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Partial dissociation of water on a MgO(100) film

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The adsorption of water at 100 K on an ordered film of MgO(100) prepared on Mo(100) is studied by low energy electron diffraction, HREELS (high resolution electron energy loss spectroscopy), and UPS (ultraviolet photoelectron spectroscopy). The appearance of the loss of OH species from HREELS and the 3σ valence features of the hydroxyl from UPS indicate that the water can be partially dissociated on MgO(100)/Mo(100) at the initial coverages. The experimental results are in good agreement with the theoretical calculations.

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I. INTRODUCTION

As we know, the mechanism of water adsorption on oxide surfaces has been widely studied due to its importance in applications in geology, atmospheric chemistry, environmental protection, corrosion, gas sensors, and heterogeneous catalysis.[1–3] In catalysis, for example, magnesium oxide is known to catalyze the H_2 and D_2 exchange reaction[4] and the dehydrogenation of formic acid or methanol.[5] Magnesium oxide has a simple rock-salt structure, a single valence state, and only one stable low-index, {100}, surface orientation.[2] Recent density-functional theory calculations[6] and first-principles molecular dynamics simulations[7] suggest that intermolecular hydrogen bonding plays an important role in water dissociation. Based on our recent study,[8] two kinds of hydrogen bonds (a strong H bond in the top layer and two weak H bonds in the bottom layer) are found in the water molecular bilayer when water adsorbs on a solid surface. *Ab initio* calculations[9] also show that lateral interactions between the adsorbed water molecules and the formation of hydrogen bonds can lead to partial dissociation of water on a perfect MgO(100) surface. On the other hand, on a defective surface the dissociation can be stabilized.[10,11]

In this paper we use LEED (low energy electron diffraction), HREELS (high resolution electron energy loss spectroscopy), and UPS (ultraviolet photoelectron spectroscopy) to study adsorption of water on the ordered MgO(100) film prepared on a Mo(100) surface. From HREELS, the frequencies of the stretching mode related to the OH groups and the bending mode of molecular water adsorbed on MgO(100) are detected. From UPS, we find that the water is characterized by 3σ valence feature of OH species related to dissociated water, suggesting partial dissociation of water on the ordered MgO(100) film.

II. EXPERIMENTAL PROCEDURE

The experiments are carried out in a UHV (ultrahigh vacuum) chamber (Leybold-Heraeus GmbH, base pressure 1×10^{-10} mbar) equipped with HREEL, UP spectrometers and a LEED facility. The HREELS measurements are performed with an ELS 22 spectrometer. As discussed in previous work,[12–17] HREELS analysis of oxide materials is often complicated due to the presence of primary phonon and multiple phonon losses with higher intensity, which dominates most of the energy-loss region making it difficult to detect the vibrational modes of adsorbed species. From Poisson distribution theory and experimental study,[15,18] we know that an off-specular scattering geometry can cause the intensities of the multiple phonon losses to depart from a Poisson distribution, and that the higher primary energy of the electron beam leads to the lower intensities of Fuchs-Kliewer phonons from magnesium oxide. However, the higher primary energy may degrade the resolution of the spectrum. Therefore, in our HREELS experiments, the analyzer is set in a slightly off-specular direction by about 5°, and the energy of the primary electron beam is 8 eV with a resolution of about 12 meV with the full width at half maximum of the elastic peak.

The magnesium oxide used here is thin films (5–8 nm thick) of MgO(100) grown *in situ* upon a Mo(100) surface. The substrate Mo(100) surface is cleaned by oxidation in oxygen at 1200 K and then heated to about 2000 K using an electron-beam heater for several cycles. The MgO(100) film is prepared by deposition of Mg in 10^{-7}-mbar O_2 at a substrate temperature of 600–700 K. A flat and ordered MgO(100) film on a Mo(100) substrate can be obtained after annealing to 1150 K.[19] The MgO(100) film as prepared in our case, however, shows a LEED pattern with broad spots indicating a defective surface. The specimen can be heated resistively and cooled down by liquid nitrogen. A W-5% Re/W-26% Re thermocouple was spot welded to the edge of the specimen for temperature monitoring. Deionized water (18 MΩ) was further purified by several freeze-pump-thaw cycles before dosing to the samples. The dosages are measured using a non-calibrated ion gauge. The surface coverage is assumed to be equivalent to the water exposure, since the film intersects virtually all of the incoming vapor and the sticking coefficient of water on the crystal at 100 K is near to unity.[20]

III. RESULTS

Figure 1 shows HREEL spectra obtained for different water coverages. The trace labeled (a) corresponds to the spec-

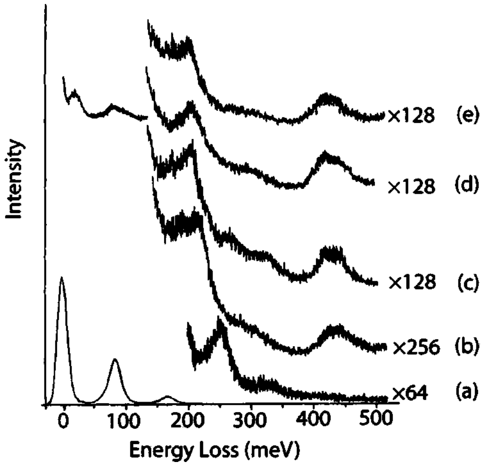

FIG. 1. HREELS data from various exposures of water on the MgO(100)/Mo(100) at 100 K. (a) 0 L; (b) 0.1 L; (c) 0.6 L; (d) 1.3 L; (e) 3 L. $E_p = 8$ eV.

trum from the clean MgO(100) film at 100 K. For magnesium oxide, the primary phonon loss (at 82 meV) yields multiple scattering loss events at 165 and 248 meV, and the fourth scattering loss of the phonon can be clearly seen (at 330 meV) even though a primary energy of 8 eV was used with analyzer off-specular direction. The MgO(100) surface is exposed to water at 100 K, and the water exposures from trace (b) to trace (e) are 0.1, 0.6, 1.3, and 3 L (Langmuir), respectively. With a 0.1-L coverage of water [Fig. 1(b)], a broad loss at ~438 meV (the stretching band of water) was found, and a loss at about 205 meV (the bending mode, also called the scissor mode of water) appears [Fig. 1(b)]. Increasing the coverage of water to 0.6 L causes the loss of 438 meV to increase in intensity. As for the adsorption of water on the metal surface,[21–23] the broad stretching band may imply intermolecular hydrogen bonding. After increasing water coverage to 1.3 L [Fig. 1(d)], a hindered translational mode of water (at 30 meV) also appears, seemingly indicating a multilayer of water molecular adsorption.

As shown in Fig. 1, with the exposures at 0.1 and 0.6 L, the stretching mode of water molecules (at 438 meV) may be a combination of the 428 and 446-meV features that can be observed when water is adsorbed on quartz.[24] At exposures of 1.3 and 3 L the stretching mode still exists, but the 438-meV mode is slightly shifted to 425 meV. We will discuss this in Sec. IV.

Figure 2 shows the UP spectra for a MgO(100)/Mo(100) surface at 100 K with water exposures of 0, 1.3, 1.8, and 3 L, respectively. The curve labeled (a) corresponds to the clean MgO(100) film, and a peak at 5.8 eV can be assigned to the emission of an O $2p$ valence band from the MgO(100) film.[25] The curve labeled (b) with 1.3-L coverage shows bands consisting of four peaks at 5.6, 7.2, ~9.2, and ~10.0 eV. With increasing coverage of water to 1.8 L, the binding energies of the bands are 5.4, 7.4, and 9.8 eV, as shown in Fig. 2(c). After adsorption of water to 3 L [Fig. 2(d)], however, the bands are similar to that obtained at 1.8 L.

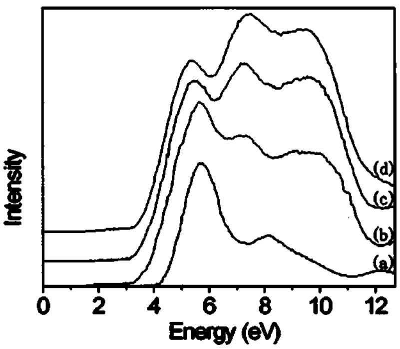

FIG. 2. UP spectra of water on the MgO(100)/Mo(100) as a function of water exposure at 100 K. (a) 0 L; (b) 1.3 L; (c) 1.8 L; (d) 3 L. He (I)=21.2 eV.

IV. DISCUSSION

At coverages higher than 0.6 L, the stretching mode of water molecule is still apparent; however, it is redshifted slightly in comparison with lower coverages. This could be caused by many physical phenomena such as different bonding geometries of water on the surface, intermolecular hydrogen bonding, or even surface charging effects. The films in our experiments are 5–8 nm in thickness; they can dissipate the charging problem via the conducting substrate. That the multilayer of water causes this peak to broaden was also seen in previous studies.[15] At this coverage and temperature, the water becomes solid layers. No matter what kind of geometric adsorption on the substrate the water has, the hydrogen bonding is dominant. The hydrogen bonding causing a broadening of the vibrational peak of OH has been documented.[26] In vibrational spectra, the vibrational energy levels move closer together, and the transitions associated with the O-H stretch shift to lower frequencies.[1] Moreover, the bending mode (at about 205 meV) is also detected, which implies that the water molecular is present. The UP spectrum (Fig. 2) shows that the binding energies at 7.2 and ~9.2 eV at 1.3-L coverage are due to the $1b_1$ and $3a_1$ molecular orbitals (MOs) of water, respectively, which has been observed in previous UPS work.[27] Furthermore, at 3-L exposure, the 9.8-eV feature related to the $3a_1$ orbital of icelike water, possibly condensed water, agrees with the results from water adsorption on the $Fe_3O_4(111)$ surface.[28] Because of the emission of the secondary electrons of magnesium oxide, the $1b_2$ MO of water cannot be well resolved in our experiment.

Figure 3 shows the HREEL spectra after annealing the sample with 3-L water exposure at 100 K. Annealing temperatures listed in the curves labeled (b)–(d) are 175, 273, and 350 K, respectively. Previous TPD (temperature-programmed desorption) experiments[17] suggested that water multilayer desorption at 160 K with a second desorption feature arises from water formed via a recombination of surface hydroxyls at 220–340 K. So when the MgO(100) surface with 3 L of water is annealed to 175 K [Fig. 3(b)], the number of hydrogen bonds decreases and the 425-meV loss shifts slightly to 430 meV. However, after annealing to 273 and 350 K [Figs. 3(c) and 3(d)], a new peak at 456 meV appears, and meanwhile the 205 and 430-meV loss peaks (the stretching mode of water molecule) cannot be observed. The vanishing of the bending mode and stretching mode of water molecule implies that water molecules are desorbed from the

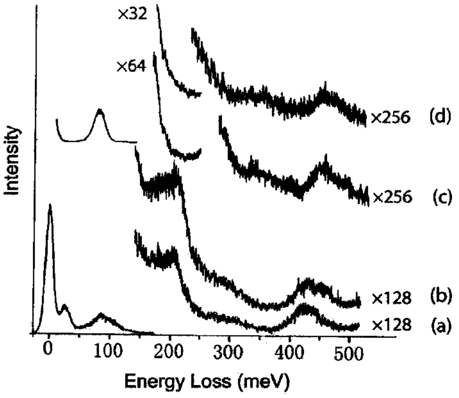

FIG. 3. HREEL spectra from MgO(100)/Mo(100) with 3 L of water as a function of annealing temperature for 3–5 sec at (a) 100 K, (b) 175 K, (c) 273 K, and (d) 350 K.

surface. This reveals that the 456-meV loss might be ascribed to the OH species related to the decomposed water and not to the isolated OH groups (nonhydrogen bonding) of water. It is interesting that the OH species related to the decomposed water seem to form hydrogen bonding with subsequently adsorbed water molecules. Our result agrees well with the theoretical calculations that suggest that the mixed molecular and dissociative adsorption of water molecules are most favorable because of the increased number of intermolecular hydrogen bonds.[6] Comparing with a previous study,[15] we cannot clearly see the OH loss at 100 K with low coverage. This might be caused by either the different geometry structure of the water adsorbed on the surface or the bonding status of the water. We do not think surface defects play a key role, because it has been shown that water can be partially dissociated on both perfect and defective surfaces.[6,7,9–11] In theoretical studies, it has been pointed out that the mixture of molecular and dissociative adsorption is stabilized by the intermolecular hydrogen bonding. The adsorbed molecular water with one hydrogen bond to a surface oxygen is the most stable configuration. Owing to the hydrogen bonding between molecular water and dissociated OH it is difficult to detect the OH loss at lower coverage in HREELS measurements. However, after annealing, the water was desorbed and the hydroxyl group was detected. This further reveals that the OH bonding from hydroxyl species is stronger than the hydrogen bonding.

It is unclear why only one stretching mode is observed in the HREEL spectrum after dissociation of water. Two different OH groups should be formed if water decomposes to H and OH. One group corresponds to the hydroxyl that resulted from the dissociation of water, and the other originates from the adsorbed proton, which forms an adlayer involving $O_{surface}$-H and $Mg_{surface}$-OH species at the surface of the magnesium oxide film. In UP spectra [Fig. 2(b)], comparing our results with a previous UPS study on water/$Fe_3O_4(111)$,[28] the 10.0-eV feature should be assigned to the 3σ orbital of hydroxyl. It is noticeable that the intensity ratio of the hydroxyl (3σ) and the H_2O ($3a_1$) feature in UPS is circa 1:1. So it is not likely that defect sites alone are responsible for the dissociation of water.[19] The 3σ orbital of hydroxyl indicates that the adsorbed water molecules at initial coverages can be dissociated at 100 K.

Because the loss intensity in HREELS is affected very much by the surface geometry structure and the orientation of the adsorbed species on the substrate; some of the loss peaks cannot be detected under normal operating conditions. Therefore, the combined results of UPS and HREELS are more informative. We conclude that the partial dissociation of the water occurs at low temperature on an ordered MgO(100) film. Our results agree well with recent investigations by metastable impact electron spectroscopy, UPS, and TPD, in that water adsorbs dissociatively and molecularly within the first monolayer on well-ordered MgO(100) surfaces.[19] Consequently, H_2O molecules adsorb both dissociatively and molecularly at the same time on the MgO(100) surface, thus forming a mixed (H_2O+OH) phase. This result corresponds to recent theoretical calculations[7,9] that predict a more stable mixed (H_2O+OH) monolayer rather than a monolayer of water. However, from the experimental results, the adsorptive sites of water molecules and OH groups cannot be well known. Certainly, the evidence still gives no clear account of the interaction between the molecular water and the OH species related to the dissociative water. The study of Giordano *et al.*,[9] however, indicates that the dissociation of water molecules may arise from interactions within densely packed H_2O adlayers. Our experimental results prove that the theoretical predictions[6–11] about the water adsorbed on the magnesium oxide are correct.

V. CONCLUSIONS

The combined HREELS and UPS results support theoretical calculations and suggest that water can be partially dissociated on an ordered surface of MgO(100) films at initial coverages under UHV conditions. The redshifted and broad stretching mode indicates an intermolecular hydrogen bonding interaction.

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