

The interaction of water with silica thin films grown on Mo(1 1 2)

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Abstract

The adsorption of water on ultrathin SiO₂ films at low temperatures has been studied with metastable impact electron spectroscopy (MIES) and ultraviolet photoelectron spectroscopy (UPS (HeI)). High-resolution electron energy-loss spectroscopy (HREELS), work function measurements ($\Delta\phi$), and temperature programmed desorption (TPD) were also utilized to study the interaction of water with silica. Evidence for molecular absorption of water on low- and high-defect silica surfaces is presented. The data are consistent with the growth of 3-D water clusters even at low coverage, i.e., the water–water hydrogen bonding is stronger than the water–silica interaction. No evidence for dissociation of water was found in contrast to previous UPS results.

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1. Introduction

Water is the most abundant compound in our environment, covers most solid surfaces, and

therefore is vitally important to disciplines from corrosion to geochemistry. Furthermore, water plays a key role in electrochemistry, catalysis and electronic devices. Therefore, a molecular-level understanding of the adsorption and reaction of water on solid surfaces is a goal of modern surface science [1,2]. An important general question is whether water adsorbs molecularly or whether it dissociates. Many studies during the last 25 years

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have addressed the adsorption and reaction of water on single crystalline metal surfaces. For Ru(0001) the adsorptive behavior of water is in dispute [3] even though this system has been extensively investigated [1,2].

The adsorption of water on metal oxide surfaces has also received considerable attention [1,2]. The investigation of oxide surfaces is more complex than metals since most metal oxides are not conducting and the preparation of well-defined surfaces is often problematic. Generally it has been assumed that water preferentially dissociates on defect sites of oxide surfaces [1]. For TiO_2 -(110)—the most extensively studied oxide surface—earlier studies report a small amount of water dissociation supporting the view that point defects are the active sites for water dissociation [4,5]. This view was recently strengthened by scanning tunneling microscopy (STM) and UPS experiments together with density functional theory (DFT) calculations [6,7]. For MgO (100), however, several theoretical studies recently have proposed that a mixed (water + hydroxyl) layer is energetically more stable than pure water layers [8–11]. To probe this important question, whether water partly dissociates on ideal oxide surfaces, additional studies are required on well-ordered oxide surfaces with very low-defect concentrations.

Because of its extensive technological importance numerous studies have been directed toward the study of silica (SiO_2). To a large extent these studies have focused on high-surface-area silicas such as powders or silica gels, although to a lesser extent some studies have addressed the initial film growth of amorphous SiO_2 on Si surfaces and on the SiO_2 /Si interface. However, only a few studies have used ultrahigh vacuum (UHV) methodologies to address the interaction of adsorbates with well-defined silica surfaces. The insulating properties of oxides limit the use of charged particle surface analytical probes because of sample charging. Such difficulties can be circumvented by using thin films grown on refractory metal substrates [12]—a methodology used successfully for a number of insulating metal oxides including MgO , TiO_2 and Al_2O_3 [13–15]. Silica films have been prepared, and although stoichiometric, these films were amorphous rather than single crystalline and thus less

than ideal. Only recently, well-ordered SiO_2 thin films with a thickness of 0.5–0.8 nm (one to two monolayers) have been successfully prepared on $\text{Mo}(112)$ [16,17]. Based on HREELS data, the ultrathin SiO_2 thin film can be characterized as a $\text{Mo}(112)\text{-c}(2 \times 2)\text{-}[\text{SiO}_4]$ monolayer where all four oxygen atoms bind directly to Mo substrate atoms [18]. Moreover, it has been shown with STM that ultrathin SiO_2 thin films grown on $\text{Mo}(112)$ are remarkable flat and homogeneous [19].

Previously, the adsorption state of water has been studied on amorphous films prepared by oxidation of $\text{Si}(100)$ and $\text{Si}(111)$ surfaces, respectively [20,21]. Using infrared reflection–adsorption spectroscopy (IRAS), Chabal and Christman found evidence for molecular physisorbed water at 80 K on $\text{Si}(100)$ covered with its native oxide [20]. In contrast, Nishijima et al., based on EELS measurements, proposed that water partially dissociates on a thin SiO_x layer over $\text{Si}(111)$ at 300 K [21]. Several theoretical studies have focused on the interaction of water with α -quartz [22,23] and with amorphous SiO_2 [24,25]. Thermodynamically the dissociation of water on α -quartz and on amorphous SiO_2 is favored. However, dissociation of water may be inhibited on SiO_2 since dehydrated silica (gel, powder or silica glass fracture surfaces) is not readily hydrolyzed when exposed to air or water [26–28]. It is known that the reactivity of silica surfaces strongly depends on the presence of hydroxyl (silanol [29]) groups [30–32]. Sneh and George, for instance, investigated the reactivity of 5 μm thick silica films as a function of hydroxyl coverage. It is noteworthy that in this study a H_2O plasma discharge was used to produce a hydroxylated SiO_2 surface [32]. To explain the hydrophobic or hydrophilic properties of vitreous silica surfaces, the role of defect sites has been addressed in several theoretical studies [25,33,34]. However, many questions remain regarding the interaction of water with silica surfaces.

In this paper we present MIES/UPS, HREELS, $\Delta\phi$, and TPD results addressing the interaction of water with ultrathin, SiO_2 surfaces in UHV. Evidence is provided for molecular adsorption of water on various SiO_2 thin films grown on $\text{Mo}(112)$. The data can be explained best by 3-D growth of water clusters even at low coverage.

Under the conditions used in these experiments no evidence for the dissociation of water is found. This conclusion conflicts with a previous report based on MIES/UPS data [35]. In Ref. [35] it was concluded that hydroxyl groups form at the silica/water interface in the presence of multilayer water. However, the results upon which this conclusion was reached are in error due to an artifact in the method used to separate the MIES–UPS data.

2. Experimental

The experiments were performed in two turbo-pumped UHV chambers. One chamber is equipped with Auger electron spectroscopy (AES), high-resolution electron energy-loss spectroscopy (HREELS, LK-2000), electron optics for low energy electron diffraction (LEED), and a quadrupole mass spectrometer (QMS) for temperature programmed desorption (TPD). The primary electron beam in the HREELS study was 4 eV and the angle of incidence 60° with respect to the surface normal of the sample. Under the chosen conditions the spectral resolution of the instrument was $64\text{--}96\text{ cm}^{-1}$ (8–12 meV). The second chamber is equipped with a cold-cathode gas discharge source producing both ultraviolet photons (He I: $E^* = 21.2\text{ eV}$) and metastable He 2^3S ($E^* = 19.8\text{ eV}$) atoms with thermal kinetic energy [36]. The axis of the cylindrical mirror analyzer (CMA) was perpendicular to the incoming photon/metastable beam. MIES and UPS spectra were acquired with photon/metastable beams incident at 48° with respect to the surface normal. The MIES/UPS spectra were measured simultaneously using a mechanical chopper (time-of-flight method) [36]. Auger spectra were acquired using an electron gun integral to the CMA. The resolution of the analyzer, estimated from the width of the Fermi edge, is $\approx 0.3\text{ eV}$. The work functions were estimated from the low-energy onset of the secondary electrons in the UPS spectra. This chamber was also equipped with LEED optics and TPD. The QMS was differentially pumped with an 8 mm aperture facing the sample at a distance of 1–2 mm.

For wide bandgap materials or metals with work functions lower than $\approx 3.5\text{ eV}$, Auger-deexcitation (AD) is the dominant mechanism by which

the MIES signal arises. In this case, a plot of the intensity of the ejected electrons versus their kinetic energies yields the surface density of states (SDOS) for the topmost layer of the surface [37]. In the spectra reported here, all binding energies are referenced to the Fermi level of the Mo substrate. A Mo(112) crystal, used as the substrate for the SiO_2 thin films, was spot-welded on an u-shaped tantalum wire allowing resistive heating. The temperature of the sample could be varied from 90 K (by cooling with liquid N_2) to 2200 K (by e-beam heating). The sample temperature was measured by a (W–5%Re/W–26%Re) thermocouple spot welded to the back side of the sample. The Mo(112) sample was cleaned by multiple flashes to 2100 K, and the cleanliness verified with AES. The clean Mo(112) surface showed a rectangular LEED pattern with intense spots and low background intensity.

The preparation of the SiO_2 thin films on Mo(112) was carried out as follows: (i) prior to Si deposition oxygen was dosed at $5 \times 10^{-8}\text{ Torr}$ with the Mo(112) substrate at 850 K for $\approx 10\text{ min}$. Following this procedure, a $p(2 \times 3)\text{O}$ surface was obtained [38]; (ii) after deposition of Si at room temperature, the surface was heated to 800 K in an oxygen atmosphere ($p = 1 \times 10^{-7}\text{ Torr}$); and (iii) the SiO_2 films were further annealed at the same oxygen pressure at 1050 and 1150–1200 K, respectively. The AES spectra of the SiO_2 thin films showed a Si^{4+} feature at 76 eV and no Si^0 feature at $\approx 90\text{ eV}$, indicating that the silicon surface was completely oxidized. Attenuation of the Mo MNN (187 eV) AES feature was used to compute the film thickness. Assuming a mean free path of 0.95 nm for 187 eV electrons in SiO_2 [39], the thickness of the SiO_2 thin films is estimated to be 0.5–0.7 nm for an anneal at 1050 K, and 0.3–0.5 nm for an anneal at 1150–1200 K. LEED showed a sharp $c(2 \times 2)$ structure, indicating the formation of well-ordered surface [16,18]. MIES and UPS spectra for low- and high-defect SiO_2 surfaces have been described previously [40]. Briefly, the low-defect SiO_2 surface produced by an anneal at 1150 K in oxygen shows in MIES two O(2p) features at 6–9 eV, and features at 10–12 eV related to the Si–O bond (lowest spectrum in Fig. 1A). In UPS, the O(2p) peaks of SiO_2 are evident at 6 and 8 eV

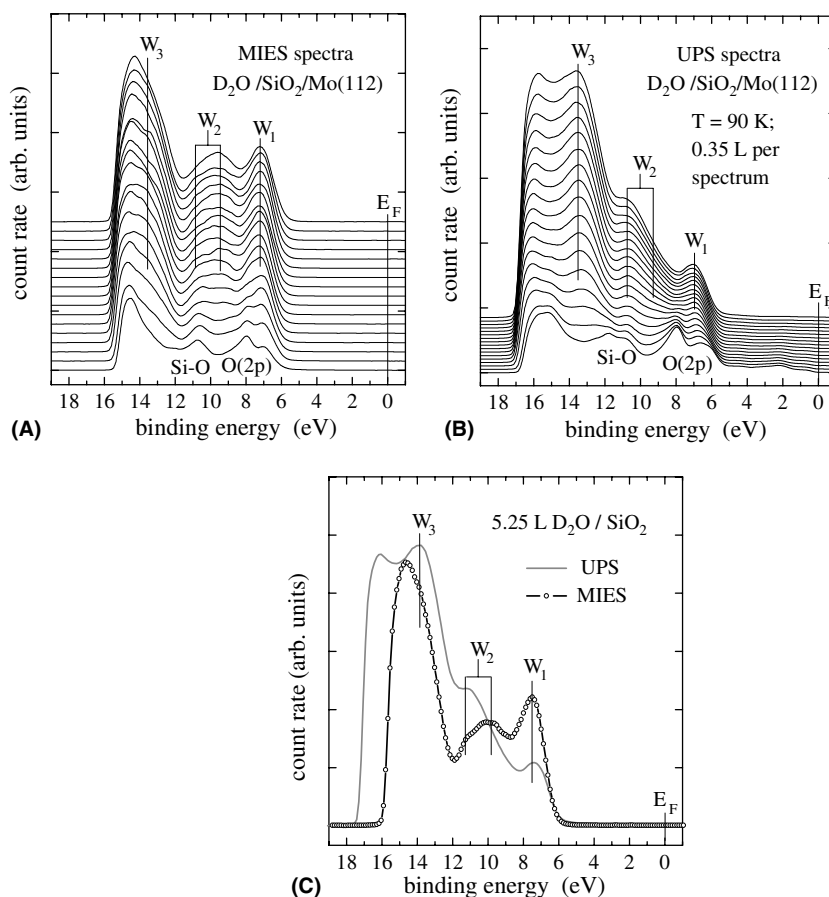


Fig. 1. (A) MIES spectra and (B) UPS (He I) spectra collected from a low-defect $\text{SiO}_2/\text{Mo}(112)$ surface as a function of water exposure at 90 K. The MIES and UPS spectra were acquired simultaneously. The shift toward higher binding energies as a function of water exposure (charging) has been removed from all spectra. Enlarged region of the UPS spectra near at the Fermi edge was used to estimate the degree of shifting. (C) Direct comparison of the MIES and UPS spectra after an exposure of 5.25 L water corresponding to multilayer coverage.

and the Si–O bonding states at 10–13 eV (lowest spectrum in Fig. 1B). Shapes of the MIES and UPS spectra are different for oxidized $\text{SiO}_2/\text{Mo}(112)$ surfaces which were annealed at only 1050 K. In this case, the O(2p) features at 6–9 eV in MIES and UPS are not resolved, consistent with a higher density of extended defects in comparison to the SiO_2 thin films which were annealed at 1150–1200 K [40,41]. The SiO_2 thin films have a low density of point defects regardless of the annealing temperature. Point defects should yield states in the bandgap region [15]. No such states were detected for the SiO_2 thin films used in this

study. Furthermore, no indication for the formation of any Mo silicide was found under the conditions used to synthesize the SiO_2 thin films on $\text{Mo}(112)$.

3. Water adsorption and desorption experiments on various SiO_2 surfaces

3.1. Low-defect SiO_2 surfaces

Fig. 1A shows MIES spectra collected as a function of water exposure to a low-defect $\text{SiO}_2/$

Mo(112) of 0.3–0.5 nm thickness at 90 K. The surface was exposed successively to 0.35 L water for each spectrum ($L = \text{Langmuir}$, with $1 L = 1 \times 10^{-6}$ Torr s). Upon water exposure, the substrate signal attenuates and concomitantly three new peaks appear, labeled as W_1 , W_2 and W_3 . In UPS (Fig. 1B) the same trend is evident, i.e. diminution of the substrate features (including Mo features between 0 and 5 eV) and appearance of three water-induced features. The positions of the features W_1 and W_3 in MIES and UPS are very similar, suggesting that these features have the same origin. In contrast, the W_2 feature with the highest intensity occurs at different energies in MIES and UPS. A direct comparison of the MIES and UPS is shown in Fig. 1C acquired after a 5.25 L water exposure. At this exposure the three water-induced features are fully developed (Fig. 2). In MIES a broad W_2 feature is visible at 9.6 eV, and a shoulder at 11.3 eV is discernible. The shoulder in MIES roughly coincides with the maximum of W_2 in UPS. Nevertheless, the MIES spectrum in Fig. 1C resembles the gas-phase photoemission spectrum of molecular water [42], allowing identification of the characteristic features W_1 , W_2 and W_3 . The W_1 feature at 7.25 eV is due to deexcitation of the $1b_1$ lone pair molecular orbital (MO). The W_2 feature at 9.6 eV is due to deexcitation

of the $3a_1$ MO (partly bonding and partly non-bonding (lone pair)), and the W_3 feature at ≈ 13.5 eV is due to deexcitation of the $1b_2$ MO (bonding orbital). The $3a_1/1b_1$ separation for the molecular species is 2.35 eV, very similar to the separation for gas-phase H_2O of 2.2 eV [42]. The MIES spectra in Fig. 1 are consistent with molecular adsorption of water on ultrathin, low-defect SiO_2 films on Mo(112).

In Fig. 2 the MIES intensities corresponding to the molecular orbitals $1b_1$, $3a_1$ and $1b_2$ are shown as a function of water exposure at 90 K. The silica surface is completely covered after a 3 L water exposure since the intensities of the $1b_1$ and $3a_1$ features are maximized at this exposure. Furthermore, no contributions are apparent from the silica substrate in MIES. That the $1b_2$ induced feature does not maximize is related to the increasing number of secondary electrons from the additional water adsorption. It is noteworthy that upon water exposure up to 10 L the $c(2 \times 2)$ LEED pattern of the $SiO_2/Mo(112)$ surface was still visible. No new water-induced LEED spots were evident, consistent with there being no long-range order in the water-covered $SiO_2/Mo(112)$ surface.

In Fig. 3 MIES and UPS difference spectra are shown for the data of Fig. 1. Prior to subtraction of the SiO_2 -spectrum from the D_2O/SiO_2 -spectrum, the SiO_2 -spectra were attenuated taking into account the D_2O -induced damping of the SiO_2 -features. In addition, the background due to secondary electrons was subtracted from the UPS spectra. Since the number of secondary electrons in MIES is substantially smaller than in UPS, a background subtraction was not performed for the MIES difference spectra. Therefore, there is a sharp feature due to the secondary electrons at 15 eV in the MIES spectra that is absent in the UPS difference spectra. In the MIES data, the positions of the water features are identical to those in the spectra of Fig. 1. On the other hand, in the UPS data the W_2 feature shifts from 9.4 eV at low water coverage to 10.4 eV at high coverage, whereas the W_1 and W_3 features are invariant. The shifting of the W_2 feature in the UPS difference spectra is not readily apparent in the UPS spectra of Fig. 1B. At low coverage (corresponding

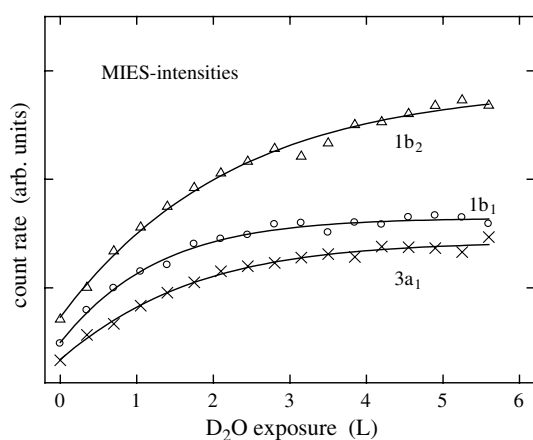


Fig. 2. Intensities of the water induced features in the MIES spectra from Fig. 1 as a function of water exposure. The orbitals of molecular water, which causes the features seen in MIES, are noted at the curves.

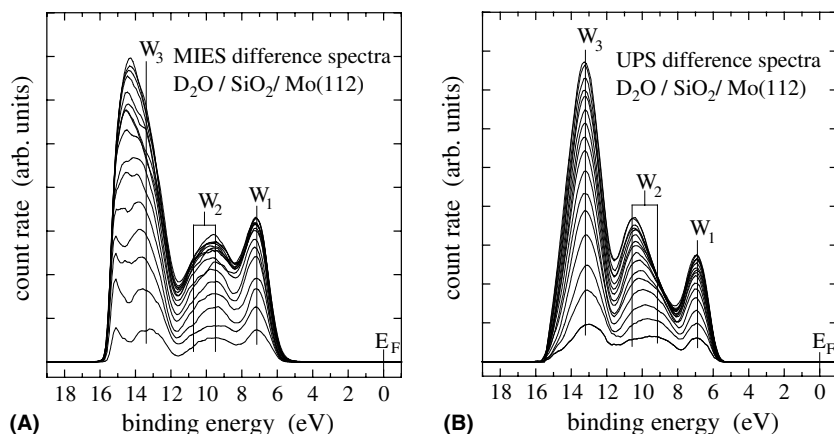


Fig. 3. (A) MIES difference spectra and (B) UPS difference spectra of the data shown in Fig. 1. Before subtracting the SiO₂-spectrum from the D₂O/SiO₂-spectrum, the SiO₂-spectrum was attenuated taking into account the D₂O-induced damping of the SiO₂-features. In addition, the background was subtracted from the UPS spectra using an exponential approach.

to a water exposure of 0.35 L) all water-induced features appear in the MIES and UPS difference spectra at very similar energy positions.

Fig. 4A shows water TPD spectra for a low-defect SiO₂ thin film after water adsorption at 90 K. For a water exposure of 0.1 L, a small peak at 160 K is evident. For a higher water exposure the maximum of the peak shifts to a higher temperature consistent with zero-order desorption kinetics. There is no discernible transition from the monolayer to the multilayer typically seen for

water on solid surfaces [1,2]. TPD therefore cannot be used for coverage determination. Even for higher temperatures than those shown in Fig. 5A, no additional features are evident. The activation energy for desorption was estimated using a simple exponential relation for the rate of desorption (Fig. 4B). The TPD trace corresponding to 5 L was used for the Arrhenius-plot in Fig. 4B. It is noteworthy that 63.9 ± 2 kJ/mol is higher than the heat of sublimation of D₂O-ice estimated to be as high as 44–50 kJ/mol [1,2].

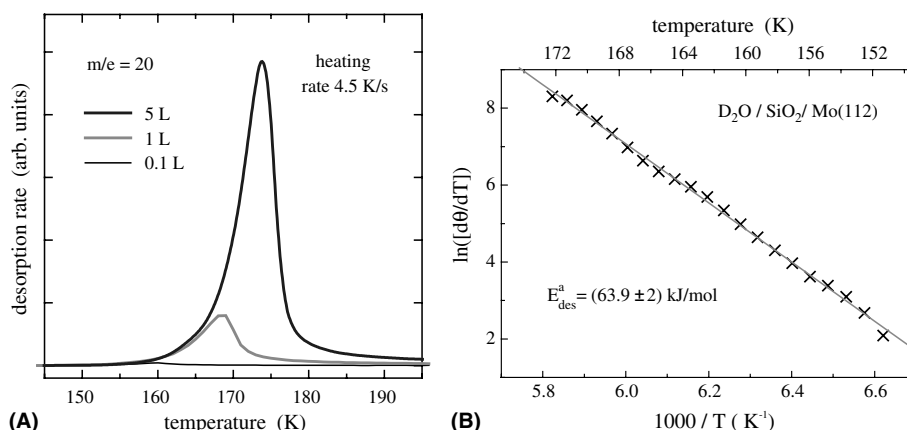


Fig. 4. (A) Water TPD spectra of a low-defect SiO₂/Mo(112) surface for 0.1, 1.0 and 5 L water exposure at 90 K. (B) Plot of the desorption rate (logarithmic) versus the reciprocal temperature for the TPD data taken after exposure of 5 L water. Such a water exposure corresponds to multilayers of water on SiO₂/Mo(112).

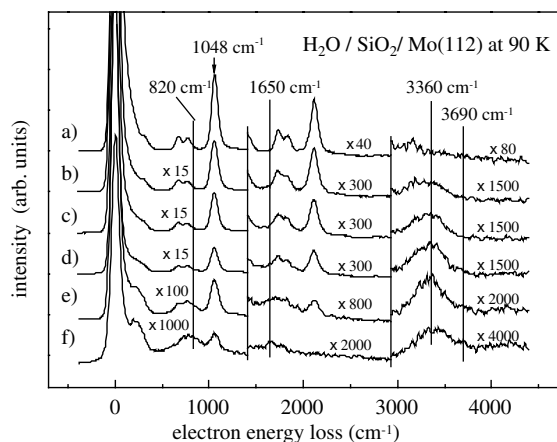


Fig. 5. HREELS spectra collected from a low-defect $\text{SiO}_2/\text{Mo}(112)$ surface as a function of water exposure at 90 K: (a) bare SiO_2 surface, (b) after exposing to 0.5 L, (c) 1.0 L, (d) 2.0 L, (e) 5.0 L and (f) 10 L H_2O . The sensitivity of the ion gauge in the HREELS chamber is comparable to that in the UHV chamber in which the MIES/UPS measurements were performed.

In Fig. 5 HREELS spectra are shown collected as a function of water exposure at 90 K on a low-defect SiO_2 film of 0.3–0.5 nm thickness. Spectrum (a) is that from the bare $\text{SiO}_2/\text{Mo}(112)$ surface and has been discussed previously [18]. The spectrum is dominated by a loss at 1048 cm^{-1} , assigned to the asymmetric Si–O stretch mode. Further losses appear at 2112 cm^{-1} (overtone of the asymmetric Si–O stretch mode) as well as doublets at $630\text{--}830$ and $1680\text{--}1870\text{ cm}^{-1}$. Comparing this spectrum to that acquired for a $\text{SiO}_2(0001)$ single crystal [43], the loss at 1048 cm^{-1} is red-shifted by approximately 126 cm^{-1} . This shift has been explained by the dominance of Si–O–Mo linkages over Si–O–Si linkages in the one ML thin film [18]. Curves b, c, d, e and f are for exposures of 0.5, 1.0, 2.0, 5.0 and 10 L, respectively. With increasing water exposure the substrate losses attenuate and features at 3360 cm^{-1} appear (spectra b–f). For high water exposures the spectral intensity dramatically decreases—thus complicating the interpretation of the spectra. Nevertheless, for an exposure of 10 L H_2O (spectrum f) new features are evident at 3690, 1650, and at 820 cm^{-1} . These losses are assigned to condensed water considering previous HREELS

data for various substrates (see for example Refs. [44–47]).

3.2. SiO_2 surfaces with extended defects

Because defect sites likely play a decisive role in the dissociation of water, MIES/UPS adsorption experiments were also performed on thicker silica films which exhibit broad O(2p) features in MIES and UPS at 6–9 and 5–9 eV, respectively (see the lowest spectrum in Fig. 7A and B). The broad O(2p) features are interpreted to be indicative of extended defects, e.g., steps, corners, etc. [40]. Broad O(2p) features are typical for amorphous silica films [41,48], consistent with the presence of extended defects. Recent STM and SPALEED results of Schroeder et al., describe the defect structure of the $\text{SiO}_2/\text{Mo}(112)$ surface as steps and antiphase domain boundaries [17]. These results are consistent with the interpretation of the MIES and UPS spectra, observed for SiO_2 films which were annealed at different temperatures [40]. In this respect it is noteworthy that the defect density is a strong function of the film thickness. Narrow O(2p) features indicative of a flat surface with a very low density of extended defects were only found for ultrathin SiO_2 films ($\approx 0.4\text{ nm}$), whereas broad O(2p) features, i.e. a high density of extended defects, were found for 0.6 nm thick and thicker SiO_2 films [41]. For a $\approx 0.6\text{ nm}$ thick SiO_2 film we performed the same adsorption experiment as for a low-defect SiO_2 film presented in Fig. 1. The data for water exposures up to 6 L at 90 K to a SiO_2 film with extended defects (not shown) are very similar to those for the low-defect SiO_2 thin film. Even at low water coverages only features originating from molecularly adsorbed water molecules are apparent. This is evident in Fig. 6A where the difference spectra for a water exposure of 0.35 L of the two films are shown. For an easier comparison of the spectra the background was subtracted from the UPS spectra. A substantially larger broadening of the $3a_1$ feature in comparison with the $1b_1$ and $1b_2$ features can be seen from the difference spectra. The lower intensity of the UPS difference spectrum of the film with extended defects (curve b) compared to the low-defect film (curve a) is due to the slightly different pressure

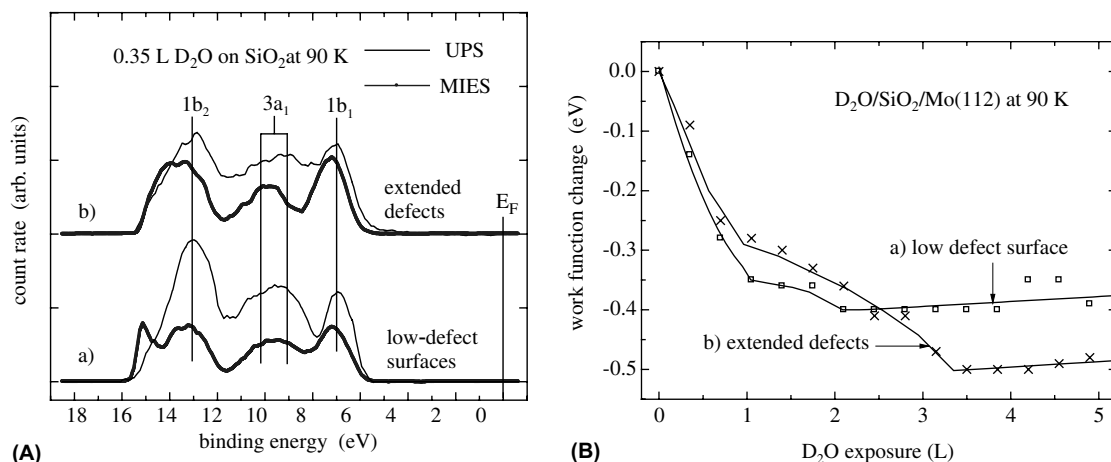


Fig. 6. (A) Initial water adsorption (0.35 L D₂O) at 90 K on two differently prepared SiO₂ thin films: (a) Low-defect SiO₂ film produced by deposition of Si at room temperature followed by a 1150 K anneal; (b) SiO₂ film prepared by annealing at 1050 K with a high density of extended defects at the surface. The MIES and UPS difference spectra are compared. The background was subtracted from the UPS spectra using an exponential approach. (B) Work function change $\Delta\phi$ upon water exposure at 90 K for the two differently prepared SiO₂ thin films on Mo(112): (a) Low-defect SiO₂ film and (b) SiO₂ film with extended defects.

conditions used in the cold-cathode He discharge source for these measurements.

The work function changes $\Delta\phi$ upon water adsorption on the different SiO₂ films are displayed in Fig. 6B. Curve (a) was extracted from the UPS

data set shown in Fig. 1B and curve (b) from the second UPS data set where a ≈ 0.6 nm thick SiO₂ film was used. For both SiO₂ thin films the work function change upon water adsorption is negative. For the low-defect, ultrathin SiO₂ film the

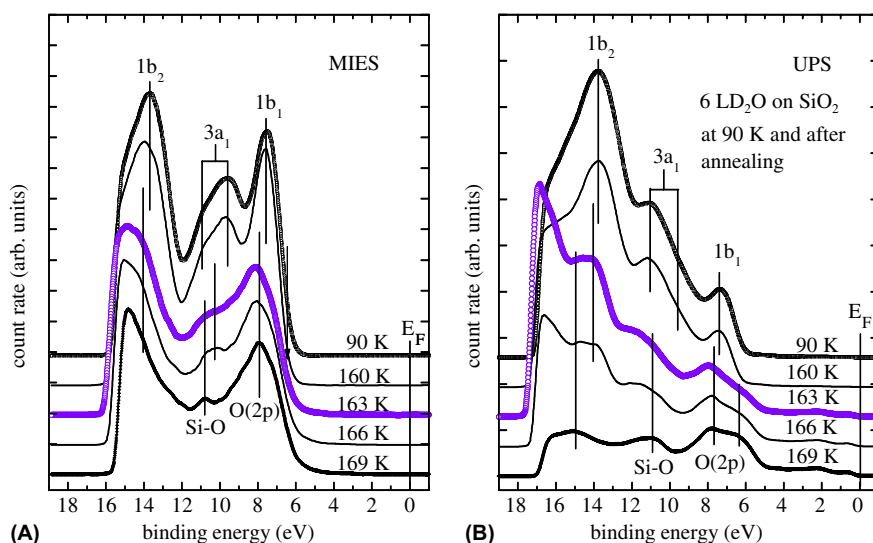


Fig. 7. (A) MIES spectra and (B) UPS spectra collected from a SiO₂/Mo(112) surface initially covered with 6 L water at 90 K as a function of the anneal temperature. The SiO₂ surface was prepared by annealing in oxygen at 1050 K and possesses a high density of extended defects.

work function decreases gradually then remains constant after ≈ 2 L exposure of water. The work function of a ≈ 0.6 nm thick SiO_2 film with a high density of extended defects decreases more slowly than that of a low-defect SiO_2 film. Furthermore, the work function remains constant only after a 3.5 L exposure of water. For a 0.6 nm thick SiO_2 film with a high density of extended defects, the work function change is 0.5 eV, approximately 0.1 eV greater than for water adsorption on a low-defect SiO_2 thin film.

Fig. 7 shows MIES (A) and UPS spectra (B) from a water-covered SiO_2 film with a high density of extended defects as a function of the annealing temperature. The upper spectra are those of the water-covered surface at 90 K after exposure of 6 L water. This exposure corresponds to multilayer of water evident when compared with Fig. 1C. After a brief anneal at 160 K, the spectra still resemble multilayer water. After a second brief anneal at 163 K, significant changes occur related to the onset of multilayer sublimation. Annealing to even higher temperatures indicated in Fig. 7, the spectra more resemble the MIES/UPS spectra of a bare SiO_2 film with a high density of extended defects. In each case all detected features in the spectra can be assigned to the electronic structure of molecular water or SiO_2 . Note that at the low energy edge of the MIES spectra, where the 1π feature of hydroxyl was apparent in the MIES spectra for water on other oxide surfaces [49,50] (see arrow), no feature is evident.

4. Discussion

First we focus on the results obtained with various techniques. Subsequently, we discuss our main conclusions with respect to previous work.

4.1. MIES and UPS data

We start our discussion with the MIES and UPS difference spectra for small coverages (Fig. 6A). The apparent features can be assigned to molecularly adsorbed water. However, since features in UPS and MIES are rather broad, and since additionally features of molecular water

and hydroxyl groups appear in the same energy range it is generally difficult to exclude water dissociation completely. Therefore, it is useful to estimate the upper limit of detectable hydroxyl groups using MIES and UPS. To estimate this limit we performed a 3 curve data-fit using Gauss curves to reproduce the MIES difference spectra of Fig. 6A in the range from 5 to 11.5 eV (Fig. 8). The three curves represent the broad $3a_1$, the $1b_1$ of molecular water, and the 1π orbital feature of the hydroxyl species. The 1π orbital feature typically appears at ≈ 1 eV lower binding energy than the $1b_1$ feature of molecular water, and the 3σ feature (not considered here because of the lack of intensity of the 1π feature) appears at ≈ 4 eV higher binding energy (see for comparison Refs. [1,2,49,50]). Hence, for a mixed (water + hydroxyl) layer a shoulder in the low-binding energy side of the $1b_1$ feature is expected. In the present case we did not detect such a shoulder even for the lowest water exposure. In spite of this fact, a small fraction of dissociated water molecules can be overlooked as one can see from Fig. 8. For the low-defect SiO_2 surface we estimate an upper limit of 9% of detectable hydroxyl groups using MIES. For the surface with extended defects the limit is only 3%. To estimate these values it was assumed that the FWHM of $1b_1$ feature is 1.3–1.4 eV and the (hypothetical) 1π feature is at 0.9 eV lower binding energy than the $1b_1$ feature. Furthermore it was assumed that the deexcitation cross sections of water and hydroxyl are comparable. For UPS the limits are likely similar. Our assumptions are conservative. This is especially true for the important assumption regarding the FWHM of the $1b_1$ feature.

Our result that there is no apparent feature in the MIES and UPS spectra that can be assigned to hydroxyl groups at the water/ SiO_2 interface is at variance to the results by Kim et al., where multilayer-induced dissociation of water on $\text{SiO}_2/\text{Mo}(112)$ at 90 K was reported [35]. Kim et al., reached this conclusion based on data that showed four, rather than three, features in the UPS spectrum following water adsorption [35]. The MIES data in Ref. [35] are in good agreement with the data presented here. The discrepancy in the UPS data of Ref. [35] is believed to be due to a

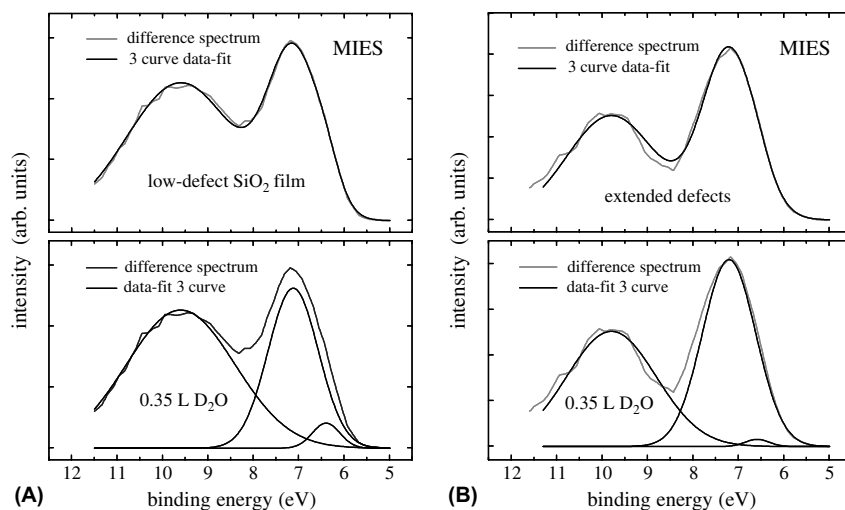


Fig. 8. (A) Data-fit to the MIES difference spectrum for initial water adsorption (0.35 L D₂O) at 90 K on low-defect SiO₂: single curves (lower panel), and 3 curve data-fit (upper panel). (B) Data-fit to the MIES difference spectrum for initial water adsorption (0.35 L D₂O) at 90 K on the SiO₂ surface possessing extended defects. In all panels the MIES difference spectrum (5–11.5 eV) is shown for comparison.

MIES contribution to the UPS spectra. One of the four features in the UPS data, located at identical kinetic energy as the 1b₁ feature in MIES, was assigned to correspond to the 1b₁ orbital of molecularly adsorbed water. The actual 1b₁ feature at a binding energy of ≈ 7 eV in the UPS spectra was erroneously assigned to the 1- π orbital of hydroxyl groups.

The substantially larger broadening of the 3a₁ feature in comparison with the 1b₁ and 1b₂ features (Figs. 1, 3 and 6A) is caused by hydrogen bonds between neighboring water molecules, i.e., clustering of water molecules [51,52]. The 3a₁ feature is more strongly influenced when forming a hydrogen network since hydrogen orbitals as well as the oxygen lone pairs contribute to the 3a₁ molecular orbital of water (partly bonding and partly non-bonding), whereas the 1b₁ orbital is purely non-bonding and the 1b₂ orbital is a purely bonding orbital [1]. For small coverages (Fig. 6A), the network of hydrogen-bonded water molecules on the low-defect silica surface (a) is more extensive than on the silica surface with extended defects (b). A possible explanation for this is the initial adsorption of water molecules along step sites whereby the forming of a hydrogen network is partly obstructed. Since the 0.6 nm thick SiO₂

film has more step sites than the 0.4 nm thin film, the shape of the difference spectra for relative low water exposures may be different for these two surfaces.

The shift of 3a₁ feature (W₂) in the UPS difference spectra as a function of exposure (Fig. 3B) is likewise consistent with the formation of hydrogen-bonded water clusters. It is noteworthy that the peak positions of the other features do not shift. The 3a₁ feature in the UPS (He I) begins to shift after the lowest water exposure of 0.35 L and continues to shift monotonically with further exposure. This finding indicates that clustering or multilayer growth occurs even at low coverages, and is consistent with facile diffusion of water on SiO₂/Mo(112) at 90 K. It is also noted that a shift of the 3a₁ feature in the UPS (He I) difference spectra as a function of water coverage has been found for other oxide surfaces [53].

The importance of hydrogen bonds for explaining the spectra is further confirmed considering the different energy positions of the 3a₁ feature (W₂) in MIES and UPS for water multilayers (Fig. 1C). The 3a₁ feature appears in UPS (He I) at ≈ 1 eV higher binding energy than in MIES. Similar peak positions were found in previous water adsorption studies that are summarized in Table 1. This indi-

Table 1
Energy positions of the three valence orbitals for water ice as observed with MIES and UPS

System	Technique	Molecular orbitals			Reference
		1b ₁	3a ₁	1b ₂	
D ₂ O/SiO ₂ /Mo(112)	MIES	7.25	9.6	13.5	This work
	UPS (He I)	7.05	10.5	13.5	
H ₂ O/TiO ₂ (110)	MIES	7.8	10.0	13.2	[49]
	UPS (He I)	7.9	11.2	13.5	
	UPS (He II)	7.8	9.8	13.2	
D ₂ O/MgO(100)	MIES	7.2	9.2	13.6	[50]
	UPS (He I)	7.0	10.0	13.6	

Binding energies are in eV with respect to the Fermi level. In all cases the sample temperature during water exposure was 90–100 K.

cates that the relative peak positions of the 3a₁ orbital in MIES and UPS (He I) are related to water multilayers in general regardless of the substrate. The different peak positions can be explained by considering the difference in surface sensitivities of MIES and UPS (He I) with respect to hydrogen bonding in water clusters (ice). As observed previously, the broad 3a₁ feature in UPS consists of at least two contributions [51]. Schmeisser et al. [51], explained a splitting of the 3a₁ orbital up to ≈2 eV using a model of flat lying linear water dimers in conjunction with calculations [54], taking into account hydrogen bonding. In the linear water dimers one water molecule acts as proton-donor and the other as proton acceptor. For multilayer water, i.e. ice, a broadening of the 3a₁ feature can be explained by the equivalence of the water molecules, i.e. the molecules act as proton-donors as well as acceptors [51]. Adapting this model for the data presented here, we conclude that the outermost surface of water multilayers, i.e. ice, act more as donors whereas the in bulk ice, the water molecules act as donors and acceptors. It is noteworthy that MIES probes exclusively the outermost surface [37] whereas UPS (He I) spectra contain contributions from the bulk. Donator-like properties of an ice surface means that the proton accepting oxygen ends of the water molecules are on the average directed into the bulk and are not visible by the MIES probe. In any case, the difference in the surface sensitivities of MIES and UPS (He I) is the key to understanding the various peak positions of the 3a₁ features. This conclusion is

supported by the UPS measurements of water multilayers at various photon energies carried out by Schmeisser et al. (Ref. [51], Fig. 4). Using photons of 21 eV (relatively less surface sensitive), the broad 3a₁ feature maximizes at relatively high binding energy. However, at photon energies >30 eV (more surface sensitive), maxima of the 3a₁ feature appear at lower binding energy values.

4.2. TPD data

The TPD data are consistent with molecular desorption from clustered water whereby the water–water hydrogen bonding is stronger than the water–surface interaction. Typical for molecular desorption from clustered water is pseudo-zeroth-order behavior in the monolayer range (Ref. [2], p. 39). Furthermore, no separation between TPD features stemming from monolayer and multilayer coverage ranges is evident, i.e., water desorption occur exclusively below 200 K. The latter is clearly the case for SiO₂/Mo(112), suggesting that this system is comparable with Ag [55], Au [56] and Cu [57,58] where such a behavior was previously observed. The similarity with these surfaces is also appropriate when comparing the activation energy of desorption. Hinch and Dubois observed for Cu(111) that dynamic adsorption/desorption of water at 155 K results in the formation of small metastable water islands at low coverages that coalesce into large crystalline clusters with increasing coverage [57,58]. The rate of desorption from the water islands at low

coverages was found to be noticeably greater than that from crystalline clusters at high coverages. A similar result was found for Ag addressing water desorption in the submonolayer range [59]. Considering these results we conclude that the interaction of water with SiO₂ thin films is indeed similar to that of water with Ag, Au and Cu. Furthermore, we speculate that 5 L D₂O in our system correspond to a coverage not significant higher than one monolayer in agreement with the data shown in Figs. 2 and 6B. We emphasize that water desorption was only found in the temperature range 160–180 K. However, it is known that hydroxyl groups (silanol groups) are strongly bound to silica surfaces [32] and hence should desorb (after recombination to water) at much higher temperatures than 160–180 K. Therefore, the TPD results support our conclusion that water adsorbs molecularly on SiO₂/Mo(112).

4.3. HREELS data

The SiO₂ thin film, which was used for the HREELS measurement, is comparable with the low-defect film in the other chamber where the MIES/UPS measurements were performed. In both cases the thickness was estimated to be 0.3–0.5 nm and sharp $c(2 \times 2)$ LEED patterns were observed. The loss spectrum of Fig. 4f resembles the HREELS spectrum of water multilayers (ice) in superposition with features of the substrate. The broad loss at 3360 cm⁻¹ is due to OH stretching modes (OH) and the loss at 1650 cm⁻¹ due to the scissor mode $\delta(\text{HOH})$. The librational modes of molecular water are expected at around 820 cm⁻¹ and may also contribute to the spectrum. The frequency of the small loss at 3690 cm⁻¹ is too large for a hydrogen-bonded OH species and is in the region of the stretching mode for free OH groups [2]. However, a feature at this frequency with low intensity in comparison to the bands at around 3360 cm⁻¹ is generally seen in HREELS data for multilayer ice surfaces [4,44–46]. This loss feature has been assigned to non-hydrogen-bonded OH stretches of H₂O molecules [44,45]. The occurrence of broad losses around 3360 cm⁻¹ for low water exposure and no loss at 3690 cm⁻¹ for these low coverages (Fig. 4, curves

b and c) also shows that water adsorbs molecularly on SiO₂/Mo(112) and, further, that water molecules cluster even at low coverages.

4.4. Work function data

The work function change $\Delta\phi$ upon water adsorption onto low- and high-defect SiO₂ thin films (Fig. 6B) is likewise evidence for molecular adsorption. A negative work function change is generally associated with the adsorption of molecular water [1]. A work function decrease can be caused by charge donation from the adsorbed water to the substrate, by polarization of the water molecule, and by an adsorption geometry with the oxygen atoms oriented towards the substrate. Since the work function decreases of 0.4 and 0.5 eV, respectively, are rather small, it is not likely that all of the above mentioned effects contribute significantly to the bonding of water to SiO₂/Mo(112). Discontinuities of the $\Delta\phi$ curves may indicate the complete covering of the SiO₂/Mo(112) surface. In this regard it is understandable that curve (b) in Fig. 6B remains constant at a higher value compared to curve (a) since the surface area should be larger on a SiO₂ film having extended defects in comparison to a flat, low-defect film.

4.5. Comparison to previous results

Comparing the results found here that water adsorbed molecularly rather than dissociatively on SiO₂/Mo(112) with previous results for silica is difficult considering that surface structure of typical high surface area silicas is unknown or hypothetical. Since Nishijima et al., found partly dissociated water on a thin SiO_x layer over Si(111) [21], we assume dissociation is not kinetically limited. One explanation of the differences in the results in the literature and the results presented here is that defect sites on silica surfaces are extremely important yet are variable from silica to silica. First of all, it can be argued that the exclusively non-dissociative adsorption found in the present work and that by Chabal and Christman [20] can be traced to the uniform stoichiometry of the silica films. Whereas the films used

by Nishijima et al., were non-stoichiometric silica film grown on Si(111), the SiO_2 thin films in the present study grown on Mo(112) films are stoichiometric. In this regard, theoretical work by Feuston [33] and Bakaev [34] deserve special consideration. Feuston et al. [33], concluded there to be a considerable concentration of topological and bonding defects in vitreous silica surfaces. It was proposed that non-bridging oxygen atoms constitute a large component of these defects. Later Bakaev and Steele concluded that single and triple coordinated oxygen atoms as well as distorted SiO_4 tetrahedra at the surface of vitreous silica create a strong electrostatic field and that these defects increase the hydrophilicity of the surface [34]. It is important to note that a simulated surface which consists only of bridging oxygen atoms was found to be completely hydrophobic [34]. Considering this and those studies in which the hydrophobic character of pure silica surfaces (not containing OH groups, i.e. silanol groups) have been reported [26–28], we conclude that defect sites are decisive. The silica thin films prepared on Mo(112) are not only well-ordered, but most probably are free of defects leading to water dissociation. The presence of extended defects, i.e. steps and corners, do not cause detectable amounts of OH groups upon water adsorption as is evident in Figs. 6A, 7 and 8. Point defects such as single and triply coordinated oxygen atoms may lead to hydroxylation of silica surfaces. In view of this point, it is not surprising that a H_2O plasma discharge was necessary to transform a hydrophobic SiO_2 surface into a hydroxylated silica surface as reported by Sneh and George [32].

5. Conclusions

Based on MIES, UPS (He I), HREELS, TPD and $\Delta\phi$ measurements we present conclusive evidence that water adsorbs molecularly on SiO_2 thin films prepared on Mo(112). Considering the lower limit of the detectability of hydroxyl-features by MIES and UPS, we estimate that the fraction of dissociated water molecules is at most 9%. However, since there is no evidence for water dissociation it is likely that water does not react with SiO_2

thin films prepared under UHV conditions and annealed at elevated temperatures. This result is consistent with previous studies where hydrophobic properties of dehydroxylated silica surfaces were reported. Furthermore, the non-dissociative adsorption of water is consistent with theoretical studies that purport point defects to be crucial for the hydroxylation of silica surfaces. Extended defects, i.e. steps and corners, are not sufficient to cause water dissociation on SiO_2 thin films prepared on Mo(112). The results indicate that clustering of water, i.e. 3-D growth, begins at very low coverages. The water–water interaction via hydrogen bonding is stronger than the interaction of water with the silica thin film. Varying peak positions of the $3a_1$ orbital in MIES and UPS (He I) for multilayers of water (ice) can be explained invoking different surface sensitivities of MIES and UPS (He I).

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