



# Work function tuning of an ultrathin MgO film on an Ag substrate by generating oxygen impurities at the interface

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## ABSTRACT

Density functional theory was used to investigate the electrostatic effect of various oxygen impurities at the interface of MgO/Ag, including interstitial oxygen defects, substitutional oxygen defects, and reconstructed substitutional oxygen defects. When interstitial and reconstructed substitutional oxygen impurities were generated at the interface, an additional bond with the film was formed and the work function of the interface increased. On the other hand, in the case of substitutional oxygen generated at the interface, the oxygen impurities migrated into the Ag subinterface layer and the work function of the interface was slightly decreased. It can be inferred that the origin of the work function change is the dipole moment induced by oxygen impurities. The results of this study indicate that the work function of MgO/Ag (001) can be finely tuned with interfacial oxygen impurities.

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## 1. Introduction

Ultrathin oxide films on metallic substrates have received considerable attention for application in the field of catalyst [1,2]. In particular, MgO thin films epitaxially grown on Ag are one of the most commonly studied catalytic substrates due to its simple structure and slight lattice mismatch [3]. The MgO/Ag combination permits the chemical reactions such as  $N_2O$  reduction [4], water dissociation [5], and charging of adsorbates [6] which are not observed on the corresponding single crystal surface. It is believed that such chemical activations are triggered by charge transfer from the interface to adsorbate in experimental [7,8] and theoretical analyses [9]. The charge transfer is explained by a reduced work function of the metal induced by the “compression effect” [10]. The compression effect occurs when the dielectric layer pushes partially spread electrons out of the surface back into the metal layer, thus changing the surface dipole and lowering the metal work function. The modified work function increases the tunneling properties from the interface to the adsorbate. Therefore, the value of the work function is one of the key parameters in determining the charging behavior of the adsorbates and direct measuring of the work function has been intensively studied [11,12].

Recently, Jung et al. reported enhanced chemical reactivity by artificially manipulating the oxide/metal interface structure [13]. Such manipulated interface structure can be generated from the deposition process. Before film deposition, surface vacancies [14], rippling [15], and dislocation [16,17] can be generated through the presputtering process onto single crystal Ag. Also, adsorbed oxygen can occupy hollow site and

vacancy sites of the Ag surface in the oxygen rich atmosphere [18]. Moreover, such point defects on metallic substrates can be artificially generated by directly picking up single Ag, Mg, or O atoms with atomic force microscopy tips [19]. Through such a process, the interstitial and substitutional oxygen impurities can be generated at the interface.

Even though buried oxygen defects are suggested in other studies, their electronic structure and induced electrostatic effects are not fully understood due to its practical difficulty of direct observation. In this study, the electronic structure and electrostatic effect of oxygen impurities at the MgO/Ag interface were investigated using ab-initio modeling. The oxygen impurities considered were interstitial ( $O_i$ ), substitutional ( $O_{Ag}$ ), and reconstructed substitutional ( $O_h$ ) oxygen defects on the Ag-side interface layer.

## 2. Calculation details

First-principle calculations were performed based on the Kohn–Sham equation as implemented in the Vienna ab-initio simulation package code (VASP) [20]. The projector augmented wave (PAW) method [21] was used for describing ionic potentials, and the exchange-correlation function between the electrons were adopted for the Perdew, Burke, and Ernzerhof (PBE) potential [22]. The basis set of the plane waves was expanded to a cut-off energy of 400 eV and Gaussian smearing was used with a 0.1 eV of sigma value.

The  $(2 \times 2)$  periodicity of supercells was constructed to describe the MgO film and Ag substrate. The supercell consisted of 2 layers of MgO and 4 layers of Ag wherein at the bottom the two layers were fixed at the bulk position. A vacuum thickness of 22 Å was set and the dipole correction was applied in all calculations. In a defect-free structure, substrate layers consisted of 8 Ag atoms and film layers contained 8 Mg and

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8 O atoms. The oxygen impurities were generated on the Ag-side interface layer. The  $O_{Ag}$  was generated by substituting O atom with fourth layer of Ag atom. The  $O_i$  and  $O_h$  were generated by positioning oxygen on the hollow site of the face centered cubic (FCC) Ag (001). The difference between  $O_i$  and  $O_h$  is that  $O_h$  is a reconstructed substitutional oxygen defect which has a neighboring vacancy of the Ag site. The constituent atoms in MgO/Ag systems were fully relaxed until the maximum Hellmann–Feynman forces were in the range of 0.1 eV/Å. A Brillouin-zone integration scheme was used on a grid of  $(2 \times 2 \times 1)$  Monkhorst–Pack points for ionic relaxation [23]. Then,  $(6 \times 6 \times 1)$  k-point sampling scheme was employed for an accurate electronic structure. From the electronic structure, the electrostatic potential is the sum of the Hartree potential and the ionic potential. The xy plane averaged electrostatic potential was obtained using

$$\bar{V}(z) = \iint_A V(x, y, z) dx dy. \quad (1)$$

The work function of the system is defined as the electrostatic energy of vacuum level with respect to the Fermi energy.

$$\phi = V_{vac} - E_F \quad (2)$$

### 3. Results and discussion

#### 3.1. Structural features

The  $O_i$ ,  $O_{Ag}$ , and  $O_h$  have different interfacial distances and neighboring ions as shown in Fig. 1. The  $O_i$  is positioned on the hollow site of Ag (001) and the neighboring ion in the film is Mg cation. This position of oxygen induces the increase of interfacial distance by 0.06 Å. The interface distance is defined as the averaged distance between Ag and MgO atoms at the interface. The  $O_{Ag}$  is on the substitutional site of vacant site of interfacial Ag which has neighboring oxygen ion in the MgO film and is surrounded by Ag atoms in the interface and subinterface layers. Because of the repulsive force from neighboring oxygen ion, the  $O_{Ag}$  moves down to the subinterface layer. If the  $O_{Ag}$  overcome the repulsive force from oxygen ions in the film, a reconstructed structure,  $O_h$ , is generated. After the reconstruction, the oxygen impurity migrates to the hollow site of FCC Ag (001) neighboring Mg ion in the film. However, in the case of  $O_h$ , the interfacial distance did not increase because

the oxygen impurity can partially occupy the neighboring vacant site. All types of oxygen impurities at the MgO/Ag interface were positioned on the Ag side layer interface but they show different structural features.

#### 3.2. Density of states

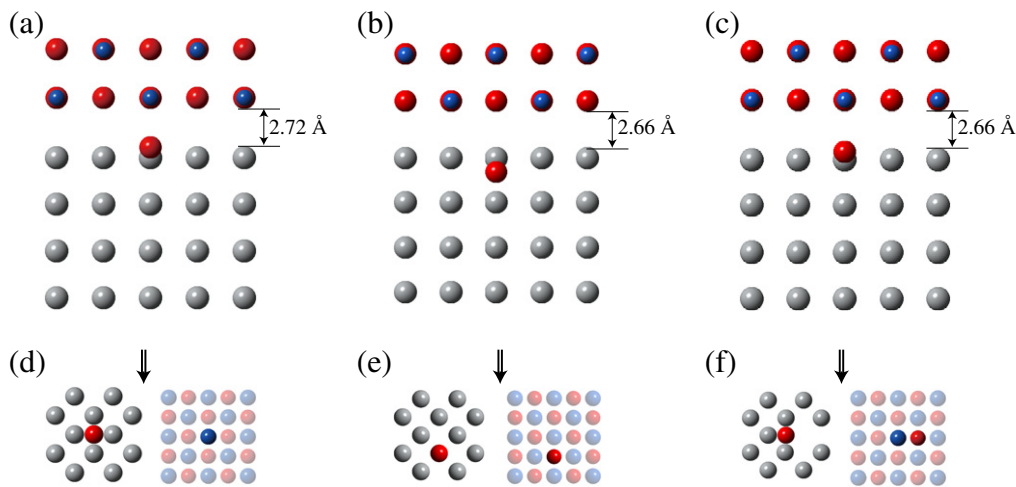
To understand the additional bonding between oxygen impurities and their neighboring ions, their density of state (DOS) is analyzed as shown in Fig. 2. For the case of defect-free MgO/Ag, oxygen atoms in the film have ionic bonding with Mg and weak covalent bonding with Ag [24]. When the oxygen impurity is generated, the states of oxygen atom in the film showed a similar DOS with that of defect-free MgO. On the other hand, the DOS of the interfacial oxygen impurities showed a significant change due to their neighboring ions [25]. The states of  $O_i$  and  $O_h$  were hybridized with the states of the interfacial Ag atoms and the  $O_{Ag}$  was hybridized with that of subinterface Ag atoms. The reason why  $O_{Ag}$  interacts with the subinterface Ag is that the subinterface Ag atom is the nearest neighbor to the sinking of the  $O_{Ag}$  from the interfacial Ag layer. Thus, all types of oxygen impurities are associated with the Ag substrate. On the other hand, the interaction with the film is not for all types of oxygen impurity. The states of  $O_i$  show hybridization with the MgO film around the  $-5$  eV. However, for the case of  $O_{Ag}$  and  $O_h$ , there was no significant hybridization between the oxygen impurities and MgO film as shown in Fig. 2(b) and (c). The DOS analysis indicates that all types of interfacial oxygen impurities were associated with Ag substrate but only  $O_i$  directly interacts with the MgO film.

#### 3.3. Work function

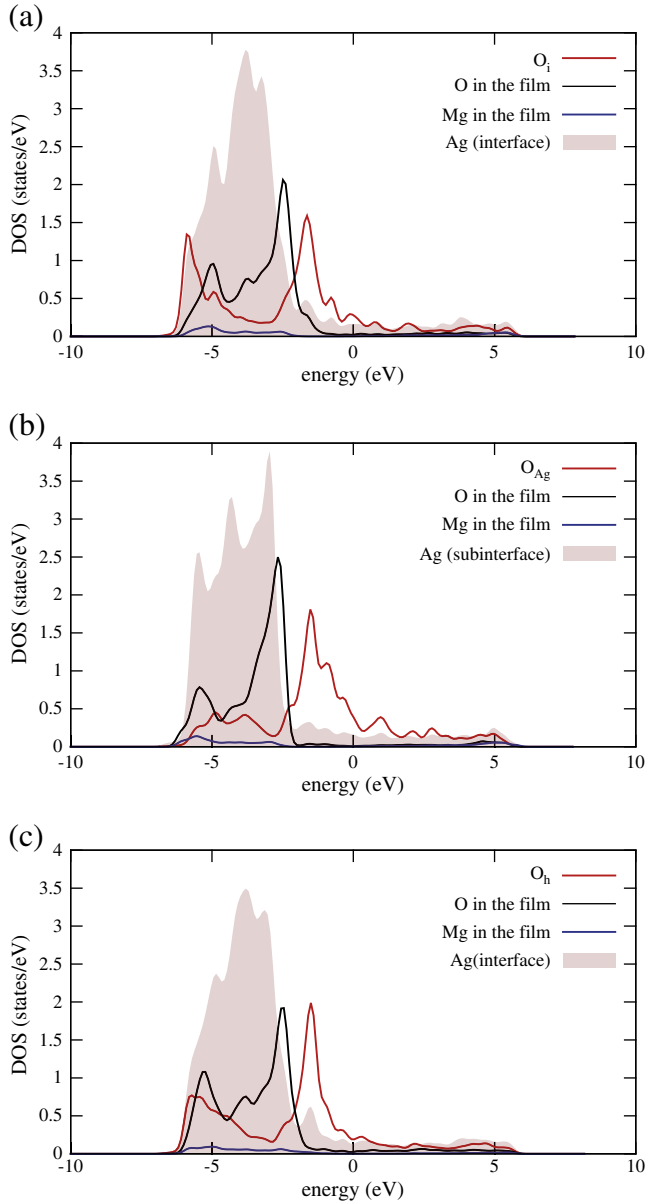
When oxygen impurities are generated at the MgO/Ag interface, the electronic structure of the interface is modified and the work function of the interface is also changed. The altered work function is summarized in Table 1. When the work function of the clean Ag substrate is the reference, the changed work function can be expressed as below.

$$\Delta\phi = \phi - \phi_{Ag}. \quad (3)$$

According to our calculation, the work function of Ag was 4.18 eV (experimental value is 4.22 eV [27]). The work function decreased by 1.19 eV in defect-free MgO/Ag structure. In the interfacial oxygen impurity-containing structure, the work function is further changed compared with the defect-free structure. The  $O_i$  and  $O_h$  induced an



**Fig. 1.** Side cut view and top view of (a)  $O_i$ , (b)  $O_{Ag}$ , and (c)  $O_h$ -containing MgO/Ag structure. Note that the interfacial distance of  $O_i$  is longer than others. Top view of the substrate side interface layer (left) and film side interface layer (right) of (d)  $O_i$ , (e)  $O_{Ag}$ , and (f)  $O_h$ -containing MgO/Ag structure. The arrows in (d, e, f) are the perspective of the side cut view of (a, b, c), respectively. The highlighted atoms of the film side interface layer are neighboring ions with oxygen impurities or vacant site. The gray, red, and blue spheres represent the Ag, O, and Mg atoms, respectively.



**Fig. 2.** Density of states of (a)  $O_i$ , (b)  $O_{Ag}$ , (c)  $O_h$ , and their neighboring Ag atom in substrates and neighboring O and Mg ions in the films. All of the oxygen impurities are associated with the Ag substrate but only  $O_i$  directly has a directly hybridized state with the film.

additional increase of the interface work function and  $O_{Ag}$  induces a slight decrease of the interface work function. The relative planar-averaged electrostatic potential in Fig. 3 obviously shows the work function change. The relative potential in a vacuum on the left side represents the work function of the substrate. The potential on the

**Table 1**  
Structural and electronic properties of the defect-free,  $O_i$ ,  $O_{Ag}$ , and  $O_h$ -containing MgO/Ag (100).

Structure	$d_{\text{interface}}$ (Å)	$q(O_{\text{impurity}})$ (e)	$\phi$ (eV)	$\Delta\phi$ (eV)
MgO/Ag	2.66	–	2.86	–1.32
MgO/ $O_i$ -Ag	2.72	7.14	3.27	–0.91
MgO/ $O_{Ag}$ -Ag	2.66	6.9	2.81	–1.37
MgO/ $O_h$ -Ag	2.66	7.08	3.14	–1.04

Note: The  $d_{\text{interface}}$  is the distance between the interface. The  $q(O_{\text{impurity}})$  is the calculated Bader charge of the oxygen defect. The  $\phi$  is the calculated work function and  $\Delta\phi$  is the work function change with respect to the Ag (001) surface.

right side is associated with the modified work function induced by the interaction between the oxygen impurity and the MgO film.

### 3.4. Interface effect

The origin of  $\Delta\phi$  is the potential level pinning induced by a surface dipole which is generated by the interface defect and film. According to the Helmholtz equation, the relation between the work function and the dipole can be expressed as [26]:

$$\Delta\phi = \frac{e\mu \cos\theta}{\epsilon_0 A} = -180.95 \frac{\mu_z}{A} \quad (4)$$

where  $\epsilon_0$  is the permittivity of the vacuum level,  $A$  is surface area, and  $\mu$  is surface dipole moment directed along the surface normal (eÅ). Since the work function is determined by the relative vacuum level potential, the  $\mu_z$  is the only component that affects the work function. The  $\mu_z$  can be expressed as the sum of the dipole moment of the substrate ( $\mu_s$ ) that is the dipole of the oxygen impurity-containing the Ag substrate in the absence of the MgO film and the dipole moment created through the charge-redistribution that accompanies film deposition ( $\mu_d$ ), according to

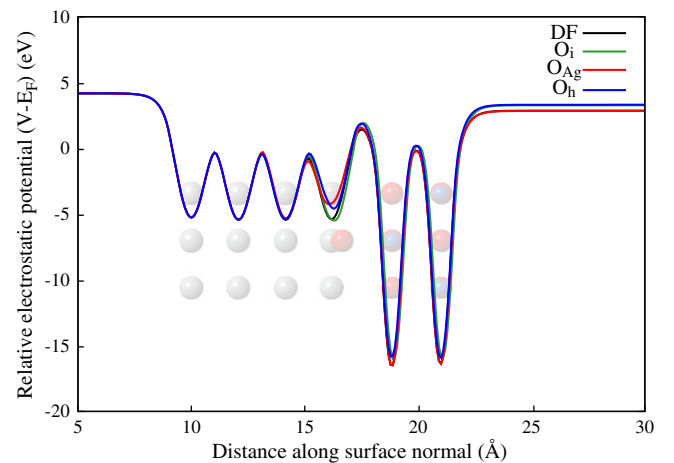
$$\Delta\phi = -180.95 \frac{\mu_s + \mu_d}{A} \quad (5)$$

By using the Helmholtz principle, the  $\mu_s$  can be computed from the asymptotic vacuum level of each substrate as

$$\Delta V_{\text{substrate}} = V_{\text{right}} - V_{\text{left}} = \frac{e\mu_s}{\epsilon_0 A} \quad (6)$$

where  $V_{\text{right}}$  and  $V_{\text{left}}$  are the planar-averaged electrostatic potentials of the vacuum level on the impurity-containing surface side and clean substrate side. Table 2 summarizes the calculated  $\mu_s$ ,  $\mu_d$ , and  $\mu_z$  values.

From the calculated results, it can be seen that the surface dipole moment can be generated where the dipole moment of the substrate is zero. In the defect-free structure, such a dipole moment is generated only by the contribution of  $\mu_d$ . The origin of the  $\mu_d$  can be understood with the two contributions. One is charge redistribution due to the formation of interface bonding between the film and substrate. The other is the “compression effect” that pushes back the electrons which are spilled out from the metal surface where the dielectric layer is deposited. The compression effect is sensitive to the interfacial distance and generates larger surface dipole moment than interface bonding in the MgO/Ag system [10]. In the defect-free MgO/Ag structure, the work function change is induced by  $\mu_d$ .



**Fig. 3.** Relative planar-averaged electrostatic potential for interface defective MgO/Ag systems as a function of position in the direction perpendicular to the surface.

**Table 2**

Vacuum level potential difference and related dipole moment of the defect-free,  $O_i$ ,  $O_{Ag}$ , and  $O_h$ -containing MgO/Ag (100) system.

Structure	$\Delta V_{\text{substrate}}$ (eV)	$\mu_s/A$ (me/Å)	$\mu_d/A$ (me/Å)	$\mu_z/A$ (me/Å)	$\Delta\phi$ (eV)
MgO/Ag	0	0	6.58	6.58	−1.32
MgO/ $O_i$ -Ag	0.202	−1.12	5.43	4.31	−0.91
MgO/ $O_{Ag}$ -Ag	0	0	6.47	6.47	−1.37
MgO/ $O_h$ -Ag	0.294	−1.62	6.65	5.03	−1.04

Note:  $\Delta V_{\text{substrate}}$  is the difference in the asymptotic vacuum level potential of the substrate. The  $\mu_s/A$ ,  $\mu_d/A$ , and  $\mu_z/A$  are calculated substrate induced dipole, deposition induced dipole, and surface dipole, respectively.  $\Delta\phi$  is the work function change with respect to the Ag (001) surface.

The induced  $\mu_d$  in the defect-free MgO/Ag still remains where  $O_{Ag}$  and  $O_h$  are generated. For the case of  $O_{Ag}$ -contained MgO/Ag,  $\mu_s$  is completely screened because of the sinking of  $O_{Ag}$  and the surface reconstruction. Relative to the defect-free MgO/Ag, the  $\mu_d$  of  $O_{Ag}$ -contained MgO/Ag slightly decreased and  $\Delta\phi$  decreased by 0.05 eV. On the other hand,  $O_h$  and its neighboring vacancy induce  $\mu_s$  of −1.62 me/Å. The  $\mu_s$  induced by  $O_h$  still remained after the deposition and contributed to the work function change. The  $\mu_d$  was increased by 0.07 me/Å relative to the defect-free MgO/Ag. For the case of  $O_{Ag}$  and  $O_h$ , the  $\mu_d$  remained similar to that of the defect-free structure.

On the other hand,  $O_i$  not only created  $\mu_s$  but also induced changes of  $\mu_d$ , relative to the defect-free structure. It can be inferred that the origin of the  $\mu_d$  change is its increased interfacial distance and the interface bonding between  $O_i$  and MgO. Since the compression effect is sensitive to the interfacial distance, surface dipoles were induced by electron redistribution changes. Also, as shown in the DOS analysis, the formed interface bonding between  $O_i$  and MgO generated a surface dipole moment. Thus,  $O_i$ -containing MgO/Ag shows different  $\mu_d$  with that of the defect-free structure.

#### 4. Conclusion

In conclusion, the electrostatic effects of the three types of oxygen defects at the MgO/Ag (001) interface were investigated. The origin of the work function change was analyzed with a dipole contribution decoupled into the substrate and interface electron terms. Each term of the dipole moment has been associated with their structural features and interface bonding properties. The results of this study indicate that the type of oxygen impurities induces a significant effect on the electronic structure and work function of the interface.

The change of the work function indicates that the interface work function could be tunable by controlling the interfacial oxygen impurities. This work provides an important clue to designing ultra-thin oxide films on metal by controlling oxygen defects.

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