# Computational study of the effect of surface defects and steps on field-stimulated exoelectron emission from aluminum

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The electronic structures of a clean Al (001) surface, of a stepped Al (001) surface, and of an Al(001) surface with vacancies were investigated by the first-principles calculation to elucidate the emission mechanism of field-stimulated exoelectrons from Al tip surfaces. The results show that vacancies at the Al (001) surface slightly increase local density of states (LDOS) in the occupied states, and that monoatomic steps significantly increase LDOS at 0.36 eV above Fermi level in the unoccupied states. The LDOS peak position in the unoccupied states at the stepped surface is close to the trap level of field-stimulated exoelectrons measured in our previous experiments, and it is concluded that the monoatomic steps at Al surfaces can play a role of exoelectron traps.

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## I. INTRODUCTION

Even at energies lower than the work function, nonstationary electron emissions are often observed from gas adsorbed surfaces[1] and from damaged metal surfaces.[2,3] These phenomena have been identified as exoelectron emission.[4] Although a large number of studies on exoelectron emission have been performed, the concrete emission mechanism has not yet been established. The two-process model proposed by Shigekawa and Hyodo[5] is the emission mechanism that successfully describes the ''storage effect'' of exoelectron emission, that is characteristic to the photostimulated exoelectron emission from Al surfaces.[5] In this model, electrons are pumped up to trap levels from the Fermi level ($E_F$), and then emitted into the vacuum upon irradiation by ultraviolet light with energies lower than the work function of the Al specimen surface. Although the trap level for exoelectrons formed between $E_F$ and the vacuum level ($E_{vac}$) is the key of the two-process model, the origin of the trap level has not been clarified.

Tagawa *et al.* confirmed the storage effect in field-stimulated exoelectron emission from Al tip surfaces.[6] The emission characteristics were explained well by the two-process model.[6] Moreover, they measured the energy distribution of field-stimulated exoelectron and estimated the electron trap levels.[7] It was found that exoelectrons were trapped by two levels at 4.0 eV and 3.8 eV below $E_{vac}$. The intensity of the exoelectron emission from the trap at 4.0 eV increased with oxygen exposure, while that at 3.8 eV did not change, suggesting that the adsorbed oxygen on the Al surface created the trap level at 4.0 eV below $E_{vac}$. Moreover, our recent first-principles calculation corroborates that oxygen adsorption on the Al (001) surface creates the trap level at 4.0 eV below $E_{vac}$.[8] On the other hand, since the exoelectron emission intensity from the trap level at 3.8 eV below $E_{vac}$ was not affected by oxygen adsorption, this trap level was thought to have originated from intrinsic characteristics of the Al surface such as impurities, vacancies, or steps.[7] However, the origin of this trap level remained unclear.

In this study, we have investigated the effect of vacancies and monoatomic steps on the formation of trap level for field-stimulated exoelectrons through first-principles calculations. The electronic structures of a clean Al (001) surface, of a stepped Al (001) surface and of an Al (001) surface, with vacancies were calculated. The origin of the trap level at 3.8 eV below $E_{vac}$ was discussed in this paper by comparing the calculated results with the previous experimental data on field-stimulated exoelectron emission from Al surfaces.[7]

## II. CALCULATIONS

The first-principles calculation in this study was based upon the density-functional theory within the local-density approximation (LDA) and was performed by using TAPP (Tokyo *ab initio* program package).[9] An ultrasoft pseudopotential scheme proposed by Vanderbilt[10] was applied in the calculation. Details of the calculation are described in the literature.[8]

The electronic structures of a clean Al (001) surface and of an Al (001) surface with vacancies were calculated using supercells depicted in Figs. 1(a) and 1(b), respectively. The filled circles are Al atoms in these figures. In Fig. 1(b), Al atoms at the center of the topmost and the lowest Al planes were removed to simulate an Al surface with vacancies. Each supercell consisted of five layers of the Al (001) plane. In the previous study, a nine-layer Al slab was used to calculate the

 

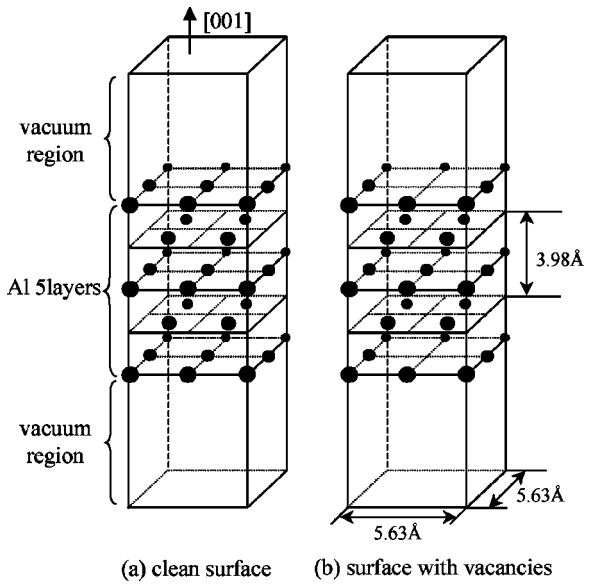


FIG. 1. The supercells simulating a clean Al(001) surface (a) and an Al(001) surface with vacancies (b).

electronic structure of a clean Al (001) surface.[8] The calculated results using the nine-layer Al slab reproduced well the experimental data, and agreed with the computational results reported previously. In this study, supercells with larger size had to be used to construct the model of an Al surface with vacancies. Due to the limitation of the computational time, the five-layer Al slab was used in this study. In order to confirm an accuracy of the calculated electronic structure of an Al (001) surface, the total energy per atom and the charge distribution calculated using the five-layer Al slab were compared with those using the nine-layer Al slab. The difference in the total energy was only 0.005 eV/atom, and any remarkable changes in the charge distribution were not observed. Thus, the calculated results using the five-layer Al slab reproduced well the electronic structure of the Al (001) surface. The vacuum region with a thickness of 5 Å was placed at both of top and bottom in each supercell as shown in Fig. 1. Since supercells were periodically arranged in three dimensions, the separation between two Al surfaces facing through the vacuum region was 10 Å. It was confirmed in the previous study that the interaction between such surfaces was small enough.[8] The surface was not relaxed in the model used here because we confirmed that the surface relaxation did not change the density of state, the charge distribution, and the band structure of a clean Al (001) surface. The calculation was carried out with a cutoff energy of 25 Ry and with a set of 388 *k* points in the irreducible Brillouin zone. These parameters provided well-converged results.

The surface model shown in Fig. 2 was used to calculate the electronic structure of an Al (001) surface with monoatomic steps. The Al (001) surface with monoatomic steps consisted of terraces with a width of 7 Å. In order to calculate the electronic structure of a stepped low index surface, a supercell simulating an equivalent high index surface has usually been used[11–13] because the use of such a supercell facilitates the calculation due to the higher symmetry of the supercell. The [110] view of the supercell used for the Al

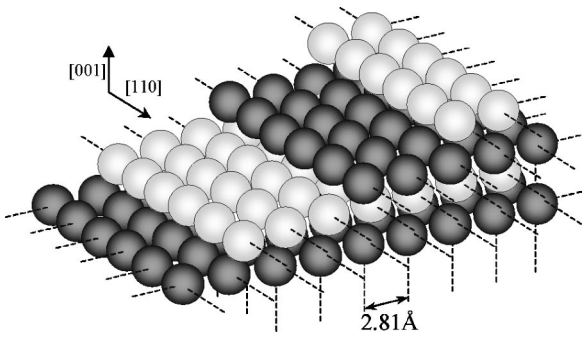


FIG. 2. The stepped Al(001) surface model consisting of terraces with a width of 7Å and monoatomic steps.

(001) surface with monoatomic steps is shown in Fig. 3. The supercell used for the calculation is surrounded by dashed lines. The calculated stepped Al (001) plane is equivalent to the Al (115) plane. The surface relaxation was not also considered in this model. Although a relaxation at step edges may change an electronic structure at the stepped Al surface, we believe from our calculation results described above that there is little effect of the relaxation on the electronic structure of the surface. To clarify the effect of the relaxation on the electronic structure at the stepped Al surface completely, further calculations will be required. The thickness of the vacuum region between two surfaces was 13.4 Å, which was thick enough to avoid interaction between facing two surfaces as described above. In this calculation, the cutoff energy and the number of sample *k* points were 25 Ry and 242 points, respectively. These parameters were also confirmed to provide well-converged results.

## III. RESULTS

Local density of states (LDOS) of the clean Al (001) surface, of the stepped Al (001) surface, and of the Al (001) surface with vacancies were calculated to investigate the energy distribution of electrons of the surfaces. The LDOS of the surface was defined as a density of states localizing within two atomic layers from the topmost surface atom.

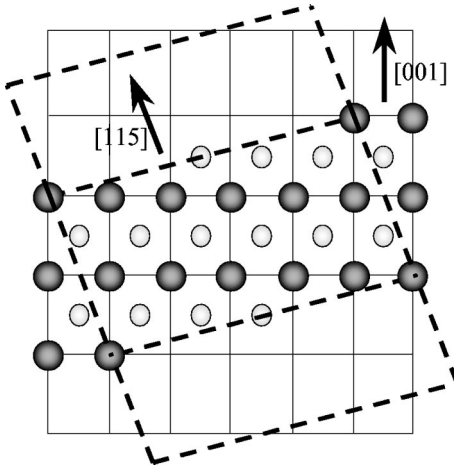


FIG. 3. The [110] view of the supercell used in the calculation for the stepped Al(001) surface, shown by dotted lines.

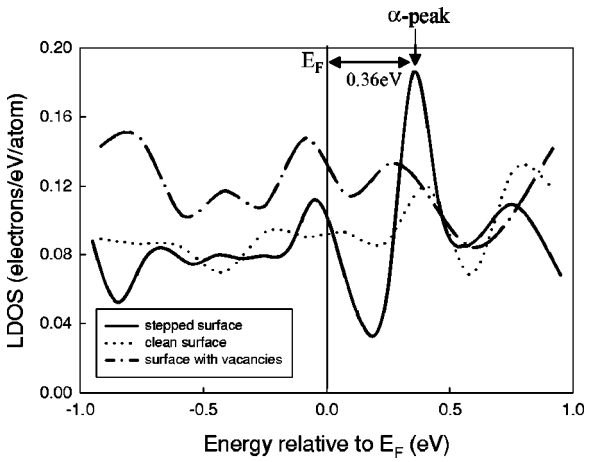


FIG. 4. The calculated LDOS of the clean Al(001) (dotted line), the stepped Al(001) (solid line), and the Al(001) surface with vacancies (broken line). The abscissa shows the energy of the states relative to $E_F$ of each surface.

Figure 4 shows the calculated LDOS. Compared with the LDOS of the clean Al (001) surface, the LDOS of the Al (001) surface with vacancies slightly increases at energies lower than $E_F$ (at the occupied states), however, it does not change greatly at energies higher than $E_F$ (at the unoccupied states). Thus, vacancies at the Al (001) surface hardly influence the electronic structure of the surface. The density of the vacancies used in this study might be high, and the calculations using supercells with larger size will be required to investigate the electronic structure of the surface with a realistic density of vacancies. In contrast, a remarkable difference in the LDOS between the stepped and the clean Al (001) surfaces is observed in the unoccupied states; the LDOS of the stepped surface has a high peak at 0.36 eV above $E_F$. Hereafter this peak is denoted the "*α peak.*" Tagawa *et al.* reported that the trap levels for field-stimulated exoelectrons at Al surfaces were distributed between $E_F$ and $E_{vac}$.[6,7] Therefore, vacancies at an Al (001) surface do not contribute to the field-stimulated exoelectron emission, while it is possible that the *α peak* induced by monoatomic steps at an Al (001) surface is the origin of the trap level for field-stimulated exoelectrons.

## IV. DISCUSSIONS

Previous experimental results on field-stimulated exoelectron emission from Al surfaces show that electrons are trapped at 3.8 eV below $E_{vac}$ and then emitted through stimulation by a strong negative electric field.[7] Although it was believed that the trap level at 3.8 eV below $E_{vac}$ was induced by intrinsic characteristics of the Al surface, the origin of the trap level has not been identified. In the previous experiments, emission of exoelectrons from Al surfaces was induced by applying a strong negative electric field of order $10^8$ V/m to a specimen. In order to apply such a high electric field to the specimen surface, the specimen should have a sharp tip. The surface of such Al tips consists of an accumulation of Al (001) planes,[14] and hence there are many monoatomic steps on the tip surface. Therefore, we surmised that the step-induced surface state (*α peak*) was the possible origin of the exoelectron trap level at 3.8 eV measured in the experiments.

In order to compare the calculated results with the previous experimental data, the $E_F$ of the stepped Al (001) surface simulated in this calculation was determined. The work function of the step-free Al (001) surface is 4.4 eV,[15] and hence the *α peak* position (see Fig. 4) is estimated to be 4.04 eV below $E_{vac}$, 0.24 eV lower than the trap level measured in the experiment. However, surface steps at a metal surface reduces the work function of the surface.[16–18] Ishida and Liebsch carried out systematic self-consistent density-functional calculations on the electronic structure of stepped jellium surfaces, and showed that the step density and step height influenced the work function of the stepped Al surface.[17] According to their results, the work function of a stepped Al (001) surface with monoatomic steps with a terrace width of 7 Å is 0.11 eV lower than that of a step-free Al (001) surface. Since the work function of a clean Al (001) surface is 4.4 eV, the $E_F$ of a stepped Al (001) surface should be 4.29 eV below $E_{vac}$, and, therefore, the *α peak* position should be 3.93 eV below $E_{vac}$. If a step density of the Al surface in the previous experiment was higher than that in this calculation, the reduction of the work function would be larger, and the *α peak* position becomes higher than 3.93 eV. Moreover, the error in the calculation within LDA should be considered. The energy difference between the occupied and the unoccupied orbitals calculated within LDA is much smaller than in the experimental data. The actual energy difference between the *α peak* and the $E_F$ is larger than 0.36 eV. Therefore, it is reasonable that the *α peak* position calculated within LDA is lower than the trap level measured in the previous experiment. Considering the reduction of the

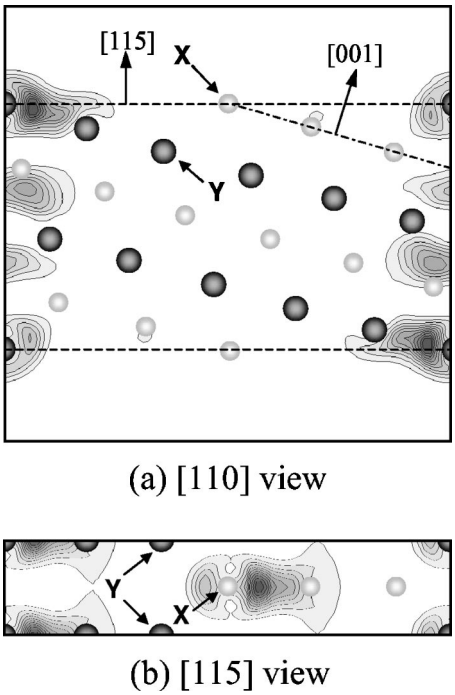


FIG. 5. The [110] (a) and the [115] (b) views of a contour map of the LDOS contained in the *α peak*.

work function due to the surface steps and the error in the LDA calculation, it is concluded that the *α peak* is a candidate for the exoelectron trap on Al surfaces.

To further corroborate the role of the *α peak* as an exoelectron trap, the spatial distribution of the unoccupied states forming the *α peak* was examined on the stepped Al (001) surface. A contour map of the density of states between 0.285 eV and 0.435 eV above $E_F$ was calculated. Figures 5(a) and 5(b) show the [110] and the [115] views of the contour map, respectively. In these figures, a high electron density is depicted as dark, and the atoms marked *''X''* and *''Y''* in Fig. 5(a) correspond to those in Fig. 5(b). The density of the unoccupied states forming the *α peak* is high at the step edge atoms. Since the applied electric field is concentrated at the step edge atoms,[19] the probability of electron emission becomes higher at the step edges. Due to the high electron density and the high electric-field strength, electrons trapped at the step edges may be emitted as exoelectrons. The computational results suggest that the exoelectron trap at 3.8 eV below $E_{vac}$ observed in the experiment comes from step structures on the Al tip surface.

## V. CONCLUSIONS

The effect of vacancies and of monoatomic steps on the electronic structure of the Al (001) surface was investigated by a first-principles calculation to identify the origin of the trap levels for field-stimulated exoelectrons. The LDOS of an Al (001) surface with vacancies was similar to that of a clean surface, while the density of unoccupied states of an Al (001) with monoatomic steps dramatically increased at 0.36 eV above $E_F$ (the *α peak*). The *α peak* position was close to the trap level for the field-stimulated exoelectrons measured in previous experiments. It is inferred that vacancies at an Al (001) surface do not contribute to exoelectron emission, but monoatomic steps at the surface can act as traps for exoelectrons.

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