

First-principles study of ionization and diffusion of metal atoms at metal/solid interfaces in electric fields: toward semiconductor and organic substrates

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Metal/solid interfaces are essential structures for various electronic/optical devices. During the fabrication and operation of devices, however, a variety of defects are often generated, particularly from their interfaces in electric fields, which produces various carrier traps and promotes the degradation of devices. However, there are little theoretical works on defect formations around metal/solid interfaces. In this works, we studied the formations of various point defects, such as interstitial metal atoms, atom vacancies, and impurity dopants, around metal/solid interfaces in electric fields using first-principles calculations.

To simulate the interfaces, we adopt (2×2) – (4×4) metal/solid repeated-slab models made of 4 ML metal atoms and 16 ML inorganic/organic solids. The formation energy of a point defect was calculated as a function of the distance from the interface 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 for all interfaces.

Figs. 1(a)–1(c) show the formation energies of C-vacancy, P-dopant, and Al-dopant defects in SiC layers around Au/2H-SiC interfaces, respectively, as a function of the distance from the interface, for various values of electric fields. The formation energies of point defects gradually increase with increasing the distance from the interface in the case without an electric field, which is a general trend observed for point defects around metal/solid interfaces. The most remarkable feature is that, with increasing the electric field, the formation

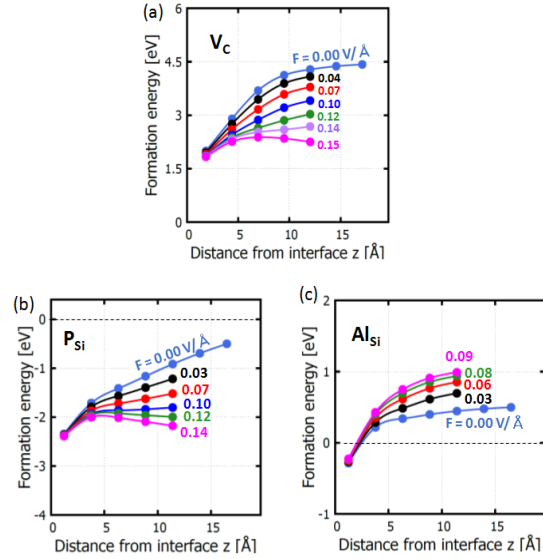


Fig.1. Calculated formation energies of (a) C-vacancy, (b) P dopant, and (c) Al dopant as a function of the distance z of a defect from the Au/2H-SiC interface. The cases with various electric fields ($F = 0$ – 0.15 V/Å) are shown in different colors.

energies in inner 2H-SiC layers decrease for the former two defects, while it increases for the latter defect. We also studied various point defects and found that formation of anion vacancies and donor-type dopants is easy, while the formation of acceptor-type dopants becomes difficult around the metal/solid interfaces when the positive voltage is applied to the metal electrode.

To understand the variation of formation energy, we show the ionization charges of C-vacancy in Fig. 2(a), as a function of the distance from the interface. We can clearly see that the ionization charge increases with increasing the electric field. This variation is explained by considering the capacitor model shown in Fig. 2(b). When the C vacancy is produced in 2H-SiC layers, the electron-

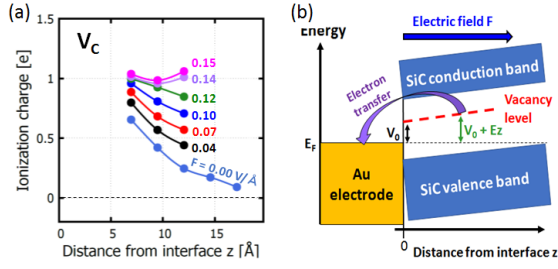


Fig.2. (a) Calculated ionization charge of C-vacancy as a function of the distance from the Au/2H-SiC interface for various values of electric fields ($F = 0-0.15$ V/Å). (b) Schematic picture to explain the electron transfer between electronic state of defect and metal electrode around metal/solid interface in electric field, for the cases of C-vacancy.

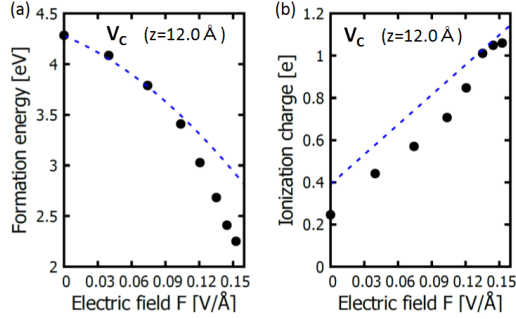


Fig.3. (a) Calculated formation energy and (b) ionization charge of C-vacancy at $z = 12$ Å around the Au/2H-SiC interface, as a function of the electric field. Dots are obtained by the first-principles calculation, while blue dashed lines are by the capacitor model.

occupied vacancy state appears in the band gap of 2H-SiC. Since the Fermi energy of Au electrode E_F is located below this state, the electron transfer q occurs from the vacancy state to the Au layers as shown by the arrow in Fig. 2(b). By considering the energy gain and loss by this electron transfer, we obtain the formation energy and ionization charge of C-vacancy as $E_{\text{form}}(F, z) = E_0 - \epsilon SF^2 z/2 - \epsilon SFV_0 - \epsilon SV_0^2/2z$ and $q = \epsilon SF + \epsilon SV_0/z$, where E_0 is the formation energy in bulk SiC, F the electric field, z the distance from the interface, S the effective area of ionization charge, V_0 the energy position of vacancy state, and ϵ the dielectric constant of SiC.

Figures 3(a) and 3(b) show the variations of the formation energy and ionization charge of C vacancy at the fixed $z = 12$ Å position. We can

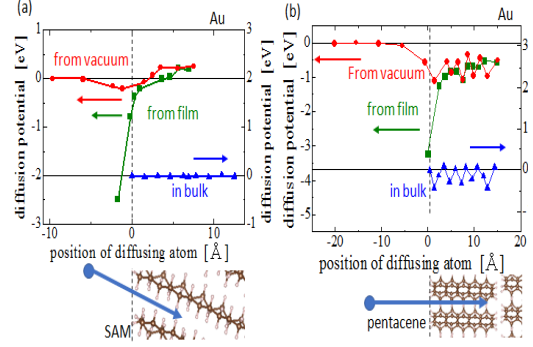


Fig.4. Calculated diffusion potentials for Au metal atom in (a) SAM and (b) pentacene solids, as a function of metal-atom position. Lower pictures display the corresponding position.

see that such variations are well explained by the present capacitor model. In this way, the electron transfer between defect and metal electrode is the key to understand the variation of defect formation energies around the metal interface in electric field.

Then, we consider the cases of metal/organic solid interfaces. Figures 4(a) and 4(b) show the diffusion potentials of Au atom around Au/SAM and Au/pentacene interfaces. In the case of SAM, metal atom easily penetrates and diffuses in solids reflecting the weak interaction between metal atom and molecules. In case of pentacene, on the other hand, since the interaction between metal atom and molecules is attractive and strong, metal atom actively enters into solids and is tightly bonded to molecules. The difference in metal-atom behavior comes from the difference in electronic structure between SAM and pentacene, which are respectively σ - and π -orbital molecular systems.

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 \times 2.5GHz), larger-size memory (around 128GB), and larger-size storage (more than 1 TB) is indispensable. These conditions are realized only by the ISSP supercomputing systems.