Quasi-ice monolayer on atomically smooth amorphous SiO2 at room temperature observed with a high-finesse optical resonator

Citation for published version (APA):

DOI:
10.1103/PhysRevLett.95.166104

Document status and date:
Published: 01/01/2005

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.
• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain.
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.
Quasi-Ice Monolayer on Atomically Smooth Amorphous SiO$_2$ at Room Temperature Observed with a High-Finesse Optical Resonator

I. M. P. Aarts, A. C. R. Pipino, J. P. M. Hoefnagels, W. M. M. Kessels, and M. C. M. van de Sanden

Department of Applied Physics, Eindhoven University of Technology, Eindhoven, The Netherlands
National Institute of Standards and Technology (NIST), Gaithersburg, Maryland 20899, USA

(Received 4 May 2005; published 13 October 2005)

The structure of an H$_2$O monolayer bound to atomically smooth hydroxylated amorphous silica is probed under ambient conditions by near-infrared evanescent-wave cavity ring-down absorption spectroscopy. Employing a miniature monolithic optical resonator, we find sharp (=10 cm$^{-1}$) and polarized (>10:1) vibration-combination bands for surface OH and adsorbed H$_2$O, which reveal ordered species in distinct local environments. Indicating first-monolayer uniqueness, the absorption bands for adsorbed H$_2$O show intensity saturation and line narrowing with completion of one monolayer. Formation of the ordered H$_2$O monolayer likely arises from H bonding to a quasicrystalline surface OH network.

DOI: 10.1103/PhysRevLett.95.166104

PACS numbers: 82.65.+r, 78.30.–j, 82.45.Mp

Thin H$_2$O layers on surfaces have a profound effect on industrial and environmental processes [1] and may catalyze prebiotic chemistry on interstellar media [2]. Although experimental investigations of the molecular-level structure of H$_2$O films on well-defined metal surfaces abound [3], comparable studies on oxide surfaces have been emerging only more recently [4–9]. Ubiquitous in science, technology, and the environment, the amorphous-SiO$_2$ (a-SiO$_2$) surface is particularly important [9,10]. As is well known, the surface chemistry of a-SiO$_2$ is controlled principally by surface hydroxyl (or silanol) groups, which play a major role in many broad areas of interest, such as heterogeneous catalysis [11], chromatography [12], atomic layer deposition (ALD) [13], and ordering of liquids [14]. Models of the a-SiO$_2$ surface are often based on B-cristobalite, which is a crystalline phase of SiO$_2$ having similar density and refractive index. The a-SiO$_2$ surface is approximated as a random patchwork of (100) and (111) B-cristobalite facets, which support geminal [=Si(OH)$_2$] and isolated (≡SiOH) surface hydroxyls, respectively. Recent theoretical studies of water adsorption on hydroxylated (100) $\alpha$ and $\beta$ cristobalite [15,16] as well as other oxide surfaces [17–19] have predicted the formation of unique “ice” monolayers at room temperature, where full hydrogen bonding (4-coordinated oxygen) is achieved through interaction with surface hydroxyl groups as well as nearest H$_2$O neighbors. Yet a paucity of experimental techniques is available to probe oxide surfaces with submonolayer sensitivity, especially amorphous oxide surfaces under ambient conditions [20].

Here, the structure of a water monolayer on atomically smooth a-SiO$_2$ is investigated under ambient conditions using a variant of cavity ring-down spectroscopy (CRDS) [21–25] to probe a vibration-combination transition in the near IR, revealing unique structural insight.

Vibrational spectroscopic techniques, including sum-frequency generation [4,8,26] and infrared absorption [1], have been used to study H$_2$O films on planar oxide surfaces by probing the fundamental OH-stretching (νOH) absorption in the mid-IR, where the presence of ordering at the interface has been associated with the appearance of a broad bulk-ice-like absorption feature at room temperature. However, the uniquely ordered H$_2$O monolayers predicted to exist on hydroxylated oxide surfaces [15–19] should have distinct vibrational signatures compared to bulk ice. The νOH spectra of H-bonded surface hydroxyl and adsorbed water are typically broad (=100 cm$^{-1}$), overlapping, and approach conventional detection limits at one monolayer coverage, obscuring subtle first-monolayer structural details. Moreover, the νOH mode shows large changes in oscillator strength with the H-bonding environment [27], which complicates quantitative analysis of spectral intensities. Although weaker than fundamentals, overtone and combination modes in the near IR can provide greater conformational resolution and sensitivity to the local environment [28], while oscillator strengths remain nearly conserved between different H-bonding environments [27]. However, detection of these weak modes on a smooth surface requires unusually high sensitivity. For example, the peak absorption cross section for the 2νOH + δOH mode of surface hydroxyl, which derives from the combined excitation of the first OH-stretching overtone (2νOH) and the in-plane OH-bending mode (δOH), is estimated to be $5 \times 10^{-22}$ cm$^2$/OH, based on measurements using high-surface-area porous $\alpha$-SiO$_2$ [10,29]. For a monolayer having surface density of $5 \times 10^{14}$OH/cm$^2$, the expected absorption loss is $1 \times 10^{-6}$, which is well beyond the detection limit of conventional near-IR spectrometers, but within the operable range of CRDS [21].

Employing evanescent-wave CRDS [22–25], we probe the small absolute optical losses arising from the 2νOH + δOH vibration-combination mode of surface species on the atomically smooth total-internal reflection (TIR) surface of a high-finesse (ultra-low-loss) monolithic folded optical resonator [23,24]. Depicted in Fig. 1, the resonator
was fabricated from a single, right-triangular monolith of ultrapure \( \alpha \)-SiO\(_2\) (\(<50\) ppb bulk OH by weight; optical loss \(<2.3 \times 10^{-6}/\text{cm at 1200 nm}\)), having a 2.0 cm edge dimension and a thickness of 0.5 cm. The two planar, high-reflectivity coated (>99.998%) surfaces and convex TIR surface (9.0 cm radius of curvature) were chemomechanically polished to 0.05 nm root-mean-square roughness. The surface (9.0 cm radius of curvature) were chemomechanically polished to 0.05 nm root-mean-square roughness. The per pass loss of the resonator was coating limited, reaching a minimum of \(2.0 \times 10^{-5}\) at 1205 nm, which yielded a base ring-down time of 4.3 \(\mu\)s. The area probed by the evanescent field at the apex of the TIR surface is \(\pi \sqrt{2(85 \times 99)} \mu \text{m}^2\) for the fundamental mode at 1200 nm, which is fixed in position by the monolithic design, providing a precisely defined sample region. Having been exposed to ambient conditions for a protracted time, the resonator was cleaned with high purity methanol, but was not subjected to any postfabrication heating. Spectra of the surface hydroxyl layer and adsorbed water were obtained as a function of relative humidity (RH) at ambient temperature (22 °C) by mounting the resonator in a simple flow cell supplied with dry N\(_2\) gas or N\(_2\)/H\(_2\)O mixtures of known RH [30]. Using the idler of a seeded-tripled-Nd:YAG-pumped optical parametric oscillator operating at 30 Hz, laser pulses (\(=0.5 \text{ mJ/pulse, 6 ns, linewidth } <10 \text{ cm}^{-1}\)) were weakly focused at normal incidence on a planar surface of the resonator to excite a distribution of low-order modes. Spectral scans were reproducible to within \(\pm 1 \text{ cm}^{-1}\), although the absolute accuracy of our wave number scale has been established only to within \(\pm 15 \text{ cm}^{-1}\). Input and output polarizations were selected with Glan-laser polarizing beam splitters to provide similar amplitude ring-down transients in simultaneously measured \(s\)- and \(p\)-polarized channels [31]. Each data point was an average of 75 loss measurements using a weighted least-squares fit to extract each decay time, which yielded a typical 1\(\sigma\) noise level of \(3 \times 10^{-8}\) optical loss.

As shown in Fig. 2, this sensitivity level reveals considerable structure in the \(2\nu\text{OH} + \delta\text{OH}\) region, which is superimposed on a quartic background arising mostly from coated-surface reflectivity loss. The two solid plots in Figs. 2(a) and 2(b) show simultaneously measured \(s\)- and \(p\)-polarized spectra obtained after a prolonged exposure (days) of the resonator to dry N\(_2\) at room temperature. The corresponding dashed plots were obtained by then exposing the (relatively) dry surface to N\(_2\) gas with 10% RH, where a stable response was obtained within seconds. In Fig. 2(a), the two peaks observed at 8119 and 8154 \(\text{cm}^{-1}\) correspond reasonably well to a doublet observed on high-surface-area porous \(\alpha\)-SiO\(_2\) and assigned to the \(2\nu\text{OH} + \delta\text{OH}\) mode [29]. Moreover, these peaks show little change with exposure to water vapor at 10% RH (dashed plots). Therefore, we tentatively assign these features to the \(2\nu\text{OH} + \delta\text{OH}\) mode of surface hydroxyl on atomically smooth \(\alpha\)-SiO\(_2\). Yet, the peaks in Fig. 2(a) are much sharper than observed on porous \(\alpha\)-SiO\(_2\) [29] and may be instrumentally broadened, having linewidths comparable to the laser source (<10 cm\(^{-1}\)). Further, the spectral features are distinctly polarized with each peak showing only a trace signal in the orthogonal polarization state. Because the \(s\)- and \(p\)-polarized surface electric fields are oriented parallel and perpendicular to the surface plane, respectively, the highly polarized spectra in Fig. 2(a) indicate distinctly oriented surface species [22–25].

In Fig. 2(b), four new peaks are observed at (solid plots) 8199(\(p\)), 8241(\(s\)), 8260(\(p\)), and 8389(\(s\)) \text{cm}^{-1} having apparent widths of 11.3, 14.1, 29.2, and 16.6 \text{cm}^{-1}, respectively, which are also highly polarized and show a strong response to the 10% RH flow stream. We assign these peaks to oriented water molecules, which are H bonded.
to the surface hydroxyls and possibly to each other. Notice some surface-bound water remains even after prolonged exposure to dry N\textsubscript{2} (solid plots) at ambient temperature. The four peaks observed in Fig. 2(b) have no experimental precedent to our knowledge. Perry and Li [32] observed a broad absorption maximum at 8418 cm\textsuperscript{-1}, which was assigned to partially H-bonded water on wet \textit{\alpha}-SiO\textsubscript{2}. Similarly, we also observe a broad peak at 8413 cm\textsuperscript{-1}, which we interpret as multilayer adsorption [33] based on its proximate frequency and broad linewidth. In Figs. 3(a) and 3(b), a wider range of humidity is explored for \textit{s} and \textit{p} polarizations, respectively, where a global least-squares-fit quartic background has been subtracted. Note that peak of the 8199 cm\textsuperscript{-1} area is incurred. For the surface hydroxyl peaks, a small lowing exposure to 10\% RH, although a 61\% increase in tion of a full maximum surface density. A similar saturation behavior of Fig. 3(a) shows an expanded view of the mum intensity but is ultimately lost in the noise. The inset of Fig. 3(a) shows an expanded view of the 8241 cm\textsuperscript{-1} H\textsubscript{2}O peak, clearly revealing the saturation effect. Intensity saturation is expected if the peaks derive from genuine first-monolayer surface modes, having a well-defined maximum surface density. A similar saturation behavior was observed for the icelike \nu O\textsubscript{D} fundamental of adsorbed D\textsubscript{2}O on mica as a function of RH at room temperature [8]. Moreover, a decrease (= 1 cm\textsuperscript{-1}) in linewidth of the four H\textsubscript{2}O peaks is observed upon exposure to 10\% RH, which suggests an increase in surface order occurs with completion of a full H\textsubscript{2}O monolayer [33]. For example, the width of the 8199 cm\textsuperscript{-1} H\textsubscript{2}O peak decreases by 0.9 cm\textsuperscript{-1} following exposure to 10\% RH, although a 61\% increase in area is incurred. For the surface hydroxyl peaks, a small width increase (= 1 cm\textsuperscript{-1}) is observed with exposure to 10\% RH (e.g., 1.3 cm\textsuperscript{-1} increase for the 8154 cm\textsuperscript{-1} peak), which we interpret as an increase in the coverage of surface hydroxyls having bound water. Small redshifts are also observed for all peaks with increasing RH, which likely result from local field changes as the average water coverage increases. Also in Figs. 2 and 3 weak peaks are observed at (dry N\textsubscript{2}) 8360(p), 8275(s), and 8300(s) cm\textsuperscript{-1}. Showing only a redshift with increasing RH, these peaks may arise from the second C-H stretch overtone of residual hydrocarbon, which is often observed by traditional surface science techniques on otherwise clean surfaces.

In previous studies of surface-hydroxyl overtone and combination modes, which required high-surface-area forms of \textit{\alpha}-SiO\textsubscript{2} to enable signal detection, interpretation of the 2\nu OH + \delta OH region was controversial [29,32,34]. To account for the observed doublet, Morrow and MacFarlan [34] proposed the presence of two chemically distinct forms of surface hydroxyl (isolated and vicinal H-bonded pairs), while Burneau and Carteret [29] argued the doublet arises from the splitting of the fundamental \delta OH mode by coupling to a nearby surface-siloxane (O-Si-O) stretching mode. Although deuterium exchange studies apparently support the assignment of Burneau and Carteret [29], a variety of other investigations indicate the importance of geminal hydroxyls [9,35], which were not consid-
of Yang et al. [15,16] for H2O adsorbed on hydroxylated (100) α, β-cristobalite. Using \textit{ab initio} total energy density-functional theory and molecular-dynamic calculations with periodic boundary conditions, Yang et al. predicted the formation of an icelike monolayer consisting of interconnected square assembles of water molecules. The monolayer was predicted to remain intact at room temperature, although some calculations suggest otherwise [36]. In their simulated fundamental (mid-IR) spectrum of the icelike monolayer, Yang et al. observed a νOH doublet originating from surface hydroxyl groups and four blueshifted H2O νOH modes that resulted in three peaks due to a degenerate pair (appearing at 3275 cm\(^{-1}\)), where the degenerate modes were assigned to in-plane and out-of-plane OH vibrations. Correspondingly, we observe a surface hydroxyl doublet and four blueshifted 2νOH + δOH H2O peaks, including a nearly degenerate, oppositely polarized pair at 8241(s) and 8260(p) cm\(^{-1}\). However, the 8260(p) cm\(^{-1}\) peak, which is lost at 75% RH, would then be associated with the rather strong linkage to the hydroxylated surface. Indeed, the unique properties of the δOH bending mode complicate direct comparison of the νOH and 2νOH + δOH spectral regions [37], but the sharp, polarized spectra we observe showing linewidth reduction and intensity saturation at low RH support the existence of an ordered and distinct first monolayer.

In summary, we have demonstrated unprecedented vibrational spectroscopy of an insulator surface by probing combination modes of hydroxyl and adsorbed water on atomically smooth α-SiO\(_2\) under ambient conditions with submonolayer sensitivity. We find strong evidence of ordering of the α-SiO\(_2\) surface and adsorbed H2O monolayer. Considering the importance, prevalence, and variability of α-SiO\(_2\), the ultrasmooth α-SiO\(_2\) surface explored here could serve as a relatively well-defined system, for example, to test theoretical models of surface structure and reactivity. The technique employed can also potentially be extended to other oxide surfaces by using the surface hydroxyl groups as reactive sites to grow thin oxide films by ALD [13]. Moreover, first- and second-order overtones and vibration combinations of other important oscillators, such as C-H and N-H are also accessible within the low-loss region of selected α-SiO\(_2\), permitting a wide range of submonolayer surface chemistry to be probed.

We thank R. Sattmann and G. Lu of Hereaus-Tenevo for supplying material. Financial support is acknowledged from DOE-EMSP, NIST intramural ATP, The Netherlands FOM, and the Royal Netherlands Academy of Arts and Sciences (W. M. M. K.)

[30] Relative humidity was determined by a commercial hygrometer (±2%; 25%–95% RH) and a known dilution factor for the lowest RH conditions at 22 °C.
[31] The near-IR ring-down transients were free-space coupled to a high-speed, 125 MHz bandwidth, InGaAs detector with a 300 μm diameter active area and digitized by a 12-bit, 100 MHz, data acquisition system.
[33] On many glass or silica surfaces at ambient temperature a coverage of \( \approx 1 \) monolayer of water is estimated at 10% RH, while multilayer adsorption begins to dominate above 60% RH. See, for example, A. L. Summer et al., Phys. Chem. Chem. Phys. \textbf{6}, 604 (2004). However, for an average coverage of 1 monolayer small islands of multilayer adsorption and corresponding vacancies in the first monolayer would likely exist.