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A first-principles study of the structure, electronic properties, and oxygen binding of FeO/Pt(111) and FeO₂/Pt(111)

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ABSTRACT

The ultrathin oxide films of bilayer FeO and trilayer FeO₂ superstructures on Pt(111) with periodicity of $(\sqrt{84} \times \sqrt{84})R10.9^\circ$ are studied in detail by density functional theory, and the corresponding structural properties, electronic properties, and oxygen activities in different domains (FCC, HCP, and TOP) are calculated. It is found that for both superstructures, the in-plane lattice constants slightly increase in the order FCC < HCP < TOP. The calculated order of the surface corrugation (O-Fe rumpling) is FCC > HCP > TOP for FeO/Pt(111), and FCC > TOP > HCP for FeO₂/Pt(111). The surface electrostatic potentials and the binding energies of the surface oxygen atoms are found to follow the same order as the surface corrugation. There is net charge transfer from the supported FeO film to the Pt substrate for FeO/Pt(111), and the calculated oxidation state of iron is +2.36. In contrast, for FeO₂/Pt(111), there is charge transfer from the Pt substrate to the supported FeO₂ film, and the calculated oxidation state of iron is +2.95 (ferric state). Compared with Pt(111), the change of the surface work function of FeO/Pt(111) is negligible, while it is 1.24 eV for FeO₂/Pt(111). The role of the surface dipole of the supported oxide film and the charge transfer of the ultrathin oxide film are discussed.

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1. Introduction

Ultrathin oxide films grown on metal substrates have attracted considerable attention in past decades because of their unique structural and electronic properties, and their potential applications in many areas [1–10]. Depending on the preparation conditions, films of several atomic layers can form complex superstructures that are completely different from the bulk materials [11–19]. These structures have significantly different surface geometries, stoichiometries and electronic properties. As a type of reverse model system and promising new material, metal oxide thin films, e.g., ZnO, MgO, TiO₂, and NiO, on metal substrates have been extensively studied in surface science

research as electronic devices and as heterogeneous catalysts.

Among ultrathin films, iron oxide films grown on Pt have attracted special interest, especially in their surface structures, magnetic properties, and model catalytic reactions [11,12,17,18,20–30]. Well-defined bilayers of FeO on Pt(111) (FeO/Pt) have been prepared in ultra-high vacuum (UHV) chambers and carefully characterized by scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED). At one monolayer load of Fe, different concomitant FeO/Pt(111) structures, such as $(\sqrt{84} \times \sqrt{84})R10.9^\circ$ and $(\sqrt{91} \times \sqrt{91})R5.2^\circ$, have been observed [11,12]. The superstructures lead to the formation of large surface Moiré patterns in STM images because of the lattice mismatch between the oxide

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film and substrate. The different domains in the Moiré pattern can have significantly different structural and electronic properties because of the variation of the registration between the grown thin film and metal substrate. Moreover, these domains affect the corresponding activity of exposed surface oxygen atoms and chemical reactions on the surfaces. These structures are sensitive to the preparation conditions, especially the temperature and the oxygen partial pressure [18]. For example, bilayer FeO is further oxidized at elevated oxygen potential, and there is evidence for trilayer O-Fe-O film formation (FeO₂/Pt(111)) [22,31].

Despite extensive experimental studies, the computational study of these superstructures is prohibitive because of the large supercell of the Moiré pattern [20,21,32,33]. This prevents the microscopic understanding of the function of these ultrathin oxide films. It is still unclear how the local registry of the different domains affects the surface corrugation, electronic properties (oxidation state of iron and the work function change), and oxygen activity. In particular, how the properties and oxygen activity change when the polar FeO/Pt(111) surface is oxidized to nonpolar FeO₂/Pt(111). To address these questions, we report a detailed density functional theory study of FeO/Pt(111) and FeO₂/Pt(111) based on the realistic ($\sqrt{84}\times\sqrt{84}$)R10.9° superstructure found by experiment. The structural properties, electronic properties, and oxygen activity of FeO/Pt(111) and FeO₂/Pt(111) are investigated and analyzed in detail.

2. Computational details

Spin-polarized density functional theory calculations were performed using the Vienna ab-initio simulation package (VASP) [34,35] with all-electron projected augmented wave (PAW) potentials [36,37] and the Perdew-Wang 91 (PW91) [38] exchange-correlation functional. The wave function was expanded by plane wave with kinetic cutoff of 400 eV and density cutoff of 800 eV. During iterative diagonalization of the Kohn-Sham Hamiltonian, Gaussian smearing of the population of partial occupancies with a width of 0.1 eV was used to improve the convergence, and the total energy was extrapolated to absolute zero. The FeO/Pt(111) surface was simulated by the ($\sqrt{84}\times\sqrt{84}$)R10.9°-FeO/Pt(111) superstructure from experiment [11], with a FeO film consisting of 67 oxygen and iron atoms and an oxygen overlayer of hexagonal symmetry supported on Pt(111)-($\sqrt{84}\times\sqrt{84}$) with three layer thickness. The FeO₂/Pt(111) surface was constructed by adding an extra 67 O atoms between the Fe and Pt atoms in such a way to form O-Fe-O fcc stacking with the same hexagonal symmetry and ($\sqrt{84}\times\sqrt{84}$)R10.9°-FeO₂/Pt(111) superstructure. Only the Γ point was considered for surface Brillouin zone sampling because of the large superstructure for both surfaces. The correction of the on-site Coulomb repulsion was made for iron using the DFT+U method [39] with the well tested values of $U = 4$ and $J = 1$ from the literature [20,32,33,40]. The initial magnetic structures of FeO/Pt(111) and FeO₂/Pt(111) were set to be antiferromagnetic. During the structure relaxation, all of the atoms were allowed to fully relax until the residual force was

less than 0.3 eV/nm, except for the bottom two Pt layers, which were fixed at the bulk truncated positions. Dipole corrections were applied to minimize the artificial interaction through the vacuum due to the periodicity. The work function was calculated by the difference between the vacuum energy level and the Fermi level. The oxidation states of the O, Fe, and Pt atoms of interest and electron transfer were analyzed based on Bader charges [41,42]. To obtain the formal oxidation states, the calculated Bader charges were normalized based on the following bulk reference: Fe in body-centered-cubic (bcc) as Fe⁰, Fe in type-II antiferromagnetic (AFM-II) FeO as Fe²⁺ (ferrous state), Fe in α -Fe₂O₃ as Fe³⁺ (ferric state).

3. Results and discussion

3.1. Structure properties

The FeO/Pt(111) superstructure has been extensively studied both experimentally and theoretically. Because of the lattice mismatch between FeO(111) (0.310 nm) and Pt(111) (0.277 nm), a Moiré superstructure of ($\sqrt{84}\times\sqrt{84}$)R10.9°-FeO/Pt(111) with periodicity of 2.54 nm forms (Fig. 1(a)). There are three domains inside the superstructure, denoted as the FCC, HCP, and TOP domains based on the adsorption site of the central interfacial Fe atoms on the Pt(111) surface. The FeO₂/Pt(111) superstructure has not yet been well characterized. As an approximation, a trilayer O-Fe-O film on Pt(111) was constructed based on ($\sqrt{84}\times\sqrt{84}$)R10.9°-FeO/Pt(111), in which an additional O layer was intercalated between the Fe layer and Pt layer to form O-Fe-O fcc stacking with the same hexagonal symmetry. The same FCC, HCP, and TOP domains are inherited from the FeO₂/Pt(111) structure and used to distinguish the iron locations on the Pt substrate. All of the Fe cations are 6-fold coordinated by O anions, and all of the O atoms have three Fe neighbors.

The average of the calculated in-plane lattice constants (\bar{a}) of FeO and FeO₂ per cell are the same (0.310 nm). The O-Fe

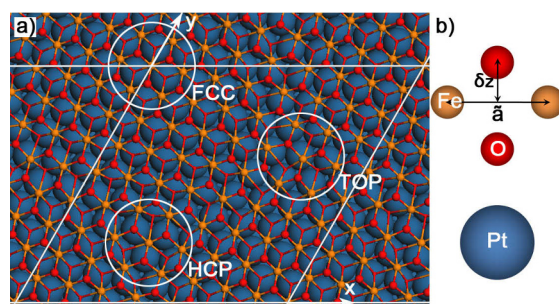


Fig. 1. (a) Schematic structure (top) of FeO/Pt(111) and FeO₂/Pt(111) superstructures with periodicity of ($\sqrt{84}\times\sqrt{84}$)R10.9° indicated by a white parallelogram. The blue, red (large), red (small), and yellow spheres (color online) represent Pt, O (surface), O (interface), and Fe atoms, respectively. The FeO/Pt(111) superstructure can be obtained by removing the small red spheres (interface oxygen atoms). The FCC, HCP, and TOP domains defined by the adsorption site of the central Fe atoms on Pt(111) are indicated by the white circles including the central seven iron cations. (b) Defined structural parameters of the in-plane lattice constant \bar{a} and the surface O-Fe rumpling δ_z (side view) are indicated.

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