First-principles study of ionization and diffusion of metal atoms at metal/solid interfaces in electric fields

Takashi NAKAYAMA
Department of Physics, Chiba University
1-33 Yayoi, Inage, Chiba 263-8522

Metal/solid interfaces are essential structures for various electronic/optical devices. However, metal atoms often diffuse from electrodes into solids such as SiO_2 by the thermal annealing processes and applied electric fields. This diffusion causes serious damage to recently developed nanoscale devices. In this view, the microscopic understanding of diffusion is important, especially in an electric field. However, there is little theoretical work on metal-atom diffusion around metal/solid interfaces. In this works, we studied the ionization and diffusion of various metal atoms in an electric field around metal/SiO_2 interfaces using first-principles calculations.

To simulate the interfaces, we adopt a (2×2) metal/SiO_2 (001) repeated-slab model made of 3-4 ML metal atoms and 16 ML α-quartz SiO_2. We consider eleven metals: Ta, Ag, Pt, Au, Al, Ni, W, Nb, V, Ti, and Cu. The adiabatic diffusion potential of a metal atom from the interface into SiO_2 was calculated by the standard first-principles method in the density functional theory. We employ a primitive method to produce an electric field perpendicular to the interface by simply removing electrons from the present slab system. All atom positions are optimized during the diffusion.

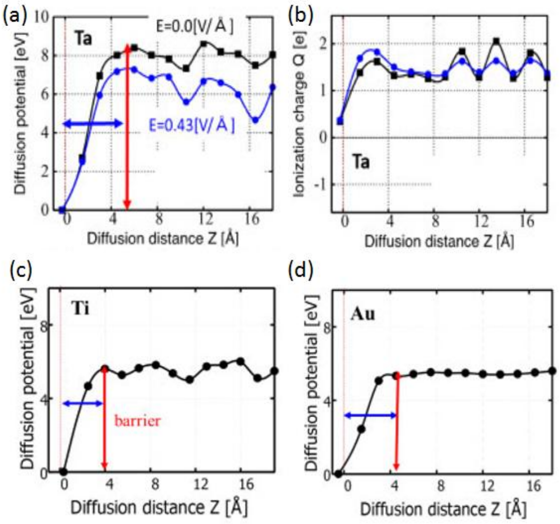

Fig.1. Adiabatic diffusion potentials at metal/SiO_2 interfaces as a function of distance from the interface, for (a) Ta, (c) Ti, and (d) Au atoms. (b) shows the ionization charge of Ta atom during the diffusion. In (a) and (b), the results in an electric field are also shown by blue lines.

Figs. 1(a) and 1(b) show the diffusion potential and ionization charge of the Ta atom, respectively, as a function of the distance z from the Ta/SiO_2 interface, while Figs. 1(c) and 1(d) are the potentials for the Ti and Au atoms. From these figures, we note two features: (1) the diffusion barrier height ϕ_B for penetrating into SiO_2 depends on the kind of atom. Fig. 2(a) shows the relationship between ϕ_B and $-\mu$ (chemical potential of a metal atom in metal). From these analyses, we found that the cohesive energy of metal atom layers is the leading factor for the penetration barrier ϕ_B.

(2) As shown in Figs. 1(a), 1(c), and 1(d), most of the metal atoms show the increase of potential in a similar 0-4 Å region near the interface. This region is closely related to the metal-induced gap states (MIGSs). Fig. 2(b) shows the electron density profile of one MIGS at a clean Ta/SiO_2 interface, and those of the electron-occupied states of a diffusing Ta atom when such a Ta atom is located at z=4.5 and 7.5 Å away from the interface. It is clearly seen that the electronic state of Ta decreases the hybridization with MIGS as the Ta atom leaves the interface. Since the hybridization of the Ta state with MIGS stabilizes the Ta atom, the hybridization with MIGS is the origin of the

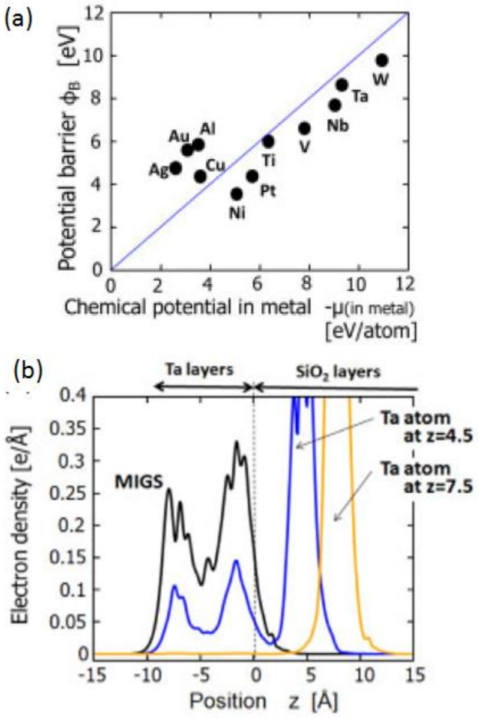

Fig.2. (a) Calculated potential barrier for metal-atom penetration into SiO_2 as a function of metal-atom chemical potential in bulk metal. (b) Electron density profile of original MIGS of Ta metal layers and Ta-atom states around Ta/SiO_2 interface.

region of potential increase with a similar width.

Next, we consider how the electric field accelerates the metal-atom penetration into SiO_2. Fig. 3(a) shows the diffusion penetration barrier for various atoms as a function of electric field strength. It is seen that the barrier height $\phi_B(E)$ decreases almost linearly with increasing electric field strength. We showed that the diffusion potential and the diffusion barrier in an electric field E are described as $\phi(E, z) = \phi_0(z) - QE$. and $\phi_B(E) = \phi_B - QE\alpha\ [1 - \log(QE\alpha/\phi_B)]$, respectively, as shown in Fig. 3(b). Here, ϕ_B, Q, and α are the potential barrier in the case of no electric field, the ionization charge of metal atom in SiO_2, and the penetration length of MIGS into SiO_2.

In this way, the barrier height $\phi_B(E)$ in an electric field is described by the universal formula, not depending on the kind of substrates and metal atoms. It is interesting to note that the MIGS are known to determine the Schottky barrier height and the defect density at metal/solid interfaces. By the present study, we also demonstrated that the MIGS work to determine the ionization and metal-atom penetration into SiO_2 in electric fields.

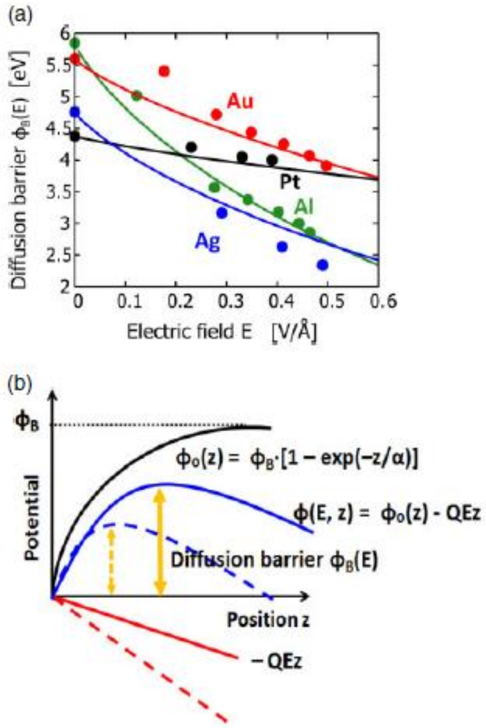

Fig.3. (a) Calculated diffusion barrier for the metal-atom penetration into SiO_2 as a function of electric field. The dots are obtained by first-principles calculations, while the lines are estimated using the model formula. (b) Model potential representing the metal-atom diffusion into insulators in electric fields. $\phi_B(E)$ is the potential barrier, while $\phi_0(z)$ and $-QEz$ are the diffusion potential in the case of no electric field and the electrostatic potential produced by the electric field, respectively. The solid and broken lines represent the cases of small and large electric fields, respectively.

All these calculations were performed using the xTAPP, VASP, and pspwf codes. In order to realize the calculations for the present interface systems in electric fields, because the system is made of a large number of atoms (300-1000 atoms), the advanced computing facility having multi-task and higher-speed CPU (more than 64 cores × 2.5GHz), larger-size memory (around 128GB), and larger-size strange (more than 1 TB) is indispensable. These conditions are realized only by the ISSP supercomputing systems.