Quantum Molecular Dynamics Study on Energy Transfer to the Secondary Electron in Surface Collision Process of an Ion

Masahiko Shibahara¹, Shin-ichi Satake² and Jun Taniguchi²
¹Department of Mechanical Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan.
²Department of Applied Electronics, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba, 278-8510, Japan.

E-mail: siba@mech.eng.osaka-u.ac.jp

Abstract. In the present study the quantum molecular dynamics method was applied to an energy transfer problem to an electron during ionic surface collision process in order to elucidate how energy of ionic collision transfers to the emitted electrons. Effects of various physical parameters, such as the collision velocity and interaction strength between the observed electron and the classical particles on the energy transfer to the electron were investigated by the quantum molecular dynamics method when the potassium ion was collided with the surface so as to elucidate the energy path to the electron and the predominant factor of energy transfer to the electron. Effects of potential energy between the ion and the electron and that between the surface molecule and the electron on the electronic energy transfer were shown in the present paper. The energy transfer to the observed secondary electron through the potential energy term between the ion and the electron was much dependent on the ion collision energy although the energy increase to the observed secondary electron was not monotonous through the potential energy between the ion and surface molecules with the change of the ion collision energy.

1. Nomenclature

- Ce-Xe: non-dimension potential energy between a secondary electron and a surface molecule
- Ck-e: non-dimension potential energy between an ion and a secondary electron
- C₄: a potential parameter
- C₆: a potential parameter
- C₉: a potential parameter
- Δt: time step
- e: elementary electric charge
- E: energy of the system
- Eₑ: energy of electrons
- Eₙ: energy of nuclei
- Eₑₑ: energy of a secondary electron
- ε: a potential parameter
- ε₀: vacuum dielectric constant
- H: Hamiltonian of a system
- Hₐ: Hamiltonian of classical particles

© 2008 IOP Publishing Ltd
2. Introduction

It is well known that an emission of secondary electrons is observed in an ion collision process to a surface, such as the focused ion beam (FIB) process. Molecular dynamics simulations were sometimes conducted to predict the surface states during and after FIB process [1,2]. However, the physical effect of secondary emission on energy and mass transfer is seldom considered and there are few examples of analysis of the secondary electron emission. It is one of interesting problems as an extreme small scale energy transfer problem how energy is transferred to the electron emitted from the surface by ionic collisions. In the present study the quantum molecular dynamics method [3-6] was applied to an energy transfer problem to an electron during ionic surface collision process in order to elucidate how energy of ionic collision transfers to the emitted electrons. In the present paper, the energy transfer to the electron was discussed during the collision process of an ion with changing the interaction between the electron and ions and that between the electron and surface molecules by the quantum molecular dynamics method.

3. Numerical method

We tried to derive fundamental equations for a calculation of a dynamic behavior of a secondary electron in a surface collision process of an ion. In a system that was composed of electrons and nuclei, the time independent Schrodinger equation of the system can be written as follows,

\[ \hat{H} \Psi = E \Psi, \tag{1} \]

where the system Hamiltonian, the system energy and the wave function of the system were \( \hat{H} \), \( E \) and \( \Psi \), respectively. When we assume that the system wave function can be separable into the wave
function of the nuclei and that of electrons because of difference of their mass and motions, the time
independent Schrodinger equation (1) can be written as
\[ H \Psi_n \cdot \Psi_e = E \Psi_n \cdot \Psi_e. \]  
(2)
The Hamiltonian in equation (1) can be written as,
\[ H = K_e + K_n + V_{e-e} + V_{e-n} + V_{n-n}, \]  
(3)
where \( K_e, K_n, V_{e-e}, V_{e-n} \) and \( V_{n-n} \) were kinetic energy term of electrons, that of nuclei, potential energy between electrons, that between electrons and nuclei and that between nuclei, respectively. From
equations (2) and (3), the following equation can be derived.
\[ (K_e + K_n + V_{e-e} + V_{e-n} + V_{n-n}) \Psi_n \cdot \Psi_e = E \Psi_n \cdot \Psi_e \]  
(4)
By multiplying \( \Psi_n^* \) to both sides in equation (4) and assuming \( \langle \Psi_n | \Psi_n \rangle = 1 \) equation (4) can be written as follows,
\[ (K_e + V_{e-e} + V_{e-n} + V_{n-n}) \Psi_n = E_n \Psi_n. \]  
(5)
When the wave function of the observed electron can be separated from the wave function of other
electrons and effects of other electrons can be included in the potential energy term between the
observed electron and classical particles \( V_{e-a} \), equation (5) can be written as follows,
\[ (K_e + V_{e-a}) \Psi_{se} = E_{se} \Psi_{se} \]  
\( |r, R\rangle \),  
(6)
where \( \Psi_{se} \) is the wave function of the observed electron. When we want to observe the dynamic
behavior of the observed electron, equation (6) can be written as a time dependent formula as
\[ i\hbar \frac{\partial \Psi_{se}}{\partial t} = H_{se} \Psi_{se}, \]  
(7)
where
\[ H_{se} = K_e + V_{e-a}. \]  
(8)
On the other hand, by multiplying \( \Psi_e^* \) to both sides of equation (4) and assuming \( \langle \Psi_e | \Psi_e \rangle = 1 \) equation (4) can be written as follows,
\[ (K_e + V_{e-e} + V_{e-n} + V_{n-n}) \Psi_e = E_e \Psi_e. \]  
(9)
When electrons and nuclei can be considered to be composed of the observed electron and classical
particles(ion, atom, molecules) and the effect of the observed electron on the classical particles can be
averaged over time, the potential energy term in equation (9) can be written as a potential energy
function of coordinates of the observed electron and classical particles,
\[ V_a(|r, R\rangle) = \langle \Psi_e | V_{e-e} + V_{e-n} + V_{n-n} | \Psi_e \rangle. \]  
(10)
In the present study the effect of the observed electron in the potential energy term in equation (10)
was ignored because the mass of the observed secondary electron was relatively small in comparison
with those of the classical particles. Hence, the potential energy in equation (10) can be written as a
classical particle,
\[ V_a(|r, R\rangle) = \langle \Psi_e | V_{e-e} + V_{e-n} + V_{n-n} | \Psi_e \rangle. \]  
(11)
Equation (9) can be written as follows,
\[ (K_e + V_a(R)) \Psi_n = E \Psi_n, \]  
(12)
where
\[ H_a = K_e + V_a(R). \]  
(13)
Hence, the Hamiltonian for the system \( H_a \) was assumed to be separable into the Hamiltonian of the
observed electron \( H_{se} \) and that of classical particles \( H_a \) as follows,
\[ H = H_a + H_{se}. \]  
(14)
The Hamiltonian for the observed secondary electron can be written as a summation of a kinetic
ergy term and a potential energy term as written in equation (8),
\[ H_{se} = \frac{p^2}{2m} + V_{se}(|r, R\rangle), \]  
(15)
where the first and the second terms on right hand side correspond to the kinetic energy term and the
potential term of the electron, respectively. \( r \) and \( R \) represented the coordinates of the observed
particles.
secondary electron and the classical particles, respectively. Wave function of the electron depending on time can be written as follows.

\[ \Psi_{se}(t) = \exp(-iH_{sc}t/\hbar)\Psi_{se}(0) \].  

(16)

In the present study, the wave function of the observed electron was expressed as a numerical function of complex numbers on 128*128 grid points and equation (16) was solved by the split operator method [7] so as to get time propagation of the wave function of the observed secondary electron as follows,

\[ \Psi_{se}(t + \Delta t) = \exp(-i\Delta K/2\hbar)\exp(-iV_{ee}\Delta t/\hbar)\exp(-i\Delta K/2\hbar)\Psi_{se}(t) \].  

(17)

where K corresponds to the spacial differential term. Fast Fourier Transform (FFT) method was employed for the spacial differential calculation in equation (17). The distance between grid points and the time interval for the integration were 0.64 and 0.01fs, respectively.

The Hamiltonian for the classical particles \( H_a \) can be written as written in equation (13),

\[ H_a = \sum_{a=1}^{N_p} \frac{p_a^2}{2M_a} + V_a(R), \]  

(18)

where "a" represents the classical particles such as ions and surface molecules in the system. In the present study, motions of the classical particles were calculated by solving the Newton’s equations with the time interval of 0.2fs. Hence, the equation (17) was time propagated for 20 steps when the Newton’s equations for the classical particles were integrated for 1 step. Figure 1 showed the calculation model employed in the present study. We assumed that an ion (potassium) which had a certain velocity was collided with the other ion (potassium) with the observed secondary electron on the surface (xenon). The wave function of the observed electron was solved by equation (17) and the motions of ions and surface molecules were solved by the Newton’s equations in order to investigate the behavior and energy transfer of the observed electron.

The potential functions between particles in the reference [3] were employed in the present study and the potential parameters between the observed electron and an ion and those between the observed electron and surface molecules were treated as calculation parameters and changed from the standard value in the reference [3]. The potential functions employed are shown as follows,

\[ V_{ee}(r, R) = V_{ei} + V_{es}, \]  

(19)

\[ V_a(R) = V_{ai} + V_{as} + V_{ii}, \]  

(20)

**Table 1. Calculation parameters.**

| \( C_{ke} \) | \( C_{e-xe} \) |
|---|---|
| 0.2 | 1.0 |
| 0.5 | 2.0 |
| 0.75 | 3.0 |
| 1.0 | 4.0 |
| 1.5 | 7.5 |

**Figure 1.** A calculation model for energy transfer to the secondary electron during surface collision process of an ion.
\[ V_{el}(r) = -e^2 / (4\pi\varepsilon_0 r_e) \quad |r_e| < |r| = 0.5 \hat{A} \]
\[ V_{is}(r) = -e^2 / (4\pi\varepsilon_0 r_i) \quad |r_i| > |r| = 0.5 \hat{A} \]
\[ V_{es} = \sum_{n} \left( a / R_n^4 \right) \left[ (c + R_n^6) - 1 \right] \quad R_n = \max\{X_n, R_e\} \]
\[ V_{ss} = \left( \frac{1}{2} \right) \sum_{n,m} 4e \left[ -\left( \sigma / R_{nm} \right)^6 + \left( \sigma / R_{nm} \right)^{12} \right] , \]
\[ V_{is} = \sum_{n} \left( C_9 / R_n^9 - C_6 / R_n^6 - C_4 / R_n^4 \right) , \]
\[ V_{ii}(r) = e^2 / (4\pi\varepsilon_0 r) \]

where \( V_{es} \) and \( V_{is} \) were the potential function of the observed electron in equation (15) and that of the classical particles in equation (18), respectively. \( V_{ei}, V_{es}, V_{ss}, V_{is} \) and \( V_{ii} \) were the potential function between the electron and the ions, that between the electron and surface molecules, that between surface molecules, that between the ions and the surface molecules and that between the ions, respectively. The standard parameters in equations (19)-(25) were the same as those in reference [3].

4. Results and discussions

Effects of various physical parameters, such as colliding position of the ion and the interaction strength between the observed electron and the classical particles on the energy transfer to the observed secondary electron were investigated by the quantum molecular dynamics method when an ion was collided with the surface so as to elucidate the energy path to the electron and the predominant factor of energy transfer to the electron. Effects of potential energy between the ion and the electron and that between the surface molecule and the electron on the electronic energy transfer were shown in the present study. The collision velocity of the ion that can be converted to the ion translational energy is one of the important physical parameters. The calculation results were shown only when the ion translational energy was 102eV in the present study and other calculation results under higher collision velocity conditions were shown in the reference [8]. The magnitude of potential energy between the ion and the electron and that between the surface molecule and the electron were expressed as \( C_{k-e} \) and \( C_{e-xe} \), respectively, that were expressed as non dimension value by dividing the standard value in the reference [3]. The effects of \( C_{k-e} \) and \( C_{e-xe} \) on trajectories of the electronic center of mass and the energy transfer to the electron were calculated numerically. The magnitudes of \( C_{k-e} \) and \( C_{e-xe} \) are related to potential energy terms \( V_{es} \) and \( V_{es} \) that are included in the time dependent Schrodinger equation (15), respectively. Hence, the secondary electron receives energy from the colliding ion through \( V_{ai} \) or \( V_{es} \). \( C_{k-e} \) and \( C_{e-xe} \) employed in the present study are shown in Table 1. Figure 2 shows the initial electron probability density calculated by equations (16) and (17).

4.1. Effect of potential energy between ions and the secondary electron on the energy transfer to the electron

Figure 3 showed the electronic trajectories during 1.0ps when \( C_{k-e} \) was 0.2 and 1. Figure 4 showed effects of potential energy between ions and the secondary electron on the energy increase of the observed electron during 1.0ps when the magnitudes of \( C_{k-e} \) were changed from 0.2 to 1.0. The energy of the observed electron increased monotonously with the increase of the magnitude.
of the potential energy between the ion and the electron, $C_{k-e}$. In Figure 3 the trajectories of the observed electron were almost similar each other and the observed electron moved to upper right direction in all cases. This is because the electronic trajectories were affected by the trajectories of the colliding ion. The magnitude of potential energy between the ion and the electron, $C_{k-e}$, related to the magnitude of $V_{ei}$ in Equation (19). These results showed that the energy transfer to the observed electron was directly dependent on the potential energy term between the ion and the electron, $V_{ei}$.

4.2. Effect of potential energy between surface molecules and the secondary electron on the energy transfer to the electron

Figure 5 showed the electronic trajectories during 1.0ps when $C_{e-xe}$ was 2.0 and 7.5. Figure 6 showed effects of potential energy between surface molecules and the secondary electron on the energy increase of the observed electron during 1ps when the magnitudes of $C_{e-xe}$ were changed from 2.0 to 7.5. In Figure 6 the energy of the observed electron increased with the increase of the magnitude of potential energy between surface molecules and the electron, $C_{e-xe}$. When the potential energy between the surface molecule and the electron was changed as calculation parameters, the stable electronic distribution was changed as a result. In Figure 5 displacements of the center of mass of the
observed electron became larger with the decrease of the magnitude of the potential energy between molecules and the electron, \( C_{e-xe} \). This is because the absolute value of the potential energy \( V_{es} \) in Equation (19) became large with the increase of \( C_{e-xe} \).

**4.3. Effect of colliding position on the energy transfer to the secondary electron**

Figure 7 showed the effect of the colliding position of the ion on the energy transfer to the electron during 1.0ps when \( C_{e-xe} \) and \( C_{k-e} \) were unity. The origin of x coordinate was defined as the initial position of the ion on the surface. The target position of the colliding ion was changed from 0.0 to 2.0 nm in Figure 7. In Figure 7 the energy increase of the observed electron were much dependent on the surface colliding position. When the x coordinate was 1.0nm, the energy increase of the observed electron was 4 times as large as those at \( x = 0.0 \text{nm or 2.0nm} \). The electron distribution on the surface as well as the ion position on the surface can be changeable because the ion and surface molecules have thermal energy. Therefore, the colliding position of the ion was very important physical factor for the energy transfer of the secondary electron. When the x coordinate was 1.0nm, we can suppose that the colliding position of the ion was just directly on the electronic distribution. The energy transfer to the observed electron was reduced when the target position was apart from \( x = 1.0 \text{nm} \).

**5. Conclusions**

The quantum molecular dynamics method was applied to an energy transfer problem to a secondary electron during ionic surface collision process in order to elucidate how energy of the ionic collision transfers to the emitted electron from the surface. First we derived time dependent Schrodinger equation of for a secondary electron and Newton’s equations for ions and surface molecules from the Schrodinger equation of the system. We assumed that an ion which had a certain translational velocity was collided with the other ion with the observed secondary electron on the surface. The wave function of the observed secondary electron was solved by time dependent equation and the motions of ions and surface molecules were solved by the Newton’s equations numerically. The energy transfer paths to the electron in the time dependent Schrodinger equation was discussed during the collision process of an ion with changing the magnitude of potential energy between the electron and ions and that between the electron and surface molecules. The main findings are as follows:

1. There were two energy paths to the observed secondary electron from the colliding ion. One was through the potential energy term between the ion and the electron and the other was through the potential energy term between the surface molecules and the electron.
2. Energy transfer to the observed secondary electron and trajectories of the observed secondary electron were much dependent on the potential energy between particles and the colliding position of the ion on the surface.

**Acknowledgments**

This work was partially supported by the Ministry of Education, Science, Sports and Culture (MEXT), Japan, “Grant-in-Aid for Exploratory Research No. 18656066” and “Grant-in-Aid for Young Scientists (A) No. 19686017”.

**References**

[1] Satake, S., Inoue, N., Taniguchi, J. and Shibahara, M., 2006, *Energy Nanotechnology International Conference*, paper No. ENIC2006-19061, 102.
[2] Satake, S., Inoue, N., Taniguchi, J. and Shibahara, M., 2006, *The 15th conference on Ion Beam Modification of Materials*.

[3] Haug, K. and Metiu, H., 1993, *J. Chem. Phys.*, Vol.99, No.9, 6253-6263.

[4] Haug, K. and Metiu, H., 1992, *J. Chem. Phys.*, Vol.97, No.7, 4781-4791.

[5] Shibahara, M. and Kotake, S., 1997, *International Journal of Heat and Mass Transfer*, Vol.40, No.13, 3209-3222.

[6] Shibahara, M. and Kotake, S., 1998, *International Journal of Heat and Mass Transfer*, Vol.41 Nos.6-7, 839-849.

[7] Feit, M. D., Fleck, J. A. Jr. and Steiger, Q., 1982, *J. Comp. Phys.*, Vol. 47, 412.

[8] Shibahara, M., Satake, S. and Taniguchi, J., 2007, *Proceedings of 2007 ASME-JSME Thermal Engineering Conference*, CD-ROM.