simulations. Experimental analysis of interfacial mixing in multilayer metals, however, always deal with a series of ion impacts. For instance, Auger depth profiling analysis of multilayers should lead to the removal of the target during analysis [9]. As a first step, we in this study focus on understanding the single-ion process. To go beyond this level we will employ a series of ion impacts in the next study.

The other common feature of the studies available is that they use a normal angle of incidence. We should like to model ion milling and destructive depth profiling techniques [9]. Based on experimental evidences we know that for the optimum application of these methods one should apply low energy ion bombardment with grazing angle of incidence (to minimize the surface morphology development). This arrangement, however, is far from the previous one. First, the angle of incidence is grazing in contrast to normal angle of incidence. Second, Pinzon et al. [8] recently showed by MD calculation that the damage structure changes with angle of incidence. At grazing angle of incidence ion bombardment the defects are confined close to the surface.

Another interesting aspect of ion-beam mixing is theoretical. It is still unclear whether the mechanism of IM is purely ballistic or heat spikes play essential role in the magnitude of interfacial mixing [1,2]. In particular within the thermal spike (TS) model [2] the heat of mixing (ΔHₘ) is found to be a key quantity in determining the magnitude of mixing. The role of heat of mixing on governing mixing processes is questioned by R. Kelly et al. [10]. They emphasized the role of residual defects in mixing (long ranged effects). Although the thermal spike concept is widely accepted, its applicability for low-energy bombardments is not straightforward. MD simulation of cascades have been reported with evidence that local melting occurs during the thermal spike phases which persists for several ps in the 3–5 keV energy regime [11].
Our intention is to study IM in the case of low energy impact at 1 keV. This energy regime is around the lower limit of the TS model [17], and the number of simulation studies in this field is limited [5]. Gades and Urbassek [5] reported MD simulations for pure Cu at 1 keV which supports the phenomenological model of Cheng et al. However, it is not clear whether the TS model will apply for multilayers with different constituents at low ion energies. The reason we are particularly interested in 1 keV Ar bombardment is its relevance to Auger depth profiling [9].

The reported MD simulations, in accordance with the model of Cheng et al. [2], show that the interfacial mixing (IFM) exhibits an inverse-square dependence on the cohesive energy; however they also show a non-linear variation of the interface broadening with $\Delta H_m$. It is therefore interesting to study the effect of thermodynamic properties such as the heat of mixing $\Delta H_m$ on mixing at low ion energies. Studying high energy IM of Ti/Pt Kim et al. [12] concluded that the mixing is governed by TS. Cirlin et al. [13] measured the depth resolution of AES depth profiling on Ti/Pt system and concluded that even at 1 keV the mixing is partially determined by TS.

In this communication we report on MD calculation of Ti/Pt layered structure applying grazing angle of incidence Ar$^+$ bombardment at 1 keV. Though the crystal lattice and the mass of atoms will be determined according to the basic feature of Ti and Pt, the Pt-Ti mixed part of the potential will be varied to determine the effect of $\Delta H_m$ on the mixing.

**II. THE MULTILAYER SAMPLE AND THE SIMULATION METHOD**

Classical molecular dynamics simulations were used to simulate collisional mixing using the PARCAS code developed by Nordlund et al. [19]. Here we only shortly summarize the most important aspects. Its detailed description is given in [6,19]. The classical equations of motion were solved according to the Gear fifth-order predictor-corrector algorithm. A velocity dependent variable time step of integration was used. Periodic boundary conditions were applied to the fixed-size simulation cells. The electronic stopping power was included in the runs as a nonlocal frictional force affecting all atoms with a kinetic energy higher then 10 eV.

The sample consists of 37289 atoms for the interface system with 4 Ti top layers and a bulk which is Pt. The Ti (hcp) and Pt (fcc) layers at the interface are separated by 2.8 Å. The computational cell has a size of roughly 85 x 85 x 85 Å. This simulation cell is of our particular interest because preliminary calculations indicate that 1 keV Ar$^+$ with grazing angle of incidence provides the interesting situation when the recoils penetrates approximately 4 layers deep below the surface. Therefore the average center of the cascade is positioned close the interface. The lattice mismatch is optimized properly at the interface in order to reduce the interfacial strain to less then 2 %. The best match of Ti (hcp) and Pt (fcc) layers are carried out by probing various structures put together by hand. The most favorably matched system have been selected for further simulations.

The crystallite is kept at 0 K at the beginning of the simulations. The entire interfacial system is equilibrated prior to the irradiation simulations and the temperature scaled softly down towards zero at the outermost three atomic layers during the cascade events [19]. Since in the present study we are interested in the fundamental mechanism of interfacial mixing, we choose 0 K as the ambient temperature seems to be appropriate to prevent any thermally activated effects from complicating the analysis. A study of temperature dependence of IFM is planned in a further study. The collision cascade were initiated by placing an Ar atom outside the surface and giving it a kinetic energy of 1 keV towards the surface. The initial velocity direction of the impacting atom was 83 degree with respect to the surface normal.

To obtain a representative statistics, the impact position of the incoming ion is varied randomly up to 15 events. We find considerable variation of mixing as a function of the impact position of the recoil. The simulations are terminated at about 20 ps after the projectile impact.

During the simulations, an atom was labeled "liquid" if the average kinetic energy of it and its nearest neighbours was above an energy corresponding to the melting point of the material through the usual relation between temperature and kinetic energy, $E = \frac{1}{2}kT$. It is then possible to carry out liquid atom analysis, which allows us to estimate the spatial extent of the cascade or the thermal spike region (the local melt). The liquid phase (typically occurs at 0.1 – 0.5 ps with a sharp "ballistic" peak [1,6]) is the direct result of thermalization of ballistic recoils and in this sense these liquid atoms do not correspond to the classical concept of a liquid in any meaningful way [22]. However, if the temperature of the atoms persists above the melting temperature longer then 1-2 ps then it can be called as a liquid which corresponds to a thermal spike. The liquid region corresponds to a classical liquid in the sense that the pair distribution function resembles that of a liquid in equilibrium [22].

The Berendsen temperature control is used throughout the simulations [20]. A complete analysis of the structural output file (movie file) has been carried out for each irradiation event for some chosen time steps (mixing, liquid, vacancy, adatom etc. analysis).

An atom is labeled mixed if it moves beyond the interface during the simulation by more then the half of the Ti-Pt interfacial distance in the initial sample (~1.4 Å).

Vacancies were recognized in the simulations using a very simple analysis. A lattice site with an empty cell sphere is set to ∼ 2 Å (the radius of a sphere around the relocated atom around its original position) which is about 60% of the average atomic distance in this system.
We find this criterion is suitable for counting the number of vacancies. We monitored the change in the surface location, and it is less than 0.3 Å during the simulation time. It is therefore does not affect the efficiency of the method used for vacancy, adatom and mixing analysis.

FIG. 1. Cross-sectional view at the Ti/Pt interface system at the end of the simulation (∼20 ps). The coordinates are in Å unit. (The upper 4 layers were originally Ti and the bulk is Pt.) The cross section is taken along the z-axis (depth profile). Heavily mixed sample taken from statistics ($N_{mix} \approx 52$).

FIG. 2. Cross-sectional view at the Ti/Pt interface system at the beginning of the cooling period (∼2 ps). Heavily mixed sample taken from statistics ($N_{mix} \approx 52$).

FIG. 3. Cross-sectional view at the Ti/Pt interface system at the end of the simulation (∼20 ps) for the low mixing sample ($N_{mix} \approx 9$).

FIG. 4. Cross-sectional view at the Ti/Pt interface system at the beginning of the cooling period (∼2 ps). Weakly mixed sample taken from statistics ($N_{mix} \approx 9$).
FIG. 5. The time evolution of the thermal spike. The number of liquid atoms as a function of time under 1 keV Ar+ bombardment for low \(N_{\text{mix}} \approx 9\) and high degrees of interface mixing \(N_{\text{mix}} \approx 35, 52; \Delta H_m \approx 75 \text{ kJ/mol}\).

Our simulation method [19] used in this study allows us to assign the value of heat of mixing of the metal pair relatively easily. The attractive part of the Cleri-Rosato many-body potential [14] used in this study

\[
V_i(r_{ij}) = -\left( \sum_j \xi^2 e^{-2Q(r_{ij}/r_0 - 1)} \right)^{1/2},
\]

where \(r_{ij}\) represents the interatomic distance between atoms \(i\) and \(j\), \(r_0\) is the first-neighbour distance. The total cohesive energy of the system is then

\[
E_c = \sum_i (E_{R}^i + E_B^i),
\]

where \(E_R^i\) is a repulsive term of the Born-Mayer type [14,16].

By varying the parameter \(\xi\) in Eq. (1) the heat of mixing can easily be varied without influencing other parameters of the crystall. The heat of mixing is calculated in the usual way,

\[
\Delta H_m = 0.5(E_A + E_B) - E_{AB},
\]

where \(E_A\), \(E_B\) and \(E_{AB}\) are the total energies/atom of the corresponding constituents. The heat of mixing of Ti/Pt is substantial \((-75 \text{ kJ/mol})\) according to the Miedema calculation [21,25]. Varying \(\xi\) in the range of \(0 - 2.55\) the heat of mixing calculated from Eq. (3) varies in the range of \(+75 - 141 \text{ kJ/mol}\), the Miedema value can be achieved by taking \(\xi \approx 2.35\).

III. SINGLE ION IMPACT ON THE TI/PT SYSTEM

The most important technical problem of the simulation is that the various parameters describing the change of the sample due to ion impact including mixing strongly depends on the position of the ion impact. Thus we always consider 15 events with random impact positions and the average and the scatter of the parameters will be given. FIGs (1)-(4) show final and intermediate states of the samples after 20 and at 2 ps after a single ion impact for \(\xi = 2.35\). FIGs (1)-(2) depict a strongly and (FIGs (3)-(4)) a weakly mixed sample with different impact positions. Originally the upper 4 layers were pure Ti. For the present case we can conclude that a single ion causes a heavy distortion in the sample. Pt and Ti appears in the originally pure Ti and Pt regions, respectively, that is, considerable mixing occurs. Besides the mixed atoms we can recognize several vacancies, interstitials and adatoms. For the shown cases in these events the number of mixed atoms, \(N_{\text{mix}} \approx 52\) and 9, respectively.

Comparing FIGs (1)-(2) we see the heavily distorted structure at 2 ps and the considerable mass transport of Pt in the Ti phase. Comparing FIGs (3)-(4) the difference between the relaxed (20 ps) and the distorted structures is even more remarkable. In particular FIG (1) shows us that the system remained distorted even after relaxation. From the point of view of the mechanism, however, these figures are not satisfactorily informative. If we would like to correlate IFM with the TS, we should consider time evolution of the number of liquid atoms and the average local temperature of the liquid atoms. This is shown in FIGs (5)-(6) for various events, in case for low, medium and high mixing rates. For simplicity we display only two mixing cases on FIG (6). The curves are rather similar. All are dominated by a huge peak at around 150 fs (characteristic ballistic peak). The thermal spike period can be attributed [3,17] to the tails of the curves. Its length and magnitude depends on the...

FIG. 6. The time evolution of the local temperature (K) in the thermal spike for the low and high degrees of interface mixing \((N_{\text{mix}} \approx 9 \text{ and } 52)\).
FIG. 7. The evolution of mixing as a function of simulation time (ps) for Pt and Ti at large mixing rate ($N_{mix} \approx 52, \Delta H_m \approx 75 \text{ kJ/mol}$).

number of mixed atoms. The higher the number of mixed atoms the longer is the TS period. However, all liquid atoms disappear at around 1.5 ps. Thus if the mixing is governed by TS then it should occur until $\sim 1.5$ ps. The average local temperature of the liquid atoms (FIG (6)) remains above the melting temperature during the TS which indicates that there is a local melt already at 1 keV which persists until 1-1.5 ps. The number of liquid atoms abruptly scales down to zero at $t \approx 1.75$ ps (the end of the TS) due to the solidification of the local melt.

In FIGs (7)- (8) the time evolution of IFM, that is the number of mixed Ti and Pt atoms as a function of time is given for a weakly and strongly mixed sample. It is obvious that the two figures show similar features and thus we can conclude that the time evolution does not depend on the magnitude of mixing.

These curves show some unexpected features. First of all mixing is strongly asymmetric. In case of high mixing (FIG (7)) the number of the mixed (heavier) Pt atoms starts to increase just after the ballistic process is terminated and reaches a maximum during the TS period ($\sim 1$ ps). With the decrease of the number of liquid atoms to zero at $\sim 1.75$ ps the number of mixed Pt atoms also decreases. But after this local minimum an additional increase comes. It reaches about the same value at about $\sim 2$ ps which is at 1 ps but at 2 ps there is no liquid atom present. This feature is shown in an even more striking way in FIG (8). In the case of low mixing the first peak of Pt appears at about 0.5 ps, while the number of liquid atoms disappears at $\sim 0.25$ ps (see FIG (5)). On the other hand the general behaviour of the curves in FIG (7) and FIG (8) are similar and it seems that the time evolution of the number of mixed atoms is independent of the magnitude of mixing for Pt. However, we see somewhat different behaviour for Ti. In FIG (8) Ti reaches its maximum more rapidly then in FIG (7). The number of the mixed Ti atoms starts to increase when the number of mixed Pt atoms reached a maximum. With the increase of the number of mixed Ti atoms the decrease of the number of mixed Pt atoms takes place, however, we see no evidence for such a process for the weakly mixed sample on FIG (8). During these processes the number of liquid atoms is zero. To sum up we see the decoupling of mixing of Pt and Ti during the TS and coupling sets in after a while the TS.

The time evolution of the adatoms, shown in FIG (9), somewhat resembles that of mixed Pt atoms. It is a double peaked curve, which abruptly decreases at $\sim 3$ ps when the number of mixed Pt atoms reaches a quasi-constant value. On the other hand the time evolution of the vacancies differs from that of adatoms (FIG (10)). There is a smaller peak in the vacancy time evolution in the $0-1$ ps range. Between 1 $\sim 3$ ps the number of vacancies reaches a minimum with a low value of $\sim 4$, and it begins to rise at $\sim 3$ ps to reach a constant value of about $\sim 20$ at 5 ps. We note that the increase of the number of mixed Ti atoms starts somewhat earlier (at 2 ps) and reaches a constant value at 3 ps.

Based on these observations it seems to be clear that a simple TS model cannot account for the mixing process. Rather it seems that the mixing occurs as a relaxation process. Surprisingly, IFM starts with a considerable mass transport of Pt and partly coincides with the TS, but as it is shown for the weakly mixed sample (FIG (8)), it might be independent from it.

The reasonable correlation with the number of the Ti adatoms suggests that the IFM process of Pt is strongly influenced by the presence of the free surface. After the first phase of Pt mixing is over the Ti atoms starts to move and with some delay considerable number of vacancies appear. Both changes can be explained as a relaxation process, which decreases the energy of the system.

Based on the above discussion we might conclude that the IFM is independent of the TS. If it is so, then the
mixing cannot depend on the heat of mixing. With the change of the Ti-Pt interaction potential by means of changing $\xi$ we can produce systems which are basically similar is mass, crystal structure etc. but their heat of mixing is different. FIG (11) shows the dependence of the number of mixed atoms on $\Delta H_m$ based on 15 simulations with random impact positions/point. As we have already mentioned, the magnitude of mixing is strongly impact position dependent. Anyhow, having this statistics we cannot see any dependence on $\Delta H_m$, which supports the discussion above although the high rate of uncertainties at each of the points seen in FIG (11) does not prove solidly our findings above. In particular our findings are in contrast with the results of Gades et al. [5]. They found a strong dependence of mixing on $\Delta H_m$ in agreement with the phenomenological models [2]. Although that study is confined to the case of mixing of pure Cu and of various model metals having the same crystall structure and therefore the unsymmetrical nature of mixing does not occur. What could be the role of TS if any in this mixing process? To answer this question we also show the time evolution of the center of the liquid zone in FIG (12). The dotted lines at $z = 35.5$ and at 27 ($z$ is the depth position in Å) mark the free surface and the interface, respectively. For higher mixing rate the center of the liquid zone (the average of the $z$-coordinate of the hot atoms) is nearly confined close to the interface, while for the case of lowest mixing it moves towards the surface. As it was mentioned in the case of the weakly mixed sample, the magnitude of the overall mixing scales with the duration of the liquid phase. Since the center of the liquid phase is at the interface, one might argue that considerable energy is concentrated around the interface which later partly after the freezing of the TS relaxes causing IFM.

But the liquid phase energy depends only on the conditions of ion impact and will not change upon $\Delta H_m$. Thus we explained that though the liquid phase creation is strongly connected to the magnitude of mixing, still the mixing is independent of $\Delta H_m$.

IV. CONCLUSION

Molecular-dynamic simulation was carried out for the Ti/Pt system to explain the ion bombardment induced mixing at 1 keV $Ar^+$ ion bombardment at grazing angle of incidence. We have found that the mixing does not depend on the heat of mixing, as might have been expected. That is, it is not the thermal spike process which governs the mixing in this case. Though we found that the magnitude of mixing is scaling with the number and position of the liquid atoms, this does not depend on the heat of mixing. Rather the majority of the mixing processes are taking place in that time, when liquid atoms are not present. Moreover it was found that the mixing of Ti and Pt are not correlated. We propose that...
FIG. 11. The total number of mixed atoms as a function of heat of mixing in the first irradiation step as obtained varying $\xi$ from 0.0 to 2.55. The error bars indicate the scatter obtained within 15 events at each point. The lower and the upper point of the error bar correspond to the lowest and the highest number of mixed atoms.

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