

Tuning Surface Reactivity via Electron Quantum Confinement

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The effect of electron quantum confinement on the surface reactivity of ultrathin metal films is explored by comparing the initial oxidation rate of atomically flat magnesium films of different thickness, using complementary microscopy techniques. Pronounced thickness-dependent variations in the oxidation rate are observed for well ordered films of up to 15 atomic layers. Quantitative comparison reveals direct correlation between the surface reactivity and the periodic changes in the density of electronic states induced by quantum-well states crossing the Fermi level.

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The quantitative understanding of chemical reactivity of surfaces, a crucial property of many technological materials, has attracted enormous theoretical effort, which demonstrated the essential role of the substrate electronic structure, in particular, the density of electronic states around the Fermi level [1–4]. In fact, chemisorption of molecules and atoms, the first reaction step playing a decisive role in catalysis, corrosion, gas sensing, etc., is fully controlled by surface reactivity. A distinct feature of many catalysts, protective coatings, and gas sensors is that they are nanoparticles or thin films, i.e., materials with strongly reduced dimensions in one or more directions. Because of the “size” dependence of the electronic structure the nanomaterials have physical and chemical properties different from those of their bulk parents [5,6]. For example, the high activity of supported gold clusters of particular dimensions in CO oxidation was tentatively attributed to quantum effects specific for these sizes [7]. Yet, despite its importance the quantitative understanding of the size dependence of the electronic structure and surface reactivity is in its infancy. Most of the attempts to tailor the surface reactivity of nanomaterials have focused on the creation of specific surface structures, where the electronic perturbations are induced by edge effects [8], perturbed packing density or chemical modification [9]. Typical examples are supported transition metal mono- and bilayer films, where the interactions with the supporting substrate and the lattice strain cause a shift of the d band, thus changing the surface reactivity [10–12]. Still poorly explored is the role of electron confinement in ultrathin films, which induces discrete states in the electron density curves evolving with film thickness [13,14]. These so-called quantum-well states (QWSs) have been demonstrated to cause oscillatory variations of *bulk* properties, such as film stability [15], resistivity [16], reflectivity [17], and magnetic coupling [18], using also films with wedge-shaped thickness profiles [19]. Considering the periodic modulations in the valence band electronic structure with film thickness an effect on the surface reactivity can also be expected.

Here we demonstrate the essential role of electron confinement in ultrathin films on the chemical activity of the surface, linking the observed quantum size effect (QSE) quantitatively to the electron density of states around the Fermi level. Our study of the oxidation of epitaxial Mg films shows that films with the thickness at which the density of states at the Fermi level is increased due to QSE exhibit a dramatic increase in surface reactivity. This effect was observed at film thickness above 4 atomic layers, for which the chemically active surface layer is already insensitive to the presence of the substrate, and the strain due to lattice mismatch has been relieved [11,12]. Thus, surface reactivity can be tailored by simply changing the number of atomic layers that build the film. Measuring the effect of QWSs on surface reactivity is a challenging task: it requires atomically flat films and exactly the same reaction conditions in order to derive unambiguous conclusions. Mg films grown on a W(110) substrate is an ideal model system, because they grow epitaxially, develop well-defined QWSs [20] and have a high affinity to oxygen. Mg oxidation begins with dissociative adsorption of O₂, followed by an intermediate stage of oxygen incorporation and growth of MgO islands that coalesce, ending with the formation of a MgO bulklike phase [21–23]. We expect that the changes in the electron density due to QWSs in the Mg films will influence the O₂ dissociative adsorption, which controls the initial oxidation rate. The complementary microscopic methods, low-energy electron microscopy (LEEM) and x-ray photoelectron emission microscopy (XPEEM), allowed us to characterize the morphology, local structure, and local chemical state of the Mg films at a mesoscopic length scale [24].

The growth of Mg films was followed in real time with LEEM [25,26] and was optimized to have step-flow growth with development of adjacent microregions of different thickness. The microspot low-energy electron diffraction (LEED) pattern showed a bulklike Mg (0001)–(1 × 1) structure already for three atomic layers. The thickness distribution usually varied by two or three atomic layers in the early growth stages and broadened

upon further growth. Such type of morphology allowed us to probe simultaneously the oxidation of Mg microregions of different thickness, excluding side effects due to variations in the O_2 exposure or temperature.

The LEEM image in Fig. 1(a) shows a typical Mg film with regions from 5 to 15 atomic layers. The XPEEM image in Fig. 1(b) shows the lateral heterogeneity in the extent of Mg oxidation for the same film after an O_2 exposure of 9 Langmuir (L). Comparison with Fig. 1(a) reveals a clear modulation of the oxidation rate with thickness: the regions of 6 to 8 and 13 to 15 atomic layers are brighter, i.e., more heavily oxidized. This modulation is directly correlated to the periodic changes in the density of electronic states induced by QWSs crossing the Fermi level of the Mg film, as described below.

Using XPEEM [24,26] we recorded laterally resolved valence band spectra. Figure 2 shows spectra of single thickness regions with pronounced QWS, in agreement with photoelectron spectra of macroscopic Mg films [20]. Along with the 1.6 eV surface state two sets of QWSs are

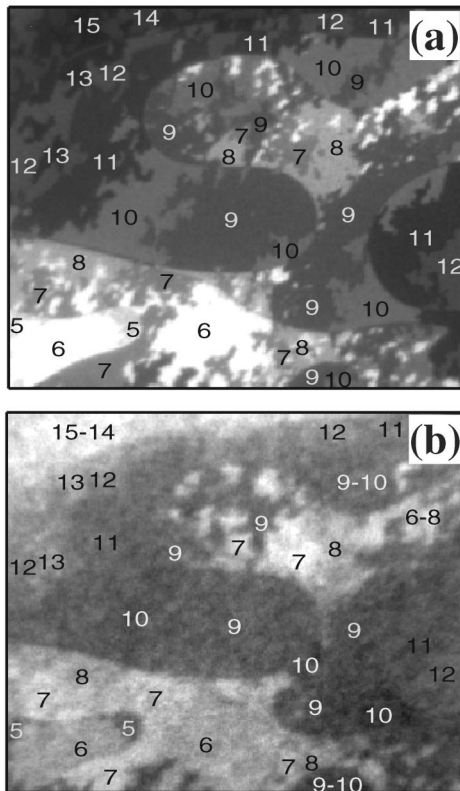


FIG. 1. $6 \times 5 \mu\text{m}^2$ images of a Mg film in an advanced growth stage. (a) 1.3 eV LEEM image: the indicated number of atomic layers corresponding to the microregions was determined following the reflectivity changes [24] during the film growth at 120°C with deposition rate of 0.1 atomic layer/min. (b) XPEEM image of the same Mg film after exposure to 9 L of O_2 at 50°C , where the contrast corresponds to the extent of local Mg oxidation. The image is obtained by measuring the Mg $2p$ intensity of oxidized Mg (I_{ox}).

visible: one appears below the gap at three atomic layers, and the other crosses the Fermi level moving towards higher binding energy a thickness of seven layers, as predicted by the Bohr-Sommerfeld rule [14] (see the inset of Fig. 2). A new QWS crosses the Fermi level when the Mg film thickness is a multiple of $7/8$ atomic layers [20,27].

To probe the local surface reactivity we compared the initial oxidation of regions having different thickness, at O_2 exposures up to ~ 13 L. At these relatively low O_2 doses the oxidation is limited to the topmost two layers [21,23], concomitant with the very high surface sensitivity of our XPEEM measurements (photoelectron escape depth of $\sim 2.8 \text{ \AA}$). In this early oxidation stage the surface state and the QWSs were still visible in the valence spectra. As a fingerprint of the oxidation rate we used the Mg atoms bound to oxygen. As shown in Fig. 3, they are characterized by a distinct broad feature in the Mg $2p$ spectra growing at the high binding energy side of the metallic Mg $2p$ peak at 49.8 eV. The intensity of this “oxide” component, I_{ox} , is proportional to the number Mg atoms bound to O and can be distinguished for oxygen density less than 0.1 atomic layers. Its relative intensity is thus a measure of the oxidation rate in the different microregions, as manifested by the I_{ox} XPEEM image in Fig. 1(b). The contrast is reversed if the XPEEM image is acquired at the energy of the Mg $2p$ metallic compo-

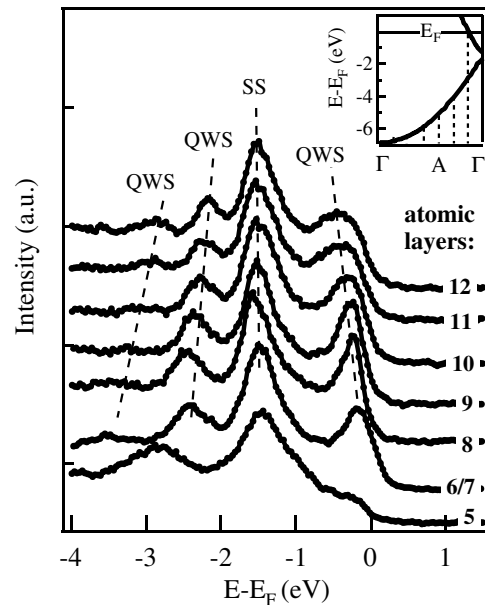


FIG. 2. Valence band spectra obtained from microregions with the indicated thickness. The inset shows the Mg (0001) band structure in the ΓA direction (normal to the film). The allowed wave-vector-energy (k_{\perp}, E) values for 7 atomic layers are calculated from the simple Bohr-Sommerfeld rule [14] assuming perfect reflectivity at the surface and interface and are indicated by dotted vertical lines.

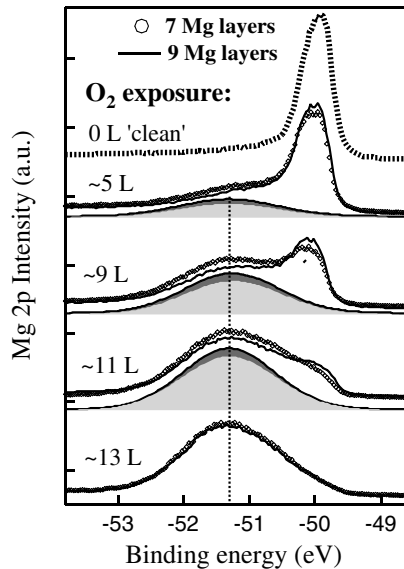


FIG. 3. The evolution of the Mg $2p$ spectra upon increasing the oxygen dose for films of seven and nine atomic layers. The broad component corresponds to the photoelectron emission from the Mg atoms bonded to oxygen.

ment. Before exposing to O_2 the Mg $2p$ image is featureless.

The dependence of the oxidation rate on the number of atomic layers is quantitatively confirmed by a large set of experiments with Mg films of other thickness combinations. The results are summarized in Fig. 4. Films of thickness higher than 15 atomic layers were not analyzed because the regions become too small to quantify their oxidation state with XPEEM [26]. The lateral variations in the extent of oxidation are highest at lower oxygen exposures and smear out when the oxide thickness exceeds our probing depth.

Figure 4 reveals a striking coincidence of the period of oscillation in the Mg surface reactivity and the period of crossing of the Fermi level by a QWS. The maximum in reactivity observed at 6–8 atomic layers occurs when the first QWS crossing the Fermi level increases the electron density of states, as shown in the top panel of Fig. 4. The reactivity decreases to a local minimum at 9–12 layers and grows again at 14–15 layers when the second QWS crosses the Fermi level.

The QWSs in Mg films evolve in the s - p band, and thus cannot be considered as laterally localized electronic states to which an orbital picture of the chemical interaction could be applied [1]. The observed “tuning” of the oxidation rate by varying the thickness of the Mg film can be attributed to QWS-induced oscillations in the magnitude of the electron density at the Fermi level. In accordance with theoretical concepts [3,4] such electronic variations should play an essential role for the interaction between the O_2 molecule and the Mg surface, which

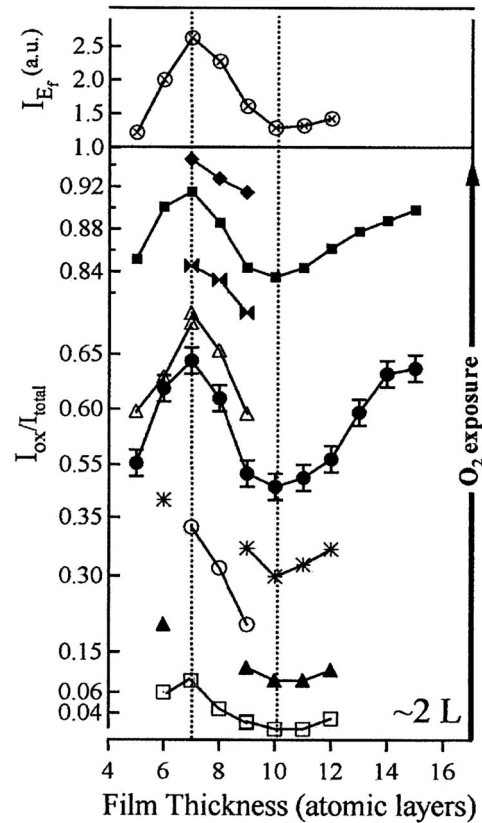


FIG. 4. (Lower panel) Plots of the relative weight of the Mg $2p$ oxide component, I_{ox}/I_{total} , obtained in several experimental runs. Data indicated with the same symbols correspond to the same O_2 exposure. (Upper panel) Photoemission intensity at the Fermi level measured for different microregion thickness before oxygen exposure with energy resolution of 0.25 eV.

involves a significant charge transfer to the unoccupied $1\pi_g$ molecular orbital and formation of O_2^- species [22]. This weakens the O-O bond leading to dissociation. The relatively low sticking coefficient [28] suggests an energy barrier along the potential energy surface for dissociative adsorption. In the presence of alkali metals, considered as electron donors, the enhancement of the Mg oxidation rate was attributed to an increase of the O_2 sticking coefficient [28]. Hence, the oscillations in the initial oxidation rate with the Mg film thickness can be understood assuming oscillations in the dissociation “barrier” governed by the oscillating changes in the electronic density of states at the Fermi level. At thickness where the QWSs enhance the density of states the charge transfer from the Mg surface to the antibonding orbitals of the oxygen molecule is facilitated and the dissociative adsorption becomes more efficient. From the results for the very initial oxidation, when most of the film is still metallic (bottom curve in Fig. 4), we deduce that the initial oxidation rate is linearly proportional to the density of states at the Fermi level, I_{Ef} , shown in the top panel

in Fig. 4. For example, it decreases by a factor of 2 from 7 to 10 atomic layers, which is close to the ratio $I_{\text{Ef}}^7/I_{\text{Ef}}^{10}$.

In a broader perspective such electronic QSE is relevant for structures confined in one or more directions, such as islands and terraces on metal surfaces [29,30]. Similar size dependence of the catalytic activity of Ni nanostructures in hydrogenolysis of ethane was also reported in Ref. [31], but the authors did not consider electronic QSE in their discussion. In fact, for low dimensional structures of transition metals with localized d bonds strongly interacting with molecular orbitals the correlation between QWSs and surface reactivity can be more complicated than in the case of a simple metal. However, a correlation between the density of states at the Fermi level and surface reactivity also exists for transition metals [3,4]. Hence one could use a simple condition for resonance of valence electrons at the Fermi level to tentatively predict the size of a nanostructure with higher surface activity: $2k_{\text{F}}aN + \phi = 2\pi n$, where k_{F} is the wave vector at the Fermi level, n is a quantum number and aN accounts for the size of the nanoobject (a is the lattice constant and N is the number of atomic layers) [14]. A major difficulty is calculating the phase shifts Φ upon electron reflection from the borders that are often poorly defined. Even in the simple case of a thin film with sharp interfaces, Φ might depend on the substrate band structure in a nontrivial manner [32]. Other important factors are the coherence and the reflectivity of valence electrons from the borders of the nanostructure [14]. In fact, the finite width of QWSs in Mg films due to nonperfect reflectivity and coherence of the valence electrons causes a finite width of the reactivity peak versus film thickness, reflected by the enhanced reactivity for the films of 6–8 atomic layers. This might explain why oscillations of the chemical activity of catalytic nanostructures versus their size have not been reported yet. We assume that due to poorly defined morphology and defects in the atomic structure the coherence length of valence electrons in realistic nanostructures is very short and an increase of the reactivity was observed only for the smallest sizes, i.e., where the reflection of Fermi electrons from the borders is still resonant.

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