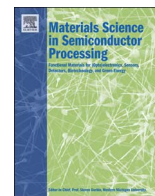




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# Ionization and diffusion of metal atoms under electric field at metal/insulator interfaces; First-principles study

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## ABSTRACT

The ionization and diffusion of metal atoms at metal/SiO<sub>2</sub> interfaces under an electric field are studied by first-principles calculation. It is shown that the ionization of metal atoms occurs when the hybridization of metal-atom electronic states with metal-induced gap states (MIGS) is broken. Moreover, we show that an electric field markedly decreases the penetration barrier of metal atoms from a metal electrode into SiO<sub>2</sub> and enhances the diffusion of metal atoms.

## 1. Introduction

Metal/insulator interfaces are essential structures in most electronic and optical devices, and thus the stability of such interfaces is important for the reliability of devices [1–3]. It has long been known that the metal atoms in a gate electrode often penetrate into insulators by thermal diffusion during the annealing processes in device fabrication. In addition, such diffusion is enhanced under an applied voltage during device operation. McBrayer et al. found by Rutherford backscattering measurement of (Cu, Ag)/SiO<sub>2</sub>/Si gate structures that metal-atom diffusion occurs only when the gate electrode is positively charged and that the amount of diffused atoms is proportional to the applied electric field [4]. This result clearly indicates that metal atoms are positively ionized and the diffusion is enhanced under electric fields. Diffusing metal atoms often produce defect electronic states, promote leakage currents, and cause serious damage in electronic devices, particularly in recent nanoscale devices such as metal nanodot memories [5–8]. On the other hand, such diffusion behavior is positively utilized to produce metal nanowires in insulators for resistive switching memory applications [9–11]. However, the microscopic understanding of ionized metal-atom diffusion has not been obtained. In this work, we concentrate on the starting point of ion diffusion and clarify the ionization behavior of metal atoms around metal/insulator interfaces under an electric field by first-principles calculation.

## 2. Calculation model and method

We select Al and Pt as representative metals, which have small and large electronegativities, respectively, while  $\beta$ -cristobalite SiO<sub>2</sub> is

adopted as an insulator. To simulate metal/insulator interfaces, we use the  $(\sqrt{2} \times \sqrt{2}) M_3/(\text{SiO}_2)_{12}$  (100) repeated-slab system shown in Fig. 1(a), where M denotes metal atoms [2,12,13]. Metal (100) layers with a bulk fcc structure are stacked on a SiO<sub>2</sub> (100) substrate, while the back surface of SiO<sub>2</sub> is terminated by H atoms. A vacuum region with about 20 Å thickness is inserted between the slabs. We add one metal atom at the interface and allow it to diffuse in the interstitial space from the interface into the SiO<sub>2</sub> layers [14]. All atom positions are optimized during the metal-atom diffusion except those in the front M<sub>3</sub> and back (SiO<sub>2</sub>)<sub>4</sub> layers, which are fixed at initial optimized positions to remove the contribution of surface changes to the calculated total energy [12,13].

The electronic structures and adiabatic diffusion potentials of the metal atoms are calculated using the first-principles code: Vienna Ab-initio Simulation Package (VASP) [15–17], which is based on the density functional theory. We employ the Perdew-Burke-Ernzerhof (PBE) exchange-correlation potential in a generalized gradient approximation (GGA), a cutoff energy of 700 eV for the projector-augmented-wave (PAW) expansion of wavefunctions, ultrasoft pseudopotentials for all atoms, and  $4 \times 4 \times 1$  k-point sampling for integration of the electron density in the Brillouin zone. Details of the calculation method are described in our previous publications [12–14,18].

There are a variety of methods of realizing an electric field in first-principles calculations [19–21]. The most sophisticated method is to arrange two electrodes and impose a thermodynamic boundary condition with a constant chemical potential difference between the electrodes [22,23], which is often used to study liquid/solid interfaces. In this work, we consider solid/solid interfaces and the diffusion of a metal atom that is originally included in an electrode; thus, we employ a naïve

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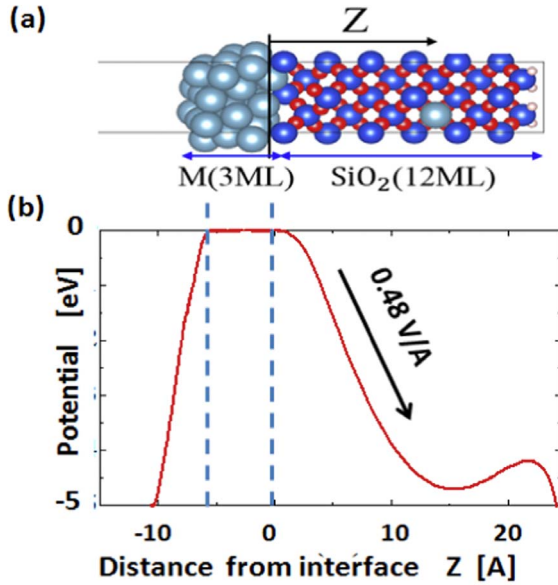
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**Fig. 1.** (a) Al/SiO<sub>2</sub> interface slab model adopted in this work. (b) Electrostatic potential profile for +e-charged ion under an electric field perpendicular to the Al/SiO<sub>2</sub> interface. This is realized by extracting one electron from the repeated-slab unit cell.

recipe to produce an electric field perpendicular to the interface by simply supplying electric charges to the present slab system. Since such additional charges are unequally distributed on the front and back surfaces of the slab, an electric field is produced in SiO<sub>2</sub>, as shown in Fig. 1(b), where one electron is removed from the slab and the electrostatic potential for a +e-charged ion is displayed. Here, we can observe a uniform electric field of about 0.48 V/Å in the region 0–14 Å from the interface. We found that such an electric field changes slightly

even when the metal atom is diffusing in this region. Thus, we adopt this method as a first-order qualitative approximation to study the metal-atom ionization during diffusion in an electric field.

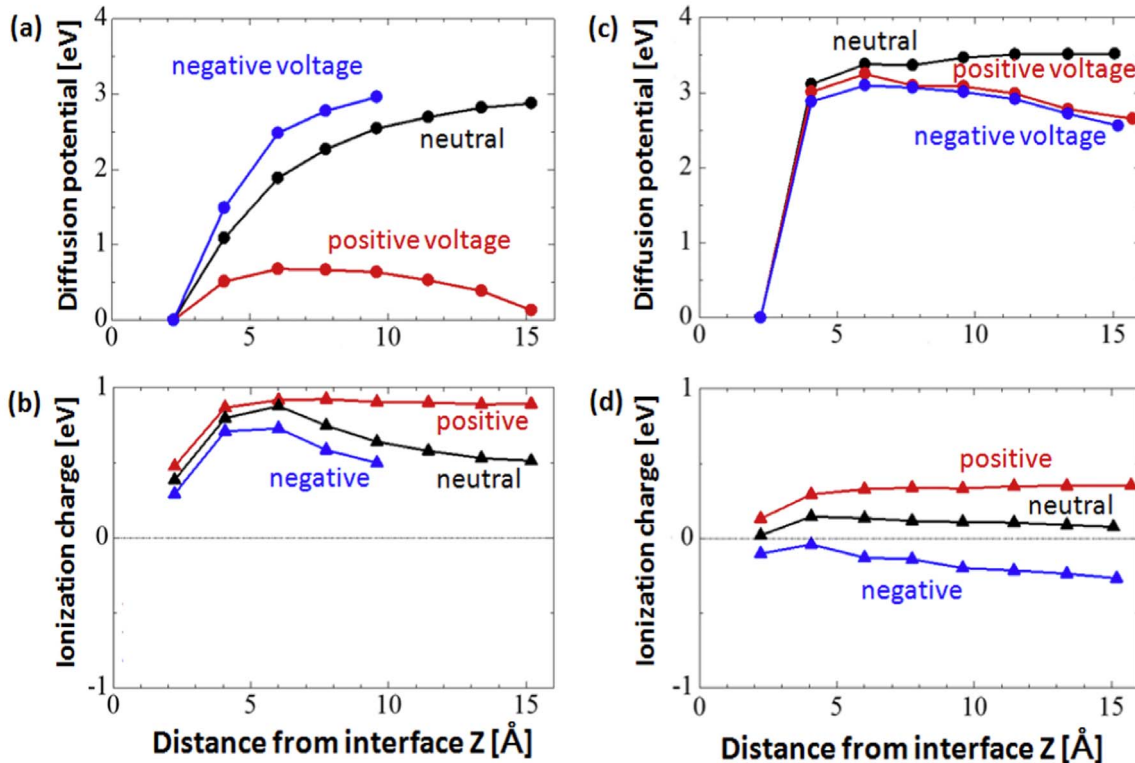
### 3. Results and discussion

#### 3.1. Diffusion under electric field

First, we consider the diffusion of an Al atom around the Al/SiO<sub>2</sub> interface. Fig. 2(a) shows the calculated adiabatic potentials for Al atom diffusion as a function of the distance of the Al atom from the interface, while the ionization charge of the Al atom is displayed at corresponding positions in Fig. 2(b), which was estimated by Bader charge analysis [24]. Here, black, red, and blue lines correspond to the cases of Al electrodes with zero, positive, and negative bias voltages, respectively.

In the case of zero-voltage application (neutral Al electrode), as the Al atom leaves the interface, the potential gradually increases and approaches a nearly constant value in the inner SiO<sub>2</sub> bulk layers. This is because the Al atom is stable in bulk Al rather than in bulk SiO<sub>2</sub> layers provided it is located interstitially in SiO<sub>2</sub> [12,13]. Even in this case without an electric field, on the other hand, the Al atom is positively ionized to approximately +0.5e in the inner SiO<sub>2</sub> layers. This occurs because the Al atom has small negativity and its electrons are extracted by the surrounding SiO<sub>2</sub>. This feature was also confirmed by calculating the stability of an Al atom in bulk SiO<sub>2</sub> against ionization. Fig. 3 shows the formation energy of an ionized Al atom in bulk SiO<sub>2</sub> as a function of the chemical potential of the electrons [1,25]. We can see that the Al atom is easily positively ionized in bulk SiO<sub>2</sub>, while it is difficult for it to be negatively ionized, reflecting its small negativity.

When a positive voltage is applied to the Al electrode, the diffusion potential shows a large decrease of approximately 2 eV; thus, the diffusion into the SiO<sub>2</sub> layers readily occurs, consistent with the results of experiments [4]. This is because the Al atom is more positively ionized (to approximately +0.9e) and there is an electric field from the



**Fig. 2.** Calculated diffusion potentials and ionization charges of Al (a and b) and Pt (c and d) atoms around metal/SiO<sub>2</sub> interfaces as a function of the distance of the metal atom from the interface. The cases with zero (neutral), positive, and negative voltage application are shown. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

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