Predicting Kinetic Electron Emission in Molecular Dynamics Simulations of Sputtering†

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We present a molecular dynamics (MD) based computer simulation model for particle bombardment of metal surfaces. In addition to the description of the atomic collision cascade initiated by the particle impact, our model incorporates the electronic degree of freedom of the target and therefore is capable of simultaneously predicting secondary ion formation in sputtering as well as ion-bombardment-induced kinetic electron emission (KEE). Hence, our simulation concept may be regarded as an approach to close the gap between classical MD simulations usually excluding electronic effects and ab initio many-body quantum mechanics breaking down for system sizes needed to describe atomic collision cascades. In this study, we apply our model to the keV self-bombardment of a (111)-oriented silver surface in order to predict kinetic electron emission yields.

1. Introduction

If an atomic particle with a kinetic energy of a few keV impinges upon a metal surface, a sequence of collisions among near-surface atoms (atomic collision cascade) is initiated. In the course of the evolution of this atomic collision cascade in time and space, particles may be released from the surface (sputtering) into the gas phase.32,33 In general, the flux of emitted particles not only consists of neutrals but also comprises excited atoms, ions,35 or even electrons.2,3,5,16 This phenomenon clearly indicates that the development of the atomic collision cascade within the solid is accompanied by electronic substrate excitations. Although investigated for decades, the underlying mechanisms of this kinetic excitation of the bombarded solid and the effects associated therewith are still not yet completely understood.4

From a fundamental point of view, a rigorous description of the particle dynamics together with the kinetic excitation requires one to numerically solve the corresponding time-dependent Schrödinger equation for the entire particle system. The microscopic particle dynamics within the atomic collision cascade is assumed to be embedded into a free electron gas characterized by its Fermi energy $E_F$. The microscopic particle dynamics within the atomic collision cascade initiated by keV Ag $\rightarrow$ Ag(111) bombardment under normal incidence are obtained by means of MD simulations described in detail earlier.6,7,23,34 Briefly, the coupled Newtonian equations of motion are numerically integrated for the projectile and all target atoms in order to obtain the time evolution (“trajectory”) of the entire particle system. The interatomic forces are modeled via a many-body MD/MC-CEM potential fitted to the properties of solid silver.18

The incorporation of the electronic system of the metal is realized in terms of a quasi-free Fermi gas picture; i.e., the atomic collision cascade is assumed to be embedded into a free electron gas characterized by its Fermi energy $E_F$ and density $n_e$.

The kinetic excitation via direct atom–electron collisions (see Figure 1a) is described within the framework of the Lindhard theory of electronic stopping,24,25 yielding a velocity-proportional friction force acting on every moving cascade atom. Consequently, the electronic energy loss $dE$ within the time interval $dt$ for the $i$th particle is proportional to its kinetic energy $E_i$.

This energy loss is treated as a source of excitation energy fed into the electronic system. Thus, the atomic collision cascade generates a space- and time-dependent source of excitation energy given by

$$\left(\frac{dE}{dt}\right)_{\text{nic}}(\vec{r}, t) = A \cdot \sum_{i=1}^{N} E_i \cdot \delta(\vec{r}-\vec{r}_i(t)) \quad (1)$$

with $\vec{r}_i(t)$ denoting the position of particle $i$ at time $t$, $N$ denoting

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the total number of atoms, and $A$ being a friction parameter evaluated as $2.88 \times 10^{12}$ $1/s^2$ for an Ag atom moving within a silver solid. Note that there exists some controversy regarding the applicability of the Lindhard friction concept for low energy recoils within the cascade. For a similar model system as studied here, \textit{ab initio} time dependent density functional theory computations have indicated the validity of our treatment even for slow cascade atoms with energies below 10 eV.\textsuperscript{24}

For the inclusion of electron promotion processes during hard inelastic collisions into MD simulations of atomic collision cascades, we apply a model\textsuperscript{9} that extends the curve crossing approach of Fano and Lichten\textsuperscript{14}—originally developed for atomic gas-phase collisions—such to apply for violent inelastic collisions within a solid (Figure 1b).\textsuperscript{17} Details of this model have recently been published elsewhere,\textsuperscript{9} so that only a short outline will be given here.

We assume that quasi-molecular orbitals (MOs) are generated due to the mixing of atomic wave functions during a close encounter of two colliding atoms within the solid. The eigenenergies $E_{\text{MO}}$ of these MOs strongly depend on the interatomic distance $r$. In a diabatic picture, some selected orbitals may be promoted to higher energy such to exceed the Fermi level of the metal and therefore allow for resonant electronic transition from the quasi-MO into free conduction band states. The transition rate $\Gamma$ corresponds to a finite level width $\Delta$ of the promoted MO. In principle, $\Gamma$ can be derived from Fermi’s golden rule. However, a physically meaningful calculation of the transition matrix elements would require the calculation of the diabatic molecular orbitals during the hard collision, which is extremely complicated and out of the scope of the present paper. In view of the many other approximations applied here, we therefore assume a constant level width $\Delta$ which is inferred from experimental photoemission spectroscopy data.\textsuperscript{28}

Within the MD simulation, the probabilistic nature of the electronic transition from the MO into a free conduction band state is implemented using a Monte Carlo scheme as follows: At each MD time step $i$ of length $\Delta t$, the pair correlation function of the entire system is calculated. In the case that there exists a pair of atoms with $r < r_c$ (see Figure 1b), an electronic transition is assumed to occur if $\xi < A \Delta t / \hbar$, where $\xi$ denotes a random number in the interval $[0,1]$. Once the transition has occurred, an additional autoionization process of the originally doubly occupied MO is prohibited, since the deoccupation in the first process energetically shifts the MO to energies below $E_F$. This condition is forced by flagging each collision and transition. Note that the autoionizing transition leaves a vacancy in the quasi-MO that will delocalize in the d-band on a time scale of a few fs. In the case of silver, the corresponding d-hole energy $E_h$ amounts to approximately 5 eV. Let $t'$ be the time index where the autoionization occurs, then the collisional excitation energy is given by

$$E^{\text{exc}} = E_{\text{MO}}(r(t')) - E_F$$

In order to enforce energy conservation, this energy is subtracted from the potential energy by instantaneously increasing the distance of the colliding atoms such that the potential energy deficit equals the excitation energy.

The transport of excitation energy generated by electronic friction or autoionization from its point of generation is treated in terms of the nonlinear diffusion equation

$$\frac{\partial E(\vec{r}, t)}{\partial t} - \nabla \cdot (D(\vec{r}, t) \cdot \nabla E(\vec{r}, t)) = \left( \frac{\partial E}{\partial t} \right)_{\text{fric}}(\vec{r}, t) + \sum_{\kappa} \frac{E_{\text{MO}}(r(\kappa)) - E_F}{\Delta t} \cdot \delta(t - t_{\text{fric}}) \cdot \delta(\vec{r} - \vec{r}(\kappa))$$

(2)

The left-hand side of eq 2 constitutes the transport term, whereas the right-hand side contains all (time- and space-dependent) sources of excitation energy. The second sum on the right-hand side loops over all close collisions $\kappa$ that lead to an autoionizing transition during the evolution of the cascade.

The transport dynamics are governed by the excitation energy diffusivity $D$, which in general may depend on the lattice temperature $T_l$, the local electron temperature $T_e$, and a lattice order parameter $\Lambda$. Equation 2 is numerically solved by means of a finite differences scheme using Neumann boundary conditions at the surface in combination with pseudoinfinite boundary conditions at all other system boundaries.\textsuperscript{13} For each trajectory, the numerical solution of eq 2 yields a space- and time-dependent excitation energy density profile $E(\vec{r}, t)$ within the cascade volume that may be transformed into an electron temperature distribution $T_e(\vec{r}, t)$. This electron temperature $T_e$ should be primarily taken as an effective parameter to characterize the local excitation energy density rather than a “real” electron temperature. Nevertheless, very recently, Race et al.\textsuperscript{27} carried out time-dependent tight-binding simulations of radiation
damage cascades in copper and found that the electronic excitations closely resemble a Fermi–Dirac distribution at some elevated temperature, even in the absence of direct electron–electron interactions that would be required in order to drive a nonequilibrium distribution into an equilibrium state.

In order to obtain the kinetic electron emission yield \( \gamma \), we treat the KEE within the framework of a simple thermal emission model as proposed by Sroubek (“hot-spot model”). Following Kovacs et al., the electron current density \( j_e \) at the surface is given by

\[
j_e(\vec{r}, t) = \frac{e m}{2 \pi^2 h^2} (k_B T_e(\vec{r}, t))^2 \sum_{n=1}^{\infty} (-1)^{n-1} \frac{1}{n^2} e^{-n \Phi(\vec{r},t)/k_B T_e(\vec{r},t)}
\]

(3)

with \( e \) denoting the elementary charge, \( m \) the (effective) electron mass, and \( \Phi = \Phi_E + \Phi_F - \mu \) being derived from the work function \( \Phi \). The chemical potential \( \mu \) is a functional of the temperature distribution and, according to the Sommerfeld model, calculated as

\[
\mu(\vec{r}, t) = E_F \left[ 1 - \frac{\pi^2}{12} \left( \frac{T_e(\vec{r}, t)}{T_F} \right)^2 \right]
\]

(4)

The electron temperature profile \( T_e(\vec{r}, t) \) at the surface delivered from the electronic extraction and transport calculations is the crucial physical input entering eq 3. Note that, in the limiting case of low electron temperatures, i.e., \( k_B T_e \ll E_F \), eq 3 reduces to the well-known Richardson–Dushman formula for thermonic emission. The kinetic electron emission yield \( \gamma \) is obtained by numerically integrating eq 3 over surface area \( A \) and the duration time \( t_c \) of the cascade, i.e.,

\[
\gamma = \frac{1}{e} \int_0^{t_c} \int_A j_e(\vec{r}, t) \, dA \, dt
\]

(5)

3. Results

The computations described in section 2 have been carried out for \( \text{Ag} \rightarrow \text{Ag(111)} \) bombardment with impact energies \( E_0 \) ranging from 0.125 to 5 keV. For each energy, a set of 120 different impact spots evenly distributed within the smallest irreducible zone of the 2D Wigner–Seitz surface cell have been selected. In order to ensure statistical significance regarding the probabilistic treatment of electron promotion, a total of 10 trajectories have been calculated for each impact point, each with a different initialization of the random number generator. Therefore, 1200 individual atomic collision cascades have been analyzed for each bombarding energy.

For each atomic collision cascade \( \nu \), an individual electron temperature distribution \( T_{e,\nu}(\vec{r}, t) \) was calculated and employed to numerically evaluate eq 5, yielding an individual KEE yield \( \gamma_\nu \). The mean KEE yield \( \gamma \) is then obtained by averaging over all trajectories. The employed Ag(111) model crystallite has dimensions of \( 22 \, \text{Å} \times 22 \, \text{Å} \times 2 \, \text{Å} \) and consists of 720 atoms arranged in 10 layers. Equation 5 is integrated up to \( t_c = 50 \, \text{fs} \) after the impact using a spatial discretization with voxels of \( 3 \, \text{Å} \times 3 \, \text{Å} \times 3 \, \text{Å} \) dimension. These numerical system parameters constitute a trade-off between accuracy and computational effort. Preliminary calculations have shown that a finer discretization of the model crystallite does not change the obtained results within a range of 10%. Furthermore, for 5 keV bombarding energy, we additionally calculated each trajectory on a larger crystal containing 4500 atoms and followed the kinetic electron emission process up to a total time of 750 fs. The obtained mean KEE yield did not significantly differ (<8%) from the results obtained from the shorter calculations on the smaller crystal.

As an example, Figure 4 depicts four temporal snapshots of an exemplary atomic collision cascade initiated by a 5 keV Ag atom impinging onto the Ag(111) model crystallite. On the left side of Figure 4, the microscopic particle dynamics in the collision cascade are shown. In each snapshot, those atoms which take part in a hard collision accompanied by an autoionizing electronic transition are highlighted in orange color. The snapshots arranged on the right-hand side of Figure 4 additionally feature a representation of the local excitation energy density \( E(\vec{r}, t) \) according to the indicated color map. At \( t = 12 \, \text{fs} \), the projectile impact leads to a pronounced local “hot spot” of high excitation energy density (about 0.025 eV/\( \text{Å}^3 \)) corresponding to an electron temperature of approximately \( 10^4 \, \text{K} \). This initial peak originates from the frictional electronic energy loss of the fast projectile. At \( t = 18 \, \text{fs} \), the projectile collides with a third-layer atom at rest, resulting in the generation of a fast recoil atom that pushes forward a second branch of the cascade propagating to the left. A detailed analysis shows that during this violent collision (at \( t = 16.7 \, \text{fs} \)) a hot electron is generated with an excitation energy of approximately 20 eV, manifesting itself in a further pronounced hot spot located 10 Å below the surface. Inspecting the situations at \( t = 28 \, \text{fs} \) and \( t = 41 \, \text{fs} \) after the impact, we observe that in both branches of the cascades further autoionizing electronic transitions take place, giving rise to distinct hot spots with electron temperatures of several thousand Kelvin. Note that, due to the color code used here, the continuous heating of the electron gas via Lindhard friction does not really become obvious. Nevertheless, in the time interval from 0 to 50 fs, a total excitation energy of 520 eV has been generated by electronic friction, whereas the total collisional excitation energy amounts to 300 eV.

Figure 3 shows the average kinetic electron emission yields \( \gamma \) as a function of the bombarding energy ranging from 0.125 keV (1.2 \times 10^{-3} \, \text{keV/amu}) to 5 keV (0.046 keV/amu). The calculations have been performed employing a constant excitation energy diffusivity of \( D = 1 \, \text{cm}^2/\text{s} \) in the entire crystal volume. This particular choice originates from previous investigations on the space and time dependence of \( D \), which reveal that for the time scale and the limited volume considered here a constant value of 1 cm²/s appears to be appropriate. In principle, our model is capable of treating the diffusion parameter \( D \) in a self-consistent manner as a function of space and time as outlined in the previous section. However, in the present study, we keep \( D \) constant in order to eliminate any discretization effects in the numerical treatment of eq 2 that may occur directly upon particle impact when the total amount of kinetic energy is located within one single integration cell.

Two different sets of calculations have been carried out: In one case, both electronic friction as well as electron promotion have been taken into account as sources of excitation energy. In the second set of calculations, electron promotion processes have been completely disregarded. If both excitation mechanisms are activated, we obtain average KEE yields ranging from \( 3 \times 10^{-4} \) (0.125 keV) up to about 0.5 (5 keV). The calculated data may be compared to experiments for \( \text{Xe} \rightarrow \text{Au} \) bombardment carried out by Lakits et al. and Alonso et al., respectively. Qualitatively, the results compare well—that is, both curves reveal similar curve characteristics over the entire range of bombarding energies. Quantitatively, the results from our
model calculation for silver self-bombardment exceed the experimental values for the Xe → Au system by factors of 3–10 depending on the bombarding energy. The most important observation, however, is that particularly at low bombarding energies below the classical threshold $E_{\text{th}}$ for KEE (for Ag → Ag: $E_{\text{th}} \approx 0.3$ keV/amu) the experimental data cannot be explained without electron promotion processes. If electron promotion is neglected as a source of excitation energy, the calculated yields underestimate the experimental results by approximately 2–4 orders of magnitude for bombarding energies below 0.5 keV. This finding indicates a non-negligible influence of electron promotion processes in KEE from silver surfaces under keV self-bombardment.

Now, in order to further profit by our MD approach to KEE, we have analyzed the statistics of kinetic electron emission being inaccessible from experiments. For 5 keV bombarding energy and a total of 1200 trajectories, Figure 4 shows the distribution of individual yields $\gamma_i$, each originating from one particular impact. The spectrum of values of $\gamma_i$ varies from 0.16 to a maximum of 1.9. Thus, the KEE yield distribution exhibits a much narrower spread compared to sputtering yield distributions usually obtained under similar bombarding conditions. Furthermore, we have analyzed the underlying temporal dynamics of the KEE emission process, which cannot be resolved in experiments. Figure 5 shows the KEE emission rate $d\gamma/dt$ as a function of time after impact. First of all, we observe that the entire KEE takes place on a time scale below 50 fs, which is by one order of magnitude smaller compared to atomic sputtering. Moreover, the graph exhibits an interesting fine structure. The maximum peak at 6 fs coincides with the projectile impact and, thus, with the overall maximum of electron temperature in the cascade. For $t \geq 6$ fs, $d\gamma/dt$ strongly decreases and finally vanishes within the next 10 fs. However, this decrease is perturbed by rather pronounced peaks at 9 and 13 fs. These peaks originate from electron promotion processes. The red curve in Figure 4 shows this excitation energy generated by electron promotion per unit time averaged over the total set of trajectories, which in the following will be denoted as $dE_p/dt$. While the aforementioned correlation between $d\gamma/dt$ and the occurrence of electron promotion processes becomes qualitatively obvious, the reciprocity in the peak intensities of $d\gamma/dt$ and $dE_p/dt$ appears to be striking at first sight. A detailed analysis, however, shows that on average the electron promotion
events at 13 and 9 fs take place at larger depth and, thus, the transport of excitation energy away from the spots of generation makes these processes less effective for KEE.

In order to further improve the accuracy of our model, the next step in the development will be the consideration of deviations of the electron temperature dependence of thermophysical properties of silver from the predictions of the classical Sommerfeld model, as discussed in ref 22. Corresponding calculations are currently under way in our lab.

4. Conclusion

We have presented a computer simulation model for the calculation of kinetic electron emission yields at ion-bombarded metal surfaces. The model treats the atomistic particle kinetics by means of molecular dynamics. The electronic degree of freedom is represented by a free electron gas. As sources of electronic excitation, electronic friction as well as electron promotion in kinetic excitation of solids. The electronic degree of freedom is represented by a free electron gas. As sources of electronic excitation, electronic friction as well as electron promotion in kinetic excitation of solids.

In contrast to other kinetic electron emission models, the computations presented here take into account the full time- and space-dependent particle dynamics within the atomic collision cascade. Furthermore, the model presented here does not treat the kinetic electron emission as a multiple step process in which the transport of electrons to the surface is decoupled from the electronic excitation. Instead, our model inherently incorporates the transport process by means of the self-consistent diffusive treatment. The model is employed to calculate kinetic electron emission yields for silver self-sputtering with bombarding energies ranging from 0.125 to 5 keV. The obtained results show good qualitative agreement with available experimental data. By switching the electron promotion processes either off or on within the simulation model, the significance of these collisional excitation events for KEE has been studied. The results indicate that hot electron generation in close binary encounters constitutes a non-negligible mechanism in the kinetic electron emission from silver surfaces under self-bombardment.

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References and Notes


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