Lévy-flight intermixing: anomalous nanoscale diffusion in Pt/Ti

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Anomalous diffusion has long been known since the classical Richardson’s study on turbulent diffusion [1]. Since than anomalously large diffusion rates have been observed in various systems under different conditions [2, 3, 5, 6, 7, 8]. The common feature of the observed enhanced diffusion rates are the nonlinear growth of the mean squared displacement in the course of time leading to a power-law time scaling pattern [2]. Hence we are faced with non-Brownian motion of particles with non-Gaussian diffusion rates giving rise to anomalous behaviors which are termed as strange kinetics [9]. Superdiffusion takes place with Lévy flight characteristics (LF, Lévy jump diffusion with broad spatial jump distributions) above the Brownian motion regime [2]. In particular, LF behaviour has been found in turbulent mixing in fluids (review in refs. [2, 6, 7]) or in elongated micelles [6], for photon trajectories in incoherent atomic radiation trapping [10] and it became clear that Lévy processes can be important in the analysis of chaotic dynamics [3]. The research of LF behaviors covers many disciplines of natural and social sciences hence this topic is of high interest [2, 3, 4, 5, 7, 11]. Our primary purpose is to present experimental and computational evidences that the nanoscale transient enhanced intermixing and diffusion, a common phenomenon in many nanostructured materials, could also be fitted in the category of Lévy flight superdiffusion.

There are a growing number of evidences emerged in the last decades that anomalous nanoscale broadening of interfaces or high diffusivity tail in the impurity concentration profile occur during ion-irradiation or sputtering [12, 13, 14, 15, 16, 17, 20], sputter deposition and thin film growth [17, 18]. The anomalous nanoscale bulk diffusional effects could be due to still not clearly established atomistic accelerative effects leading to anomalously fast and possibly athermal atomic transport (long range diffusion) at interfaces or during impurity diffusion [12, 13, 14, 15, 16, 17, 20].

In the present work, using computer atomistic simulations, the recently observed enhanced intermixing in a nanoscale bilayer film/substrate system (Pt/Ti) reported in ref. [10] is attempted to interpret as a Lévy-superdiffusive atomic transport process in the bulk. Superdiffusion in the nanoscale has only been reported until now on solid surfaces [21, 22] and no reports have been found for bulk superdiffusion in the solid state of matter.

Classical molecular dynamics simulations have been used to simulate the ion-sputtering (repeated low-energy ion bombardments of the film) induced atomic intermixing at the Pt/Ti interface using the PARCAS code [23]. Here we only shortly summarize the most important aspects. A variable timestep and the Berendsen temperature control is used to maintain the thermal equilibrium of the entire system at 300 K (see refs. at [16]). The detailed description of other technical aspects of the MD simulations are given in refs. [23] and details specific to the current system in recent communications [16, 21, 23].

Our primary purpose is to simulate the conditions occur during ion-sputtering [10] and Auger electron spectroscopy depth profiling analysis (AES-DP) [10] using molecular dynamics simulations. Following our previous work [10] we ion bombard the film of the bilayers Pt/Ti and Ti/Pt (film/substrate systems) with 0.5 keV Ar+ ions repeatedly (consecutively) with a time interval of 10-20 ps between each of the ion-impacts at 300 K which we find sufficiently long time for most of the structural relaxations and the termination of atomic mixing, such as sputtering induced intermixing (IM) [25]. Since we focus on the occurrence of transient intermixing atomic transport processes, the relaxation time of 10 – 20 ps...
should be appropriate for getting adequate information on transient enhanced intermixing. Pair potentials have been used for the interaction of the Ar$^+$ ions with the metal atoms derived using \textit{ab inito} density functional calculations. The initial velocity direction of the impacting ion was 10 degrees with respect to the surface of the film (grazing angle of incidence) to avoid channeling directions and to simulate the conditions applied during ion-sputtering \cite{16}. The impact positions have been randomly varied on the surface of the film/substrate system and the azimuth angle $\phi$ (the direction of the ion-beam). In order to simulate ion-sputtering a large number of ion irradiation are applied using script governed simulations conducted subsequently together with analyzing the history files (movie files) in each irradiation steps. The impact positions of the 400 ions are randomly distributed over a 20 × 20 Å$^2$ area on the surface.

We used a tight-binding many body potential on the basis of the second moment approximation (TB-SMA) to the density of states \cite{20}, to describe interatomic interactions. In ref. \cite{16} it has been shown that the TB-SMA potential gives the reasonable description of IM in Pt/Ti and gives interfacial broadening comparable with AES-DP measurements. The crosspotential energy has been calculated for the Ti-Pt dimer using \textit{ab inito} local spin density functional calculations \cite{27} together with quadratic convergence self-consistent field (SCF) method. The G03 code is well suited for molecular calculations, hence it can be used for checking pair-potentials. We used the Perdew-Burke-Ernzerhof (PBE) gradient corrected exchange-correlation potential \cite{28}. We find that the interpolated TB-SMA potential \cite{16} nearly perfectly matches the \textit{ab initio} one hence we are convinced that the TB-SMA model accurately describes the heteronuclear interaction in the Ti-Pt dimer. The employed parameter set is given in Table 1.

The crossectional computer animations of simulated ion-sputtering can be seen in our web page \cite{29}. The cartoons of the simulation cells (crossectional slabs as a 3D view) can be seen in ref. \cite{16} which show the strong intermixing at the interface in Pt/Ti and a much weaker mixing in Ti/Pt. In Fig. 1 the evolution of the mean-square atomic displacements (MSD) (the variance of displacements) $\langle R^2(t) \rangle_z = \sum_j N_{ion} \sum_{atom} \langle r_j^2(t) - r_j(t = 0) \rangle_z^2$, of all intermixing atoms obtained by molecular dynamics simulations, where $\langle r_j(t) \rangle_z$ is the position vector of atom 'j' at time $t$, $N_{atom}(t)$ is the total number of intermixing atoms in the jth irradiation step included in the sum, can be followed as a function of the ion fluence (the number of ions $N_{ion}$). Lateral components ($x, y$) are excluded from $\langle R^2 \rangle_z$ and only contributions from IM atomic displacements perpendicular to the layers are included ($z$ or depth components). We follow during simulations the time evolution of $\langle R^2 \rangle_z$ which reflects the atomic migrations through the interface (no other atomic transport processes are included).

In Fig. 1 we present $\langle R^2 \rangle_z$ as a function of the number of ion impacts $N_{ion}$ (ion-number fluence). $\langle R^2 \rangle_z(N_{ion})$ corresponds to the final value of $\langle R^2 \rangle_z$ obtained during the $N_{ion}$th simulation. The final relaxed structure of the simulation of the $(N_{ion} - 1)$th ion-bombardment is used as the input structure for the $N_{ion}$th ion-irradiation. The asymmetry of mixing can clearly be seen when $\langle R^2 \rangle_z(N_{ion})$ and the depth profiles given in ref. \cite{16} are compared in Ti/Pt and in Pt/Ti. The computer animations of the simulations \cite{29} together with the plotted broadening values at the interface in ref. \cite{16} also reveal the stronger IM in Pt/Ti. Moreover we find the strong divergence of $\langle R^2 \rangle_z$ from linear scaling for Pt/Ti and a much weaker nonlinear scaling has been found for Ti/Pt. As it has already been shown in ref. \cite{16} AES-DP found a relatively weak IM in Ti/Pt (the interface

| TABLE I: The semiempirical parameters used in the tight binding interatomic potential for Pt/Ti \cite{16, 20} |
|---|---|---|---|---|
| Ti | Pt | Ti-Pt |
| $\xi$ | 1.416 | 2.695 | 4.2 |
| q | 1.643 | 4.004 | 2.822 |
| $A$ | 0.074 | 0.298 | 0.149 |
| p | 11.418 | 10.612 | 11.015 |
| $r_0$ | 2.95 | 2.78 | 2.87 |

$^a$The parameters for Ti and Pt have been given by Cleri and Rosato \cite{26}. The parameters of the crosspotential have been obtained by fitting the interpolated crosspotential given in ref. \cite{16} to \textit{ab inito} diatomic calculations. The preexponential parameter $\xi$ has been fitted to the \textit{ab inito} curve (see also in ref. \cite{19}). The notations used for the parameters are the same as given in refs. \cite{16, 19, 26}.

![Fig. 1: The simulated ion number fluence](image-url)
energetic particles of which the kinetic energy is larger than to Pt/Ti and to Ti/Pt, respectively. The positions of the energetic particles of which the kinetic energy is larger than ~1 eV are collected during typical single ion impact events at 500 eV ion energy. The ions have been initialized 10 Å above the interface. The vertical axis corresponds to the depth position given in Å. The position at \( z = 0 \) is the depth position of the interface with a horizontal dashed line and the initial positions of the atoms (before irradiation) are also shown.

broadening \( \sigma \approx 20 \) Å) while an unusually high IM occurs in the Pt/Ti bilayer (\( \sigma \approx 70 \) Å). In order to clarify the mechanism of intermixing and to understand how much the nanoscale interfacial mass-anisotropy influences IM, simulations have been carried out with atomic mass ratio \( \delta = m_{Pt}/m_{Ti} \) (where \( m_{Pt} \) and \( m_{Ti} \) are the atomic masses) is artificially set to \( \delta \approx 1 \) (mass-isotropy). We find that the magnitude of IM is strongly sensitive to \( \delta \) at mass-anisotropic, called \( \delta \)-interfaces. The corresponding animation can be also be seen at \([24]\). We reach the conclusion that the mass-effect is robust and the magnitude of IM is weakened significantly in artificially isotropic Pt/Ti in agreement with our earlier finding \([24, 25]\). The huge difference in IM between Pt/Ti and Ti/Pt can be understood as the effect of \( \delta \)-inversion on IM. Actually the system undergoes the transition in the asymptotics of \( \langle R^2 \rangle \propto t^{1.35} \rightarrow \langle R^2 \rangle \propto t^{1.0} \) (from nonlinear dynamics to linear) when the mass anisotropy is inverted (the film and the substrate is interchanged).

To further test mass-effect on IM, we carried out simulations for the Pt/Ti system in which the atomic masses have been interchanged (Ti possesses the atomic mass of Pt and vice versa) setting in an artificial mass ratio (the inverse of the normal one) while keeping all the other parameters unchanged. Note, that we keep the interatomic potentials, only the atomic mass ratio is inverted. We find that this artificial setup of atomic masses results in the suppression of IM in Pt/Ti with inverted \( \delta \). These findings together with our AES measurements (with the long-range tail shown in ref. \([16]\)) confirms our recent results reported for various bilayers in which a strong correlation has been obtained between the experimental and simulated mixing efficiencies and mass anisotropy in various metallic bilayers \([24]\).

In Fig. 1 for Pt/Ti it can clearly be seen that \( \langle R^2 \rangle_z \) (MSD) grows nonlinearly with \( N_{ion} \). The horizontal axis is proportional to the time of ion-sputtering, hence \( \langle R^2 \rangle_z \propto t^\alpha \) with \( \alpha > 1 \). \([2]\). During thermally activated interdiffusion \( \langle R^2 \rangle \) scales linearly with time hence our system violates this temporal behavior. The \( \langle R^2 \rangle_z \propto t^\alpha \), scaling, where \( \alpha \geq 1 \), used to be considered as the signature of anomalous diffusion (superdiffusion) in the literature \([2, 3, 4]\). In our case we find that \( \alpha \approx 1.35 \pm 0.1 \) exponent fits the simulated curve for Pt/Ti. We find for Ti/Pt a linear behavior (\( \alpha \approx 1.0 \pm 0.05 \)) hence no superdiffusive features can be identified in this system.

We would like to show that it might also be the case that transient IM takes place in Pt/Ti which resembles in many respect the Lévy superdiffusive atomic transport processes known on solid surfaces \([2]\). Superdiffusion occur when the particle trajectories exhibit long displacements (flights) termed Lévy flights \([2]\), characterized by power-like asymptotical distribution of the displacements of trajectories (and with heavy-tailed distribution) \([2]\). For these ballistic processes \( \langle R^2 \rangle(t) \) is divergent with time. Normal diffusion is characterized by the linear time evolution of \( \langle R^2 \rangle \) in the long-time limit and with Gaussian distribution \([2]\).

The obtained results are in agreement with the findings presented in ref. \([16]\). However, in that paper it has not been realized that the fingerprint of superdiffusive feature of IM is detected by AES as a long-range diffusivity tail in the concentration profile at the Pt/Ti interface in the Pt/Ti bilayer. No such tail occurs in the concent-

FIG. 2: The normal to the surface cross-sectional view of collisional displacement cascades with atomic trajectories (cross-sectional slab cut in the middle of the simulation cell) in Pt/Ti and in Ti/Pt. The right and left panels correspond to Pt/Ti and to Ti/Pt, respectively. The positions of the energetic particles of which the kinetic energy is larger than ~1 eV are collected during typical single ion impact events at 500 eV ion energy. The ions have been initialized 10 Å above the interface. The vertical axis corresponds to the depth position given in Å. The position at \( z = 0 \) is the depth position of the interface with a horizontal dashed line and the initial positions of the atoms (before irradiation) are also shown.

FIG. 3: The normal to the surface cross-sectional view of trajectories of Lévy flights obtained during 50 consecutive ion-impact events in Pt/Ti using 0.5 keV ion energy for Pt (left panel). The atomic trajectories of hyperthermal Ti atoms are also shown collected during the same irradiation events (panel on the right). The atomic layers above the interface with depth position \( z > 0 \) are Pt layers. The positions of energetic atoms have been plotted which have larger than ~2 eV kinetic energy. The ions have been initialized 10 Å above the interface. The interface is at \( z = 0 \) depth position (the increments are in Å). The initial positions of the atoms (before irradiation) are also shown.
tronization profile of Ti/Pt as shown in ref. [10]. Hence we conclude that the experimental fingerprint of Lévy jumps could also be detected as a high diffusivity tail in the AES concentration profile of many other anisotropic materials. The trajectories corresponding to Lévy flights can be seen in the left panel in Fig. 2. In the panel of Pt/Ti in Fig. 2 we can see the ballistic trajectories of intermixing hyperthermal Pt atoms which exhibit Lévy flights with long trajectories through the interface. We find 8 events out of 10 which exhibit Lévy flights. No such trajectories can be seen in the panel of Ti/Pt in Fig. 2 and in the other dozens of events generated (not shown). The ions have been initialized during these single ion impact events 10 Å above the interface in order to place the range of the ions directly in the depth position of the interface. This way of direct deposition of the ion energy at the interface does not influence the main physics what we find with simulations when ions have been initialized at the surface. This is because the first few tens of ions simply sputter remove the top layers of the film and intermixing develops when the range of ions approaches the interface. Fig. 3, depict us what we see in Fig. 1 that Lévy flights cause the nonlinear time scaling of \( \langle R^2 \rangle_z \). The initial kinetic energy of few of these particles can reach the few tens of eV and which hyperthermal Pt atoms exhibit long trajectories.

In the left panel of Fig. 3 we show all the flight trajectories of Pt atoms obtained during a simulation with 50 repeated ion impacts with 10 ps time delay between each of the events in Pt/Ti. This figure clearly depicts us that Lévy jumps of energetic Pt atoms take place which boost intermixing. Such kind of an interfacial broadening can also be called Lévy interdiffusion. In the right panel of Fig. 3 the trajectories of energetic Ti atoms are also shown obtained during the same simulation. No Lévy jumps can be seen for Ti atoms. These atoms not even move across the interface except during few events. In Ti/Pt no LF behavior can be found both for Pt and Ti atoms. Concerning the atomic mobility of the hyperthermal Pt particles, some of these particles can have a huge initial kinetic energy exceeding 100 eV in few cases. This could be due to the accelerative effect of head on collision of the ion or recoils with few of the Pt atoms at the δ-interface. The Pt atoms intermix preferentially both in Ti/Pt and in Pt/Ti [25]. These rapidly migrating particles slow down to few eV within 0.5 ps and which energy regime persists up to few ps. Hence a long range tail exists for the time distribution of the atomic velocity during Lévy jumps in Pt/Ti which is also a characteristic feature of non-Brownian dynamics [2, 3].

In conclusion, we reveal that atomic intermixing might take place via Lévy flights in the Pt/Ti film/substrate bilayer upon low-energy ion bombardments. This mechanism could be valid for many other interdiffusion processes in which mass anisotropic interface is present.

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