Surface Reactivity and Quantum-Size Effects on the Electronic Density Decay Length of Ultrathin Metal Films

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The origin of the correlation between surface reactivity and quantum-size effects, observed in recent experiments on the oxidation of ultrathin magnesium films, is addressed by means of *ab initio* calculations and model predictions. We show that the decay length in vacuum of the electronic local density of states at the Fermi energy exhibits systematic oscillations with film thickness, with local maxima induced when a quantum-well state at $k_{\|} = 0$ crosses the Fermi energy. The predicted changes in the decay length are expected to have a major impact on the electron transfer rate by tunneling, which has been proposed to control the initial sticking of O_2 in the oxidation process.

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There is considerable interest in identifying methods to tailor the chemical reactivity of surfaces, a crucial factor in many technologically relevant surface phenomena, including oxidation and catalysis. The recent observation of a correlation between quantum-size effects and the surface reactivity of ultrathin metal films [1] is an exciting development in this area, both because of its fundamental interest for a quantitative understanding of the structure-size dependence of the reactivity and in view of the importance of nanoscale and low-dimensional structures in modern technology. Experimentally, oscillations were observed in the oxidation rate of ultrathin Mg(0001) films on W(110), as a function of film thickness, with the largest oxidation rate occurring when a quantum-well state was found to cross the Fermi energy, in photoemission (PE) spectra [1] taken near normal incidence. In particular, the changes observed in the initial oxidation rate—when most of the film was still metallic—were found to be dramatic. The origin of these changes has not been established yet. The changes in reactivity were suggested to be due to a change in the density of states (DOS) at, or near the Fermi energy E_F [1], as the oscillations in the reactivity were found to correlate with the oscillations in the PE intensity at E_F. However, unlike the normal-incidence PE intensity, which measures the partial DOS at $k_{\|} = 0$, the total DOS of the films at E_F is bound to exhibit a monotonic, staircaselike increase with film thickness [2], and cannot thus simply account for the oscillations in the reactivity.

Here we propose a theoretical interpretation of these observations, in which the decay length in the vacuum of the electronic local density of states around the Fermi energy is identified as the key parameter responsible for the changes in the reactivity. On the basis of *ab initio* calculations, inspired by model predictions for quantum-well states, we show that the decay length λ of the local density of states at the Fermi energy exhibits an oscillatory behavior with the film thickness, with local maxima present when the highest occupied quantum-well state at $k_{\|} = 0$ is closest to the Fermi energy. The predicted changes in the decay length are significant. They are expected to have a direct, exponential impact on the electron transfer rate by tunneling, which has been proposed to control the initial sticking of O_2 on the metal surface [3]. The changes in λ should be observable by scanning tunneling microscopy (STM), near terraces steps, on surfaces characterized by regions of different film thicknesses [1].

Model predictions for λ.—Within an independent electron description and considering, for simplicity, a square-well potential along the z direction, normal to the thin film, with a constant depth V and a variable width L (film thickness), the electronic states are solutions of a separable problem in the z and (x, y) variables, and read

$$\psi^{E}_{n,k_x,k_y}(x, y, z) \sim \chi_n(z) e^{i(k_x \cdot x + k_y \cdot y)}, \tag{1}$$

with energy $E = E_n + \hbar^2(k_x^2 + k_y^2)/2m^*$, where m^* stands for the electron effective mass. E_n and $\chi_n(z)$ are the eigenvalues and eigenstates of the one-dimensional square-well potential problem, with the following properties:

$$\chi_n(z) \sim e^{-\alpha_n \cdot z} \tag{2}$$

for $z \geq L/2$, assuming the z origin at the center of the film, and

$$\alpha_n = (\sqrt{2m^*}/\hbar)\sqrt{-E_n}, \tag{3}$$

where the zero of energy is taken at the vacuum level. In the three-dimensional problem, E_n coincides with the energy E of the subband state n at $k_{\|} = 0$, measured relative to the vacuum level.

All states ψ^{E}_{n,k_x,k_y} belonging to subband n, with energy $E \geq E_n$, are thus characterized by the same decay length $1/\alpha_n \sim 1/\sqrt{-E_n}$, for a given film thickness L. If E_F is located between the levels E_n and E_{n+1}, the dominant decay length of the electronic states at E_F is $1/\alpha_n$, namely, the decay length of the highest occupied band state at $k_{\|} = 0$. With increasing width L of the well, the energies of the quantum-well states decrease with respect to E_F; hence,

the decay length λ of the electronic density at E_F first decreases as $1/2\alpha_n \sim 1/\sqrt{-E_n}$, until the next quantum-well state at $\bar{\Gamma}$ crosses the Fermi energy, at which point λ increases to the new value $1/2\alpha_{n+1} \sim 1/\sqrt{-E_{n+1}}$. The decay length then decreases again with increasing L, displaying systematic oscillations with L. Considering next a discrete number of atomic layers, the periodicity of the crossing of the Fermi energy may be derived from the Bohr-Sommerfeld rule, which for Mg(0001) yields a periodicity of 7.7 monolayers (ML) [4].

From the model description, we expect thus oscillations in λ, with local maxima occurring when the highest occupied quantum-well states at $\bar{\Gamma}$ is closest to E_F. A more realistic description of the system, however, is clearly needed to confirm the robustness of this behavior, and to quantify the effect. In particular, electron interaction, atomic orbitals and bonds, surface states, and the presence of the substrate, are all factors which are expected to influence the decay length λ. We have therefore examined the effect of quantum confinement on λ by means of *ab initio* calculations performed for epitaxial Mg(0001) films on W(110) and also, for comparison, for the corresponding unsupported Mg(0001) films in vacuum.

First-principles results.—The calculations were performed within density functional theory, using the Perdew-Burke-Ernzerhof exchange-correlation functional [5], Troullier-Martins pseudopotentials [6], and a plane-wave basis set. The Mg pseudopotential was generated in the atomic configuration: $3s^{1.8}3p^{0}3d^{0.2}$, using as core-radii cutoff $r_{s,p,d} = 2.8$ a.u.. For W we treated the $6s$, $6p$, and $5d$ orbitals as valence states, using the same parameters as in Ref. [7]. The overlap between valence and core electrons was accounted for using the nonlinear core correction to the exchange-correlation potential [8]. A kinetic-energy cutoff of 49 Ry was used for the plane-wave expansion of the electronic orbitals of the Mg/W systems. For the isolated Mg(0001) slabs we used a kinetic-energy cutoff of 14 Ry. The Brillouin zone sampling was done with a Monkhorst-Pack (MP) grid [9], and we used a Gaussian smearing of the electronic levels of 0.02 Ry to determine the Fermi energy. The films were modeled using slab geometries in supercells. For the Mg films on W, we considered slabs containing 7 W(110) ML, terminated by 5 to 12 Mg(0001) ML on one side, and by 2 Mg (0001) ML on the other side. The Mg bilayer was introduced in order to avoid the presence of an electric field—due to the different work functions of W and Mg—in the vacuum regions separating the periodic images of the slab. We used vacuum regions with a minimal thickness of 20.1 Å, in order to obtain well-converged values of λ.

Experimentally, above 3 ML, the Mg films are known to grow epitaxially on W(110) [4], with lattice parameters corresponding to their bulk values [10]. The mismatches between the experimental in-plane lattice parameters of Mg(0001) ($a_{\mathrm{Mg}} = 3.21$ Å, $b_{\mathrm{Mg}} = \sqrt{3}a_{\mathrm{Mg}}$) and W(110) ($a_{\mathrm{W}} = 3.16$ Å, $b_{\mathrm{W}} = \sqrt{2}a_{\mathrm{W}}$) are 1.6% and ~20% [4]. To model such epitaxial systems, a commensurate interface atomic structure is needed in the calculations. The inclusion of dislocations would require prohibitively large lateral dimensions of the supercell, and the details of the atomic structure at the interface are unknown in any case. In order to simulate an unstrained Mg film on W(110), we thus elected to laterally strain the W(110) slab to the in-plane lattice parameters of Mg(0001). The epitaxial alignment was made by positioning the atoms of the first W(110) layer, adjacent to the Mg, in the continuation of the Mg (0001) hcp lattice. The three outermost layers of the Mg film were relaxed, while the other interlayer spacings were kept frozen at their bulk position (using the theoretical values of the bulk lattice constants: $a_{\mathrm{Mg}} = 3.19$ Å, $c_{\mathrm{Mg}} = 5.18$ Å, and $a_{\mathrm{W}} = 3.21$ Å). It should be noted, however, that the Mg(0001) surface relaxations are small [11,12], and were found to have a negligible impact on λ. The self-consistent calculations were carried out using a (20,20,1) MP grid. For the local density of states, we used a (48,48,1) grid centered at Γ, with a Gaussian level smearing of 0.005 Ry. The decay length was derived from a fit, assuming an exponential decay of the local density of states at distances beyond ~2.15 Å from the outermost atomic plane.

In Fig. 1, we report the calculated decay length λ of the Mg films, as a function of film thickness. The results are shown for both the Mg films on W and the isolated Mg films in vacuum. The behaviors are very similar in the two cases. The decay length exhibits a pronounced oscillation, with a maximum at 9 layers and a minimum at 6–7 layers. The presence of the tungsten substrate tends to reduce the amplitude of the variation of λ, from 17% to 10%, but has no significant impact on the position of the extrema. The densities of states at $\bar{\Gamma}$ of the Mg (0001) films on W(110) are displayed in Fig. 2. With increasing film thickness, an unoccupied quantum-well state crosses the Fermi energy at ~9 layers. This coincides with the maximal decay length λ found in Fig. 1, consistent with the model prediction. In Fig. 2, we also reported the energy positions of the electronic states at $\bar{\Gamma}$ obtained from the calculations for the isolated Mg slabs in vacuum. Also in this case, a quantum-well state is found to pass through the Fermi energy at ~9 layers, which corresponds to the largest λ obtained in Fig. 1. We note that we have also examined the variation of the work function of the Mg films on W with the number of Mg layers [13], as quantum-size effects can be expected on this value [14]. For the Mg films on W, however, the calculated changes in the work function were found to be very small, namely, a variation of 0.05 eV in the range 5–12 layers. With increasing thickness, the work function was found to first decrease, in the range 5–8 layers, from 3.74 to 3.69 eV, and then to increase, in the range 8–11 layers, from 3.69 to 3.72 eV, and then saturate at 3.72 eV for higher coverage (in good agreement with the experimental value of 3.66 eV for Mg [15]).

Inspection of Fig. 2 reveals a striking correspondence between the positions of the peaks in the DOS of the Mg

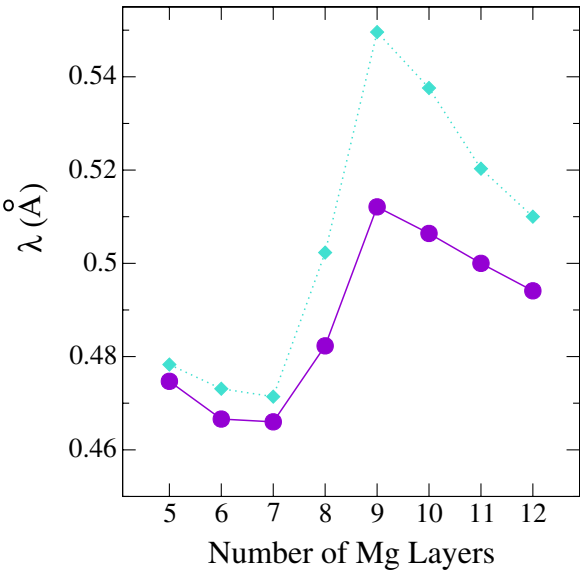

FIG. 1 (color online). Calculated decay length in vacuum of the electronic local density of states at the Fermi energy of Mg(0001) films of various thicknesses on W(110) (disks). The decay length of the corresponding Mg(0001) films isolated in vacuum is also shown for comparison (diamonds).

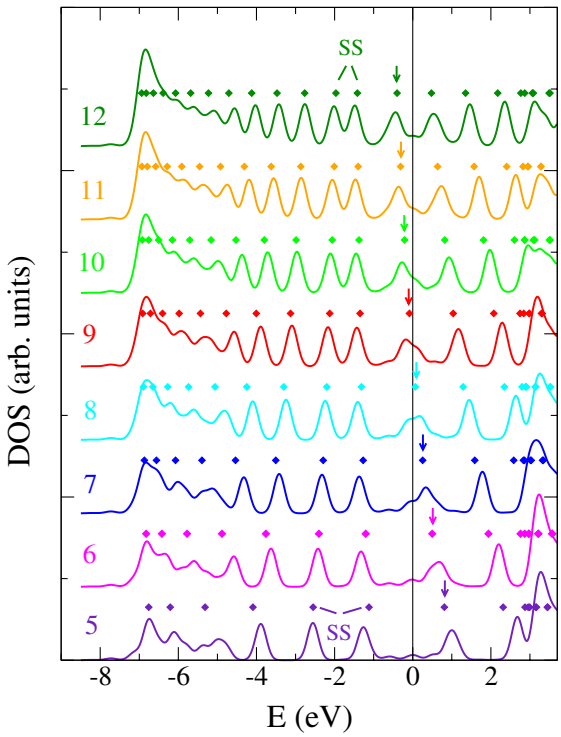

FIG. 2 (color online). Calculated density of states at $\bar{\Gamma}$ of the Mg (0001) films on W(110) (solid lines). The film thickness increases from 5 to 12 atomic layers (bottom to top curve). The densities of states have been convoluted with a Gaussian of width 0.2 eV. The symbols (diamonds) show the energies of the electronic levels at $\bar{\Gamma}$ of the isolated Mg(0001) films in vacuum. The states indicated by SS originate from the Shockley surface state of Mg(0001) (see text). The zero of energy corresponds to the Fermi level.

films on W and the positions of the levels of the isolated Mg films in vacuum. The largest difference between the two sets of energies does not exceed 0.2 eV in the range $[E_F - 8\ \text{eV}, E_F + 2\ \text{eV}]$. The states indicated by "SS" in Fig. 2 originate from the Shockley surface state of Mg(0001). In the isolated Mg(0001) slab in vacuum, the Shockley states of the two surfaces strongly interact, giving rise to a pair of split even and odd states—with respect to the center-of-slab reflection plane. The resulting splitting is as large as 1.4 eV for 5 Mg layers and 0.6 eV for 12 Mg layers. In the presence of the W substrate, these states persist as strong surface or interface resonances, with maxima in the probability density on both the outermost (surface) Mg layer and the innermost (interface) Mg layer. The ratio of the probability density on the surface relative to the interface layer of the high- (low-) energy state SS tends to increase (decrease) with increasing film thickness, and is ~1.3 (~0.85) in the 12 layer case. In the presence of the W substrate, some of the quantum-well states, and, in particular, those in the range $[E_F - 6\ \text{eV}, E_F - 3\ \text{eV}]$ [4,7], remain fully localized within the Mg films—similar to the confined quantum-well states obtained from *ab initio* calculations in Ag films on Fe [16], or sharp Fano resonances, located mostly within the Mg film. Other Mg quantum-well states, instead, and, in particular, the states corresponding to the feature which crosses E_F and is indicated by the arrow in Fig. 2, become broader resonances, corresponding to quantum-well states displaying an increased probability density within the W substrate. The resonant character of the quantum-well states which cross the Fermi energy tends to smoothen the jump in λ observed for thicknesses between 7 and 9 layers.

Hence, in spite of the presence of the surface or interface states, and the resonant character of the quantum-well states crossing the Fermi energy, the qualitative behavior of λ, inferred from the particle-in-a-box model, is fully supported by the *ab initio* calculations. The variation in the decay length we predict from the *ab initio* calculations is expected to have a direct, exponential impact of the electron transfer rate by tunneling—from the metal to the O_2 molecule—which has been proposed to control the initial sticking of the oxygen molecules impinging on the surface, via the attractive image charge potential on the ionized O_2^- molecule [3]. Assuming a transfer rate by tunneling proportional to $e^{-d/\lambda}$, with d the distance between the metal surface and the center of mass of the molecule, and considering, e.g., a distance $d \approx 3.5$ Å—within the expected physisorption range of the O_2 molecules [3,17], a 10% variation in λ produces a 100% change in the transfer rate. Such a charge is of the order of magnitude of the experimental change in the oxidation rate at low O_2 exposure [1].

The peak positions of the calculated DOS in the energy range $[E_F - 4\ \text{eV}, E_F]$, in Fig. 2, compare well with the near-normal-incidence PE measurements [1], except for a

systematic shift, by about +2 Mg ML, of the theoretical spectra with respect to the measured spectra. In our calculations, the first quantum-well state with energy higher than the surface or interface states SS, enters the occupied-state spectrum at a Mg thickness of 8–9 ML. In the experiment, this state is found, instead, to enter the valence-band spectrum at a nominal thickness of 6–7 ML. The same shift is observed between the calculated maximum or minima of λ and the experimental maximum or minima of the reactivity. Such a shift is probably due to the use of a commensurate, dislocation-free interface atomic structure, in the calculations, to describe a heavily lattice-mismatched epitaxial system. The presence of strained Mg layers or dislocations at the interface could result in the entrance of a quantum-well state at a smaller value of the number of layers of the Mg film.

The changes in λ we predict should be observable, e.g., by STM near terrace steps on a Mg surface characterized by regions of different film thicknesses [1]. Also, He scattering experiments have indicated an apparent step-height oscillation in the layer-by-layer growth of Pb on Ge due to quantum-size effects [18]. Such changes were recently shown to be due mostly to a displacement of the topmost layer charge density [19], in contrast to previous interpretations in terms of a displacement of the surface atomic planes. This recent analysis corroborates thus the present finding on the behavior of the decay length of the Mg films. We note that the changes in the decay length of the density of states near the Fermi energy may also be related to a recent observation of quantum-size effects on the chemisorption properties of Cu(001) thin films [20]. In addition, layer Korringa-Kohn-Rostoker calculations [21] have indicated that the lifetime of negative ionic states of molecules, adsorbed on supported metal thin films, varies with the thickness of the film through coupling to quantum-well states. This effect (not yet measured, to our knowledge) was associated, in the calculations, with oscillations in the amplitude, at the position of the molecule, of the density of empty states above E_F. This calculated behavior, consistent with the trend we find for λ, also supports the interpretation we propose for the reactivity changes.

In conclusion, on the basis of *ab initio* calculations for Mg(0001) ultrathin films on W(110), we have shown that the decay length in vacuum of the electronic density of states at the Fermi energy exhibits substantial oscillations with the film thickness. The decay length is maximal, as a function of film thickness, when a quantum-well state passes through the Fermi energy. The changes we predict in the decay length are expected to have a major impact on the tunneling rate in the electron transfer mechanism, which is believed to control the initial sticking of O_2 on the Mg surface. We therefore propose that the experimental tuning of the reactivity is due to quantum oscillations in the electronic density decay length, which should be observable by STM.

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