UNIVERSITÄT DUISBURG ESSEN

SFB 616

Computer Simulation of Electronic Excitation in Atomic Collision Cascades

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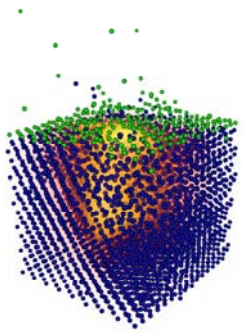
Motivation

- **keV-particle impact → atomic collision cascade**
  - elastic collisions
  - electronic excitation
  - particle emission
- **kinetic excitation**
  - hot electron-hole pair generation
  - ionization & excitation of sputtered particles
  - kinetic electron emission
- **model description**
  - electronic excitation mechanisms
  - excitation energy transport
  - secondary ion formation mechanisms
  - model for kinetic electron emission

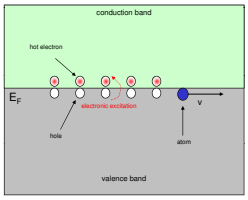


model system: Ag → Ag (111)

Electronic Excitation Model

Excitation Mechanisms

- **electronic friction**



- direct atom-electron collisions
- electronic stopping (Fig. 1)
- velocity-proportional friction force
- Fermi-like excitation spectrum → T_e (Fig. 2)

→ total excitation energy source rate:

$$\frac{dE(\mathbf{r},t)}{dt} = A\sum_i E_k^i(t)\cdot\delta(\mathbf{r}_i-\mathbf{r}) = AE_k(\mathbf{r},t)$$

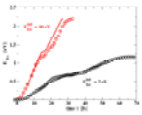


Fig. 1: Energy E_{exc} dissipated into electron hole pair excitations as a function of time for different kinetic energies of a H-atom impinging onto an Al(111) surface. Results from TDDFT simulations are compared to predictions from the Lindhard theory of electronic stopping.

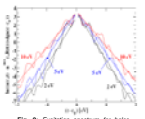
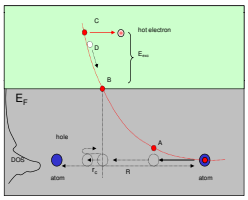


Fig. 2: Excitation spectrum for holes and electrons in the N_i simulation volume

- **electron promotion**



- close atom-atom collisions
- quasi-molecular orbital formation
- „diabatic" curve crossing (Fig. 3)
- electron promotion above Fermi level
- resonant autoionizing transitions into free conduction band states
- generation of hot electrons above E_F

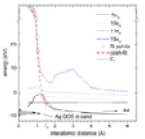
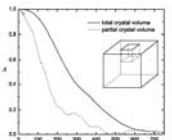


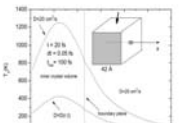
Fig. 3: Ab-initio HF-calculation of MO energies vs. interatomic distance corresponding to a quasi-molecule consisting of two Ag atoms. The red dotted line constitutes the diabatic MO-level geometrically constructed from the adiabatic ones

Transport

- free electron gas model
- nonlinear diffusive transport of excitation energy
- crucial parameter: D „excitation energy diffusivity"
- D may vary in space and time as a function of
  - lattice temperature T_l
  - electron temperature T_e
  - crystallographic order →

Local order parameter for two different crystal volumes as a function of time after the projectile impact. The relative size and position of the "partial" crystal volume dotted line within the total model crystallite solid line is schematically drawn, too.





Boundary Conditions

- Neumann conditions at the surface
- pseudo-infinite boundary conditions at other boundary planes (Green's functions method)
- crater formation dynamics treated as a moving boundary value problem

Fig. 4: Electron temperature along the central x-axis of the simulation volume 20 fs after the impact of a 5-keV Ag atom onto an Ag(111) model crystallite. The right boundary plane is located at x=42 Angstroem.

Model Equations

Excitation Energy Density $E(\vec{r},t) \Leftrightarrow T_e(\vec{r},t)$

particle dynamics (MD)

$$M\frac{d^2\vec{r}_i(t)}{dt^2} + \left(K\right)\frac{d\vec{r}_i(t)}{dt} = -\nabla_{\vec{r}_i}V(\vec{r}_1(t),\vec{r}_2(t),\ldots,\vec{r}_N(t))$$

$\vec{r}_i(t),\ \vec{v}_i(t)$

electronic system

$$\frac{\partial E(\vec{r},t)}{\partial t} - \vec{\nabla}\cdot\left(D\left(T_l(\vec{r},t),T_e(\vec{r},t),\Lambda(\vec{r},t)\right)\vec{\nabla}E(\vec{r},t)\right) = A\sum_{i=1}^{N}E_k^i(\vec{r}_i,t)\cdot\delta(\vec{r}_i(t)-\vec{r}(t)) + \sum_{\kappa}\frac{E_{\vartheta\sigma,\kappa}\left(\vec{r}_{dep}^{\,(\kappa)}(t)\right)-E_F}{\Delta t}\cdot\delta(t-t_{dep}^{(\kappa)})\cdot\delta(\vec{r}-\vec{r}_{dep}^{\,(\kappa)})$$

diffusion coefficient

$$D(\vec{r},t) = \frac{1}{1-1/\sqrt{N(\vec{r},t)}}\cdot\left\{D_0(\vec{r},t)\left[\Lambda(\vec{r},t)-1/\sqrt{N(\vec{r},t)}\right]+D_{\min}\left[1-\Lambda(\vec{r},t)\right]\right\}$$

$$\Lambda(\vec{r},t) = \frac{1}{3N}\left|\sum_i\sum_{j=1}^{3}\cos\left(\frac{2\pi}{a_j}x_j^i(t)\right)\right|$$

$$D_0(\vec{r},t) = \frac{1}{3}aT_e^2(\vec{r},t)+bT_l(\vec{r},t)$$

boundaries of the electronic system

$$I_m := \{(i,j,k)|\vec{r}_{i,j,k}\in\partial\Omega_m\}$$

$$\Delta E^{out,n} = \frac{1}{\Delta\tau}D_{out}\vec{\nabla}E\cdot\vec{n}_m\Delta t$$

$$E(\vec{r}_{i,j,k}\in\partial\Omega_m,t_n) = \sum_{\alpha=0}\sum_{\kappa,\mu,\nu\in I_m}\Delta E_{\kappa,\mu,\nu}^{s,\alpha} \times \frac{1}{(4\pi D_{out}(t_n-t_\alpha))^{\frac{3}{2}}}\exp\left(\frac{-|\vec{r}_{\kappa,\mu,\nu}-\vec{r}_{i,j,k}|^2}{4D_{out}(t_n-t_\alpha)}\right)$$

Results

Electron Promotion

- At which interatomic distance does the resonant electronic transition occur ?

Stochastic Landau-Zener (LZ) approach

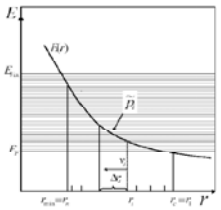


Fig. 5: Schematic drawing of the quasi MO intervening the conduction band

- avoided crossings between MO diabatic energy curve and continuum states (Fig. 5)
- LZ transition probability given by

$$p(r) = \left[1-\exp\left(\frac{-2\pi H^2}{\hbar v(r)\alpha(r)}\right)\right]$$

- probability for transition at r_i is then

$$p_i = \frac{1}{N}\cdot\frac{1}{q}\cdot\left[1-\exp\left(\frac{-2\pi H^2}{\hbar v(r_i)\alpha(r_i)}\right)\right]\times\Delta r_i\left|\frac{\partial E}{\partial r}_{r_i}\right|\times\prod_{j=1}^{i-1}(1-p_j)$$

- Normalization factor N determined by the condition that, at the latest, the transition must occur at the turning point

el. promotion vs el. friction

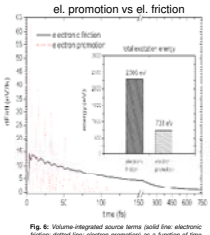


Fig. 6: Volume-integrated source terms (solid line: electronic friction; dotted line: electron promotion) as a function of time after the projectile impact. Insert: shows the total excitation energy generated within the first 750 fs after the initialization of the cascade.

Constant Rate Model

5-keV Ag → Ag (111)

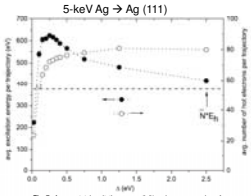


Fig. 7: Average total excitation energy (left) and average number of hot electrons (right) per trajectory for different level widths Δ.

- Overlap of diabatic MO with conduction band states
  → Virtual bound state (VBS) of finite width Δ
- transition rate given by Fermi's Golden Rule

$$\Gamma(E) = \frac{2\pi}{\hbar}|V_{ik}(E)|^2\rho(E)$$

- approximation: constant transition rate Γ taken from experimental line widths Δ
- Monte-Carlo treatment of transitions within molecular dynamics code

excitation spectrum

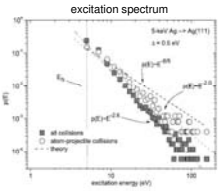


Fig. 8: Nascent excitation energy distribution of hot electrons generated in electron promotion events. Data taken from a set of 120 trajectories.

Statistical Analysis of Energy Transfer Processes

- particle bombardment of solid surfaces is stochastic process

→ averaging over large number of impact points

→ comparison of average electron temperatures with temperatures obtained from high action events (Fig. 9)

- investigation of crystallographic effects (Fig. 10)

5-keV Ag→ Ag(111): electron temperatures

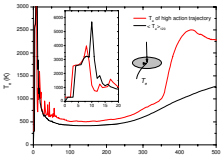


Fig 9: Comparison of the electron temperatures of a high-action trajectory (Y = 28) with electron temperatures averaged over 120 trajectories (Y = 10).

Crystallographic effects

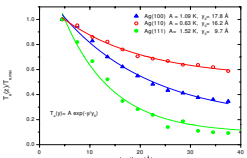
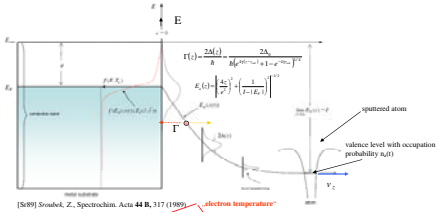


Fig 10: Temperature depth profile for different crystall orientation

Secondary Ion Formation in Sputtering



[Sr89] Sroubek, Z., Spectrochim. Acta **44 B,** 317 (1989)

$$\frac{dn_a(t)}{dt} = -\Gamma\cdot n_a(t)(1-f(E_a,T_e)) + \Gamma\cdot f(E_a,T_e)(1-n_a(t)) \quad \text{(rate equation)}$$

$$\Rightarrow P^+ = \lim_{t\to\infty}1-n_a(t) \quad \text{(ionization probability)}$$

5-keV Ag→ Ag(111) Ionization probabilities

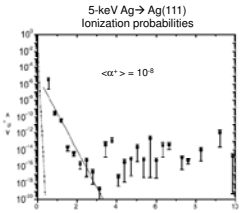


Fig 11: Calculated ionization probabilities of sputtered atoms for 5-keV Ag → Ag (111) bombardment

Kinetic Electron Emission

- thermodynamical free-electron model
- numerical integration of Richardson-Dushman equation using the time- and space dependent electron temperature distribution at the surface

$$j_e(\mathbf{r},t) = \frac{e(1)}{2\pi^2\hbar^3}(k_BT_e(\mathbf{r},t))^2\times\sum_{n=1}^{\infty}(-1)^{n-1}\frac{1}{n^2}e^{-n\Phi_e'(\mathbf{r},t)/k_BT_e(\mathbf{r},t)}$$

$$\gamma_{KEE} = \frac{1}{e}\int_0^{t_{tr}}\int_\Omega j_e(\mathbf{r},t)\,dA\,dt$$

→ kinetic electron emission yield γ per trajectory

- averaging over many trajectories (Fig. 12)

Kinetic electron emission yields

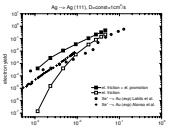


Fig. 12: Kinetic electron emission yield γ as a function of bombarding energy. γ has been averaged over 1200 trajectories. The total simulated time per impact was 50 fs.

5-keV Ag → Ag (111)

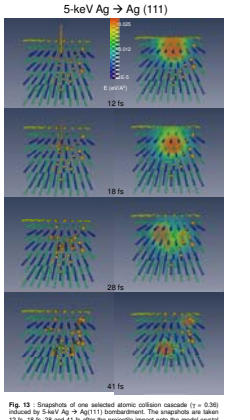


Fig. 13 : Snapshots of one selected atomic collision cascade (γ = 0.36) induced by 5-keV Ag → Ag(111) bombardment. The snapshots are taken 12 fs, 18 fs, 28 and 41 fs after the projectile impact onto the model crystal (726 atoms). **Left:** Evolution of the collision cascade in space and time. Atoms are enclosed (yellow, green, blue) according to the layer they originate from. Particles that are involved in close collisions in the course of the cascade are depicted in orange color. **Right:** In addition to the particle dynamics, the local excitation energy density is shown using the indicated color map.

Selected Publications

[1] *Computer-simulation of low-energy electronic excitation in atomic collision cascades*
A. Duvenbeck, F. Sroubek, Z. Sroubek and A. Wucher, Nucl. Instr. Meth. **B 225** (2004) 464-477

[2] *Self sputtering yields of silver under bombardment with polyatomic projectiles,*
A. Duvenbeck, M. Lindenblatt and A. Wucher, Nucl. Instr. Meth. **B 228** (2005) 170-175

[3] *Electronic excitation in atomic collision cascades,*
A. Duvenbeck, Z. Sroubek and A. Wucher, Nucl. Instr. Meth. **B 228** (2005) 325-329

[4] *Low energy electronic excitation in atomic collision cascades: a nonlinear transport model,*
A. Duvenbeck and A. Wucher, Phys. Rev. **B 72** (2005) 165408

[5] *On the role of electronic friction and electron promotion in kinetic excitation of solids,*
A. Duvenbeck, O. Weingart, V. Buss and A. Wucher, Nucl. Instr. Meth. **B 255** (2007) 281

[6] *The role of electronic friction of low-energy recoils in atomic collision cascades,*
A. Duvenbeck, O. Weingart, V. Buss and A. Wucher, Nucl. Instr. Meth. **B 258** (2007) 83

[7] *Electronic friction and electron promotion in atomic collision cascades,*
A. Duvenbeck, O. Weingart, V. Buss and A. Wucher, New. J. Phys. **9** (2007) 38

[8] *Modeling hot electron generation induced by electron promotion in atomic-collision cascades in metals*
A. Duvenbeck, B. Weidtmann, O. Weingart and A. Wucher, Phys. Rev. **B 77** (2008) 245444 (1-7)

[9] *Predicting secondary ion formation in MD simulations of sputtering,*
B. Weidtmann, A. Duvenbeck and A. Wucher, Appl. Surf. Sci. (2008) in press

[10] *Predicting kinetic electron emission in MD simulations of sputtering*
A. Duvenbeck, B. Weidtmann and A. Wucher, Nucl. Instr. and Meth. B (2008) submitted