

Waveguide terahertz time-domain spectroscopy of nanometer water layers

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Waveguide terahertz time-domain spectroscopy is demonstrated to have the sensitivity to characterize nanometer-thick water layers on the surfaces of a parallel-plate metal waveguide. The measured far-infrared absorption and index of refraction of the 20-nm water layers are in reasonable self-consistent agreement with those of bulk water. © 2004 Optical Society of America

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Recently progress has been made in the study of guided-wave propagation of subpicosecond terahertz (THz) pulses.^{1–5} The efficient coupling of broadband THz pulses into waveguides of different configurations is achieved by quasi-optics, which incorporates hyperspherical or plano-cylindrical silicon lenses. Single-mode and low-loss propagation has been demonstrated in a plastic ribbon waveguide with pulse broadening that is due to group-velocity dispersion² and in a parallel-metal-plate waveguide with nondispersive TEM mode propagation.^{3,4} These studies have made possible new applications of THz radiation. One of these applications is waveguide THz time-domain spectroscopy (THz-TDS), which can be used to measure the absorption and the dielectric constant of a thin, nanometer layer in the waveguide.

For a metal waveguide with a thin dielectric layer the total loss comes from both the metal walls and the dielectric layer.¹ By comparing the signal from the empty guide with that from the waveguide containing the dielectric layer, one can extract the changes in both amplitude and phase caused by the addition of the layer. Knowing the layer thickness, one can then obtain the absorption and the index of refraction of the layer material. The sensitivity of this measurement is proportional to the ratio between the length and the plate separation of the waveguide¹ such that, when the waveguide is properly configured, this method can be used to characterize extremely thin layers of low-loss materials.

In this Letter we report the study of nanometer water layers on a parallel-metal-plate waveguide. The water layer has a self-consistent determined thickness of 20 nm, which is equivalent to approximately 64 molecular layers, and shows an index of refraction and an absorption that are similar to those of bulk water.^{6–8} This result is consistent with other studies, in which, for thicknesses greater than 10 nm, water behaves as bulk water.⁹ In contrast, a THz-TDS study of submonolayer water adsorbed in hydrophilic silica aerogel was recently reported¹⁰ for which the adsorbed water has remarkably different absorption properties from those of bulk water.

Figure 1 shows the experimental setup of the broadband THz-TDS system, which consists of a THz transmitter and a THz receiver along with beam-shaping and steering components. The THz pulse is gener-

ated and detected by photoconductive switching of the transmitter and the receiver with 40-fs optical pulses from a Ti:sapphire laser. Between the paraboloidal mirrors is a cylindrical vacuum chamber of 188 mm (length) \times 80 mm (diameter), with two 50 mm (diameter) \times 10 mm (thickness) silicon windows for the THz beam to pass through. Placed in the middle of the vacuum chamber along the THz beam path, the waveguide assembly is composed of two identical copper plates with dimensions of 63.5 mm (length) \times 6.3 mm (thickness) \times 27.9 mm (width) and separated by 52 μ m and with two plano-cylindrical lenses to couple the THz pulses into and out of the guide.³ The copper plates were hand polished by grade-2000 sandpaper to a mirror finish with submicrometer surface flatness. Before assembling the waveguide we cleaned the plates first by plasma etching in oxygen to remove the hydrocarbons, followed by plasma etching in forming gas of 95% argon and 5% hydrogen to achieve hydrophilicity on the plates. Thermoelectric coolers and thermocouples are used to adjust the temperature of the waveguide within an accuracy of ± 0.2 °C; the temperature of the warmer silicon lenses is kept constant at 19 °C during the experiment.

In the experiment, first the vacuum chamber is pumped to below 50 mTorr and the waveguide temperature is reduced to 9.0 °C; then the chamber is filled with pure water vapor to initiate the experiment. The reference scan is then obtained with the chamber kept at 8.10 Torr of water vapor and the waveguide temperature at 9.0 °C, which is above the dew point of the water vapor so there is no water condensation on

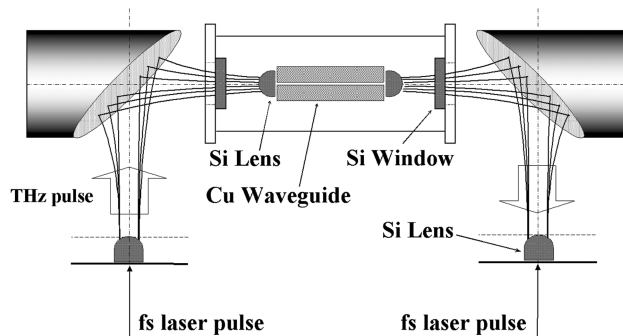


Fig. 1. Experimental setup.

the guide. After this scan, the water vapor pressure is slowly increased to 8.70 Torr, which is slightly above the saturation water vapor pressure at the waveguide temperature of 9.0 °C. The water layer is gradually formed on the inner surfaces of the waveguide under this condition, and a consequent time delay and signal drop can be observed. The water vapor pressure is then carefully adjusted to produce a balance point at which the amplitude and the timing of the THz signal pulse remain constant, indicating an unchanging water layer. The signal scan is then measured at this water vapor pressure. The corresponding measured reference and signal scans are presented in Fig. 2(a), where the reference scan has been shifted for clarity. The respective spectra are shown in Fig. 2(b), where the sharp absorption lines are due to water vapor.¹¹

It is important to note that the data scans have a relatively long time extent compared with the main transmitted pulse. We made the scans long so we would be able to display the water lines in the frequency-domain spectra with as high an experimental resolution as possible. Consequently, it is easy to separate the broadband absorption of the water layer from the sharp water lines.

The inset of Fig. 2(a) is an enlargement of the transmitted pulse, showing that the signal scan is delayed by 0.06 ps with an estimated uncertainty of ± 0.02 ps owing to the water layer on the waveguide surfaces. In the experiment, THz pulses propagate in the nondispersive TEM mode of the waveguide.³ For this case the phase difference between the signal scan and the reference scan can be calculated as¹

$$\arg\left[\frac{A_l(\omega)}{A_{\text{ref}}(\omega)}\right] = \frac{2\pi[1 - 1/\epsilon_l(\omega)]L\Delta l}{b\lambda_0}, \quad (1)$$

where \arg denotes the phase angle in radians, ω is the angular frequency, $A_l(\omega)$ and $A_{\text{ref}}(\omega)$ are the complex spectra of the signal and the reference scans, respectively, $\epsilon_l(\omega)$ is the relative dielectric constant of the water layer, $b = 52 \mu\text{m}$ is the separation between the waveguide plates, λ_0 is the free-space wavelength, $L = 63.5 \text{ mm}$ is the length of the waveguide, and Δl is the water layer thickness on each plate. Thus, given the layer thickness, the index of refraction of the layer material $n_l = (\epsilon_l)^{1/2}$ could be calculated from our measurements by use of Eq. (1). However, because it was not possible for us to measure the thickness of the water layer directly, in the calculation we adjust layer thickness Δl to get the index of refraction to match the known value for bulk water at 0.86 THz in the quiet region between the two absorption peaks of water vapor near 0.75 and 0.99 THz.^{8,10} This is physically reasonable in that water appears to behave as bulk water for thicknesses greater than 10 nm.⁹ For this case the layer thickness is then obtained as $l = 20 \text{ nm}$, to within an accuracy of $\pm 3 \text{ nm}$. The power absorption coefficient can then be calculated as¹

$$\alpha_l(\omega) = -\ln(|A_l(\omega)/A_{\text{ref}}(\omega)|) \frac{bn_l^3}{L\Delta l}. \quad (2)$$

In Eq. (2) the index of refraction of bulk water from the previous measurement,⁸ as displayed in Fig. 3(a), is used for n_l . The calculated index of refraction and power absorption coefficient determined from the experiment are shown in Figs. 3(a) and 3(b), respectively, along with the previous measurement results from bulk water.

The spikes in the index of refraction and the power absorption coefficient are caused by the sharp absorption lines of water vapor.¹¹ If both the reference and the signal scans were obtained at the same vapor pressure, in principle, these lines should be canceled out in the calculation. However, here the vapor pressures for the two scans are slightly different; any noise and instability in the system will cause these discontinuities. Keeping in mind that the data were forced to fit the index at 0.86 THz indicated by the arrow in Fig. 3(a), we found that the overall dependence of the index matches reasonably well the previous measurement from bulk water.⁸ The measured power absorption coefficient is slightly higher than the results from bulk water. The discrepancy is within the accuracy of our measurement but could also be due to surface conditions of the waveguide and to aberrations in water-layer uniformity. Indeed, the roughness of waveguide surfaces is on a submicrometer level, compared with the water-layer thickness of

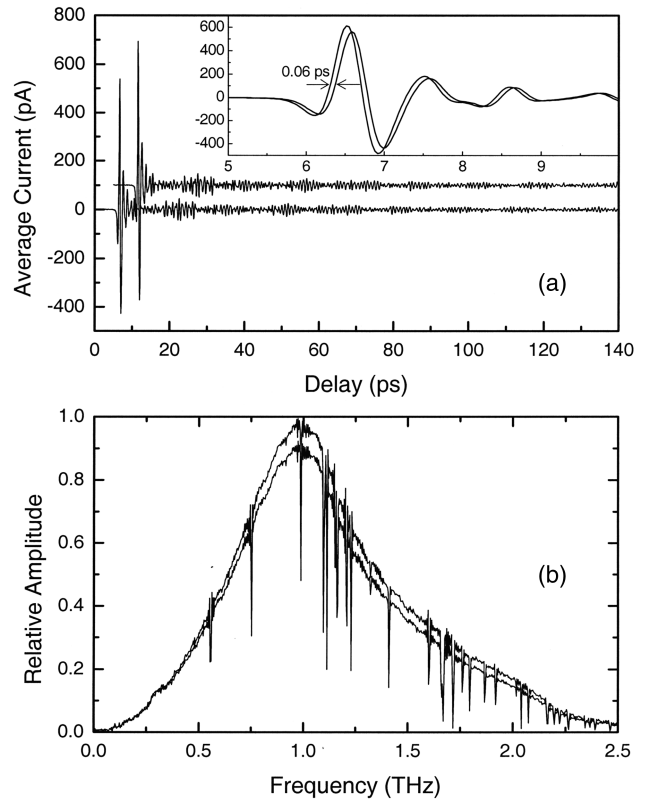


Fig. 2. (a) Measured reference and signal pulses and (b) their respective spectra. The reference pulse has been shifted for clarity. Top curves in both (a) and (b): reference, 8.10-Torr water vapor at 9.0 °C. Bottom curves: sample, 8.68-Torr water vapor at 9.0 °C. The inset of (a), enlargement of the transmitted pulses.

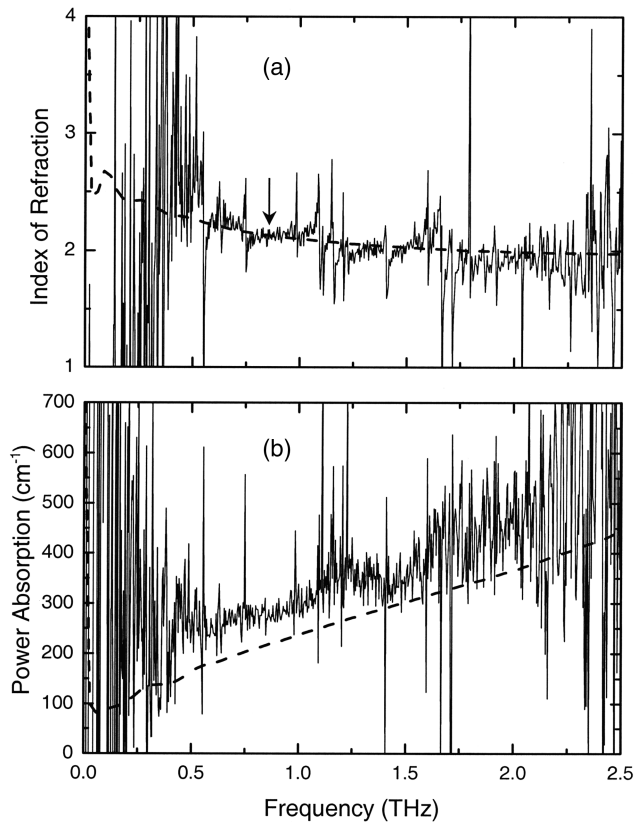


Fig. 3. (a) Index of refraction and (b) power absorption coefficient obtained with $\Delta l = 20$ nm. Dashed lines, results for bulk water.

20 nm. The roughness would increase the actual absorption because of the increased surface area. In addition, surface roughness will also affect the layer uniformity, making the calculation inaccurate when one is using Eqs. (1) and (2).

The major goal of this research has been the demonstration of the sensitivity of waveguide THz-TDS to nanometer layers of material. Here, because water layers were previously shown to have bulk water properties for thicknesses greater than ~ 10 nm,⁹ our forced fit to the bulk index of water at 0.86 THz allowed us to determine a 20-nm thickness of the measured layer, equivalent to approximately 64 monolayers. The resultant frequency-dependent index and absorption coefficient of the layer from our measurements are consistent with those of bulk water, thereby validating our simple approach. However, an independent measure of sample thickness is needed for characterizing an unknown material.

Many thin-film preparation techniques combined with separate thickness monitoring could be used to

fabricate multiple monolayer films of interest with a known thickness on the individual waveguide plates or separate sample plates. These plates would then be installed in a waveguide assembly for the THz-TDS measurement. Examples of such samples include thin films of metals, alloys, semiconductors, dielectrics, and polymers to be applied by the techniques of thermal or *e*-beam evaporation, sputtering, laser ablation, or molecular beam epitaxy. Langmuir-Blodgett films could also be applied to waveguide or sample plates to make possible measurements of aligned complex organic molecules, proteins, and DNA. Another general and versatile technique is the layer-by-layer assembly method,^{12,13} which can produce suitable layers of nanostructured composite multilayers specifically tuned for the adsorption of a particular class of material, thereby enhancing the analyte's adsorption on the waveguide's surface. The layer-by-layer method can also produce aligned layers with a known thickness of single-walled nanotubes.

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