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Common fingerprint of hydroxylated non-polar steps on MgO smoke and MgO films

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ABSTRACT

The infrared spectra of MgO smoke exposed to water are compared to high-resolution electron energy loss spectra (HREELS) of hydroxylated ultrathin MgO(1 0 0)/Ag(1 0 0) films. Very similar bands are observed at 3458–3480 cm^{-1} and 3710–3714 cm^{-1}. On the basis of first principle calculations, these bands are interpreted as the stretching modes of the two distinct OH groups that are formed at monatomic steps parallel to ⟨1 0 0⟩ crystallographic directions. The lower frequency band is due to H adsorbed on O at the step edge, while the higher frequency one originates from OH groups that are twofold coordinated with Mg. Consistently, scanning tunnelling microscopy images of MgO films, prepared in similar conditions as during the HREELS experiments, show that the MgO/Ag(1 0 0) island edges are mainly non-polar, i.e. oriented along the ⟨1 0 0⟩ direction. In spite of that, a minor contribution to the OH-stretch intensity from hydroxylated polar ⟨1 1 0⟩ steps cannot be excluded; for such geometry density functional theory predicts indeed a single OH species with a vibrational frequency very close to the high-frequency band of OH adsorbed at ⟨1 0 0⟩ steps.

1. Introduction

Surfaces of crystalline oxide involve defects such as steps, kinks, adatoms and vacancies, which are similar to those described in the Kossel model of cubic ionic crystal surfaces [1]. On metals and semiconductors, the properties of surface defects are commonly studied by means of stepped surfaces of defined orientations that are obtained experimentally by appropriately cutting bulk crystals along high Miller index (HMI) planes [2]. However, the method often fails in the case of oxides. As observed on MgO [3] and on α-Al$_2$O$_3$ [4], the annealing at a temperature high enough to reorder HMI surfaces results in steps bunching in such manner that neither step orientation nor step height can be controlled. On the other hand, cleavage produces, aside mono-atomic steps, also an uncontrolled distribution of multi-atomic steps and slip lines [5].

An alternative approach to obtain well defined surface orientations consists in producing oxide crystallites of reproducible size distribution under accurately controlled conditions. For instance, it was shown by photoluminescence [6,7] and infrared (IR) spectroscopy [7,8] that MgO smoke, which mostly consists of cubic crystallites with (1 0 0) facets of average size 100–200 nm, involves a high density of defect-free ⟨1 0 0⟩ mono-atomic steps [6,7]. During the infrared experiments, water adsorption was performed under a partial pressure of 20 Pa of water vapour, i.e. in conditions close to the ambient. Both photoluminescence [6,7] and IR data [7,8] (the latter ones also supported by calculations) consistently define unambiguous fingerprints for ⟨1 0 0⟩ MgO steps on MgO(1 0 0) surfaces and demonstrate that MgO smoke can be used as a high area model to study the behavior of these sites. Supported MgO thin films are commonly used to model MgO(1 0 0) substrates in ultra-high vacuum (UHV) experiments [9–11]. We have deposited them on Ag(1 0 0) due to the small lattice mismatch between the two crystal structures, which allows the growth of ordered layers. On Ag(1 0 0), the adsorption of oxygen atoms atop Ag atoms is energetically favoured (a situation mirrored in the opposite case of Ag films grown on MgO(1 0 0) [12]), so that the oxygen lattice of the MgO(1 0 0)/Ag(1 0 0) film matches the silver lattice [13]. Consistently, a general agreement exists about the epitaxial relationship $(1\,0\,0)_{\mathrm{MgO}} /\!\!/ (1\,0\,0)_{\mathrm{Ag}}$ with $\langle 1\,0\,0\rangle_{\mathrm{MgO}} /\!\!/ \langle 1\,0\,0\rangle_{\mathrm{Ag}}$ [9–11]. Nevertheless, the orientation of edges and steps of the MgO islands is still debated. STM images collected by Schintke et al. [10] and Sterrer et al. [11] show MgO domains with edges running mostly parallel to the non-polar ⟨1 0 0⟩ directions. A very different behavior was reported by Valeri et al. [9], whose STM data show edges predominantly oriented along the ⟨1 1 0⟩ direction. Straight ⟨1 1 0⟩ steps are formed either by O or Mg atoms so that Mg and O rows alternate along the direction normal to the step edge in a polar sequence [14,15].

The purpose of the present paper is to compare steps on MgO smoke to steps on MgO(1 0 0)/Ag(1 0 0) films and to discuss their polar or non-polar nature on the basis of the vibrational signatures

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detected upon H_2O dissociative adsorption. To this aim the vibrational spectra of MgO samples exposed to water vapour are discussed with the support of calculation performed within the density functional theory (DFT). Although the spectroscopic data and part of the numerical results have already been published [8,16], no specific analysis was performed in order to distinguish among the different orientations of the steps. Moreover, the interpretation of the high-resolution electron energy loss (HREEL) spectra of the OH/MgO films that was originally given in Ref. [16] is here revisited and strengthened through the comparison with the IR data collected on MgO smokes [8].

The hydration of MgO smokes has been analyzed at the Institut des Nanosciences de Paris. Infrared (IR) spectroscopy and DFT calculations evidenced the vibrational signatures of the fully hydroxylated non-polar $\langle 1\,0\,0\rangle$ mono-atomic steps of MgO [6,8]. The structure and the hydroxylation of ultrathin MgO(1 0 0)/Ag(1 0 0) films have been studied at the Department of Physics of Genoa by scanning tunnelling microscopy (STM) and HREELS [16,17], respectively. Most interestingly, a close comparison of the two series of experiments shows that HREEL and IR spectra present similar features. That observation renews our interest in determining the actual orientation of the borders of the Ag-supported MgO films. To clarify this point we discuss here: (i) the structure of clean MgO/Ag(1 0 0) films prepared in conditions very similar to the ones examined by HREELS, as inferred by STM investigation; (ii) the comparison of experimental IR and HREELS data with DFT predictions about the vibrational spectra for hydroxylated polar and non-polar steps of MgO(1 0 0).

The critical assessment of the spectroscopic measurements that were performed on MgO films [16], crystalline surfaces studied in ultra-high vacuum, and on MgO smoke, high surface area samples exposed to pressure close to the ambient [8], makes it possible to appraise the basic properties of extended defects, such as steps, through surface systems that differ by preparation and dimensions. This also suggests that these very properties can be interpreted as the fingerprints of the defects, irrespectively of the host surface system.

2. Experimental and theoretical methods

Only the most important aspects of the setups dedicated to STM and vibrational analysis will be recalled here, since they were previously described in detail in Refs. [7,16,18]. The features distinguishing the data on MgO smokes from those previously collected by other authors are due to the experimental protocol. The MgO powder was synthesized and manipulated in a controlled environment, that is, either in a pure argon and oxygen mixture or under vacuum. Such precautions proved to be imperative to pinpoint the photoluminescence spectra of defect-free $\langle 1\,0\,0\rangle$ steps [6] and the related IR spectra upon hydroxylation [8]. HREELS and STM experiments were performed in two different ultra-high vacuum (UHV) chambers equipped with the same instrumentation for film growth. The MgO/Ag(1 0 0) films were grown by reactive deposition at a substrate temperature $T = 453$ K and 500 K in the two chambers, respectively. This method, consisting in the Mg evaporation on Ag(1 0 0) in presence of an O_2 atmosphere, is commonly used [9,10] since it leads to films of better crystallographic quality than those obtained either by oxidation of a pre-deposited Mg film [19,20] or by sputter deposition [20]. In our experimental setup, the O_2 partial pressure was limited to $P_{O2} = 3 \times 10^{-7}$ mbar since the gas is introduced in the UHV chamber through a doser placed at 2 cm from the Ag(1 0 0) surface; the local pressure at the sample is therefore 5 to 10 times higher. The Mg flux (ϕ) was evaluated *a priori* through a quartz microbalance ($\phi = 0.23 \pm 0.03$ ML/min, in monolayers of MgO) and checked a posteriori by analysis of the frequency and intensity of the Fuchs–Kliever (FK) modes recorded by HREELS or of the STM images. Water vapour adsorption was then studied by HREELS (Delta0.5 by Specs) in ultra-high vacuum conditions [16], while structural characterization was performed using a low temperature STM (Createc) operated with liquid N_2. The use of cryogenic temperatures allows the sample to remain uncontaminated for several days and therefore to probe accurately different sample areas. The lateral size of STM images and the orientation of the surface were determined from atomically resolved measurements of the clean Ag(1 0 0) surface (see inset of Fig. 4); similarly, heights were calibrated on mono-atomic Ag steps.

The calculations were performed within the generalized gradient approximation [21] to the Density Functional Theory. After a fine optimization for various structural models, the OH frequencies and intensities were computed within the density functional perturbation theory (DFPT) using the ABINIT code [22]. Here we use the default O and H norm-conserving pseudo-potentials [23], with an energy cutoff of 30 Hartree (816 eV). More details can be found in Refs. [8,24].

The stability of water on surfaces that differ by orientation or by the type of defects (O and MgO vacancies, mono- and diatomic steps) has been evaluated as a function of temperature T and water partial pressure P through the adsorption free energy $\Delta G_{ads}(P,T)$. The latter quantity was approximated by the DFT adsorption energy, E_{ads}, computed at $T = 0$ K, plus the (P,T)-dependent chemical potential of water vapour, as detailed in Ref. [25]. Therefore, for each adsorption configuration, we can sketch (Fig. 1) the coexistence curves, which correspond to $\Delta G_{ads}(P,T) = 0$. Each curve splits the (P,T) plane in two domains: above the coexistence curve, the actual adsorbed phase is predicted to be thermodynamically stable; below, the vapour phase is stable.

3. Results and discussion

For clarity sake, in the following O_s and Mg_s will indicate atoms of the MgO substrate, while O_w will refer to an oxygen coming from a dissociated water molecule.

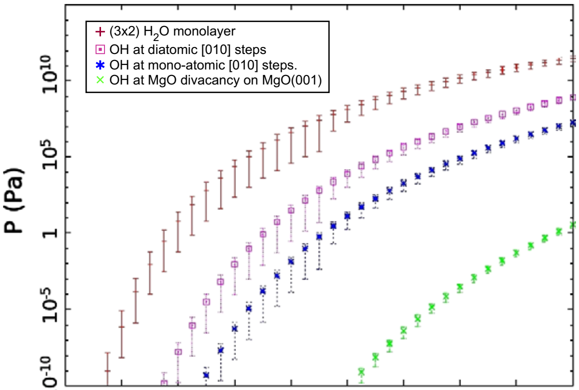

Fig. 1. Computed stability diagram of water adsorption at different MgO adsorption sites. Each curve represents the (P,T) values for which $\Delta G_{ads}(P,T) = 0$, as a function of the surface configuration (see Section 2). Above (below) the curve, the adsorbed (vapour) phase is stable. The curves are plotted together for an easier comparison and correspond to the (3×2) water monolayer on MgO(0 0 1) (dark red +), to the hydroxylated diatomic step with edges parallel to [0 1 0] (magenta ⊡), to the hydroxylated mono-atomic step with edges parallel to [0 1 0] (blue $*$) and to the hydroxylated MgO divacancy on MgO(0 0 1) (green $\times$). The corresponding curve for the hydroxylated mono-atomic step on MgO(0 0 1) with edges parallel to $\langle 1\,1\,0\rangle$ is out of scale. The error bars account for the error propagation, which is due to the estimated uncertainty in E_{ads} as computed within the GGA as well as to the dispersion of E_{ads} as a function of the density of adsorbed hydroxyls on the defects. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)