Oscillatory energetics of flat Ag films on MgO(001)

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The energetics and electronic structures of flat Ag films on the MgO(001) substrate are studied by first-principles density-functional calculations. An oscillatory variation of the film energetics showing the existence of multiple magic thicknesses for smooth growth is found. This oscillatory behavior correlates well with the quantum-well states, which themselves vary with the film thickness. The results demonstrate the importance of the confined motion of the conduction electrons in stabilizing epitaxial metal films, as emphasized in a recent ''electronic growth'' model.

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The realization of quantum-well (QW) states in metal thin films is of considerable interest due to its potential technological applications in microelectronic devices.[1] In the past decade there have been a wealth of experimental observations of QW states in noble metal films on magnetic substrates,[2–4] and such QW states have been shown to be responsible for the oscillatory exchange coupling observed in the magnetic multilayers. Recent photoemission experiments for the Cu/Ni (Ref. 5) and Ag/Fe (Ref. 6) systems have further improved our understanding of QW states with the measurement of their properties such as the spatial variation, band structure, electron reflectivity, and phase shift.

It was recently proposed that QW states can play an important role in stabilizing epitaxial growth of metal films on semiconductor substrates.[7,8] This so-called ''electronic growth'' model showed that a metal film of any given thickness can be stabilized by quantum confinement, whereas it can also be destabilized by charge spilling from the metal to the substrate. The competition between these two effects leads to the existence of a critical thickness for smooth growth, as observed in a recent study of the Ag growth on GaAs(110).[9] Here, atomically flat Ag films with the critical thickness of 15 Å can be formed by controlled manipulation of the growth processes using a *two-step process* (low-temperature deposition followed by room-temperature annealing). More recently, in the growth of Ag on Si(111) the two-step process has led to the formation of isolated islands with a strongly preferred height and flat tops.[10] The existence of the critical thickness in Ag films was quite surprising, because a rough surface had been easily formed from typical growth conditions.[11]

To observe QW states in epitaxial metal films on any substrate, the following two conditions have to be satisfied: (i) the growth of flat films and (ii) the confinement of the conduction electrons within the films. To meet condition (ii), a metal film on a ceramic substrate is naturally an attractive system, because there is a larger band gap in the substrate to ensure reflection of propagating film states and thus their confinement within the film. Here, we present our first-principles calculation results for the energetics and electronic structures of flat Ag films on MgO(001), where the films are assumed to be pseudomorphic with the substrate. As the film thickness increases, the binding energy per layer is found to oscillate, thereby defining the existence of magic thicknesses for smooth growth. This oscillatory energetics of Ag films can be attributed to the evolution of QW states with the films.

Our first-principles density-functional calculations are performed using the plane-wave-basis pseudopotential method within the generalized gradient approximation (GGA).[12,13] We use the exchange-correlation functional of Perdew, Burke, and Ernzerhof[13] for the GGA calculations. The Ag and Mg atoms are described by the norm-conserving pseudopotentials of Troullier and Martins[14] and the O atom is described by the ultrasoft pseudopotential of Vanderbilt.[15] The MgO(001) substrate is modeled by means of a periodic slab geometry consisting of three atomic layers and the Ag atoms are adsorbed on both sides of the slab, keeping the vacuum region to be the thickness of five atomic layers.[16] The electronic wave functions are expanded in a plane-wave basis set with a cutoff energy of 40 Ry, and the electron density is obtained from the wave functions calculated at 10 **k** points in the irreducible surface Brillouin zone. The position of all atoms, except the position that the center MgO layer atoms hold at their theoretical bulk positions ($a_0 = 4.23$ Å), are allowed to relax along the calculated Hellmann-Feynman forces until all the residual force components are less than 0.04 eV/Å.

First, we determine the geometric structure of Ag monolayer on MgO(001). Here, three possible adsorption sites for Ag atoms (i.e., the site above the O atom, the site above the Mg atom, and the hollow site) are considered, and their binding energies are calculated to be 0.15, 0.02, and 0.06 eV/surface atom, respectively. Thus, the site above the O atom

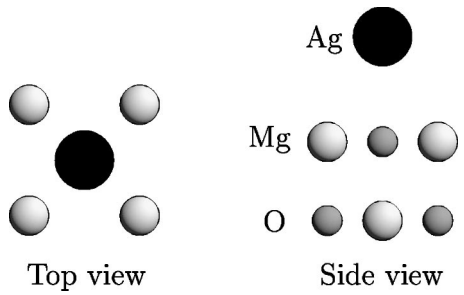

FIG. 1. Top and side views of the equilibrium structure of the Ag monolayer on MgO(001).

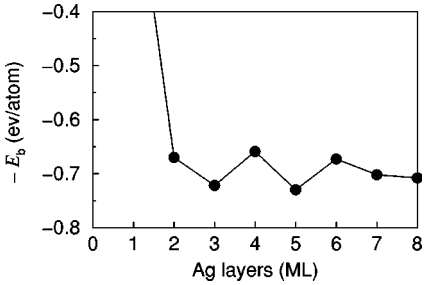

FIG. 2. Binding energy of Ag films on MgO(001) as a function of the film thickness.

(Fig. 1) is the most favorable, consistent with experiments.[17,18] Our results for the binding energy (E_{bind}) and the distance between the Ag and O atoms ($d_{\text{Ag-O}}$) at the site above the O atom are compared with those of previous calculations[19–21] and experiments[17,18] in Table I. The present values of E_{bind} and $d_{\text{Ag-O}}$ agree well with those of a previous GGA calculation.[21] Compared to the local-density-approximation (LDA) results,[19,21] the GGA tends to increase $d_{\text{Ag-O}}$, but to decrease E_{bind} (see Table I). There is a somewhat large deviation for $d_{\text{Ag-O}}$ between theories[19–21] and experiments.[17,18] This is possibly due to the theoretical inaccuracy in describing the weak interaction between the Ag film and the MgO substrate, or the experimental difficulties in generating a flat Ag film.

The relative stability of flat Ag films on MgO(001) is examined by calculating the binding energy with increasing the film thickness. The binding energy per Ag atom is given by

$$E_{\text{bind}} = -[E(N) - E(N-1) - lE_{\text{mono}}]/l, \qquad (1)$$

where $E(N-1)$ and $E(N)$ are the total energies of slabs with the Ag thickness of $(N-1)$ and N monolayers (ML), respectively, and E_{mono} is the total energy of a free-standing Ag monolayer. Here, l is equal to 2, because we consider the Ag overlayers on both sides of the slab. The binding energy with respect to the Ag thickness is plotted in Fig. 2, showing strongly oscillatory size effects. In particular, the binding energies at $N=3$ and 5 ML are larger than those at 2 and 4 ML, indicating that a Ag film of $N=3$ and 5 ML is locally stable. We note that the binding energy at $N \geqslant 2$ ML is significantly larger than that of 1 ML, because the interaction between Ag layers is stronger than that between the Ag monolayer and the MgO substrate. In contrast, for the energetics of flat Ag films on MgO(001), the atomistic simulation[21] using the discrete classical model of Finnis[22] showed that the stability of flat Ag films increases to a maximum at the thickness of ~ 4 ML and then decreases as more layers are added. Such atomistic simulations based on a classical interaction model[21] failed to predict the oscillatory behavior in the energetics of flat Ag films on MgO(001).

TABLE I. Calculated binding energy (E_{bind}) and interlayer spacing ($d_{\text{Ag-O}}$) of a Ag monolayer on MgO(001), in comparison with experimental and previous theoretical results. FLAPW denotes the full-potential linear-augmented-plane-wave method and HF CC represents the Hartree-Fock method with the electron correlation corrections.

	E_{bind} (eV)	$d_{\text{Ag-O}}$ (Å)
FLAPW LDA[a]	0.30	2.69
HF CC[b]	0.20	2.64
Pseudopotential LDA[c]	0.33	2.61
Pseudopotential GGA[c]	0.16	2.75
This work (GGA)	0.15	2.77
GIXD experiment I[d]		2.43 ± 0.02
GIXD experiment II[e]		2.52 ± 0.1

[a]Reference 19.
[b]Reference 20.
[c]Reference 21.
[d]Reference 17.
[e]Reference 18.

In a grazing incidence x-ray diffraction (GIXD) experiment,[17] it was found that the growth of Ag on MgO(001) proceeds in four steps: (i) Two-dimensional (2D) pseudomorphic growth occurs at the very beginning ($\theta \leqslant 0.4$ ML) in the form of 1 ML high platelets. (ii) It is followed by a quasi-2D growth mode up to $\theta \simeq 1$ ML. Here, the Ag film is still in the form of wide platelets with a height of 2–3 ML. (iii) Between $\theta \simeq 1$ ML and $\theta \simeq 4$ ML, the growth proceeds via the formation of 3D pseudomorphic islands, with no sign of plastic relaxation. (iv) Above $\theta \simeq 4$ ML, the strain relaxation is clearly plastic, by formation of misfit dislocations. Recently, a similar GIXD experiment[18] found that below 4–6 ML the lattice parameters of the Ag islands are pseudomorphic with that of the MgO substrate, but above 4–6 ML the islands are relaxed to the bulk Ag lattice parameters, arising from the formation of interfacial misfit dislocations. In these experiments,[17,18] the Ag growth process was performed at room temperature. It is remarkable that controlled manipulation (i.e., the two-step process) for Ag growth on Si(111) generated isolated islands with a strongly preferred Ag height of 3 ML and flat tops[10] rather than the commonly observed pyramids.[23] In this way, the present Ag/MgO(001) system is expected to produce Ag islands with a preferred height and flat tops by using the two-step process, where room-temperature annealing follows low-temperature deposition. Here, the preferred height should be 3 and 5 ML based on our prediction for the stability of the flat Ag films on MgO(001), and the preference of either one of these two magic thicknesses can be manipu-

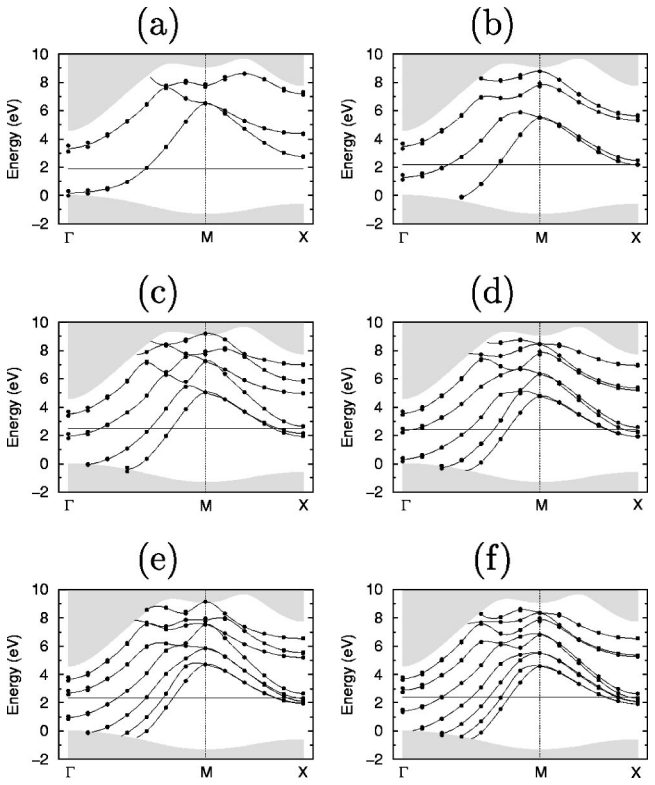

FIG. 3. Changes of surface band structures of Ag/MgO(001) with respect to the increase in Ag thickness: (a) 1 ML, (b) 2 ML, (c) 3 ML, (d) 4 ML, (e) 5 ML, and (f) 6 ML. The dark areas indicate the MgO bulk band projected onto the (001) plane. The solid lines represent the spline fitting of the average values of symmetric and asymmetric states. The ΓM and MX lines denote the directions of [110] and [010], respectively.

lated by controlling the growth conditions such as the growth temperature and the annealing time.

To explain the oscillatory energetics of the flat Ag films on MgO(001), we display the band structures at the different Ag thicknesses (ranging from 1 ML to 6 ML) in Fig. 3. We see that QW states due to the electrons confined in the Ag film appear in the band gap of bulk MgO. As the film thickness increases, the subbands are lower in energy and their spacings decrease. Note that these variations of the subbands are significant along the ΓM line, where the subbands originated from the Ag 5*s* electrons are the free-electron-like bands. We also see that along the ΓM line the energy of the lowest subband decreases steeply up to 3 ML and changes little at $N \geqslant 3$ ML (see Fig. 4). This significant lowering of the subbands up to 3 ML gives the decrease of the band energy contribution to the total energy, resulting in the stability of the Ag film at $N=3$ ML. However, at $N=4$ ML an additional subband touches E_F at the Γ point [see Fig. 3(d)], thus increasing the density of states at E_F. This increase of the density of states at E_F, together with little lowering of the subbands, gives an increase of the band energy contribution to the total energy, possibly producing the cusp of E_{bind} at $N=4$ ML. As a consequence of the instability of the Ag film at $N=4$ ML, an additional oscillation of E_{bind} occurs at $N>4$ ML. Thus, we believe that the variation of QW states

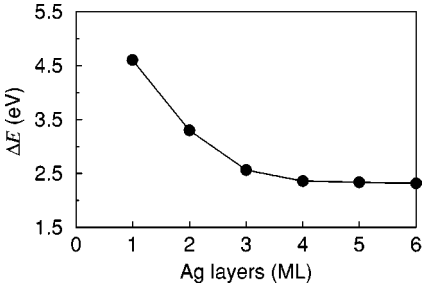

FIG. 4. Change of the lowest subband energy at the *M* point for the increase in Ag thickness. ΔE is the energy separation from the Fermi level.

with respect to the Ag thickness is an underlying factor for the oscillatory energetics in the Ag/MgO(001) system.

The photoemission peaks due to quantized electrons (i.e., QW states) in metal films were observed at a set of discrete energy values determined by the film thickness and the boundary conditions.[2–5] It is now well established that the amplitude of the electron waves confined in a metal thin film is modulated by an envelope function.[2,4,5] Here, the number of nodes in the envelope function is given by the quantum number ν, and the QW energy for a given ν value increases with increasing film thickness.[24] The normal-emission angle-resolved photoemission experiment for Ag films on the Fe(001) substrate[3] found that the QW energy for $\nu=1$ varies with the film thickness at -1.7 (1 ML), -1.0 (2 ML), and -0.3 eV (3 ML) below the Fermi level. As shown in Table II, this variation of the QW energy is close to our result for Ag/MgO(001), i.e., -1.74 (1 ML), -0.91 (2 ML), and -0.53 eV (3 ML). In addition, for both the Ag/Fe(001) and Ag/MgO(001) systems the QW energy of $\nu=1$ crosses E_F at 4 ML.[2–4] The good agreement for the variation of QW energies between Ag/Fe(001) and Ag/MgO(001) indicates that in the former system the *s* states are well confined within the Ag film because of the presence of the *s*-*d* hybridization gap in the Fe(001) substrate, as pointed out in previous studies.[2,4]

In summary, our first-principles calculations have shown that QW states in flat Ag films on MgO(001) appear in the band gap of bulk MgO and evolve as the film thickness increases. The binding energy per layer oscillates with the film thickness. This shows that flat films at thicknesses of 3 and 5 ML are locally stable. This finding calls for a more precise determination of flat plateaus of Ag islands on

TABLE II. Calculated QW energy for $\nu=1$ as a function of the Ag thickness. The values are chosen at the Γ point. The corresponding values for Ag/Fe(001), obtained from the normal-emission photoemission experiment, are also given for comparison. Energies are given in eV below the Fermi level.

Thickness	Ag/MgO(001)	Ag/Fe(001)[a]
1 ML	−1.74	−1.7
2 ML	−0.91	−1.0
3 ML	−0.53	−0.3

[a]Reference 3.

MgO(001) in future experiments by using the two-step process of low-temperature deposition following by annealing.

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