

First-principles Molecular Dynamics Simulation of Metal Surfaces Interacting with OH Molecule

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In order to reveal the etching mechanism of the metal surfaces of the electrochemical machining using ultrapure water, first-principles molecular dynamics simulations of metal surfaces (Cu(001), Fe(001) and Al(001)) interacting with an OH molecule were carried out on the basis of density-functional theory. The optimized electronic structures and atomic configurations of the OH chemisorbed surfaces were calculated. It was confirmed that the chemisorption of an OH molecule on Cu(001) surface initiates the dissociation of Cu-Cu back-bond and the etching process of the surface atom. In the cases of Fe(001) and Al(001), back bonds of the surface atoms were not dissociated. These simulated results agree with the experimental results.

Key words: first-principles molecular dynamics simulation, metal surfaces, etching, hydroxyl group, electrochemical machining, back-bond, orbital hybridization

1. INTRODUCTION

The study of the interaction of OH molecule with metal surface is an interesting subject for the basis of important application fields, such as oxidation or etching processing by electrochemical machining. According to the experimental results of the electrochemical machining using ultrapure water, the etching characteristics have difference between the materials.¹⁾ For example, Cu can be etched in ultrapure water and for Al and Fe the surface oxidation layers are formed, but in the condition of high density of electrical current, surface oxidation process of Fe changes to the etching process. There have been, however, only a few reliable theoretical studies on these processes based on the first-principles electronic state theory.^{2,3)} In this report, we apply the first-principles molecular dynamics simulation method to the chemisorption of an OH molecule on the Cu(001), Fe(001) and Al(001) surfaces. We determined the optimized structure for an OH chemisorbed system and clarified the electronic structure relevant to the oxidation and the etching mechanism.

2. SIMULATION METHOD

In the present work, the calculation is based on the Kohn-Sham local-density-functional formalism.⁴⁾ A plane-wave basis set was used, and the cut-off energy were 63Ry(Cu(001)), 39Ry(Fe(001)), 44Ry(Al(001)), which corresponds to 65536 plane waves. The exchange-correlation interaction is approximated by the Ceperley-Alder form.⁵⁾ A norm-conserving pseudopotential was used in the originally developed separable form based on the Troullier-Martins form.⁶⁾ A mean-value point in the Brillouin zone⁷⁾ was also used.

We adopt the standard molecular dynamics method for the optimization of the ionic system and the preconditioned conjugate-gradient method for the quenching procedure of the electronic degrees of freedom.⁸⁾ In the present simulation the time step is 1.0 or 2.0 fs. The criterion for the optimized configuration is that forces exerted on all the

ions are lower than 1.0×10^{-3} Hartree/au.

As a localized basis set for the calculation of the local density of states, the MINI-1 Gaussian basis set which was proposed by Huzinaga⁹⁾ was used. We have already proposed and developed the method of population analysis for the plane-wave basis set in a supercell system.¹⁰⁾

The models studied in this work consist of metal (Cu, Fe and Al), oxygen and hydrogen atoms. The length of the unit lattice vector of the super-cell parallel to the x , y , and z axes are $2a_0$, $2a_0$, $4a_0$ (Cu(001) and Al(001)) or $3a_0$, $3a_0$, $6a_0$ (Fe(001)) respectively, where a_0 denotes the lattice constant of metal bulk, and the slab consists of three (Cu and Al) or five (Fe) atomic layers. Fig.1 shows the case of Cu(001) and Al(001). The thickness of the vacuum region is equivalent to five (Cu and Al) or seven (Fe) atomic layers.

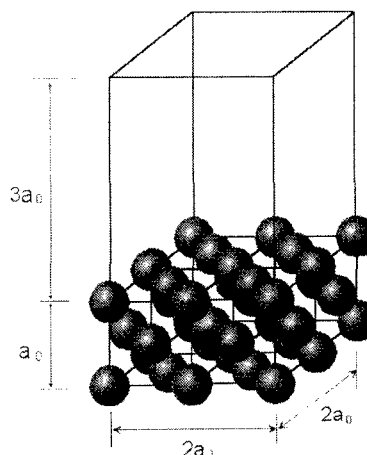


Fig.1 Atomic configuration of Cu(001) and Al(001) surface. a_0 : the lattice constant.

Cu: $a_0=3.385 \text{ \AA}$, Fe: $a_0=2.866 \text{ \AA}$, Al: $a_0=4.050 \text{ \AA}$

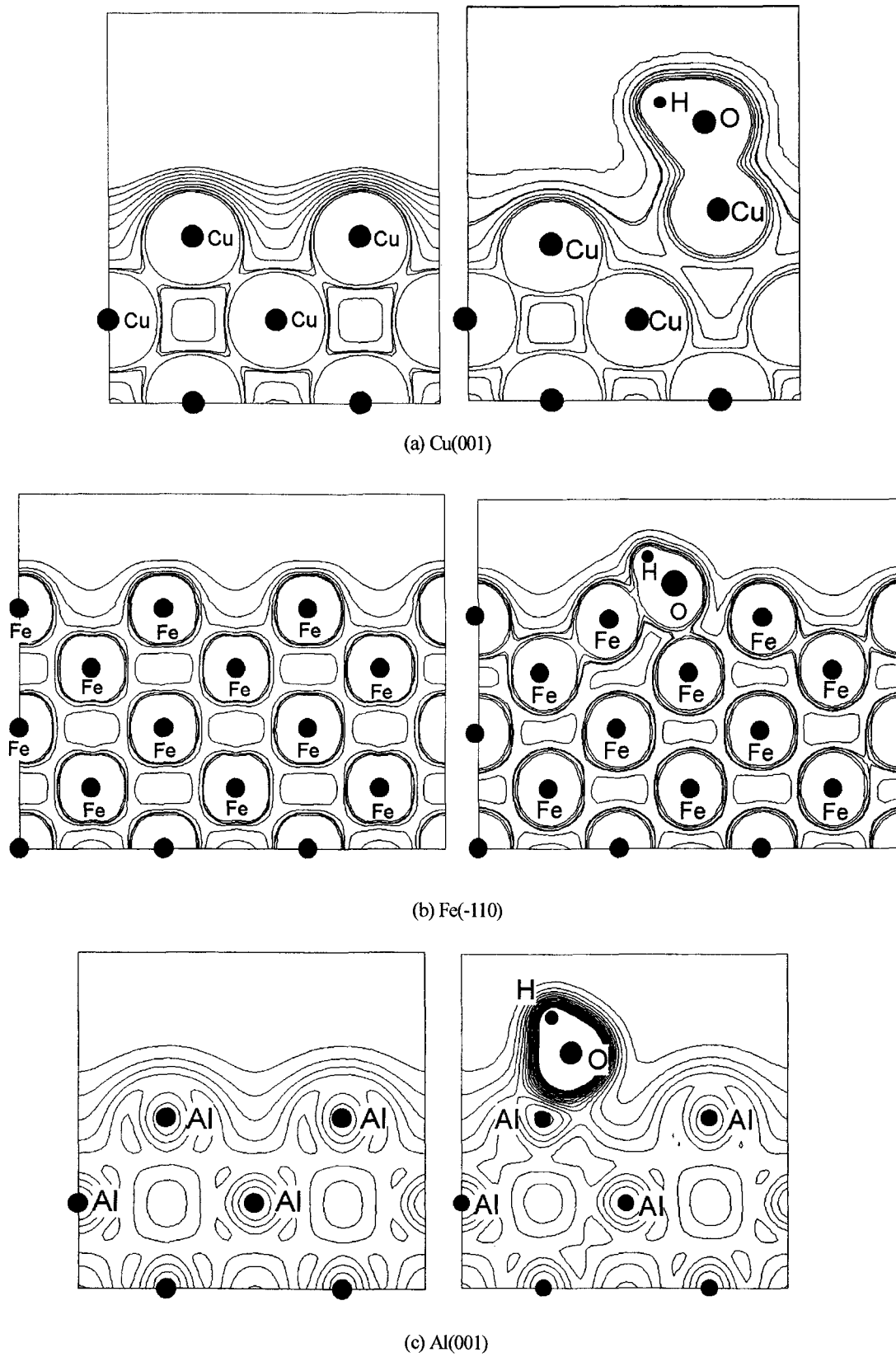


Fig.2 Charge density distribution for the optimized atomic configurations of ideal metal (001) surfaces and the one interacting with an OH molecule.
 (a)Cu(100) plane, (b)Fe(-110) plane, (c)Al(100) plane.

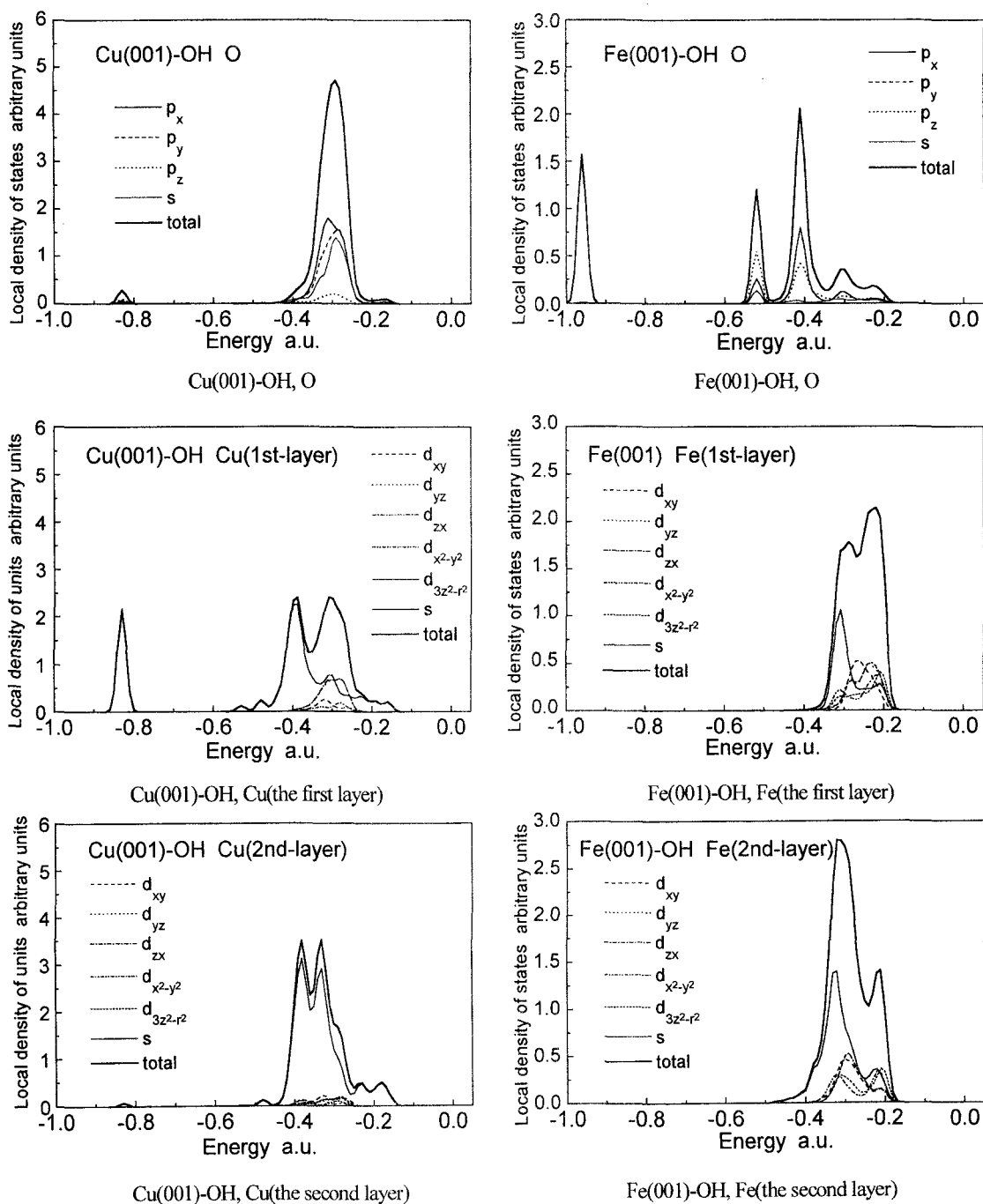


Fig.3-(a) Local density of states for oxygen, surface atom and the second layer atom of Cu(001) surface.

Fig.3-(b) Local density of states for oxygen, surface atom and the second layer atom of Fe(001) surface.

The optimized electronic structures and atomic configurations of the OH chemisorbed surfaces were calculated.

3. RESULTS AND DISCUSSION

Fig.2 (a), (b) and (c) show the calculated charge density distribution of (100) plane (for Cu and Al) or (-110) plane (for Fe) for the optimized atomic configurations of metal (001) surfaces interacting with one OH molecule,

respectively. In the case of Cu(001) surface, the strength of the back-bond of the surface Cu atom which chemisorbed by the OH molecule decreased and the surface Cu atom moved upward through the distance 1.37a.u. In the case of Fe(001) and Al(001) surfaces, the strength of the back-bond increased and the surface atom moved downward.

Fig.3 (a), (b) and (c) show the calculated local density of states for oxygen, the surface atom interacting with an OH molecule and the second-layer atom of Cu(001), Fe(001)

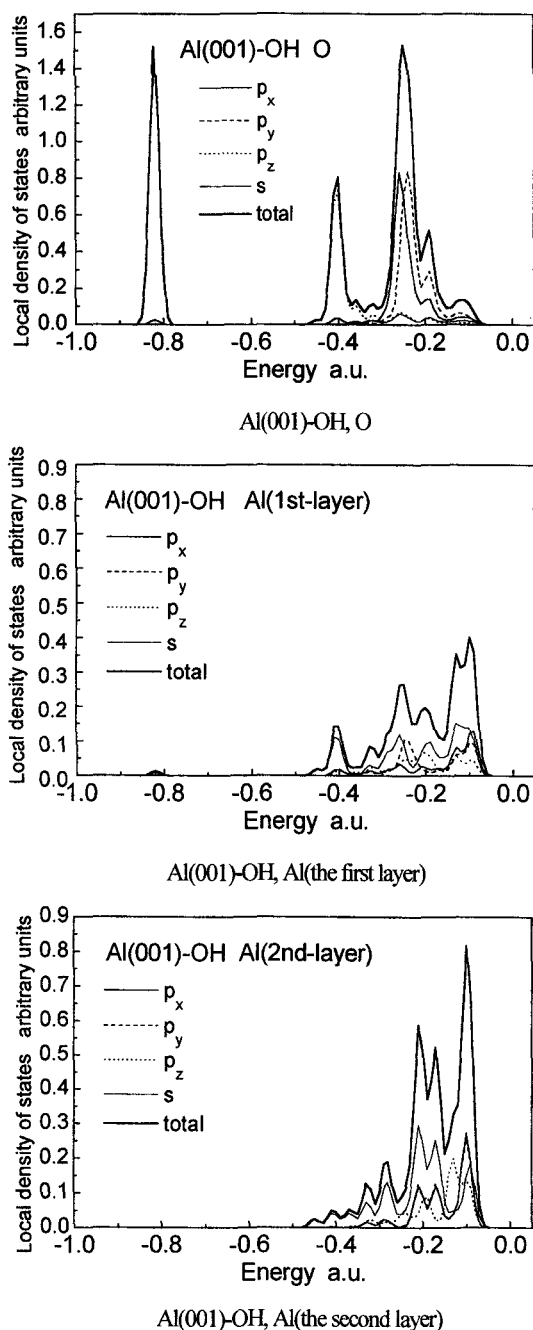


Fig.3-(c) Local density of states for oxygen, surface atom and the second layer atom of Al(001) surface.

and Al(001), respectively. The density is shown only for the states which are occupied by the valence electrons. In the case of Cu(001) surface, there exist orbital hybridizations between the p-type orbital of oxygen atom and the d-type orbital of the surface Cu atom. Therefore, the hybridization produces anti-bonding states in the back-bond of the surface Cu atom and the strength of the back-bond decreased, so the chemisorption of an OH molecule initiates the etching process.

In the case of Fe(001) and Al(001) surfaces, the bond between oxygen atom and the surface atom is ionic type, so the chemisorption of OH can not break the back-bond

and it initiates the surface oxidation process.

These simulated results agree with the experimental results of the electrochemical machining using ultrapure water. It is necessary to perform the farther simulations of the system which contains some OH or H₂O molecules for revealing the detail of the etching process. Such simulations are the plans for our future study.

4. CONCLUSIONS

Applying first-principles molecular dynamics simulation method for the metal surfaces (Cu(001), Fe(001) and Al(001)) interacting with an OH molecule, optimized configurations and its electronic structures were obtained. It was revealed that the chemisorption of an OH molecule on Cu(001) surface initiates the dissociation of Cu-Cu back bond and the etching process of the surface atom. In the cases of Fe(001) and Al(001), back bonds of the surface atoms were not dissociated. These simulated results agree with the experimental results.

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