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Surface Science 600 (2006) 2154–2162

SURFACE SCIENCE

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First-principles studies on initial growth of Ni on MgO(0 0 1) surface

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Received 26 August 2005; accepted for publication 8 March 2006
Available online 29 March 2006

Abstract

To elucidate the initial growth of metal on oxide surface, we studied adsorption of small nickel clusters, Ni_n ($n = 1$–5), on MgO(0 0 1) surface using first-principles method based on density-functional theory. It was found that the preferential adsorption site for an isolated Ni atom is directly above the surface oxygen atom. A strong covalent bond with partial ionic character is formed between the Ni adatom and the surface oxygen atom. Various structures were considered for the Ni_n isomers and 3D structures were found to be energetically more stable than 2D structures for clusters of more than two atoms. For the 2D clusters, metal–metal bonds prevail over metal-substrate bonds with increasing Ni coverage. The calculated work function and ionization energy were found to vary with Ni coverage which is attributed to the change of the surface dipole moment upon metal adsorption, while the evolution of Schottky barrier height at the initial growth stage is dominated by the adatom-induced gap states.

Keywords: Nickel; Magnesium oxides; Density-functional calculations; Adsorption; Clusters

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1. Introduction

Metal/oxide interfaces play important roles in various technological applications [1–5]. However, both interface structures and chemical bonding at metal/oxide interfaces are quite complicated. Despite intensive experimental and theoretical studies on metal–ceramic interfaces, many fundamental issues remain unresolved. It is known that MgO(0 0 1) surface, with a simple atomic structure and strong ionic bonding characteristics, has good thermal and chemical stability, which make MgO(0 0 1) an ideal system for studying metal/oxide interfaces. However, with only a few exceptions, such as Ag, there is a noticeable lattice mismatch between metals and MgO. Therefore, growing crystalline metal on MgO(0 0 1) is a challenge and understanding the growth process is crucial for the ultimate applications of metal/oxide heterostructures. In the case of nickel/MgO(0 0 1) interfaces, Barbier et al. [6] observed that in the early stages of growth, up to one monolayer of Ni was strained on the top of surface oxygen sites, which indicates that surface oxygen is the preferred adsorption site. Theoretically, Pacchioni et al. [7] studied the adsorption of Ni atoms on both ideal and defected MgO(0 0 1) surfaces by means of cluster models. They found that metal clusters are weakly oxidized by the surface oxygen (with Ni adatom slightly positively charged), and the adatom–adatom bonds are stronger than the metal–substrate bonds. In another ab initio total energy study of pseudomorphic Ni/MgO(0 0 1) interfaces, Goniakowski and Noguera [8] found that 0.08 electrons were transferred from the oxide to a metal atom, and the interface formation is mainly attributed to the polarization effects. The above findings reflect the complex bonding between nickel adatoms and the oxide substrate. Further studies are needed in order to fully understand the interaction between metal clusters and oxide surfaces. The present work was also motivated by the fact that questions related to the initial growth of metal on oxide surface, such as how the adsorbed metal atoms

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doi:10.1016/j.susc.2006.03.005

aggregate, how the chemical states of adatoms vary with increasing coverage, and how the Schottky barrier height evolves with the metal deposition, etc. have seldom been addressed, compared to adsorption of isolated metal adatoms [9–11], strained monolayers, or thin films [5,12,13].

In this work, we investigate the adsorption of small Ni_n ($n = 1$–5) clusters on MgO(001) surface. The system was modeled by a periodic slab. Total energy calculations were carried out to determine the stable geometries of the adsorbed clusters. The bond nature between Ni adatoms and the oxide substrate was investigated. The chemical state (ionic or neutral) of adatom was discussed through the metal-deposition induced variations in work function, ionization energy and Schottky barrier height (SBH). This study would shed light on the physics underlying the initial growth of Ni on MgO(001) surface.

2. Method

Total energy and force calculations were carried out within the framework of density-functional theory (DFT). We used the Vienna ab initio simulation package (VASP) [14,15] with the frozen-core projector-augmented-wave (PAW) method [16]. Spin polarization effects were included. For the alkali element Mg, the semi-core p electrons were treated as valence electrons. For the transitional metal Ni, 10 ($4s^1$ $3d^9$) electrons were treated as valence electrons. A plane-wave cut-off corresponding to a kinetic energy of 350 eV was used. For exchange and correlation, the functional proposed by Perdew and Zunger was used, with the Perdew–Becke–Ernzerhof generalized gradient approximations (GGA) [17]. A k point mesh of $3 \times 3 \times 1$ was used to sample the supercell which consists of (2×2) surface MgO units (8.506 Å × 8.506 Å). Electronic energy was minimized using a fairly robust algorithm which is a mixture of the blocked Davidson and a variant of a residual minimization and direct iterative subspace rotation method (RMM-DIIS) as implemented in VASP. Ionic relaxation was performed using the conjugate gradient (CG) algorithm. Density of states (DOS) were calculated with finer k point meshes using the tetrahedron method with Blöchl corrections as implemented in VASP.

3. Structures and energetics

The calculated lattice constants of MgO and fcc-Ni are 4.253 Å and 3.523 Å, respectively, which are within 1.0% of the experimental values of 4.211 Å and 3.524 Å. The clean MgO(001) surface was considered first. It was modeled with seven atomic layers (two atoms/layer) and a vacuum region of 12 Å thick. An inward surface relaxation of 0.09% and an outward displacement of the surface oxygens with respect to the magnesium atoms (rumpling $\varepsilon = 1.11\%$) was found after relaxation, which are in good agreement with results of other DFT calculations [18].

The MgO(001) substrate for the adsorption of Ni atoms was represented by a repeated slab geometry. For structural optimization, a thin slab was used to reduce computing time. Each slab contains three MgO layers (eight O atoms and eight Mg atoms/layer, the size of the surface unit cell is 8.506 Å × 8.506 Å) with the nickel clusters adsorbed on one side. The uppermost MgO layer and the nickel atoms were allowed to relax to minimize the total energy. In subsequent detailed study of the electronic properties (Sec. 4), seven MgO layers (eight atoms/layer) were used with two identical surfaces adsorbed with metal clusters. At least 12 Å vacuum was included in the supercell.

To describe quantitatively the energetics of the adsorbed Ni clusters on the MgO surface, we introduce the following three energy terms:

(1) The cluster adsorption energy,

$$E_\mathrm{A} = -[E_\mathrm{ads} - E_\mathrm{slab} - E_{\mathrm{Ni}\text{-}n}]/n, \tag{1}$$

where E_ads is the total energy of the adsorbate–substrate system, E_slab is that of MgO slab, and $E_{\mathrm{Ni}\text{-}n}$ is that of the floating cluster consisting of n Ni atoms. The cluster adsorption energy describes the strength of the adsorbate–substrate interaction.

(2) The binding energy,

$$E_\mathrm{B} = -[E_\mathrm{ads} - E_\mathrm{slab} - nE_\mathrm{Ni}]/n, \tag{2}$$

where E_Ni is the total energy of an isolated Ni atom. E_B reflects the relative stability of the adsorbate–substrate system.

(3) The intracluster binding energy E_IB,

$$E_\mathrm{IB} = E_\mathrm{B} - E_\mathrm{A}, \tag{3}$$

which describes the strength of adsorbate-adsorbate interaction. For convenience of comparison, all these energy terms are normalized by the number of adatoms, i.e. given per adatom.

3.1. Adsorption of isolated Ni atom

To determine the likely adsorption site of Ni atom on the MgO(001) surface, we mapped out the potential energy surface (PES) of the Ni atom on the MgO(001) surface. The Ni atom was placed at equally spaced positions above the MgO(001) surface, and for each non-symmetry-equivalent position, the uppermost MgO layer and the z coordinate of Ni atom were fully optimized. Fig. 1a shows the variation of the adsorption height with respect to the average position of the surface ions. Fig. 1b shows the potential energy surface for an isolated Ni atom. It is clear that the preferred adsorption site is directly above the surface oxygen atom, with an adsorption energy of 1.453 eV and a Ni–O bond length of 1.800 Å. The magnesium-atop site is an energy maximum, while the hollow site is a saddle point and is the transition state for diffusion. The diffusion barrier for an isolated Ni adatom is estimated to be 0.993 eV. Following Ref. [19], we estimated the temperature at which the adatom diffusion becomes active (i.e.,