PHYSICAL REVIEW B **69**, 235423 (2004)

Polar surface engineering in ultrathin MgO(111)/Ag(111): Possibility of a metal-insulator transition and magnetism

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(Received 26 December 2003; revised manuscript received 12 March 2004; published 30 June 2004)

A recent report [Kiguchi *et al.*, Phys. Rev. B **68**, 115402 (2003)] that the (111) surface of 5 MgO layers grown epitaxially on Ag(111) becomes metallic raises a question of what will happen when we have fewer MgO layers. Here we have revealed, first experimentally with electron energy-loss spectroscopy, that MgO(111) remains metallic even when one-layer thick. We have confirmed this theoretically with the density functional theory, where metallization turns out to depend on the nature of the substrate. We finally predict, with a spin-density functional calculation, that a magnetic polar surface can be possible.

DOI: 10.1103/PhysRevB.69.235423 PACS number(s): 79.60.Jv, 73.20.−r, 68.55.−a

The problem of polar surfaces, i.e., surfaces of ionic crystals where the outermost atoms are all anions (or all cations), is of fundamental as well as technological interest. While polar surfaces, with their high reactivity, have been envisaged to be a unique playground for catalysis, unusual adhesion, etc., a fundamental feature is the possibility of metallization of the surface layer, on which we focus in the present study.

The physics behind the metallization of polar surfaces is as follows. A slab having a polar surface at either end is equivalent to a stack of dipole layers, which would accompany a spontaneous appearance of a macroscopic electric field. Since this state, with its infinite surface energy, should be unstable, a sheet of compensating charges must be formed at the top and bottom surfaces. The system can accomplish this in two ways: either the surface reconstructs itself to introduce, e.g., systematic vacancies, or a charge transfer may occur across the bulk and the surface without reconstructions. In the latter case the sheets of surplus charges imply that each surface becomes metallized.

The metallized polar surface has long been investigated theoretically.[1] Specifically, for the unreconstructed MgO(111) surface, which consists of a top O^{2-} surface and a bottom Mg^{2+} surface (type-III surface in the classification by Tasker[2]), a quantum mechanical calculation has been performed with the discrete variational (DV)-X_α method[3] for a finite cluster,[4] a semiempirical Hartree-Fock study,[5] or a first-principles density functional calculation[6,7] for a slab. The metallization has been confirmed in these studies.

On the other hand, the problem has a long history of experimental investigation as well, but only recently do we have definite results. Namely, various attempts to grow rocksalt-structure compounds with unreconstructed polar surfaces have proved to be a difficult task. It has in fact been shown theoretically that reconstructions cannot be avoided unless we introduce hydroxylation[5,8] or adsorption of metals.[6,7,9] If we turn to oxide surfaces, they are even more difficult to prepare than ionic crystal surfaces, because oxygen deficiencies tend to occur and hinder spectroscopy for oxide surfaces even when nonpolar. Now, recent advances in fabrication techniques for ultrathin oxides[10,11] are enabling us to prepare atomically-controlled single-crystal films of oxides,[12] but the unreconstructed polar surfaces remained a challenge.

Recently, however, three of the present authors[13] have succeeded in growing an MgO(111) 1×1 surface with alternate adsorptions of Mg and O_2 on Ag(111), which has enabled them to fabricate a unreconstructed polar surface (which turned out to be metastable, transforming to more stable ones after annealing). The electronic structure of 5 MgO layers (or 10 monolayers as sometimes called) of MgO(111), as probed with electron energy-loss spectroscopy (EELS) and ultraviolet photoemission spectroscopy (UPS), shows that the surface is indeed unreconstructed with a nonzero density of states at the Fermi energy (E_F) indicative of a metal.

This raises an interesting question of what should happen to the metallization when we have only few monolayers: As the film thickness decreases the macroscopic electrostatic potential due to the surface charge should decrease, so the competition between the metallic state and the insulating state with an electric field retained should become more subtle and interesting. The present study exactly addresses this problem.

Here we show, first experimentally, that even one layer of MgO(111) on Ag(111), as probed with EELS, is metallic. We then theoretically show with an *ab initio* calculation that the system is indeed metallic. We further predict that the nature of the surface should depend on the nature of the substrate, i.e., the surface should be insulating for substrate with larger lattice constants. We finally predict, with a spin-density functional calculation, that the surface, whose local density of states is large at the surface of thicker films, can exhibit a magnetic instability.

Let us start with the experimental result. As for the sample preparation we follow Ref. 13. Namely, the MgO film was grown with alternate adsorptions of Mg and O_2 on the Ag substrate at $T=300$ K, where the experiment was performed in a ultrahigh vacuum throughout. The formation of a clean 1×1 MgO film on the substrate is confirmed from a sharp reflection high energy electron diffraction (RHEED),

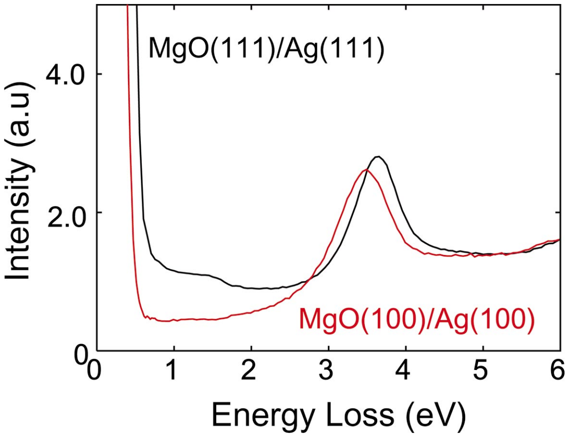

FIG. 1. (Color) EELS result, with the primary-electron energy of 60 eV, for the one MgO(111) layer on Ag(111) as compared with that for MgO(100) on Ag(100).

while the Auger-electron spectroscopy detects no contamination.

The electronic structure is then probed *in situ* with EELS. While the defects would be observed in EELS as specific peaks (at 2.3 eV for an Mg vacancy; 5 eV for an O vacancy), we have observed no such peaks and we conclude that the surfaces are basically defect-free. The result is displayed in Fig. 1 for one layer of MgO(111) on Ag(111) as compared with MgO(100)(Ref. 13) of the same thickness grown on Ag(100). We can immediately see that the MgO(111) has a long and substantial tail for the energy loss $\lesssim 2.5$ eV in marked contrast with the result for MgO(100) (while the peak around 4 eV, visible in both cases, originates from the surface plasmon of the Ag substrate). The qualitative feature observed here for one layer of MgO on Ag is quite similar[14] to those of five layers of MgO on Ag, reported in Ref. 13. So we conclude that one layer of MgO(111) on Ag already has,

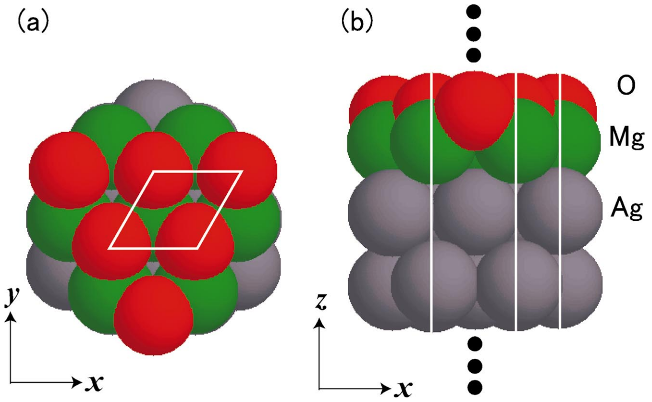

FIG. 2. (Color) Top (a) and side (b) views of the atomic configuration considered in the present study. The unit cell is indicated in white.

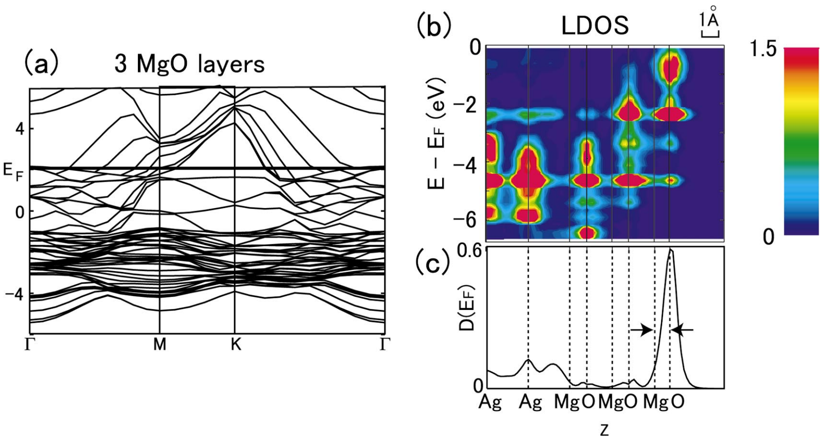

FIG. 3. (Color) The band structure (a), the local density of states (LDOS) integrated over both x and y directions displayed as a function of energy and z($\perp$ interface) (b), and the LDOS just at E_F as a function of z (c). Vertical dotted lines in (c) represent the optimized positions of atoms, with the separation between the outermost O and Mg indicated with arrows.

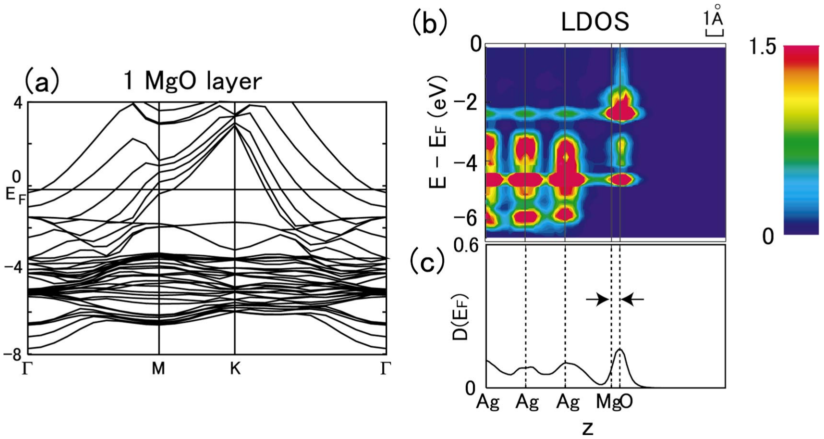

FIG. 4. (Color) A plot similar to Fig. 3 for one MgO(111) layer.

surprisingly enough, a nonzero density of states around E_F suggestive of a metallic surface.

We move on to a first-principles electronic structure calculation in the framework of the generalized gradient approximation (GGA) based on the density functional theory. We adopt the exchange-correlation functional introduced by Perdew *et al.*[15] We employ ultrasoft pseudopotentials[16,17] for Mg and O, and a norm-conserving soft pseudopotential for Ag, both in separable forms. The cut-off energy of the plane-wave expansion for the wave function is taken to be 25.0 Ry. The atomic configurations and the corresponding electronic ground states are obtained with the conjugate gradient scheme.[18]

The optimized lattice constants in the bulk obtained are 4.11 (against the experimental 4.09) Å for Ag and 4.22 (4.21) Å for MgO. We then introduce a slab model, where we put a (111)-directed 5 Ag layers sandwiched from top and bottom by MgO layers. Here we put Mg atoms on the hollow sites of the outermost Ag atoms (see Fig. 2), since the total energy is found to be lower by ~ 0.1 eV per unit cell than when we put them on the atop sites. Then we put oxygen atoms to accomplish one layer of MgO(111), and repeat this for $\geqslant 2$ layers for multi-layer cases.

In the previous study,[13] we have reported that the lattice constant of 1 ML MgO film on Ag is ~ 4.6 Å and is incommensurate with that of the bulk of Ag (~ 4.1 Å). Since the incommensurate case is intractable in a first-principles calculation, we adopt a commensurate case. In this situation, the question is which should be more reasonable; case I where the substrate (Ag) is expanded (to ~ 4.6 Å), or case II where MgO is contracted (to ~ 4.1 Å). In case I each oxygen atom would drop very deeply into the hollow space between Mg atoms, where the drop would be exaggerated since there is neither Ag (nor Mg) just below O when the interface is commensurate (see Fig. 2). So case II, in which this is prevented, should be more realistic, although the separation (d) between O and Mg atoms in the z-direction may be overestimated. Thus we take the same unit-cell size as the bulk of Ag in the xy-plane, and optimize the atomic positions. The size of the whole slab in the z direction is set to be large enough (47.46 Å). On the other hand, while larger unit-cell sizes in xy would be necessary when the surface is reconstructed, we take 1×1 unit cell here, since we focus on the unreconstructed case, which is experimentally observed as the 1×1 RHEED pattern although the state is metastable.

Let us start with the result for three MgO layers on Ag. Figure 3 shows the band structure along with the local density of states (LDOS). The LDOS at E_F, plotted in Fig. 3(c), is calculated by $\Sigma_i |\phi_i(x,y,z)|^2$, with the summation taken over the eigenstates (labelled by i) having energies $E - 0.125 < E_i < E + 0.125$ eV. The LDOS does not change significantly when the energy window (0.25 eV here) is changed to 0.5 eV. The number of sampled k points in Figs. 3(b) and 3(c) is 8 with the Monkhorst-Pack method for the integration over the Brillouin zone,[19] where the bands are fitted to sinusoidal forms and the tetrahedron method is employed. The result in fact changes little when the number is increased to 18.

We can see in the energy-resolved LDOS [Fig. 3(b)] that, while the LDOS at E_F is small, LDOS is large around $E \simeq E_F - 5$ eV, which originates from $3d$ levels of Ag. If we turn to the LDOS at E_F in Fig. 3(c), a notable peak is seen at the outermost oxygen, which suggests that the surface is in fact metallic. This is a tail (in real space) of the bands originating from the MgO. We have obtained a similar result for the case of two MgO layers (not shown). This is quite consistent with the experimental result[13] that unreconstructed polar surface becomes metallic if the MgO film is $\gtrsim 5$ MgO layers, and also with theoretical studies.[4–7]

Now, for the thinnest possible (one) MgO layer, we can see in Fig. 4(c) that the peak in the LDOS at E_F at the O site continues to exist, which indicates that the one MgO(111) layer is still metallic as consistent with the experiment. To be more precise, the tail in real space still extends to the surface for the bands originating from MgO, but the peak at the O site is much smaller than in Fig. 3(c), so the charge redistribution occurs less completely for one MgO layer than for three layers. Experimentally it is difficult to quantify the difference between one- and five-layer cases in the present EELS, but other techniques such as photoemission spectroscopy or energy loss spectroscopy with higher energy resolutions should detect the difference.

So a small electric field may remain for the incomplete charge redistribution, but we will have to implement a theoretical method to quantify the electric field.[6,7] Qualitatively, however, we can understand the incomplete charge redistribution for one MgO layer as follows. We first note in Fig. 4(c) that the outermost O atoms sink deep into the Mg layer. Namely, the optimized separation, d, in the z-direction between the O and Mg atoms on the surface is 0.50 Å, which is much shorter than that for the case of three MgO layers (with $d = 0.90$ Å). This suggests that the electric field induced by the surface charge should be smaller. In other words, the energy loss due to the lattice distortion (Δ_L) and that due to the buildup of the electric field (Δ_E) are relatively moderate for one MgO layer, so that the energy cost due to the charge redistribution (Δ_C) may exceed $\Delta_L + \Delta_E$.

This observation leads us to propose here an interesting phenomenon: if we can change the value of d which dominates $\Delta_L + \Delta_E$, the relative magnitudes of $\Delta_L + \Delta_E$ and Δ_C should be changed. This implies that we should be able to induce a *metal-insulator transition* for the polar surface by controlling d. One of the simplest ways to change the value of d is to vary the lattice constant of the substrate. Namely, if we employ a substrate having a larger lattice constant, the separation between the hollow sites becomes larger, which in turn increases the distance between Mg atoms in xy-plane. This will make O atoms sink more deeply into the Mg layer, and a smaller d will favor an insulating surface.

To confirm that the MgO surface becomes insulating for substrates having larger lattice constants, we have calculated the band structure and LDOS for the interface system where we artificially make the lattice constant larger (4.23 Å, Fig. 5) or smaller (3.90 Å, Fig. 6). We can see that the larger lattice constant indeed makes the LDOS around E_F at the outermost O (Fig. 5) notably smaller than in Fig. 4, while the quantity becomes larger for the compressed substrate (Fig. 6). In general, the metal induced gap state (MIGS) is an interesting problem for metal-insulator heterointerfaces.[20,21] In the present case, however, the DOS becomes larger for

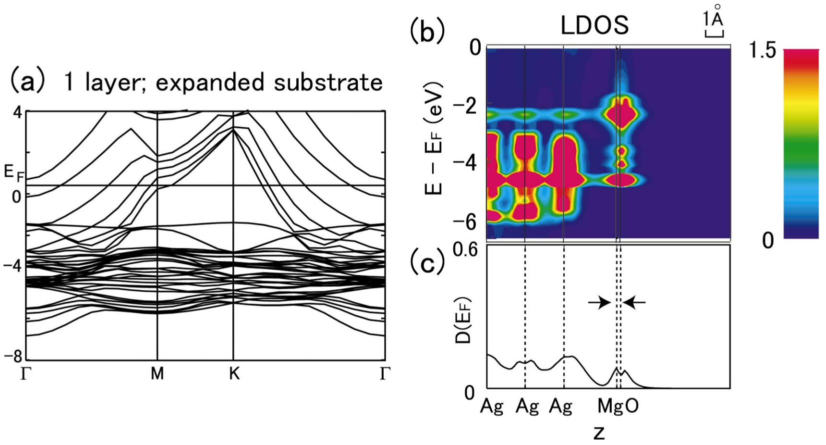

FIG. 5. (Color) A plot similar to Fig. 3 for one MgO layer with a larger lattice constant (4.23 Å) of Ag than that in Fig. 4.

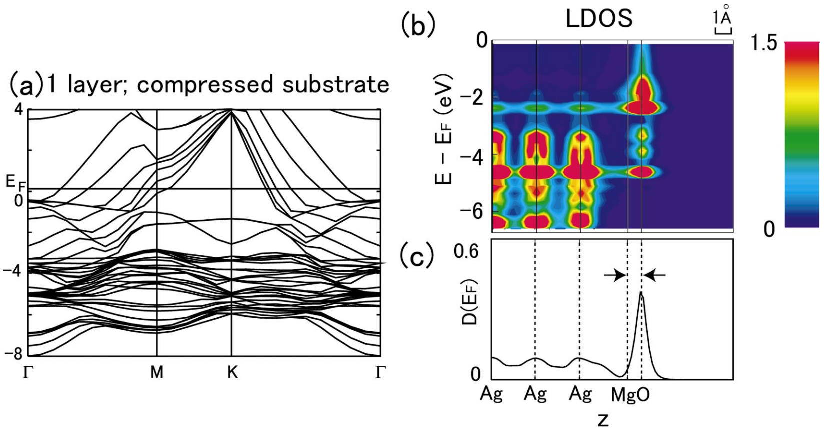

FIG. 6. (Color) A plot similar to Fig. 3 for one MgO layer with a smaller lattice constant (3.90 Å) of Ag than that in Fig. 4.

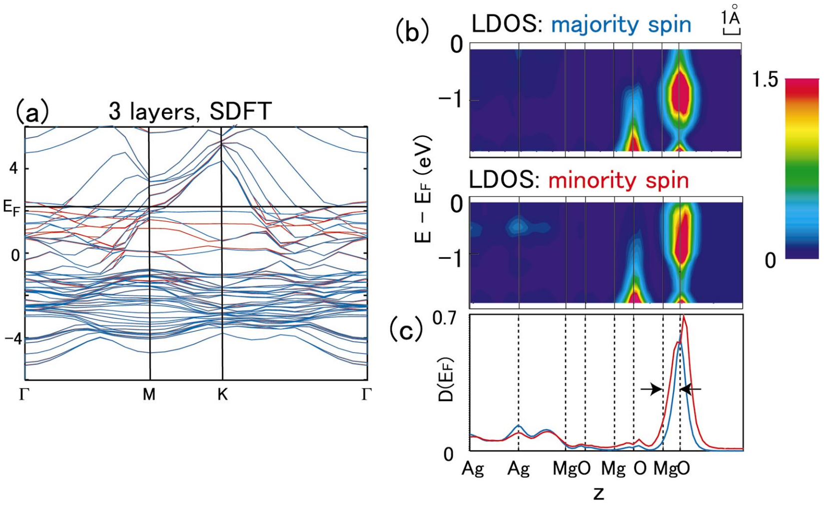

FIG. 7. (Color) A plot similar to Fig. 3, where the spin density functional theory with GGA is adopted to calculate spin-resolved band structures. Blue (red) lines in (a,c) represent the majority (minority) spin.

larger separation between O and Mg atoms in the *z*-direction, while MIGS would become prominent when O atoms are closer to the interface, so the contribution of MIGS should be irrelevant here. This shows that the system indeed resides in the vicinity of the metal-insulator transition, although the proof of the transition would require a more quantitative analysis. Even with the problem about the commensurability of the interface, the qualitative tendency for the decrease in the density of states for substrates having larger lattice constants should qualitatively hold.

From the behavior of the LDOS at E_F we can propose an even more fascinating phenomenon, i.e., the possibility of a magnetic polar surface. As we have shown, the LDOS at E_F is large for the outermost oxygen layer in thicker MgO films. When the LDOS is large enough, we may expect a ferromagnetic instability. In fact, Goniakowski *et al.*[6] have already shown, by means of a spin density functional calculation for a five atomic-layer slab (O/Mg/O/Mg/O with unbalanced numbers of cations and anions), that the unreconstructed polar surface of MgO has a ferromagnetic instability. However, the structure of MgO (especially the value of d) is not optimized in that study, so the LDOS at E_F should be overestimated.

So we have performed a spin density functional calculation for one-layer and three-layer MgO(111) on Ag with the optimization for d to study the magnetic instability. The result shows that the three-layer system does have a ferromagnetic ground state, while one MgO(111) layer is paramagnetic as expected. Figure 7 displays the band structure and the LDOS, where an exchange splitting ($\sim$0.5 eV) is seen for the bands lying $\sim$2 eV below E_F. The magnetization (the difference between the numbers of opposite spins per unit cell) is $\sim$0.1. One thing we have to note is that the unit cell in the present work as well as in Ref. 6 is 1×1 in the xy-plane, so that it cannot describe other magnetic states such as antiferromagnetic ones. Thus a calculation with larger unit cells will be required to really confirm whether the ground state can become magnetic, which is a future problem.

R.A. and Y.T. would like to thank J. Nakamura for providing them a pseudopotential for Ag. The GGA calculation was performed with TAPP (Tokyo *ab initio* program package), for which R.A. received technical advices from Y. Suwa. Numerical calculations were performed on SR8000 in ISSP, University of Tokyo. This research was partially supported by a Grant-in-Aid from the Japanese Ministry of Education.

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