Ab Initio Calculation of Surface Atom Evaporation in Electron Field Emission

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Surface atom evaporation under electron field emission was investigated by scattering-state calculations based on the density-functional theory. We found that surface atom evaporation assisted by electron field emission occurs for a certain electric-field strength that is lower than that of usual field evaporation without electron field emission. The present ab-initio study elucidates the surface atom process under field emission, which has been frequently observed in experiments, for the first time. [DOI: 10.1380/ejssnt.2007.106]

Keywords: Density functional calculations; Field emission; Field evaporation; Metallic surfaces

I. INTRODUCTION

Over the past few decades, field emission (FE) has been widely utilized in various devices in vacuum microelectronics. FE has therefore been extensively studied both experimentally and theoretically. FE is a quantum-mechanical electron-tunneling phenomenon from a tip surface with a high curvature to vacuum that accompanies high electric field and electric-current density. Such high fields and current densities tend to reconstruct the atomic geometry at the tip or even destroy the tip surface. It has been reported from experimental observations that even multi-walled carbon nanotube field emitters, which have high mechanical toughness, undergo structural damage, such as protrusions, branching and sublimation [1, 2]. The stability of the tip surface is of critical importance for applications since it determines the lifetime of the field emitters [3]. However, the mechanisms of these surface structural changes during FE have not yet been understood, because there have been few studies thus far on the microscopic analysis of forces acting on surface atoms in the presence of electron emission [4]. On the other hand, we note that the evaluation of forces on adatoms and impurity atoms under an electric current at the surface or in the bulk has been a major concern for understanding the mechanism of electromigration and has been previously investigated [5–7]. The analysis of current-induced forces on atoms of nanoscale bridges has also attracted growing interest in the field of molecular electronics [8, 9].

Our objectives in this study are to calculate the forces on surface atoms under FE and to explore FE-assisted surface evaporation, from first principles calculations.

II. METHOD AND MODEL

In order to calculate the force exerted on the surface atoms, we need a quantitatively reliable method that takes into account the current-carrying states in real atomic structures. Among first-principles calculations based on the density-functional theory (DFT) [10, 11] for the study of FE [12–16], we employed the recursion-transfer-matrix (RTM) method [14, 17] for this study, because this scheme is suitable for analysis of FE as well as ballistic transport through nanoscale bridges. The whole system is divided into three regions; electrode, surface and vacuum regions in the RTM method for FE [14] as shown in Fig. 1. The wave functions in the electrode region are expressed as plane waves. The wave functions in the vacuum region under an electric field are analytically given by Airy functions that are the solutions of Schrödinger equations under an electric field in one dimension. In solving Kohn-Sham equations in the surface region with some atomic structures, scattering waves injected from the left infinity of the electrode and emitted from the surface-vacuum boundary (B). (See Fig. 1.) As a result, the nonequilibrium electron density is obtained from the scattering waves. The scattering waves are expanded with plane waves in a direction parallel to the surface and are given at real-space grid points in the direction normal to the vacuum region under an electric field.

FIG. 1: Schematic diagram of Na (001) surface models for electron field emission. (a) and (b) have single and triple Na layers on the jellium electrodes of \( r_s = 3 \), respectively. The rectangle is a surface region, wherein the electronic states are self-consistently calculated, and repeated in the \( x \) and \( y \) directions. Yellow circles are Na atoms and the blue area denotes semi-infinite jellium electrodes. Electrons are injected from the left infinity of the electrode and emitted from the surface toward the vacuum.
the surface (Laue representation). Here, we should note that the Laue representation of scattering waves is ideal for describing tunneling electrons into the vacuum. Details of the RTM method for FE can be found in Ref. [14]. The force acting on the atom under electric current is described in Refs. [18, 19]. The force is calculated from the ion-electron interaction,

$$F^{(1)}_{\mu} = -\frac{\partial}{\partial R_{\mu}} \int V_{\text{ion}}(r) \rho(r) \, dr,$$

(1)

the ion-ion interaction,

$$F^{(2)}_{\mu} = -\frac{\partial}{\partial R_{\mu}} \sum_{\nu} \frac{Z_{\nu} Z_{\mu} e^2}{|R_{\nu} - R_{\mu}|},$$

(2)

and ion-electrode interaction,

$$F^{(3)}_{\mu} = -\frac{\partial}{\partial R_{\mu}} Z_{\mu} e \int \frac{\rho^+(r)}{|r - R_{\mu}|} \, dr.$$

(3)

Here, $-e$ is the electron charge, $\rho$ and $\rho^+$ denote the electron number density obtained from scattering waves and the positive background number density of the jellium electrode, and $V_{\text{ion}}$ is the ionic potential. $R_{\mu}$ and $Z_{\mu}$ indicate the atomic position and the valence of the $\mu$-th atom. The force on the $\mu$-th atom is $F_{\mu} = F^{(1)}_{\mu} + F^{(2)}_{\mu} + F^{(3)}_{\mu}$.

In the present study, we investigate Na (001) surfaces on the semi-infinite jellium electrode of $r_s = 3$. ($r_s$ is the Wigner-Seitz radius in units of the Bohr radius.) Figs. 1(a) and 1(b) have single and triple Na layers on jellium electrodes, respectively. We chose the jellium thickness in the surface region as 10.0 a.u. The thicknesses were set as 7.0 a.u. in Ref. [17] using the same method and 19.8 a.u. in Ref. [4] using a similar method, respectively. The work functions were set as 7.0 a.u. in Ref. [17] using the same method, respectively. The thicknesses in the surface region as 10.0 a.u. The thicknesses were set as 7.0 a.u. in Ref. [17] using the same method and 19.8 a.u. in Ref. [4] using a similar method, respectively. The work functions were set as 7.0 a.u. in Ref. [17] using the same method, respectively.

FIG. 2: Distance-dependent force acting on the outermost Na atoms under applied electric fields. A force component parallel to the $z$ direction is shown in the vertical axis. (a) and (b) correspond to each model in Fig. 1. (c) shows the field-strength ($E$) dependence of the minimum force obtained from the force curves of model (b).

III. RESULT

The force curves under applied fields for each model in Fig. 1 are given in Fig. 2. A positive value of the force denotes the force direction away from the surface. The distance $d$ is defined in Fig. 1. In this section, we discuss the results only for model (b) in Fig. 1, because the force curves for the two models are qualitatively the same. The difference in the evaporation energy between the two models will be described later. We observe two features in Fig. 2(b). The first is that a threshold electric field $E_{\text{th}}$, beyond which the Na atoms can evaporate without an energy barrier, exists between 3 and 4 V/nm. $E_{\text{th}}$ is determined with good accuracy by interpolating the values of the minimum force as a function of the electric-field strength $E$, as shown in Fig. 2(c). The value of $E_{\text{th}}$ obtained is 3.3 V/nm for model (b) (3.7 V/nm for model (a)). The force curves for these $E_{\text{th}}$ values are indicated by the red curves in Figs. 2(a) and (b). The corresponding FE-current density $J_{\text{th}}$ is 0.018 nA/nm$^2$ for model (b) (0.058 nA/nm$^2$ for model (a)). The second observation relates to the electric-field dependent equilibrium position $d_{\text{eq}}$. The $d_{\text{eq}}$ value, at which the force is zero, is found to increase (i.e., the stable position of Na atoms moves towards the vacuum) with increasing $E$ from Fig. 2(b).

These properties become more apparent in the potential energy $V$ defined by

$$V(d) = -\int_{d_0}^{d} F(z) \, dz,$$

(4)

where $d_0$ is arbitrarily chosen [24]. In the present calculation, we chose $d_0 = 2.545$ a.u. The potential-energy curves for model (b) are given in Fig. 3. $d_{\text{eq}}$ as a function of $E$ is shown in the inset. $V$ has a minimum at around $d \sim 3.1$ a.u. for zero field. A maximum (not shown in Fig. 3) appears beyond $d \sim 6$ a.u. with a finite

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electric field, while the minimum position $d_{\text{eq}}$ moves toward the vacuum. $d_{\text{eq}}$ is found to increase quadratically with increasing $E$, as shown in the inset [25]. At $E = 3.3 \text{ V/nm} \left(= E_{\text{th}}\right)$, the potential minimum merges into the maximum (red curve in Fig. 3), leading to evaporation of surface Na atoms without an activation energy as negative ions. It is difficult to evaluate the charge of the atom directly with good precision because of the wave function with plane wave basis. Instead, we determine the charge in a different way. Figure 4 shows the force as a function of $E$ at the equilibrium position for zero field. The effective charge $Z^*$ is evaluated as $-0.49e$ from the nearly linear curve, $F = Z^*E \left(E \text{ is negative}\right)$. $Z^*$, which depends on the atomic position, is predicted to be $-e$ upon evaporation into vacuum. The negatively charged states of the evaporated atom under the applied field with the same direction but without field emission have also been discussed in previous work [26]. The evaporation of surface atoms during FE is likely to occur in conventional FE experiments. In fact, the evaporation of carbon atoms from carbon nanotube emitters has been observed in an FE microscopy study [27]. The physical quantities obtained in this study are summarized in Table. I.

Lastly, we mention the reason for $E_{\text{th}}$ for model (a) being higher than that in model (b), as given in Table. I. The order of the strength must be similar to that of the activation energy for evaporation without an applied field. Unfortunately, it is difficult to obtain the potential curve precisely in the region where the atom is far from the surface in the present scheme. However, we found a difference in the binding energies for the two models from the electron-density accumulation in the area between the evaporating layer and the host surface. (This is not shown here.) The electron density in the area between the Na-atom layer and the jellium surface (see model (a) in Fig. 1) is found to be more conspicuous than that between the outermost and inner layers in model (b) in Fig. 1. Thus, we interpret the difference in $E_{\text{th}}$ for the two models in terms of the amount of electron accumulation in the area between the evaporating layer and the host surface.

### IV. DISCUSSION

We note common features between the Na-atom evaporation obtained here and usual field evaporation. The most interesting observation is that the mechanism of evaporation of Na atoms under FE based on the potential scheme is qualitatively the same as that of usual field evaporation in the absence of FE, except for the sign of the charge of atoms evaporated caused by applied fields with the opposite direction. A remarkable difference between the two evaporation processes is that $E_{\text{th}}$ for the present evaporation under FE is much lower than that of usual field evaporation [28, 29]. One of the reasons for this is that Na surface atoms are weakly bound to the host Na atoms in the bulk compared to the tight-binding nature of tungsten or carbon atoms of typical field emitter tips. Other reasons that cause $E_{\text{th}}$ to be low need to be explored using more detailed analysis. Moreover, $E_{\text{th}}$ is naturally considered to highly depend on the atom species, the geometrical configuration of the surface and the temperature. In the present model, all Na atoms in the outermost layer are assumed to evaporate simultaneously from the flat surface. But in practice, a single or few atoms tend to evaporate from a curved surface under enhanced electric fields. Therefore, it is necessary to take account of such atomic geometries of real tip-surfaces for determining the value of $E_{\text{th}}$ more correctly. These issues will be the subjects of future research.

Finally, we comment on the role of wind force [5] in the

### TABLE I: The equilibrium distance at zero field, $d_{\text{eq}}$, work function, $\phi$, threshold field strength of atom evaporation induced by FE, $E_{\text{th}}$, and the corresponding FE-current density, $J_{\text{th}}$, for each model in Fig. 1.

<table>
<thead>
<tr>
<th>Model</th>
<th>$d_{\text{eq}}$ [a.u.]</th>
<th>$\phi$ [eV]</th>
<th>$E_{\text{th}}$ [V/nm]</th>
<th>$J_{\text{th}}$ [nA/nm$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>3.07</td>
<td>2.69</td>
<td>3.7</td>
<td>0.058</td>
</tr>
<tr>
<td>(b)</td>
<td>3.06</td>
<td>2.77</td>
<td>3.3</td>
<td>0.018</td>
</tr>
</tbody>
</table>
field evaporation under FE. The present scheme based on the density-functional theory cannot incorporate the electron-ion interaction process with momentum transfer, which is responsible for wind force, in the force calculation. As a result, the effect of current-scattering states are taken into account partly in the force calculation in the present study only through the electron redistribution caused by the current. Therefore, the wind force on surface atoms under FE is still a challenging issue to be resolved.

V. SUMMARY

We have investigated FE-assisted Na surface atom evaporation by the RTM method. We obtained the threshold value of the applied field, beyond which Na surface atoms are evaporated without thermal activation, and we have derived the effective charge of a Na atom before evaporation by calculating the forces and potentials under FE. Na surface atoms are found to evaporate with lower fields than the typical strength of conventional field evaporation in the absence of FE. We believe that the present study on field evaporation under FE provides a clue to understand microscopic surface processes such as reconstruction or disintegration during FE that are frequently observed in FE microscopy studies.

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[25] $d_{eq}$ has a linear dependence of applied electric-field strength within a crude phenomenological theory with a rigid-potential approximation. In the present study, however, we determined $d_{eq}$ from the potential energy curves under electric fields and currents calculated self-consistently. The reason why $d_{eq}$ shows a quadratic behavior is not yet clear.