

Simultaneous determination of density and viscosity of liquids based on quartz-crystal resonators covered with nanoporous alumina

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Quartz-crystal resonators were coated with a layer of alumina nanopores in order to allow for simultaneous measurement of density and viscosity of a liquid. Whereas the motion of the liquid contained in the pores is locked to the movement of the crystal, the liquid located above the surface experiences internal shear. The latter portion of the liquid dissipates energy, thereby increasing the bandwidth of the resonance. Based on the increase in bandwidth, viscous loading and mass loading can be distinguished, allowing for an independent determination of the density and the viscosity of Newtonian liquids. © 2005 American Institute of Physics. [DOI: 10.1063/1.1942646]

INTRODUCTION

The quartz-crystal microbalance (QCM) is traditionally used to determine the areal mass density of films deposited on one crystal surface.¹ The analysis is mostly based on the Sauerbrey equation

$$\frac{\delta f}{f} = -\frac{m_f}{m_q}, \quad (1)$$

where m_f is the mass per unit area, $m_q = Z_q/(2f_0)$ is the mass per unit area of the quartz plate, $Z_q = 8.8 \times 10^6 \text{ kg m}^{-2} \text{ s}^{-1}$ is the acoustic impedance of the quartz, f_0 is the frequency of the fundamental resonance, δf is the frequency shift, $f = nf_0$ is the frequency of the respective overtone, and n is the overtone order. In the Sauerbrey limit, the presence of the film does not affect the bandwidth. The frequency shift δf scales as the overtone order n .

If the load is not a thin film, but rather a semi-infinite liquid, the Kanazawa relation holds^{2,3}

$$\frac{\delta f}{f_0} = \frac{\delta f + i\delta\Gamma}{f_0} = \frac{i}{\pi Z_q} Z_l = \frac{i}{\pi Z_q} \sqrt{i\omega\rho\eta} = \frac{i-1}{\sqrt{2}\pi Z_q} \sqrt{2\pi n\rho f_0}, \quad (2)$$

where δf^* is the complex frequency shift, $\delta\Gamma$ is the shift of the half-band half-width ("bandwidth," for short), Z_l is the acoustic impedance of the liquid, ρ is the density of the liquid, and η is its viscosity. Because of the relation $(i)^{1/2} = (1+i)/2^{1/2}$, the shifts in frequency and bandwidth are the same. They both scale as the square root of the overtone order n , because of the $\omega^{1/2}$ term on the right-hand side. The shifts in frequency and bandwidth are a function of the viscosity-density product $\rho\eta$. Neither of the two parameters can be individually determined on the basis of the Kanazawa relation.

We propose to use nanoporous alumina layers created on the crystal surface in order to separately determine the density and the viscosity of the liquid. The separation is based on the fact that the portion of liquid situated inside the pores does not experience shear and therefore acts like a film in the Sauerbrey sense, whereas the liquid above the alumina layer is not locked to the motion of the crystal and therefore is described by the Kanazawa relation (Fig. 1). The details of this separation are justified below. This concept in itself has been described previously. Martin *et al.* have used microfabrication techniques to generate a strongly corrugated surface serving as the rigid scaffold.^{4,5} The same group holds a patent;⁵ Schön *et al.* have used mesoporous TiO_2 for a similar purpose.⁶ A related concept has also been used with surface acoustic wave devices.⁷ Here, we report on the use of alumina nanopores. Impedance analysis gives access to the frequency as well as the bandwidth. A reference resonator is not needed. The comparison of the different overtone orders provides for redundancy and also allows for a measurement of the viscosity as a function of frequency.⁸

Porous alumina layers grown by anodization of aluminum in diluted polyprotic acids are known since half a century ago.⁹ The size of the pores can be adjusted in the range

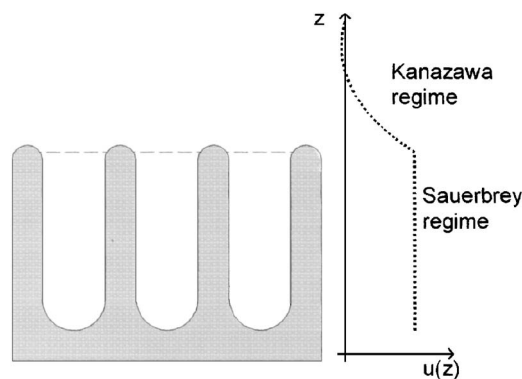


FIG. 1. Principle of measurement: the crystal surface is covered with a layer of alumina nanopores. The part of the liquid which is contained in the pores does not increase the bandwidth because it is not sheared. Based on a comparison of the shift in frequency δf and bandwidth $\delta\Gamma$, both the density and the viscosity can be determined.

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of 5–300 nm by the parameters of the anodization process. The depth of the pores is adjustable via the anodization time. The preparation of nanoporous alumina layers is relatively easy. The properties and applications of such layers are, for example, reviewed in Ref. 10. Reference 11 provides an overview of the use of alumina nanopores for sensing. In the context of the QCM, nanopores are attractive because they provide a rigid framework for the uptake of liquid, which is otherwise difficult to obtain. Alumina is chemically inert and insoluble in water and in most organic liquids. The pores are oriented perpendicular to the surface. The surface-to-volume ratio is not as large as for other scaffolds used for similar purposes. Given that uncontrolled surface chemistry and slow adsorption processes often occur at surfaces, such a small surface-to-volume ratio is beneficial. A pore size on the order of 100 nm is also helpful with regards to the issue of wetting.¹² For very small pores, the liquid may not penetrate into the pores. For the present work, we can only conclude *a posteriori* that wetting is not a major concern because the derived values come close to the literature values.

SAMPLE PREPARATION

An optically polished AT quartz crystal with a fundamental frequency of 5 MHz (Maxtek, Santa Fe Springs, CA) was cleaned in surfactant solution (Hellmanex, Germany). An aluminum electrode of about 1000-nm thickness was thermally evaporated onto the crystal surface. Subsequently, the aluminum electrode was either anodized in a 0.3M solution of oxalic acid at 0 °C and 50 V (resulting in a pore diameter of about 50 nm) or anodized in a 0.4M solution of phosphoric acid at room temperature and 80 V (resulting in a pore size of about 80 nm). The anodization times were chosen as about 85% of the time needed for complete oxidation of aluminum layer. The pore sizes were determined by atomic force microscopy.

Because the dynamic instability giving rise to the pores develops a few nanometers underneath the surface, the alumina surface appears closed and rather smooth after anodization. For the details of the growth process, we refer the reader to Ref. 10. Even for “closed” pores, the liquid can easily reach the pores through small holes in the oxide cover layer. In order to completely open the pores, the alumina layer was in some cases treated with a solution of chromic acid (0.2M) and phosphoric acid (0.4M) at 60 °C for 2 min. This process not only opens the pores but also widens them to some extent. Figure 2 shows atomic force microscopy (AFM) images of the surfaces before and after anodization.

DATA ACQUISITION

Frequency shift δf and the shift of the half-band half-width $\delta\Gamma$ were measured by means of a network analyzer (5100A from Agilent). The analyzer sweeps the frequency around the resonance frequency and determines the spectra of the conductance $G(\omega)$ and the susceptance $B(\omega)$. Resonance frequency and bandwidth are determined by fitting resonance curves to the conductance spectra. In liquids, the resolution of the instrument is about 1 Hz. This procedure was repeated for the overtone orders 3, 5, 7, 9, and 11.

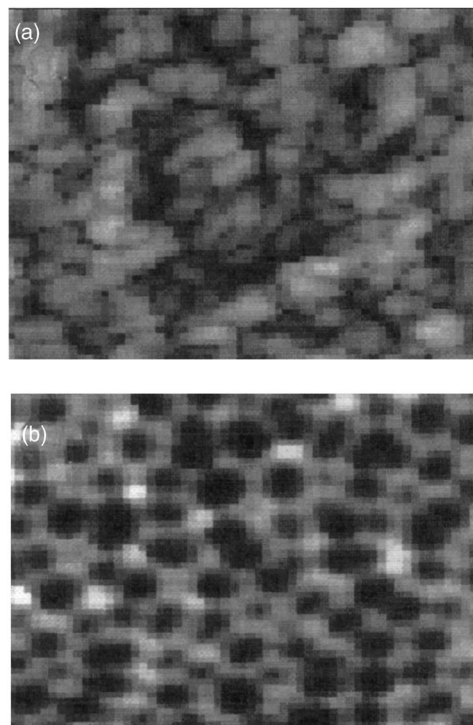


FIG. 2. AFM images of the alumina layer at different stages of the sample preparation. The lateral size is 1 μm , the vertical scale is 150 nm. (a) Thermally evaporated aluminum layer before anodization. (b) Sample after 10 min of anodization (50 V, 0.3-M oxalic acid, 0 °C, 5 min of anodization in a mixture of phosphoric acid and chromic acid at 60 °C, and a second 10-min anodization as in step 1. The intermediate step serves to open the pores. Surfaces with closed pores look similar to the untreated surface.

As a model system, mixtures of ethanol and water were chosen.¹⁰ Due to hydrogen bonding, ethanol–water mixtures display a pronounced maximum of the viscosity at an ethanol fraction of about 42%. The viscosity and density of these mixtures are tabulated in Ref. 13. The quartz plates were mounted in the holder CHC100 from Maxtek (Santa Fe Springs, CA) with the surface facing up. The liquid was just poured onto the crystal in its holder until the surface was completely covered. A typical liquid volume was 1 ml. The holder was mounted with a slight inclination with respect to the horizontal, so that the liquid surface and the crystal surface were not strictly parallel. This avoids the occurrence of standing compressional waves between the crystal surface and the air-water interface.¹⁴ We checked for the presence of such standing waves by adding of small amounts of liquid, thereby increasing the distance between the crystal and the air-water interface. Adding liquid did not change the resonance frequency.

DATA ANALYSIS

In order to derive density and viscosity from the shifts in frequency and bandwidth, a viscoelastic model is needed. We treat the layer of alumina nanopores as a viscoelastic layer with the exact same acoustic properties as the quartz. For a viscoelastic layer in a liquid environment one has¹⁵

$$\frac{\delta f^*}{f_0} \cong \frac{i}{\pi Z_q} Z_f \frac{Z_f \tan(k_f d_f) - Z_l}{Z_f + i Z_l \tan(k_f d_f)}, \quad (3)$$

where Z_f is the acoustic impedance of the film, $Z_l = (i\omega\rho\eta)^{1/2}$ is the acoustic impedance of the liquid, k_f is the wave number of shear sound in the film, and d_f is the thickness of the film.

Since the thickness of the alumina layer is much less than the wavelength of sound, one can Taylor expand Eq. (3) to first order in d_f , resulting in

$$\begin{aligned} \frac{\delta f^*}{f_0} &\cong \frac{i}{\pi Z_q} \left[Z_L + Z_f k_f d_f \left(1 - \frac{Z_L^2}{Z_f^2} \right) \right] \\ &= \frac{i}{\pi Z_q} \left[\sqrt{i\omega\rho\eta} + i\omega m_f \left(1 - \frac{Z_L^2}{Z_f^2} \right) \right] \\ &\approx \frac{1}{\pi Z_q} \frac{i-1}{\sqrt{2}} \sqrt{\omega\rho\eta} - \frac{2nf_0}{Z_q} m_f, \end{aligned} \quad (4)$$

where the relation $Z_f k_f = \rho\nu\omega / \nu = \rho\omega$ (ν the speed of sound) has been used in the second line and the approximation $Z_L^2 \ll Z_f^2$ has been used in the third. In the thin-film limit, the Sauerbrey term and the Kanazawa term are *additive*. We write $\delta f = \delta f_{\text{Sau}} + \delta f_{\text{Kan}}$ and $\delta\Gamma = \delta\Gamma_{\text{Sau}} + \delta\Gamma_{\text{Kan}}$. Equation (4) is the basis of the separation of mass and viscosity.

For Newtonian liquids one has $\delta f_{\text{Kan}} = -\delta\Gamma_{\text{Kan}}$. Since the *entire* increase in bandwidth originates from the Kanazawa term, $\delta\Gamma_{\text{Sau}}$ is zero and one can write

$$\delta f_{\text{Kan}} = -\delta\Gamma_{\text{exp}}. \quad (5)$$

The trapped portion of the liquid causes an additional frequency shift δf_{Sau} (but no shift in bandwidth). One has

$$\delta f_{\text{Sau}} = \delta f_{\text{exp}} - \delta f_{\text{Kan}}. \quad (6)$$

The mass of the trapped liquid is given by

$$m_{\text{Sau}} = -\frac{Z_q}{2nf_0^2} \delta f_{\text{Sau}}. \quad (7)$$

With a calibrated volume per unit area of the pores, V , this translates to a density

$$\rho = \frac{m_{\text{Sau}}}{V} = -\frac{Z_q}{2nf_0^2 V} \delta f_{\text{Sau}}. \quad (8)$$

Finally, with the known density, the viscosity can be extracted from the Kanazawa relation [Eq. (2)] and the bandwidth as

$$\eta = \frac{2\pi^2 Z_q^2}{\rho\omega f_0^2} \delta\Gamma^2. \quad (9)$$

RESULTS AND DISCUSSION

Figure 3 shows a set of raw data. The data on the left-hand side were acquired with an ethanol weight fraction of 96%, whereas the data on the right-hand side were obtained with a mixing ratio close the maximum of the viscosity (42% ethanol). The pore volume was 8 nl/cm². Initially, the crystal was exposed to air. At a certain time, the liquid was added. In order to emphasize the deviation from the behavior on flat

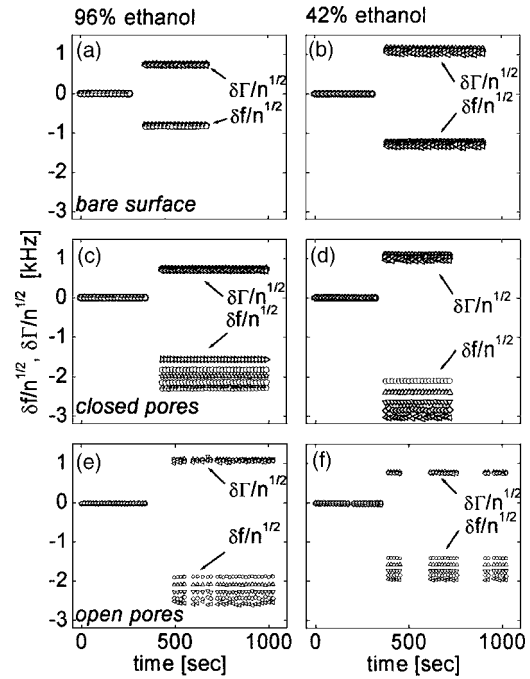


FIG. 3. Raw data (shifts frequency and bandwidth) for the bare quartz surface, a crystal with closed pores, and a crystal with open pores. The left and right columns show data acquired with an ethanol weight fraction of 96% and 42%, respectively. The different symbols correspond to the overtones: \circ : 15 MHz, \triangle : 25 MHz, ∇ : 35 MHz, \diamond : 45 MHz, and \lessdot : 55 MHz.

surfaces as described by the Kanazawa equation, frequency and bandwidth are displayed in the same graph. Also, all shifts have been divided by $n^{1/2}$. In this representation, the values from different overtone orders superimpose if the Kanazawa relation is obeyed.

For the data sets shown in panels (a) and (b), this superposition is indeed observed. Also, the magnitude of the change is about the same for frequency and bandwidth. As expected, the Kanazawa relation holds in the absence of pores. We comment on the fact that the bandwidth is slightly less than the negative frequency shift in a separate publication.¹⁶ We believe that this disparity is related to nanoscopic air bubbles. Panels (c) and (d) show the analogous data for a crystal where the pores have been grown, but are still closed. The negative frequency shift is now larger than the increase in bandwidth. The $n^{1/2}$ scaling no longer holds. This deviation from the Kanazawa behavior is caused by the part of the liquid which is trapped in the pores. Finally, panels (e) and (f) show the analogous data, where the pores have been opened by an etching process. The deviation from the Kanazawa behavior has increased somewhat because the volume of the pores has become larger.

Figures 4 and 5 show the outcome of the analysis for this experiment and for a second data set, where the pore volume had been increased by a factor of 4 relative to the data shown in Fig. 4. The comparison shows that the volume increase has a beneficial effect on the achieved precision. Eight different mixing ratios were investigated. The full line corresponds to the literature values. The experimental data agree with the literature values within 2% (density) and 5% (viscosity). The simultaneous determination of density and vis-

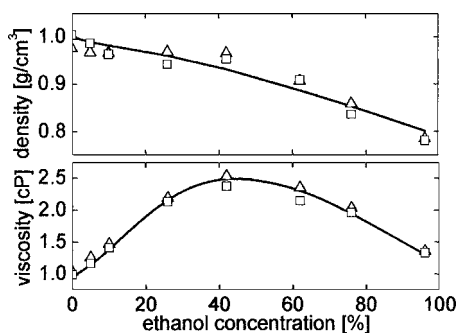


FIG. 4. Results of the simultaneous determination of density and viscosity with closed (\square) and open (\triangle) alumina pores. The solid line shows the literature values. The volume of the pores as determined by calibration with liquids of known density was 8 nl/cm^2 (corresponding to an equivalent depth of 80 nm, where “equivalent” indicates a vanishing volume of the pore walls).

cosity works well and is easily carried out. The preparation of the alumina pores is fast and easy; the measurement itself is done in less than 30 min.

Comparing the data from a crystal with open and with

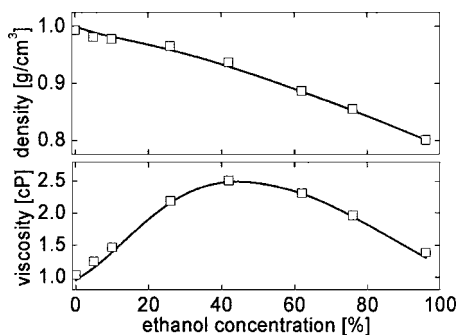


FIG. 5. Same data as in Fig. 4 with an increased in the pore volume (equivalent depth of 320 nm, closed pores). Clearly, the improved surface-to-volume ratio results in an improved accuracy.

closed pores, one finds the achieved precision is comparable. Evidently, the liquid easily penetrates through the cover layer. The detailed analysis shows that the precision is slightly better for closed pores, which we attribute to smaller effects of roughness.

CONCLUSIONS

Layers of nanoporous alumina nanopores have been created on the surface of quartz-crystal resonators. When immersing these structures into a liquid, the liquid inside the cavities moves rigidly with the crystal, whereas the liquid above the surface experiences shear strain. Based on this effect, the density and the viscosity of a liquid can be determined independently.

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