

# Charge Retention and Stability of Metal Nano Dots in SiO<sub>2</sub>; First-principles Study on Metal Dependence

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## Abstract

Metal nano dots are promising systems for future non-volatile memory devices. However, metal-atom diffusion from metal dot induces serious degradation during repetitious charge injection. We studied which kind of metal has large charge retention in SiO<sub>2</sub> and which metal dot is stable in charged states, using the first-principles calculations. We showed that d-orbital metals with small number of valence electrons, such as W, have both large retention and large structural stability. This is because these metal atoms are strongly bound to surrounding SiO<sub>2</sub> atoms reflecting the flexibility of electron-unoccupied d orbitals.

## 1. Introduction

Because of large charge-retention power, nano-scale metal dots are promising systems for near-future memory devices when they are embedded in insulating oxides such as SiO<sub>2</sub> [1]. However, there exist serious issues of charge-storage degradation; during the repetitious charge injection, metal dot is broken by the diffusion of metal atoms from metal-dot surface into insulator under applied electric field [2]. In addition, diffused metal atoms are easily ionized, which decreases charge-retention power of metal nano dots. However, there have been no microscopic studies on these phenomena. The purpose of this work is to clarify how the charge retention of metal nano dot depends on metal kind and which metal dot is stable in charged states, by using the first-principles calculations.

## 2. Models and Calculation Method

In this work, we consider a metal nano dot in amorphous SiO<sub>2</sub> insulator. When there are no defects in SiO<sub>2</sub>, charge retention power of metal dot generally depends on the size of dot and band gap of insulator. Near the metal dot, however, there exist diffused isolated metal atoms, which can be ionized by obtaining charges from the metal dot as shown in Fig.1(a). In this case, the charge retention is broken by the ionization of neighboring isolated metal atoms. Based on this viewpoint, we can calculate the charge retention window (voltage) of metal nano dot as the energy difference between positive and negative ionizations of isolated atom, as shown in Fig.1(b).

When metal nano dot is charged, electric field is induced around nano dot and the atoms on the nano-dot surface easily diffuse into SiO<sub>2</sub>, as shown in Fig.1(c), owing to repul-

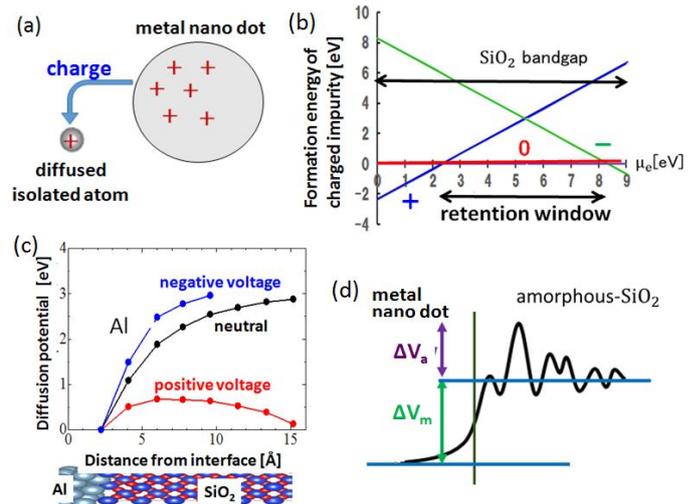


Fig. 1. (a) Ionization of isolated atom by obtaining charges from metal dot. We assume that this process limits the charge retention power of metal nano dot. (b) Schematic picture to estimate the charge retention window (voltage) of metal nano dot. 0, +, and - lines represent formation energies of charged isolated metal atom in SiO<sub>2</sub>, as a function of chemical potential of electrons. Chemical potential corresponds to the Fermi energy of metal nano dot. (c) Calculated diffusion potential of metal atom from metal dot into SiO<sub>2</sub> (cristobalite) layers for neutral and  $\pm$  charged metal-dot cases, as a function of distance from metal/SiO<sub>2</sub> interface. Lower inset shows diffusion geometry. (d) Schematic energies to determine the structural stability of metal nano dot.  $\Delta V_m$  is the dissociation energy from bulk metal and  $\Delta V_a$  is the potential fluctuation in amorphous SiO<sub>2</sub>.

sive Coulomb interaction. This diffusion promotes electronic and structural degradation of metal nano dot. We found that the energy barrier (voltage) for such diffusion is roughly estimated by two factors [3]: one is the chemical-potential difference of metal atom between in bulk metal and in amorphous SiO<sub>2</sub>,  $\Delta V_m$  shown in Fig. 1(d), while the other is the potential fluctuation in amorphous SiO<sub>2</sub>,  $\Delta V_a$ . Thus, in this work, we calculate such energy differences to judge structural stability.

Electronic structures and total energies of present systems are calculated in the density functional theory, employing Vienna ab-initio simulation package (VASP) code, ultrasoft pseudopotentials, and plane-wave basis with less than 700 eV energy. Details are described elsewhere [3,4].

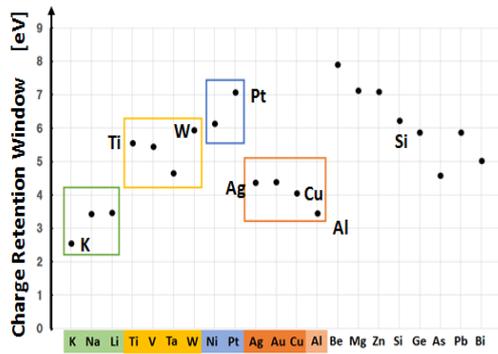


Fig. 2. Calculated charge retention windows for various kinds of metal nano dots.

### 3. Results and Discussions

#### Charge Retention Windows of Metal Nano Dots

Figure 2 shows calculated charge retention windows for various kinds of metal nano dots. It is seen that Ti, W, and Pt as well as Si have large retention, which corresponds to about five electrons in case of 1 nm dot consistent with experiments [5], while those of Ag, Cu, and Al are small.

In order to clarify the origin of charge-retention difference between various metals, we show projected densities of states (PDOS) of Ti and Ag atoms in Figs.3(a) and 3(b) when they are located in  $\text{SiO}_2$ , together with PDOS of neighboring O and Si atoms. We can see that Ti atom produce Ti-O and Ti-Si bonds by orbital hybridization. Such hybridization promotes large stability of isolated Ti atom against ionization and enlarges the retention window. On the other hand, d orbitals of Ag is fully occupied and there appears no strong orbital hybridization with surrounding O and Si atoms, thus the retention is not so large compared to Ti. In this way, we can conclude that the charge retention power in the present impurity-restricted cases reflects the bonding features of metal atoms with surrounding  $\text{SiO}_2$ .

#### Structural Stability of Metal Nano Dots against Dissociation

Figure 4 shows calculated potential barrier of metal-atom dissociation from nano dot into  $\text{SiO}_2$  for various kinds of metal nano dots. It is seen that W, Ta, V, and Ti atoms have large barriers. This is because these atoms have large cohesive energies (large  $\Delta V_m$ ). On the other hand, since sp-orbital atoms like Al and Si produce strong bonds with O in  $\text{SiO}_2$ , they have has small barrier.

It is interesting to note that there exists some correlation between the charge retention window and dissociation potential barrier ( $\Delta V_a$  effect). For example, d-orbital metals with many d electrons, like Ni and Ag, have small barriers. This is because these atoms produce weak bonds with  $\text{SiO}_2$  and thus easily diffuse in  $\text{SiO}_2$ . It should be noticed that the potential barrier obtained in this work might become smaller in experiments because the ionic charge in  $\text{SiO}_2$  depends on metal kind and it increases with increasing electric field

From Figs. 2 and 4, we can conclude that d-orbital metals such as W and V have large retention and barrier energies, thus being suitable for nano-dot memory usage.

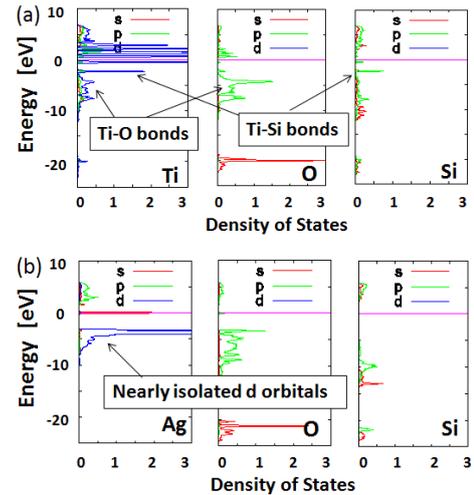


Fig. 3. Projected densities of states of (a) Ti and (b) Ag atoms in amorphous  $\text{SiO}_2$ .

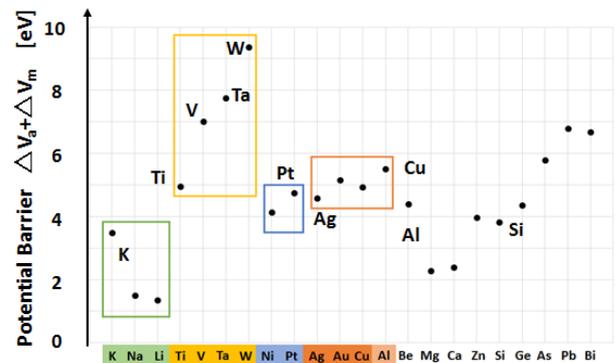


Fig. 4. Calculated potential barriers,  $\Delta V_a + \Delta V_m$ , for metal-atom dissociation from nano dots in cases of various kinds of metal nano dots.

### 4. Conclusions

We have studied the charge retention windows and dissociation stability of various metal nano dots in amorphous  $\text{SiO}_2$ , using the first-principles calculation. We found that d-orbital metals with small number of valence electrons, such as W and Ta, have large retention and large stability, thus suitable for nano-dot memory usage. This is because these atoms are strongly bound not only to each other but also to Si and O in a- $\text{SiO}_2$ ; thus, they are difficult to become ions owing to the strong electronic hybridization to  $\text{SiO}_2$ .

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