quantum-well state was found to cross the Fermi energy, states (DOS) at, or near the Fermi energy were suggested to be due to a change in the density of states, which has not been established yet. The changes in reactivity were found to be dramatic. The origin of these changes in photoemission (PE) spectra [1] taken near normal incidence. In particular, the changes observed in the initial sticking of O on the metal surface [3]. The changes in $V_{ab}$ should be observable by scanning tunneling microscopy (STM), near terrace steps, on surfaces characterized by regions of different film thicknesses [1].

Model predictions for $V$.—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:

$$
\psi_0^{E} \chi_n(z) \sim \chi_n(z) : e^{i(k_x x + k_y y)},
$$

with energy $E = E_n + \hbar^2(\vec{k}_x^2 + \vec{k}_y^2)/2m^*$, 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:

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

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

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

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 $k_\parallel = 0$, measured relative to the vacuum level.

All states $\psi_0^{E}$ 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

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 nano-scale 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 local maxima induced when a quantum well state at $k_\parallel = 0$ 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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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_{Mg} = 3.21 Å, b_{Mg} = \sqrt{3}a_{Mg}) and W(110) (a_{W} = 3.16 Å, b_{W} = \sqrt{2}a_{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 unsupported 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_{Mg} = 3.19 Å, c_{Mg} = 5.18 Å, and a_{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 \Gamma, 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 \sim 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 \sim 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 \sim 9 layers, which corresponds to the largest λ obtained in Fig. 1. We note that we have also examined the variation of the workfunction 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 are found to be very small, namely a variation of 0.05 eV in the range 5-12 layers. With increasing thickness, the workfunction first decreases, in the range 5-8 layers, from 3.74 to 3.69 eV, and then increases, in the range 8-10 layers, from 3.69 to 3.72 eV, and then saturates 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 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/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- (respectively, low-) energy state SS tend to increase (decrease) with increasing film thickness, and is \(\sim 1.3 \sim 0.85\) 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 \(\lambda\) observed for thicknesses between 7 and 9 layers.

Hence, in spite of the presence of the surface/interface states, and the resonant character of the quantum-well states crossing the Fermi energy, the qualitative behavior of \(\lambda\), 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 \(d \approx 3.5\ \text{Å}\) within the expected physisorption range of the \(O_2\) molecules [3, 17], a 10 % variation in \(\lambda\) 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 en-
tum oscillations in the electronic density decay length, which should be observable by STM.

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[2] See, e.g., J. C. Boettger and S. B. Trickey, Phys. Rev. B 45, 1363 (1992); the increase of the film DOS is implicit when the DOS is normalized to the number of atoms in the film.
[12] For 5 to 12 Mg ML on W, the relaxation of the topmost interlayer spacing (the largest relaxation) was found to be in the range +1.3 to +1.5 %. 
[13] We employed symmetric slabs with less vacuum, using the electrostatic potential as a reference in the vacuum.