Hydroxyl groups on oxide surfaces (*)

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(ricevuto il 28 Febbraio 1997; approvato l'8 Maggio 1997)

Summary. — The hydroxylation of α-Al_2O_3(0001) and MgO surfaces is studied in ultra-high vacuum by high-resolution electron energy loss spectroscopy (adsorbate and phonon losses being distinguished via resonance scattering) and X-ray photoemission spectroscopy. Hydroxyl groups which arise from the dissociative adsorption of H_2O on α-Al_2O_3(0001) surfaces and low-coordinated MgO surface sites are characterized by chemical shifts and stretching frequencies.

PACS 68.35.Ja – Surface and interface dynamics and vibrations.
PACS 79.60.Dp – Adsorbed layers and thin films.
PACS 82.30.Lp – Decomposition reactions (pyrolysis, dissociation, and group ejection).
PACS 01.30.Cc – Conference proceedings.

1. – Introduction

Widely encountered in studies of metal and semiconductor surfaces, vacuum techniques are not much used on oxide surfaces. There are many reasons [1] for that, indeed including the fact that surface analysis, which mostly relies on electron probes, faces charging effects on insulator substrates.

In the present work, hydroxyl groups at submonolayer coverages are studied in ultra-high vacuum (UHV) conditions on oxide surfaces by X-ray photoelectron spectroscopy (XPS) and high-resolution electron-energy-loss-spectroscopy (HREELS). Our purpose is twofold. i) In addition to charging effects, the vibrational analysis by HREELS of adsorbed species adsorbed on oxyde surfaces has to distinguish between phonon and adsorbate losses. We investigate the possibility to solve that problem by means of resonance scattering. ii) By combining HREELS and XPS analyses, we characterize OH groups that are formed on α-Al_2O_3(0001) and MgO surfaces by dissociative adsorption of H_2O.

(*) Paper presented at the "First International Workshop on Reactivity of Oxide Materials. Theory and Experiment", Como, 8, 9 November 1996.

2. – Experimental

Experiments are performed in an UHV system equipped with a HREELS LK2000 and an XPS VG Clam 2. Clamped on a platinum plate, $10 \times 10 \times 1$ mm^3, the crystal can be heated by an electron bombardment of the plate and cooled by circulating liquid nitrogen. Gases are introduced through a dosing pipe.

The α-Al_2O_3(0001) crystals are mechanically cut and polished. The MgO surfaces are produced by cleavage of a MgO crystal. Once introduced in the vacuum chamber, samples are cleaned by heating under a partial pressure of oxygen, either at 1000 K, as in the case of alumina (the Al_2O_3 crystals are kept below 1100 K so as to avoid surface rearrangements due to oxygen removal [2]), or at 1200 K, as in the case of MgO. During the heating of the sample, an equivalent oxygen pressure of 10^{-3} to 10^{-2} Pa is obtained by setting the surface within few millimeters of the dosing pipe, while the stationary pressure in the chamber is kept below 10^{-4} Pa. As checked by XPS, surfaces are commonly cleaned after 10 to 20 mn long treatments (the detection limit is 0.005 monolayer for carbon; 1 monolayer corresponds to 1 adatom per surface oxygen atom).

During HREELS analysis, charging effects are avoided by illuminating the samples with an additional electron beam [3]. Operated at about 1 keV and defocused

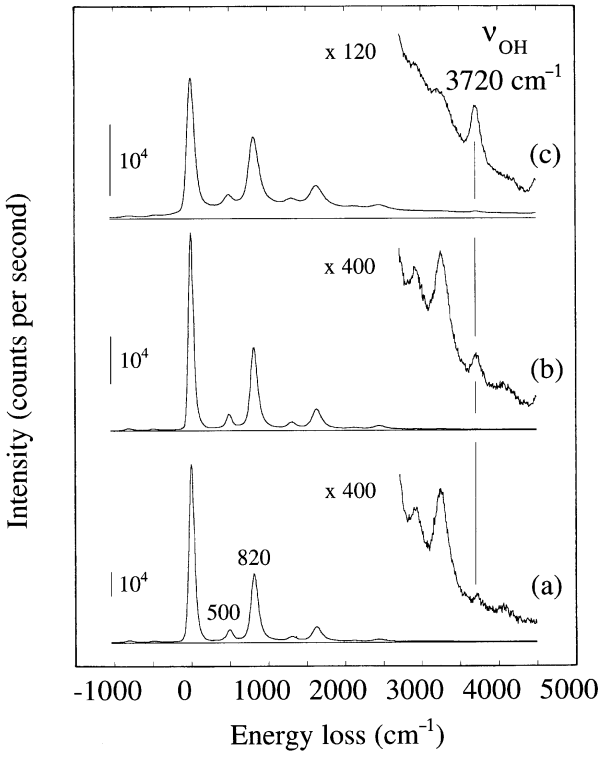

Fig. 1. – Resonance scattering of the OH stetching mode on the α-Al_2O_3(0001) surface. HREELS spectra after an exposure of 0.6 Pa s of H_2O: (a) $E_p = 12$ eV; $\theta_i = \theta_{an} = 60°$; b) $E_p = 6$ eV; $\theta_i = \theta_{an} = 60°$; (c) $E_p = 6$ eV; $\theta_i = 60°$ and $\theta_{an} = 45°$. The incident and analysis angles, θ_i and θ_{an}, are with respect to the normal to the sample.

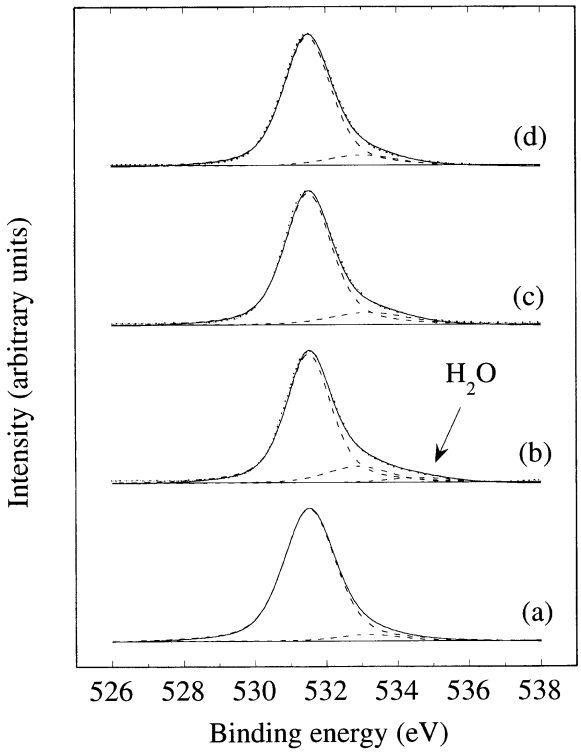

Fig. 2. – Hydroxylation of the α-Al_2O_3(0001) surface. XPS spectra: (a) clean surface; b) and (c) after an exposure of 0.6 Pa s of H_2O at 110 K, at temperatures 110 K $\geqslant T$(b) $\geqslant T$(c) $\geqslant$ 300 K; (d) following (b) and (c), at 300 K.

so as to flood the entire surface, it is suggested to stabilize the surface potential, via both secondary emission and creation of nonequilibrium carriers [3, 4]. For all the experiments reported herein, the extra current density is as low as 1 nA·cm^{-2}. As checked by XPS and HREELS, this allows to collect data for hours without damaging the adsorbed layers.

The O 1s binding energies are calibrated by using tabulated values, *i.e.* 531.9 eV and 531.5 eV for the MgO and Al_2O_3 surfaces, respectively [5]. Hydroxyl coverages are estimated by taking 1.86 nm (MgO) and 1.78 nm (Al_2O_3) for the escape depth [6] of the O 1*s* photoelectrons probed by the Mg $K\alpha$ line.

3. – Results and discussion

3˙1. HREELS *of* OH *groups via resonance scattering*: OH/α-Al_2O_3(0001). – After an exposure of 0.6 Pa·s of the Al_2O_3 surface at 300 K to H_2O, a ν_{OH} stretching loss is seen at 3720 cm^{-1} in the HREELS spectrum (fig. 1). Surrounded by multiple phonon losses, this loss is unambiguously identified through a resonance scattering [7] which takes place at low impact energy. Its relative intensity (*vs.* phonons) increases as the impact energy E_p decreases (figs. 1*a* and 1*b*) and, since the resonance scattering escapes the dipole behaviour, when exploring off-specular directions (fig. 1*c*). Resonance scattering

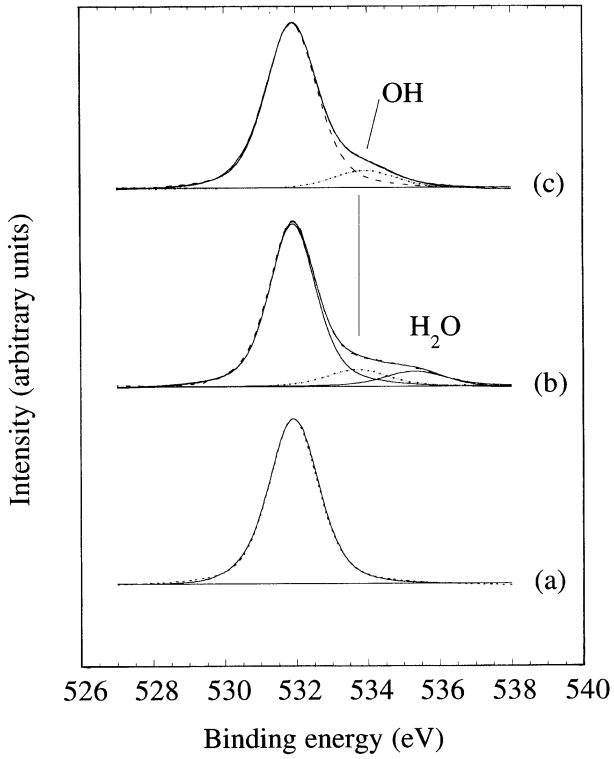

Fig. 3. – Hydroxylation of a MgO surface with a high concentration of low-coordinated sites (see text). XPS spectra: (a) clean surface; (b) after an exposure of 0.6 Pa s of H_2O at 110 K, at a temperature T(b) between 110 K and 300 K which is low enough to allow molecular adsorption of water; (c) following (b), at 300 K: molecular water is now fully desorbed and the shifted peak is due to OH groups.

arises from the capture of an incident electron by a quasi-bound molecular orbital of the target molecule, which leads to the formation of a short-lived negative ion [8]. Provided that the electron trapping occurs in given OH molecular orbitals [9], the low energy resonance which is analyzed herein on alumina surfaces can be considered as an intrinsic property of the adsorbed OH and can be widely used to study ν_{OH} on oxide surfaces (see the OH/MgO case).

The value of the above ν_{OH} frequency is close to those found on hydroxylated alumina films [10, 11] and it is within the frequency range where the stretching modes associated to hydroxyl groups bonded to octahedral aluminium cations of alumina are expected to be [12]. Moreover, the present OH layers are seen to fully desorb at 1000 K, as in the case of the hydroxylated alumina films of Frederick *et al.* [11]. However, loss spectra shown in fig. 1 do not allow to discard the adsorption of H_2O in the molecular form since, due to the first harmonic (1640 cm^{-1}) of the dominant phonon mode, the frequency region of the scissor mode δ_{HOH} cannot be explored.

Further insight is gained through the XPS analysis of the adsorption of water at low temperature. In our system, the sample cannot be cooled when XPS analyzed, but it can be cooled down to 110 K in the HREELS chamber prior to being quickly

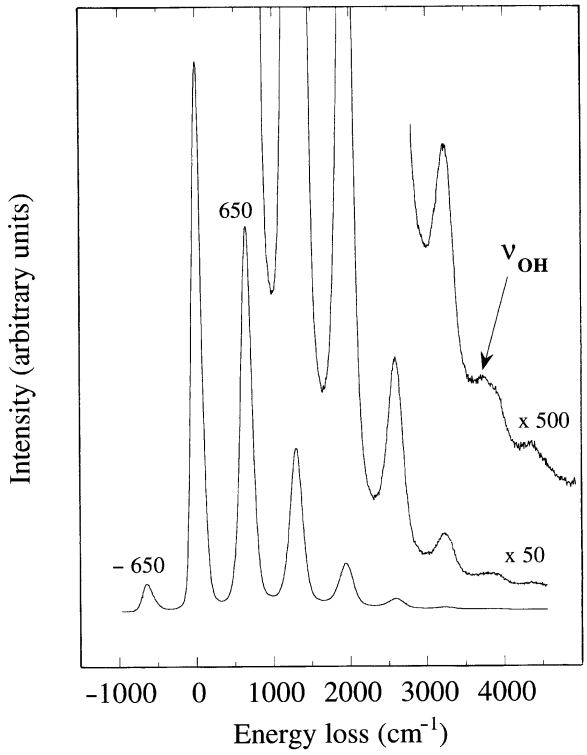

Fig. 4. – HREELS spectrum of a MgO surface (same as fig. 3) after an exposure of 0.6 Pa s of H_2O at 300 K ($E_p = 4$ eV; $\theta_i = \theta_{an} = 60°$). The phonon loss is seen at 650 cm^{-1} and the OH stretching mode at 3740 cm^{-1}.

transferred towards the XPS spectrometer so as to be analyzed at a temperature between 110 and 300 K. Under these conditions, series of O 1s spectra as those shown in fig. 2 can be recorded after the adsorption of a water multilayer on α-Al_2O_3(0001) at 110 K in the HREELS chamber. At the lowest temperature (fig. 2*b*), a pronounced feature is seen on the higher binding energy side of the O 1*s* peak. It involves two components, shifted by 1.6 ± 0.2 eV and 2.9 ± 0.2 eV with respect to bulk. The latter is assigned to molecularly adsorbed water because i) it corresponds to a weakly bound species which desorbs below 300 K (figs. 2b and 2c) and ii) its binding energy, 534.4 eV, compares well to values found for water multilayers [13].

An extra feature is already seen on the higher binding energy side of the O 1*s* spectrum of the clean alumina surface (fig. 2a). However, this feature always increases (compare figs. 2a and 2d) by a given amount when a clean alumina surface is exposed to H_2O (about 5% of the total O 1*s* area, leading to an estimate of $(5 \pm 2) \cdot 10^{14}$ OH.cm^{-2} for the OH coverage under these conditions). In addition, the 1.6 ± 0.2 eV shifted feature seen in the O 1*s* spectrum is accompanied by the appearance of the 3720 cm^{-1} ν_{OH} stretching loss. The shift and the loss thus unambiguously characterize hydroxyl groups adsorbed on the α-Al_2O_3(0001) surface (although the dissociation mechanism is still a pending question). The absence of the 2.9 eV shift in the O 1*s* spectrum at 300 K (fig. 2d) shows that there is no molecular H_2O on the surface at that temperature.

3˙2. *Reactivity of surface defects sites*: OH/MgO. – The dissociative adsorption of water is not expected to occur on five-coordinated surface sites—*i.e.* on (100) faces—but only on four- and three-coordinated sites [14-16]. When cleaved in a glove box prior to being quickly inserted in UHV, MgO(100) surfaces show 100 nm wide terraces [17]. At variance, MgO surfaces exposed to the ambient air (in fact, more likely to moisture) undergo rearrangement at the nanoscopic scale and become very rough [17], which is indicative of the formation of low-coordinated sites. Nevertheless, surfaces as rough as that in fig. 4 of ref. [17] can be cleaned by heating under oxygen pressure, in the same way as flat surfaces. These surfaces are not only carbon-free, but also hydroxyl-free, since no shifted feature can be detected in the O 1s spectrum (fig. 3a) and no loss is seen in HREELS (for the characterization of OH groups, see the discussion below). In the following, such surfaces (herein referred to as MgO surfaces, with no indication of orientation) will be used to probe the reactivity of H_2O on the low-coordinated surface sites.

After an adsorption at 110 K, an analysis below 300 K reveals a strong shoulder on the higher binding energy side of the O 1*s* spectrum (fig. 3b). It involves two

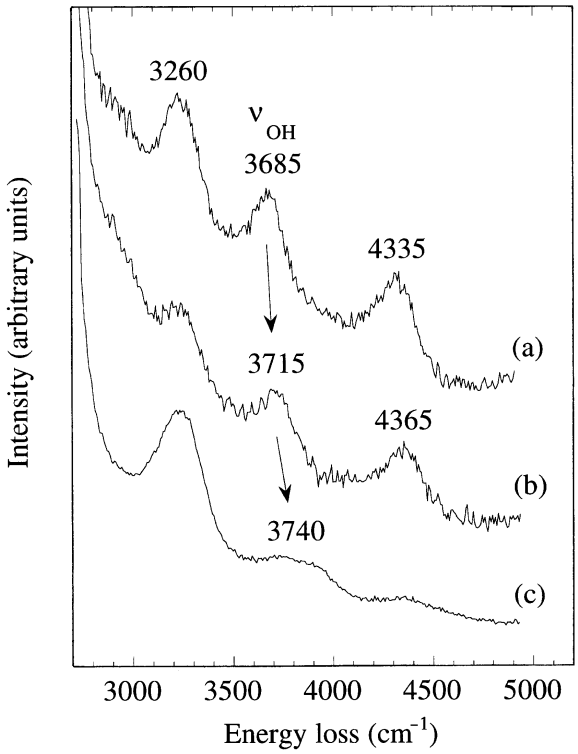

Fig. 5. – Blue shift of the ν_{OH} stretching loss on hydroxylated MgO surfaces at 300 K, upon decreasing OH coverages. HREELS spectra ($E_p = 4$ eV; $\theta_i = \theta_{an} = 60°$) of the OH stretching region: (a) θ_{sat}; (b) $0.7\,\theta_{sat}$; (c) $0.2\,\theta_{sat}$. OH coverages are defined with respect to the saturation coverage θ_{sat} (fig. 3c; an order of magnitude of θ_{sat} is obtained by noting that the extra component in fig. 3c would correspond to about 1 OH group per MgO pair on a (100) face of the same macroscopic area). The peaks at 4335 cm^{-1} and 4365 cm^{-1} are due to the (ν_{OH} + phonon) loss which is indeed blue shifted when the OH coverage decreases.

contributions, shifted by 1.9 ± 0.2 eV and 3.6 ± 0.2 eV with respect to the bulk peak, respectively. Following the same reasoning as in the case of alumina, the component at 535.5 eV, which desorbs below 300 K (fig. 3c), is assigned to molecularly adsorbed water and the peak at 533.9 eV is attributed to OH groups [18]. Therefore, OH/MgO are characterized by a chemical shift and a ν_{OH} HREELS loss near 3700 cm^{-1} (fig. 4; in figs. 4 and 5, a low impact energy (4 eV) is used so as to enhance ν_{OH} with respect to phonons, via resonance scattering). A complete removal of OH groups is observed at 1000 K. The fact that the MgO surfaces on which water dissociation occurs show a high concentration of low-coordinated sites supports the theoretical finding [14-16] that the dissociative adsorption of H_2O only takes place on these sites.

The ν_{OH} loss is recorded at 3685 cm^{-1} at the maximum OH coverage θ_{sat} (obtained after the adsorption and further desorption of a water multilayer on the MgO surface), in perfect agreement with the HREELS data of Wu *et al.* [19] on a hydroxylated MgO thin film. However, it is worth noting that, as observed by infrared on high area MgO [20, 21], the ν_{OH} mode is blue shifted when θ_{OH} decreases (fig. 5). Such a shift has been suggested to arise either from the various types of surface sites (see ref. [21] for a review) or from lateral interactions between OH groups [22, 23]. Finally, we do not see any evidence for the presence of the two types of OH groups which are expected to appear on MgO surfaces [14], perhaps because their frequency separation [24] is too small to give rise to two distinct loss peaks.

4. – Conclusion

HREELS is a powerful tool to study adsorbates on well-defined insulating surfaces. The two major experimental problems, charging effects and intense phonon losses can be solved by i) stabilizing the surface potential by an extra electron gun with a beam current low enough to not perturb the adsorbed layer and ii) using resonance scattering to distinguish adsorbate losses from phonon losses.

On α-Al_2O_3(0001) and MgO surfaces, hydroxyl groups have been unambiguously characterized by both stretching frequencies and chemical shifts of the O 1*s* photoemission line.

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