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Acceleration of Metal-atom Diffusion under Electric Field at Metal/Insulator Interfaces; First-principles Study

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Abstract

Metal-atom diffusion into gate insulator often causes serious damages in electronic devices, particularly under electric field during device operation. In this work, we studied how metal atoms diffuse under electric field at metal/SiO_2 interfaces by first-principles calculation. It is shown that the ionization of metal atom occurs owing to (i) the breakdown of hybridization with MIGS and (ii) the electron transfer to electrode. Reflecting such ionization, the electric field remarkably decreases the potential barrier of metal atoms and accelerates the diffusion of metal atoms into SiO_2. Simple formula is derived to estimate the potential barrier height in electric field.

1. Introduction

Metal-atom diffusion from metal electrode into gate insulator often promotes leakage currents and causes serious damages in electronic devices, particularly under electric field during device operation [1]. On the other hand, such diffusion property under electric field is recently utilized to produce and control metal clusters in insulators for a variety of device applications, such as for metal-nanodot memory and metal-nanowire resistive memory [2]. However, the microscopic understanding of diffusion, i.e., how metal atoms are ionized and diffuse under electric field, has not been obtained. In this work, we study the diffusion of metal atoms under electric field around metal/insulator interfaces by the first-principles calculations and clarify how the electric field accelerates the metal-atom diffusion into insulators.

2. Calculation Model and Method

We consider metal/insulator interfaces made of various metals (Al, Ag, Au, Pt, Ta, W, etc.) and crystalline/amorphous SiO_2 [3]. To simulate these interfaces, we use the ($\sqrt{2}\times\sqrt{2}$) $M_3/(SiO_2)_{12}$ (100) repeated slab shown in Fig.1(a), where M denotes metal atoms. Electronic structures, ionization charges, and adiabatic diffusion potentials of metal atoms are calculated using the first-principles code, VASP [4], based on the density functional theory, where GGA-PW exchcorr. potential, 700eV cutoff energy, and 4x4x1 k-point sampling are employed.

Electric field is applied perpendicular to the interface by supplying electric charges to the present slab-model system. Since the charges are in-equally distributed at the front and back surfaces of the slab, the electric field is produced in SiO_2 as shown in Fig.1(b). Here, we can see a uniform electric field of about 0.48 V/Å in a 0-10Å region from the interface. The strength of electric field is varied by changing the amount of supplying charge. Other calculation details are described in our previous publications [3,5].

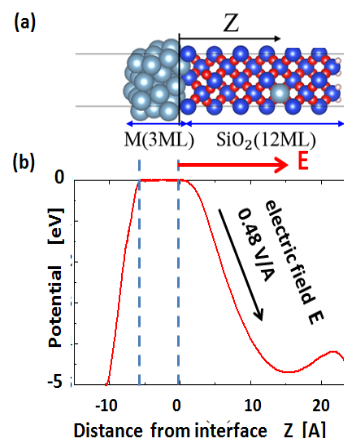

Fig.1. (a) Al/SiO_2 interface slab model adopted in this work. (b) Electrostatic potential profile for +e virtual ion under electric field perpendicular to the Al/SiO_2 interface.

3. Results and Discussions

Ionization and diffusion of metal atoms under electric field

First, we consider how the diffusion potential changes under electric field. Fig. 2(a) shows the calculated potentials for Al-atom diffusion as a function of the distance from Al/SiO_2 interface, while the ionization charge of Al atom is shown in Fig. 2(b), which is estimated by Bader charge. Here, black, red, and blue lines correspond to the electrode with no, positive, and negative bias voltages, respectively.

When no voltage is applied to Al electrode, the potential gradually increases as Al atom leaves the interface. This occurs because Al atom is stable in bulk Al rather than in SiO_2 [5]. Even in this case without electric field, however, Al looks ionized by about +0.5e in SiO_2 layers. This is because Al has small negativity and its electrons are extracted by surrounding SiO_2.

When the positive voltage is applied to Al electrode, diffusion potential shows remarkable decrease, around 2eV, thus the diffusion into SiO_2 layers becoming quite easy. This occurs because Al atom is more ionized positively, around +0.9e, and there is an electric field from metal electrode to inner SiO_2 layers. When the negative voltage is applied, on the other hand, since diffusing Al atom is still ionized posi-

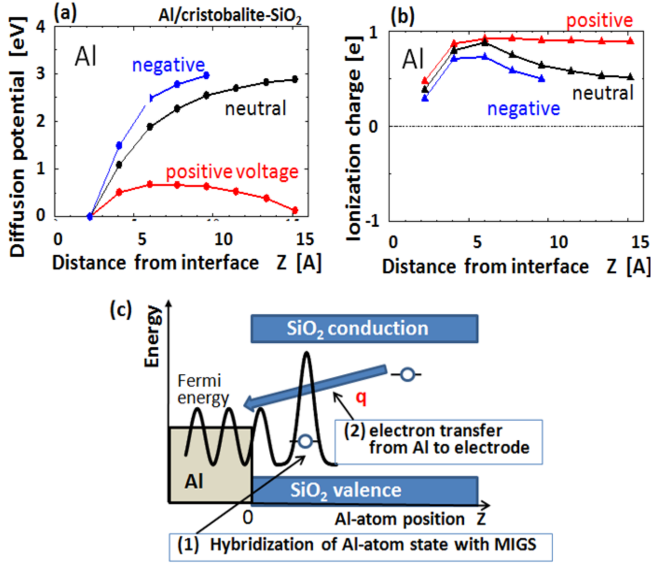

Fig. 2. (a) Calculated diffusion potentials and (b) ionization charges of Al atom at Al/cristbalite-SiO_2 interface as a function of the distance from interface. The cases with no (neutral), positive, and negative voltage applications are shown. (c) Schematic picture explaining two factors that change the ionization.

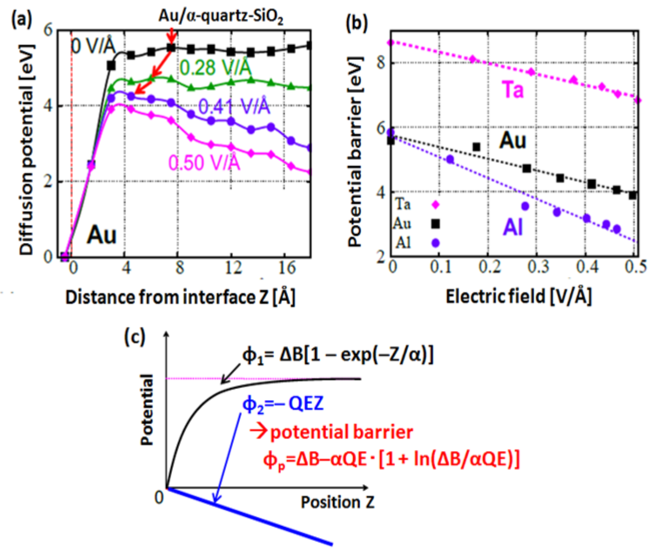

Fig. 3. (a) Calculated diffusion potential of Au atom at Au/α-quartz-SiO_2 interface for various strength of electric field, as a function of the distance from interface. (b) Diffusion barriers of Al, Au, and Ta atoms to penetrate into SiO_2, as a function of electric field. (c) Schematic potential model to derive the potential barrier height for penetration under electric field.

tively in SiO_2, the potential barrier to enter SiO_2 increases.

Then, we discuss where the ionization of metal atom occurs around metal/SiO_2 interface. From Fig. 2(b), we note that the diffusing atom is sharply ionized with leaving the interface in a 0-6Å region near the interface. This occurs owing to the breakdown of orbital hybridization between electronic states of metal atom and metal induced gap states (MIGS) of metal electrode [3,5,6]. When the substrate is changed to semiconducting Si and Sn, this region is extended to 10-15Å. Outside this MIGS-penetration region, on the other hand, the ionic charge of metal atom still varies. This variation occurs due to the electron transfers from diffusing metal atom to not only surrounding SiO_2 but also metal electrode. In this way, as shown in Fig. 2(c), there exist two factors to change the ionization, which is a crucial feature to understand the diffusion potential profile under electric field as discussed in the following.

Acceleration of metal-atom diffusion by electric field

Next, we consider how the electric field decreases the potential barrier for diffusion (penetration) into SiO_2. As shown in Fig. 3(a), the barrier gradually decreases with increasing the electric field. Fig.3(b) shows the potential barrier heights for Al, Au, and Ta-atom diffusion as a function of electric field. We found that the diffusion barrier simply decreases in a linear manner with increasing the electric field. This result indicates that the electric field remarkably accelerates the metal-atom penetration into SiO_2, as an exponential-function form of electric field. In addition, comparing the cases of Al and Au, it is seen that such acceleration works largely for metal atoms with small electronegativity, which is in good agreement with observations. This is because small-negativity atoms have large ionic charges.

Finally, we derive the simple formula to predict the potential barrier height in electric field. The potential near the interface is made of two terms: ϕ_1 and ϕ_2 shown in Fig.3(c). ϕ_1 is the MIGS-induced potential, where α represents the inverse of MIGS penetration length, while ϕ_2 is the electric-field induced potential, where Q and E are ionization charge and electric field, respectively. From this potential profile, we can derive the formula of potential barrier height (ϕ_p) in electric field for metal-atom penetration, which is shown in Fig.3(c).

4. Conclusions

Ionization and diffusion of metal atoms under electric field at metal/SiO_2 interfaces were studied by first-principles calculation. It was shown that the ionization of metal atom occurs when the hybridization with MIGS is broken and when the electron transfer from metal atom to electrode is caused by electric field. In addition, we showed that the electric field remarkably decreases the potential barrier height and accelerates the diffusion of metal atoms into insulators.

Acknowledgements

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References

[1] McBrayer et al., J. Electrochem.Soc. **133** (1986) 1242.
[2] Y.Yang et al., Nature Comm. **5** (2014) 4232.
[3] Y.Asayama et al., Materials Science Semicond. Process., DOI: 10.1016/j.mssp.2016.09.010 (2016).
[4] P.E.Blöchl, Phys. Rev. B **50** (1994) 17953.
[5] T.Hiramatsu et al., Jpn.J.Appl.Phys. **53**(2014) 058006.
[6] S.Sasaki, T.Nakayama, Jpn.J. Appl. Phys. **55**, 111302 (2016).