Enhanced Reactivity at Metal−Oxide Interface: Water Interaction with MgO Ultrathin Films

L. Savio,* E. Celasco, L. Vattuone, and M. Rocca

Istituto Nazionale di Fisica della Materia, Unita' di Genova and IMEM-CNR, Dipartimento di Fisica, Universtita' di Genova, Via Dodecaneso 33, 16146 Genova, Italy

Received: July 17, 2003; In Final Form: March 29, 2004

The interest in thin and ultrathin oxide films is increasing rapidly due to the new properties and the many possible technological applications of such materials. In this frame the interaction with water, a major constituent of our atmosphere, is an essential issue for a better characterization of oxide film-based devices. We report here a detailed high-resolution electron energy loss spectroscopy and X-ray photoelectron spectroscopy study of the reactivity of ultrathin MgO films grown on Ag(100) toward H_2O. We find that only OH groups are detected at 310 K, while at low temperature molecular adsorption prevails. In the former case we observe a strongly enhanced dissociation probability for monolayer and submonolayer MgO films, indicative of an active role of the Ag substrate in the dissociation process. The active sites are suggested to be low-coordinated ions at the border of monolayer MgO islands. Aging phenomena, previously observed on MgO ultrathin films,[1] have been confirmed. Although their origin could not be definitively determined, our data strongly suggest water adsorption not to be the major cause of this process.

1. Introduction

Ultrathin metal oxide films are employed more and more frequently as components of miniaturized electronic devices, e.g., as dielectric spacers in metal−oxide semiconductor field effect transistors (MOS−FET) or as tunneling barriers in other nanoelectronic devices.[2] More recently, applications of MgO layers in plasma display panels were also suggested.[3]

The existence of several technological applications and the observation of new catalytic properties of ultrathin films (not present for bulk oxide surfaces and due to the presence of the metal−oxide interface[4]) increased the interest in this class of materials and encouraged fundamental studies in this field. Moreover, contrary to bulk oxides, ultrathin metal−oxide films do not present charging effects when probed by means of electron-based spectroscopic techniques, which is a great advantage from an experimental point of view.[5]

MgO films are among the most studied systems since, due to their relatively simple electronic and atomic structure, they were assumed as a model for investigating metal−oxide interface properties.[6] Ag(100) is an optimal substrate for the film deposition, since the small mismatch between the Ag and the MgO lattice constants allows for epitaxial growth, as demonstrated recently by scanning tunneling microscopy (STM).[7,8] Such experiments, aimed at clarifying the structure of MgO layers in the very early stages of film growth, showed that initially both MgO islands and pyramidal structures form on the Ag(100) surface. At a nominal coverage of one monolayer of MgO (1 ML = 1.18 10^{15} Mg ions/cm^2) 58% of the substrate is covered by a single layer, 22% by a double layer, 2% by pyramids, and the remaining part is still bare.[8]

The phonon spectrum of MgO films is dominated by the presence of the Fuchs−Kliever mode (FK), a macroscopic surface optical phonon corresponding to the vibration of the Mg and O sublattices one against the other. It was detected at 658 cm^{-1} (81.7 meV) on thick MgO films,[9] but its frequency

was recently proved to downshift with decreasing film thickness.[9,10] The reported vibrational frequency for a 1 ML film is 580 cm^{-1} (72 meV). On the same film, the Wallis mode, a microscopic phonon corresponding to the vibration of O-atoms of the first MgO layer against the Mg sublattice, is detected at 508 cm^{-1} (63 meV), and a further single-layer mode is present at 427 cm^{-1} (53 meV). The last one is not observed for multilayer films and is assigned to the vibration of less coordinated oxygens at the borders of MgO islands of monolayer thickness.[10]

X-ray photoemission spectroscopy (XPS) experiments revealed an aging process of MgO ultrathin films consisting of the growth of a satellite in the O1s region, at a binding energy 2.3 eV higher than that of the main peak.[1] Such an effect, apparently stronger for 1 ML films than for multilayers, was interpreted in terms of water adsorption from the residual gas, but no direct water adsorption experiment has been performed until now to verify this hypothesis.

Water interaction with metallic and oxide surfaces has been deeply investigated in the last years.[11] In the case of MgO films, it is indeed a subject of pivotal importance in the understanding of the film properties, being an essential clue to determine the chemical stability of MgO-based devices working in air. Indeed, a lot of theoretical and experimental work has been done on bulk MgO(100) surfaces and thick films. Perfect MgO(100) planes are predicted to be inert toward water dissociation, so that at room temperature defects are expected to be the only active sites for this process.[12] This prediction is confirmed experimentally for low water exposures performed under ultrahigh vacuum conditions,[13] while the formation of a fully hydroxylated layer was detected upon exposure of MgO(100) to a water pressure above 10^{-4} mbar.[14] In the latter regime some restructuring of the surface occurs, since the water dissociation probability decreases after repeated adsorption−desorption cycles.[15] At low temperature, on the contrary, molecular and dissociative adsorption coexist at monolayer coverage, as predicted by several theoretical papers[16−20] and confirmed

* Corresponding author.

7772 *J. Phys. Chem. B, Vol. 108, No. 23, 2004*

Savio et al.

experimentally by Goodman et al.[21] for a 15 ML thick MgO film grown on Mo(100). Partial dissociation, due to hydrogen bonding between H_2O molecules, should involve one-third of the total coverage in the so-called Marseille model[17] and one-half in the calculations of ref 20. The different adsorbed species should be distinguishable from their vibrational spectrum.[18] To the best of our knowledge, however, very little experimental work on ultrathin MgO films has been reported until now on this particular topic.[22,23]

In the present paper we show a combined high-resolution electron energy loss spectroscopy (HREELS) and X-ray photoemission spectroscopy investigation of water interaction with ultrathin MgO films (0.3−4 ML thick). We find that at room temperature only dissociative adsorption occurs and that the dissociation probability is strongly enhanced in the monolayer and submonolayer regime. On the contrary, molecular adsorption is dominant at low temperature, although some dissociated OH groups are most probably present. The temporal evolution of clean films has also been investigated, confirming the existence of the aging process described in ref 1. From the comparison of our HREELS and XPS results on aged and water-covered MgO layers, we can, however, rule out water as the main cause of the process.

2. Experimental Section

The experiments were carried out in an ultrahigh vacuum (UHV) apparatus equipped with HREEL (Specs) and X-rays photoemission (Omicron) spectrometers, with a Knudsen cell for in situ epitaxial film growth, a quartz microbalance for Mg flux measurements, and all other typical vacuum facilities. The substrate is an Ag single-crystal cut within 0.1° from the (100) plane, which is carefully cleaned by sputtering and annealing to 720 K before each experiment. Several cycles are repeated until no loss features are detected in the HREEL spectra and an ordered low-energy electron diffraction (LEED) pattern is observed.

MgO films are grown by reactive deposition at a crystal temperature $T = 453$ K. O_2 is dosed through a shower placed 1.5 cm from the surface in order to have a high local pressure at the sample while the chamber pressure is kept below 3×10^{-8} mbar, thus reducing the contamination level. The film thickness is evaluated by calibration of the Mg flux through the quartz microbalance and by the analysis of the FK mode frequencies and intensities; it is affected by an error of ±8%. LEED inspection is employed to check the film order after evaporation. Bidistilled water is dosed through a dedicated gas line, which is carefully pumped before each exposure.

HREEL spectra are recorded in-specular, with a primary electron energy $E_e = 4.0$ eV, unless otherwise stated, and an angle of incidence of 60°. The typical resolution achieved in the experiments is 32 cm^{-1} (∼4.0 meV). The energy loss frequencies are determined with a precision of ±4 cm^{-1} (∼0.5 meV), while the intensities, normalized to the corresponding elastic peak, are estimated within 10%. Photoemission spectra are recorded using a conventional Al Kα X-ray source. The photons impinge on the surface at 54°, while electrons are collected close to the surface normal. The binding energies of the XPS peaks, E_B, are calibrated by fixing the Ag3d$_{5/2}$ line at 368.2 eV, in accord with the literature.[24] The O1s level of MgO is found at $E_B = 530.5$ eV (see Figure 1); we note that such a value is slightly higher than the one reported in ref 1, although the calibration procedure is the same.

3. Data Presentation

3.1. Room-Temperature Experiments. Figure 1 reports XPS spectra of the O1s, Mg1s, and Ag3d regions recorded during water adsorption experiments at $T = 310$ K. The left column refers to 2.7 ML and the right one to 0.5 ML of MgO. The clean films (dotted curves) are characterized by binding energies of the O and Mg ions E_B(O1s) = 530.5 eV and E_B(Mg1s) = 1304.2 eV for the 2.7 ML thick film and E_B(O1s) = 530.5 eV and E_B(Mg1s) = 1304.5 eV for the 1 ML film. The small shift of the Mg1s level with thickness has already been reported by Altieri et al.[4] At variance with the cited paper, we do not observe any corresponding variation in E_B(O1s). The discrepancy is currently under investigation; we underline, however, that such shift is quite unexpected since, to the best of our knowledge, it has never been detected on other oxide films. We further note that the intensity of the peaks does not scale exactly with the thickness, as the lowest MgO layers in the 2.7 ML film are partially screened.

Upon water exposure only the O1s region is strongly modified: an additional feature grows at E_B higher than the main peak while the latter shifts slightly toward lower energies. Its intensity remains unaltered for the 2.7 ML film and decreases slightly for the 0.5 ML film. Such behavior indicates that (i) additional oxygen is now present on the film and (ii) the O ions of the MgO lattice are not perturbed by the presence of the adsorbate. The Mg1s peak is initially unaffected by water adsorption, and only after 20 L of exposure a small downshift is observed. The Ag3d bands, on the contrary, are not modified even after the largest H_2O dose.

The insets of panels A and B show the O1s difference spectra between the water-covered and the clean MgO films. We note that, after 20 L of H_2O, the additional O1s peak is centered at E_B(O1s) = 532.8 eV and at E_B(O1s) = 532.6 eV for the 2.7 ML and for the 0.5 ML film, respectively. Moreover, the intensity of the additional peak is almost three times larger in the latter case. Since our control experiments on clean Ag(100) (not shown) indicate that such a surface is totally inert with respect to water exposure at room temperature, the satellite signal of panel B must originate only from the MgO islands, which cover half of the area tested by the analyzer.[8] We can therefore deduce that the signal for 1 ML of MgO would be ∼5.5 times larger than for the 2.7 ML film. Since water molecules are detected always with the same efficiency, this difference is indicative that the final coverage of the adsorbate is 5−6 times larger on 1 ML than on the multilayer films.

Although they give precious information on the reactivity of MgO films, the XPS spectra of Figure 1 do not allow us to understand the final adsorption state of water molecules. To clarify this point, we employed vibrational spectroscopy in our experiments. Figure 2A shows HREEL spectra recorded after dosing 20 L of H_2O on MgO films of different thickness at $T = 310$ K. The spectrum of the clean, 1 ML thick MgO film is shown in panel B for comparison. As already discussed in the Introduction, it is characterized by the presence of the FK, Wallis, and single-layer modes at 580 cm^{-1} (72 meV), 508 cm^{-1} (63 meV), and 423 cm^{-1} (53 meV), respectively, the frequency and intensity of which are thickness dependent.[10] We note that the region between 3200 and 4000 cm^{-1} (approximately from 400 to 500 meV), characteristic of OH stretch modes, is initially unstructured. Upon water exposure the MgO phonon intensity increases and the 423 cm^{-1} component, if present, is strongly reduced. This point will be discussed in greater details later on. More importantly, a peak grows at 3724 cm^{-1} (462 meV). Since no other water-related features are detected upon inspection of the whole region between 240 and 4000 cm^{-1} (∼30−500 meV, not shown[22]), we can safely assign such a peak to the OH-stretch frequency of dissociated water molecules.

Enhanced Reactivity at Metal–Oxide Interface

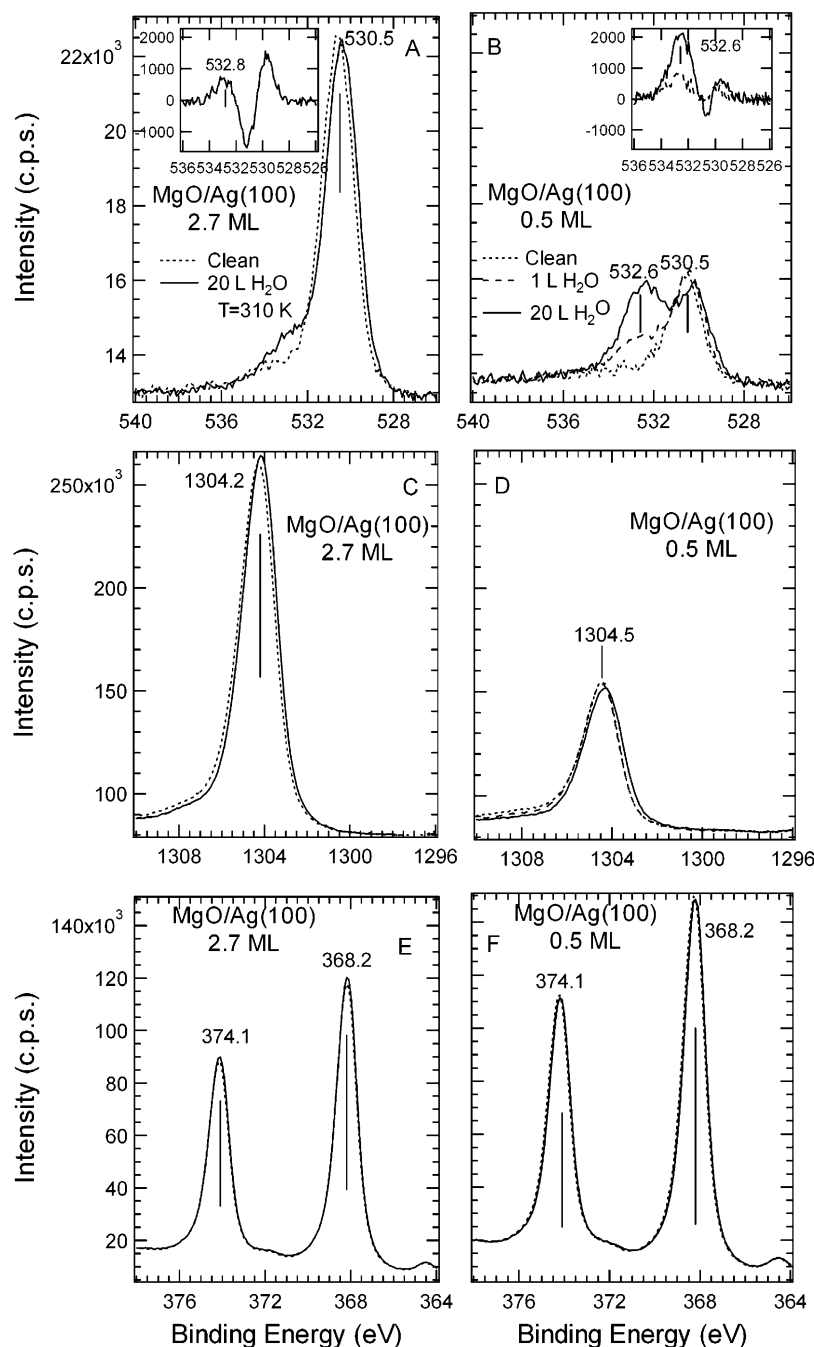*J. Phys. Chem. B, Vol. 108, No. 23, 2004* **7773**

Figure 1. XPS spectra of the O1s, Mg1s, and Ag3d regions relative to H_2O adsorption experiments performed at room temperature on MgO films of different thickness. Left column, 2.7 ML of MgO; right column, 0.5 ML of MgO. The insets of panels A and B report the difference spectra obtained by subtracting the corresponding clean film spectrum from the one recorded after adsorption. The higher reactivity of the 0.5 ML film is evident.

Therefore, our data clearly demonstrate that only dissociative adsorption occurs on MgO thin films at 310 K. The OH-stretch intensity (I_{OH}) depends strongly on MgO coverage, being much lower for the thicker films. Such behavior is more evident in panel C, where we plotted I_{OH} vs MgO film thickness (square symbols, left scale). The OH coverage deduced from the XPS experiments of Figure 1A,B (circles, right scale; see section 4 for the coverage calibration with XPS) is reported, too. We note that XPS signals are always proportional to the adsorbate coverage, while HREELS intensities may be affected by depolarization effects, which cause them not to scale linearly.[25] This is, however, not the case for the present system since (a) as evident from Figure 2C, the two techniques show a good accord once the OH-stretch intensity is calibrated with the XPS

signal of films of equal thickness and (b) the HREELS and XPS intensities for a short (1 L) and long (20 L) water exposure scale with the same ratio within experimental error. Therefore, we can safely assume I_{OH} to be proportional to the average adsorption probability and, as a consequence, to be indicative of the chemical reactivity of the films. As it is evident, the latter increases initially up to 1 ML and drops abruptly above 1.2 ML. As for the 0.5 ML film of Figure 1, we note that in the submonolayer regime only part of the substrate is covered by MgO, so only a fraction of the area tested by HREELS is reactive. If we normalized I_{OH} to a unit area, we would indeed find a nearly constant value up to 1 ML of MgO. HREELS data confirm therefore that the reactivity towards dissociative adsorption of water is enhanced by a factor of ~6 for the single
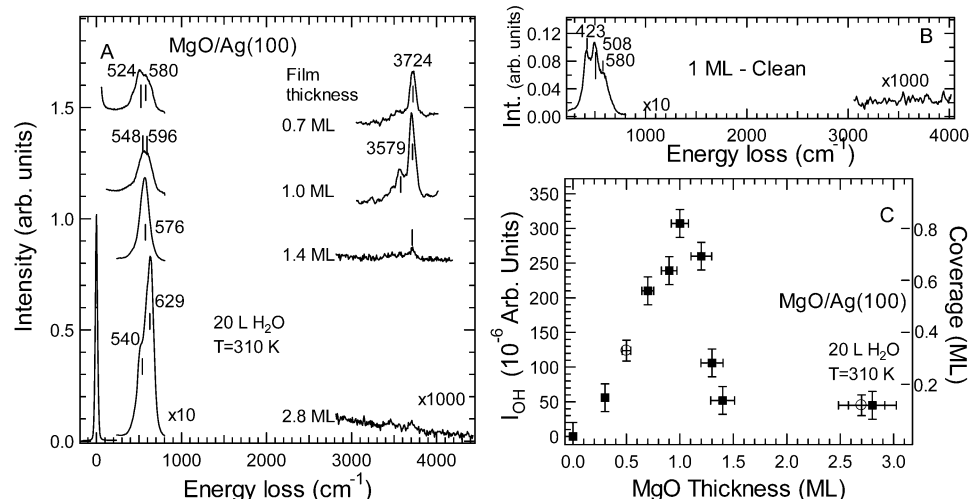
Figure 2. Panel A: HREEL spectra recorded after the exposure of MgO films of different thickness to 20 L of H_2O. The strong dependence of the OH-stretch intensity at 3724 cm^{-1} on film thickness is evident. Panel B: HREEL spectrum of the clean 1 ML thick MgO film, reported for comparison. The loss intensities are normalized to the corresponding elastic peak (not shown). Panel C: The left scale reports the intensity of the 3724 cm^{-1} peak vs film thickness (full squares) and the right one the corresponding OH coverages estimated from the XPS experiments of Figure 1 (open circles). The I_{OH} points represent an average value obtained from experiments performed on films of the same thickness. The reactivity increases between 0 and 1 ML, due to the increase of the MgO covered area, and drops abruptly above 1.2 ML.
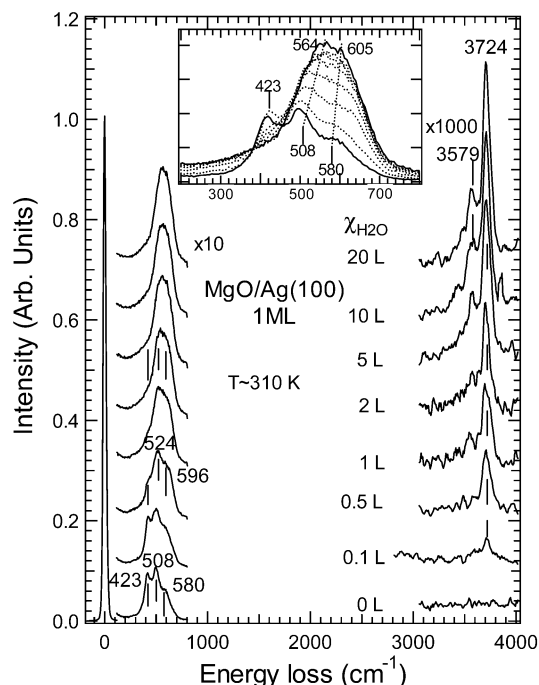

Figure 3. HREEL spectra recorded after subsequent H_2O doses on a 1 ML thick MgO film at $T = 310$ K. The peaks at 3724 and 3579 cm^{-1} correspond to the OH stretches of dissociated molecules. The inset reports an enlargement of the MgO surface phonons region to emphasize the modifications occurring to these vibrational modes upon water adsorption. The continuous lines correspond to the first and to the last spectrum of the sequence.

layer with respect to multilayer films. This is our major result and will be discussed in more detail in the following.

Let us now focus attention on the highly reactive single layer films. Figure 3 shows HREEL spectra recorded during subsequent water exposures on 1 ML of MgO at $T = 310$ K. The clean film (lowest spectrum) is the one already discussed in Figure 2B. Upon dosing 0.1 L of H_2O, a peak grows at 3724 cm^{-1}. Its intensity increases with further exposure, while a minor peak appears at 3579 cm^{-1}. The frequency of the latter mode varies for different films between 3579 and 3619 cm^{-1} (444– 449 meV). Both the 3724 and 3579 cm^{-1} features correspond

to OH stretches of dissociated water. The alternative hypothesis that a strongly bound water moiety is stable on the film at room temperature, as already observed for other oxide species,[26] is ruled out. In fact other vibrational modes, in particular the scissor mode around 1612 cm^{-1} (200 meV), would be expected in HREEL spectra, contrary to experimental evidence.[22] At least two different adsorption sites must be present to justify the two stretch modes. Previous infrared measurements of hydroxylated MgO powders[27] report OH-stretch frequencies in perfect agreement with those of Figure 3. According to this paper, we identify the high-/low-frequency stretch with OH groups bonded at defect/terrace sites, respectively. Such assignment also fits well with the later appearance of the 3579 cm^{-1} feature and with its absence on less reactive films. We stress, however, that our experimental means do not allow us to understand if only one or more kinds of defects are active toward OH adsorption.

Also, the shape and intensity of the MgO surface phonons are affected by water adsorption. To highlight the details, we report an enlarged picture of the phonon region in the inset of Figure 3. An evolution of the loss features is evident: the 423 cm^{-1} peak soon disappears, while the other vibrational modes increase in intensity and shift toward higher energies. It is well-established that MgO surface phonons are related to the structure of the film.[10] Their modification as a function of water adsorption suggests, therefore, that this last parameter is somehow affected. The disappearance of the 423 cm^{-1} structure might be indicative that border atoms are directly involved in the adsorption process; on the contrary, one tentative explanation for the increased intensity and for the upshift of the FK and Wallis modes might be that the MgO film reorganizes into thicker islands upon water adsorption. A more thorough investigation employing microscopic techniques is however needed to confirm this hypothesis. Finally, we underline that the MgO surface phonons do not recover their original shape after OH desorption (see Figure 4), indicating that the structural modification is not reversible, in agreement with what is reported in the literature for large H_2O doses on MgO(100) surfaces.[15]

Figure 4 shows the behavior of an OH-covered MgO film upon annealing the sample. The surface was prepared by exposing a 0.7 ML thick film at 310 K (bottom spectrum) to 20 L of H_2O. An intense OH-stretch signal appears therefore

Enhanced Reactivity at Metal−Oxide Interface

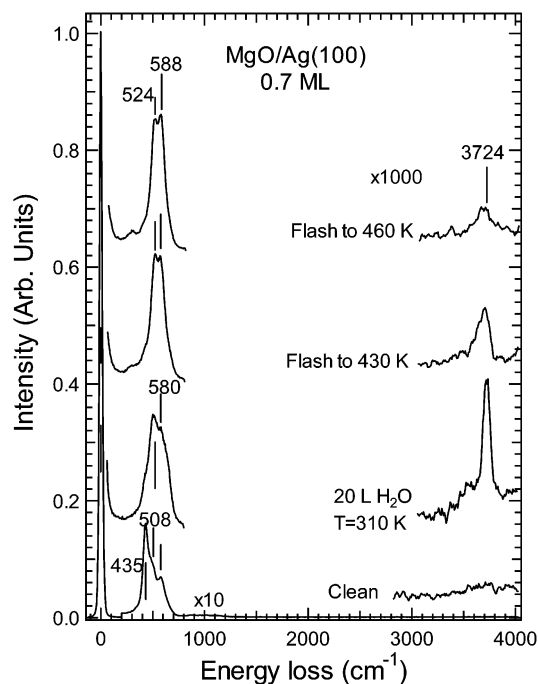*J. Phys. Chem. B, Vol. 108, No. 23, 2004* **7775**

Figure 4. HREEL spectra showing the behavior vs T of an OH layer adsorbed on a 0.7 ML thick MgO film at 310 K. At 460 K the OH-stretch intensity has already reduced by more than a factor of 5, indicating the low desorption temperature of this moiety.
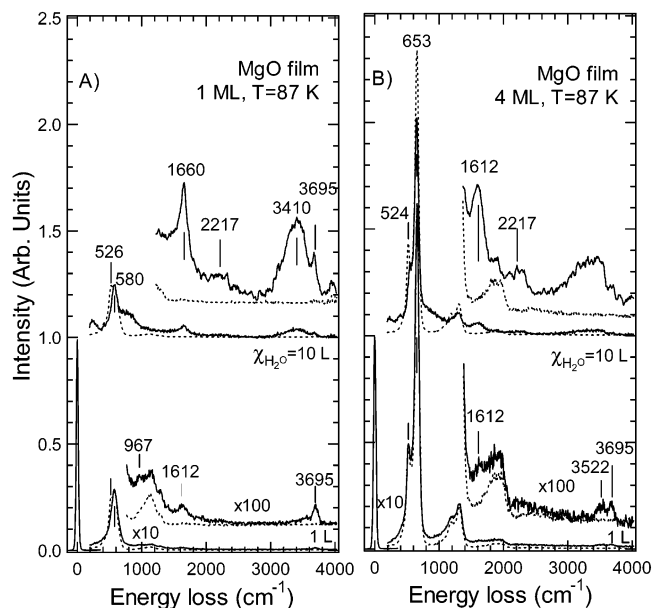

Figure 5. Water adsorption experiments performed at $T = 87$ K on MgO films of different thickness and monitored by HREELS. Panel A, 1 ML MgO; panel B, 4 ML MgO. The dashed curves refer to clean films, the continuous ones to the H_2O-covered surfaces. The presence of both dissociated and nondissociated water molecules is evident from the analysis of the vibrational frequencies.
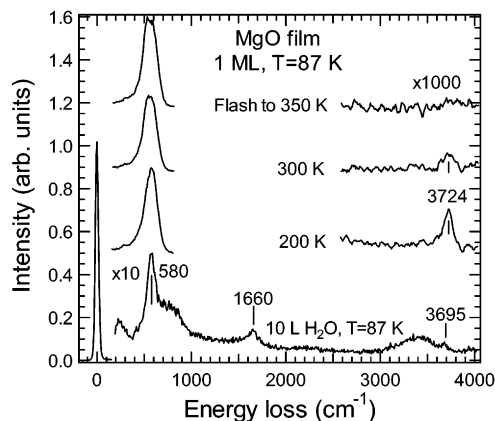
in the HREEL spectra (second spectrum from the bottom), the intensity of which decreases when annealing to 430 K and reduces to less than one-fifth at $T = 460$ K. Peng et al.[13] reported a temperature range between 400 and 610 K for the disappearance of the OH signal from flat and sputtered MgO(100) surfaces exposed to H_2O at 300 K and found that the desorption temperature is higher for the defective surface. Coherently, MgO powders undergo significant dehydroxylation only above 673 K.[28] Our result is therefore in agreement with previous data on MgO monocrystals, while the discrepancy with disordered samples is not surprising and can be ascribed to the different structure and concentration of defects in the two cases.

3.2. Low-Temperature Experiments. Figure 5 reports the HREEL spectra recorded during water adsorption experiments performed on 1 and 4 ML thick MgO films at $T = 87$ K (panels A and B, respectively). For the thinner film, the intensity in the MgO phonons region was strongly enhanced upon water adsorption. The corresponding spectra were therefore renormalized to the intensity of the FK peak of the clean film to allow for an easier comparison. Upon 1 L of exposure, we observe on both films the formation of a broad feature at 1612 cm^{-1} (200 meV), indicative of nondissociative water adsorption, and the presence of OH stretches at 3522 and 3695 cm^{-1} (437 and 458 meV), of comparable intensity in the 4 ML case. When dosing 10 L of H_2O the 1612 cm^{-1} loss grows in intensity, shifting to 1660 cm^{-1} (206 meV) for the 1 ML film, and a weak feature appears around 2217 cm^{-1} (275 meV). In the OH-stretch region a broad structure develops between 3200 and 3600 cm^{-1} (∼400−450 meV), so the previous 3695 cm^{-1} peak is now hardly resolved. The identification of the vibrational modes detected upon water adsorption both on oxide or metallic substrates has been largely debated in the literature, as witnessed by the vast production on the subject.[18,29−31] In particular, the assignment of the losses in the OH-stretch region to the dissociated or undissociated species has been controversial.[29,30,32] Comparing our spectra with the frequencies predicted by theory for MgO(100)[18] and observed for MgO thick films,[31] we identify

Figure 6. Annealing of the water-covered MgO film of Figure 5A. The surface was prepared exposing a 1 ML thick MgO film at $T = 87$ K to 10 L of H_2O. The surface was then annealed to different temperatures and cooled to 87 K again before recording the spectrum. Contrary to room temperature experiments, total desorption occurs already at 350 K.

the 1612 cm^{-1} loss with the H_2O scissor mode. The assignment of the feature around 2217 cm^{-1} is less straightforward, since it was not reported previously. The observed frequency is both compatible with the CO_2 stretch and close to the value predicted for the OH-surface stretch of hydroxyl groups of undissociated molecules hydrogen-bonded to the film O ions.[18] The former hypothesis is improbable because, if CO_2 adsorption from the residual gas were important, we would expect it to occur also for the clean MgO film at 87 K. The OH stretch at 3410 cm^{-1} (423 meV) is also ascribed to undissociated water molecules.[23,30] The losses at 3522 and 3724 cm^{-1} are more problematic, since these frequencies fit for H_2O as well as for OH.[29,30,32] From comparison of the spectra recorded after 1 and 10 L of exposure it is evident that the 3724 cm^{-1} loss is dominant in the initial stages of the adsorption process. Such behavior is compatible either with the assignment to hydroxyls at defect sites or to OH stretches of isolated water molecules, but no clean conclu-
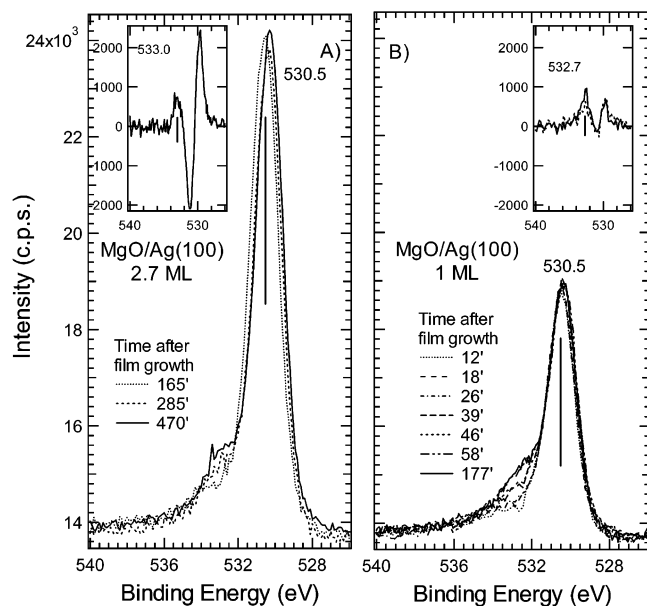
Figure 7. XPS spectra of the O1s region, showing the temporal evolution of MgO films at room temperature. Panel A, 2.7 ML thick film; panel B, 1 ML of MgO. The insets report the corresponding difference spectra between the aged and the freshly grown surface. In both cases the growth of a satellite at higher energy than the main peak is evident.

sion can be drawn with our experimental means. We note, however, that the presence of both the dissociated and the undissociated moieties on ultrathin MgO fims at low T would be in accord with what is reported for thicker layers.[21,23]

Figure 6 shows the effect of annealing the water layer of the experiment in Figure 5A, produced by dosing 10 L of H_2O on a 1 ML thick MgO film at $T = 87$ K. Already at 200 K the spectrum has changed: the structure around 3400 cm^{-1} has disappeared and the 3695 cm^{-1} peak has grown and shifted to 3724 cm^{-1}. We interpret this finding as desorption and/or dissociation of water molecules, in accord with a previous study on D_2O/MgO/Mo(100), which reported desorption of the ice multilayer below 200 K.[33] The spectrum is now very similar to

those recorded after water exposure at room temperature. Indeed, an upshift of the OH-stretch frequency upon water desorption was already reported for 30 ML thick MgO films on Mo(100).[31] At 350 K no more intensity is detected in the HREEL spectra in the OH-stretch region, indicating that complete desorption has occurred. The shape of the FK^+ mode modifies with decreasing OH coverage, but it does not recover the shape typical of the clean surface even after complete removal of the adsorbate. We notice that the desorption temperature is lower than the value of 430 K measured in room-temperature experiments, and also the residual OH-stretch intensity at 300 K is significantly weaker. On the contrary, its value agrees with the desorption peak at 260 K observed for D_2O adsorption on MgO thick films and assigned to the first layer of chemisorbed molecules.[33] We can therefore deduce that (a) hydroxyl production via thermal dissociation of a water layer dosed at low T is a mechanism less efficient than water exposure at room temperature and (b) in the competition between desorption and thermal dissociation of water molecules adsorbed at low T, the former process is favored.

3.3. Aging of Clean MgO Films. Aging phenomena on ultrathin MgO films at room temperature were observed in XPS experiments by Altieri et al.[1] According to the cited paper, the effect (a) consists of the growth with time of a satellite peak at a binding energy 2.3 eV higher than the one of the main O1s peak and close to the one of our OH signal, (b) is much more evident for 1 ML thick films than for multilayers, (c) is clearly detectable already 60 min after the film growth, and (d) saturates in a few hours. Water adsorption from the background was suggested to be the main cause of this process, but no controlled water exposure was ever performed on those films to verify the hypothesis.

We have attacked the matter with the combined HREELS and XPS approach, to check the presence of reactants (in particular water or OH) on the aged film. Figure 7 reports XPS spectra of the O1s region following the temporal evolution at room temperature of MgO films of 2.7 ML (panel A) and 1 ML (panel B) thickness. Difference spectra between the "aged" and the "freshly grown" film are shown in the insets. We note
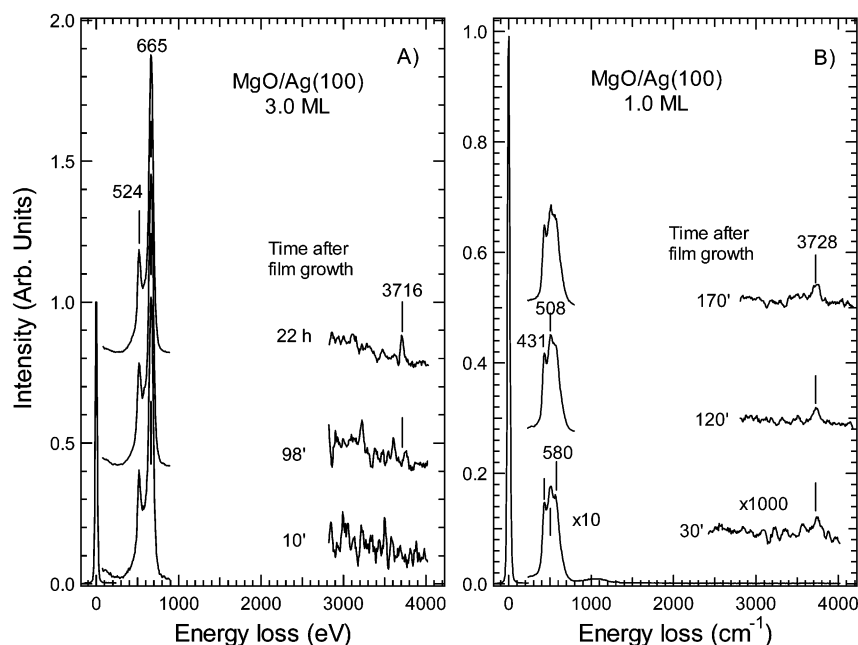

Figure 8. HREEL spectra showing the temporal evolution of two MgO films. Panel A, 3 ML of MgO; panel B, 1 ML. No significant increase of the OH-stretch signal is detected with time. The spectra of panel A are recorded with a primary electron energy $E_e = 3.0$ eV.

Enhanced Reactivity at Metal−Oxide Interface

J. Phys. Chem. B, Vol. 108, No. 23, 2004 **7777**

that a satellite peak forms with time at a binding energy $E_B = 533.0$ eV for the multilayer and $E_B = 532.7$ eV for the 1 ML film. As for water adsorption experiments (see Figure 1), no significant reduction of the main peak intensity is observed, indicating that some additional oxygen is accumulating at the film. The aging process is slightly more efficient for the single layer, although the satellite peak remains less intense than the one in ref 1. Our XPS data confirm therefore the existence of an aging process of the MgO film, in qualitative accord with ref 1. The result of the corresponding HREELS experiment is shown in Figure 8 for a 3 ML and a 1 ML thick MgO film (panels A and B, respectively). On the 3 ML film, no OH signal is detected within a few hours from evaporation and a small intensity at 3716 cm^{-1} (461 meV) is present only 22 h later. For the 1 ML film, on the contrary, a very small signal is detected at 3728 cm^{-1} already 30 min after the film growth. From comparison with the uptake experiment of Figure 3, we deduce that it must correspond to a H_2O exposure of less than 0.1 L. Its intensity does not change significantly with time and such behavior is at variance with respect to the XPS result, which shows an increase of the satellite intensity by nearly a factor of 2 between the spectra recorded after 46 and 177 minutes. Moreover, the MgO surface phonon intensity, which has been proved to be very sensitive to water adsorption, remains unchanged with time. The small OH-stretch intensity of the 1 ML film is thus most probably due to some water contamination during the evaporation process and is not related to temporal evolution. Moreover, we note that the ratio between the HREELS intensity of the OH loss and the XPS intensity of the satellite peak is significantly lower than in the water adsorption experiments.

Therefore, the overall information strongly suggests that the aging effect observed by XPS is not a water-induced process. A possible alternative explanation might involve oxygen accumulation in Ag(100) subsurface sites either through segregation from the bulk or incorporation from the gas phase. Indeed, it has been recently shown by theory that the latter process has an energy barrier lower than expected, being mediated by the substitution of an O atom provided from the gas phase to one of the MgO lattice, which undergoes subsurface migration.[34] Finally, we want to point out that the measurements reported in Figure 1 are not affected by the aging process described above, since water exposure was performed within a few minutes after evaporation, i.e., immediately after recording the XPS spectrum of the clean film.

4. Discussion

Our data clearly show that only hydroxyls are present on ultrathin MgO films at 310 K, the coverage of which can be roughly estimated from XPS spectra. We first note that (1) by comparing the O1s satellite peaks grown upon water adsorption with the main peak of the clean, 0.5 ML thick, MgO film (dotted spectrum in Figure 1B), whose intensity is not affected by screening effects, we deduce that an oxygen coverage of 0.5 ML corresponds to an intensity-to-background ratio of 0.23. (2) Since the intensity of the main line decreases little upon adsorption, the satellite intensity has to be due only to OH groups bonded at Mg atoms, while O ions of the film are very little affected by the presence of the adsorbate. From these starting points we can estimate for the 0.5 ML film of Figure 1B an amount of extra oxygen of 0.13 ML (0.33 ML) after 1 L (20 L) of exposure, corresponding to an OH−Mg coverage of 0.26 ML (0.66 ML) and as many H atoms bond at substrate O ions. The same procedure applied to the satellite peak of Figure 1A yields an OH−Mg coverage of 0.12 ML upon dosing 20 L

of H_2O on the 2.7 ML MgO film. Once the OH coverage is known, the initial and average adsorption probability can be estimated as the ratio between the coverage and the H_2O dose for the shortest (1 L) and for the largest (20 L) exposure, respectively. We find an initial (average) sticking coefficient of ∼0.6 (∼0.08) for the submonolayer MgO film and an average adsorption probability lower than 0.02 for the 2.7 ML film.

The high initial sticking observed for the submonolayer film is indicative of the existence of a physisorbed precursor living long enough to allow water molecules to search for the active sites. The alternative hypothesis of a direct dissociation mechanism is indeed not convincing, since it does not explain the high saturation coverage achieved, unless we admit that the majority of sites in single layer films are defective. This is, however, very improbable in view of the good LEED pattern of our films. In this frame we also note that the high coverage estimated from XPS spectra implies, on the contrary, saturation of the active defects and significant population of terraces. The latter ones are expected to be inert, even in the limit of monolayer film;[35] we suggest, therefore, that migration of OH groups from the active site for dissociation toward the terraces occurs. Despite that, the OH stretch detected by HREELS at 3579 cm^{-1} (and assigned to OH at terraces) is always much lower than the corresponding defect-related mode. Such observation suggests a tilted configuration of OH groups at terraces, which causes a partial screening of the dynamical dipole moment by the metallic substrate. A similar configuration has been reported also for OH groups on Fe(100).[36]

The combination of HREELS and XPS analysis clearly demonstrates an enhancement by approximately a factor of 6 of the water dissociation probability at room temperature for single layers with respect to multilayer MgO films. This is our major result. We can make several hypotheses to explain such an effect: (i) a larger defectivity of the film in the initial stages of its growth, (ii) the presence of a large number of less coordinated sites at the borders of MgO islands, and (iii) the influence of the Ag(100) substrate. The first hypothesis should be rejected because the defectivity at monolayer MgO islands is not 6 times larger than for the multilayers. Both hypotheses ii and iii, on the contrary, are partially true. In fact, MgO films of a few ML thickness are by far not perfect and are therefore rich in low coordination sites,[7,8] but the coordination number with other MgO unit cells is even lower for ions at the border of single MgO layers. The metal−oxide interface might indeed play a more active role, as recently demonstrated by Altieri et al.,[4] who found a reduction of Coulomb and charge-transfer energies for ultrathin MgO films on Ag(100). A possible picture is that the underlying metal contributes in activating the defect, e.g. by acting as a reservoir of electrons so that the MgO film can take advantage of additional charge transfer during the water dissociation process. We further note that the active sites must lie at the border of monolayer MgO islands to explain the drop in reactivity for films thicker than 1.2 ML, for which large parts of the MgO film still consist of a single layer.[8] Moreover, first-principle calculations[35] exclude that interface effects at perfect terraces can induce an increased reactivity. The final qualitative picture that we infer from the experimental data is therefore that dissociation occurs at the borders of monatomic MgO islands, mediated by the influence of the metallic substrate.

Since water dissociation on bulk MgO surfaces needs no charge transfer, giving rise to H^+ and OH^-, a different mechanism might be operative at the defects of the monolayer islands. Our data are however not sufficient to prove this hypothesis.

5. Conclusions

We have reported here on a combined HREELS and XPS study on the interaction of water with ultrathin MgO films. Our investigation demonstrates that molecular adsorption is dominant at low temperature, while only hydroxyls are stable on the surface at 310 K. Most importantly, an enhancement of the reactivity by a factor of 6 is observed, at room temperature, for the single MgO layer and the submonolayer. This result is consistent with the model of dissociation occurring at low coordinated sites at the borders of single-layer MgO islands and taking advantage of the influence of the metallic substrate. We believe this finding to be not only of general interest in the study of thin oxide films but also of great relevance for future technological applications of ultrathin layers.

Moreover, the temporal evolution of our films was studied comparatively by HREELS and XPS. The existence of an aging process was confirmed. Although its nature is not yet well-established, it was however possible to rule out water as the major cause of the phenomenon.

References and Notes

(1) Altieri, S.; Tjeng, L. H.; Sawatzky, G. A. *Phys. Rev. B* **2000**, *61*, 16948; *Thin Solid Films* **2001**, *400*, 9.

(2) Braginsky, A. I.; Gavaler, J. R.; Janocko, M. A.; Talvacchio, J. In *Superconducting Quantum Interference Devices and their Applications*; Walter de Gruyter: Berlin, 1985.

(3) Matulevich, Y. T.; et al. *Phys. Rev. Lett.* **2002**, *89*, 167601.

(4) Altieri, S.; et al. *Phys. Rev. B* **1999**, *59*, R2517.

(5) Freund, H. J.; Kuhlenbeck, H.; Staemmler, V. *Rep. Prog. Phys.* **1996**, *59*, 283.

(6) Wu, M. C.; Estrada, C. A.; Corneille, J. S.; Goodman, D. W. *J. Chem. Phys.* **1992**, *96*, 3892.

(7) Schintke, S.; et al. *Phys. Rev. Lett.* **2001**, *87*, 276801.

(8) Valeri, S.; et al. *Phys. Rev. B* **2002**, *65*, 245410.

(9) Thiry, P. A.; Ghijsen, J.; Sporken, R.; Pireaux, J. J.; Johnson, R. L.; Caudano, R. *Phys. Rev. B* **1989**, *39*, 3620.

(10) Savio, L.; Celasco, E.; Vattuone, L.; Rocca, M.; Senet, P. *Phys. Rev. B* **2003**, *67*, 075420.

(11) Henderson, M. A. *Surf. Sci. Rep.* **2002**, *46*, 1, and references therein (pages 125−126).

(12) Langel, W.; Parrinello, M. *J. Chem. Phys.* **1995**, *103*, 3240.

(13) Peng, X. D.; Barteau, M. A. *Surf. Sci.* **1990**, *233*, 283.

(14) Liu, P.; Kendelewicz, T.; Brown, G. E., Jr.; Parks, G. A. *Surf. Sci.* **1998**, *412/413*, 287.

(15) Abriou, D.; Jupille, J. *Surf. Sci. Lett.* **1999**, *430*, L527.

(16) Odelius, M. *Phys. Rev. Lett.* **1998**, *82*, 3919.

(17) Giordano, L.; Goniakovski, J.; Suzanne, J. *Phys. Rev. Lett.* **1998**, *81*, 1271.

(18) Delle Site, L.; Alavi, A.; Lynden-Bell, R. M. *J. Chem. Phys.* **2000**, *113*, 3344.

(19) Lynden-Bell, R. M.; Delle Site, L.; Alavi, A. *Surf. Sci.* **2002**, *496*, L1.

(20) Cho, J. H.; Park, J. M.; Kim, K. S. *Phys. Rev. B* **2000**, *62*, 9981.

(21) Kim, Y. D.; et al. *Chem. Phys. Lett.* **2002**, *352*, 318.

(22) Savio, L.; Celasco, E.; Vattuone, L.; Rocca, M. *J. Chem. Phys.* **2003**, *119*, 12053.

(23) Yu, Y.; Guo, Q.; Liu, S.; Wang, E. *Phys. Rev. B* **2003**, *68*, 115414.

(24) Citrin, P. H.; Wertheim, G. K.; Baer, Y. *Phys. Rev. B* **1983**, *27*, 3160.

(25) The use of HREELS intensities for quantitative analysis has been a largely debated point. In principle, HREELS intensities can indeed be affected by several external factors. Beside depolarization effects, already discussed in the text, further problems can originate, for example, from the changes in reflectivity due to the different surface conditions (temperature, adsorbate coverage and consequent work function changes, angle of incidence of the electron beam, etc.). We believe that for the quantitative analysis reported in Figure 2C all of these problems are negligible. The spectra were recorded at the same temperature and under identical geometrical conditions. Small differences are then corrected once by normalizing the loss intensities to the corresponding elastic peak. Moreover, no abrupt changes around $E_e = 4.0$ eV were observed in the reflectivity curve measured for a clean ultrathin MgO film, so we can safely assume that small adsorbate-induced variations in the work function do not affect our normalized loss intensities for more that the estimated error of 10%.

(26) Ghosal an, S.; Hemminger, J. C. *J. Phys. Chem. A* **1999**, *103*, 4777.

(27) Coluccia, S.; Marchese, L.; Lavagnino, S.; Anpo, M. *Spectrochim. Acta* **1987**, *43A*, 1573.

(28) Murphy, D. M.; et al. *J. Phys. Chem. B* **1999**, *103*, 1944.

(29) Bushby, S. J.; et al. *Surf. Sci. Lett.* **1993**, *298*, L181.

(30) Chen, J. G.; Basu, P.; Ng, L.; Yates, J. T., Jr. *Surf. Sci.* **1988**, *194*, 397.

(31) Wu, M. C.; Estrada, C. A.; Goodman, D. W. *Phys. Rev. Lett.* **1991**, *67*, 2910.

(32) Paul, J.; Hoffman, F. M. *J. Phys. Chem.* **1986**, *90*, 5321.

(33) Xu, C.; Goodman, D. W. *Chem. Phys. Lett.* **1997**, *265*, 341.

(34) Giordano, L.; Butti, G.; Montalenti, F.; Trioni, M. I. To be published.

(35) Sgroi, A.; Pisani, C.; Busso, M. *Thin Solid Films* **2001**, *400*, 64.

(36) Hung, W. H.; Schwartz, J.; Bernasek, S. L. *Surf. Sci.* **1991**, *248*, 332.