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The effect of SU-8 patterned surfaces on the response of the quartz crystal microbalance

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Abstract

In this work we present data showing the effect of patterning layers of SU-8 photoresist on a quartz crystal microbalance (QCM) and subsequent chemical treatment to increase their hydrophobicity. Patterns with 5 μm diameter pillars spaced every 10 μm have been fabricated with heights of 3 μm, 5 μm and 10μm in addition to equivalent thickness flat layers. Contact angle measurements have been made before and after the hydrophobic chemical treatment. The change in resonant frequency of the QCM has been investigated as the surfaces were submerged in solutions of water/PEG with changing viscosity-density product.

Keywords: QCM, TSM, SU-8, hydrophobic, superhydrophobic, contact angle

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1. Introduction

The majority of acoustic wave sensors designed for operation in the liquid phase use a shear mode of oscillation. Amongst the most widely used acoustic wave devices is the thickness shear mode (TSM) quartz crystal microbalance (QCM). The first quantitative model for solid films attached to a quartz surface was given by Sauerbrey [1]. This model gives a frequency change proportional to the change in surface area mass density and the square of frequency. However if the interface is between a liquid and a solid, rather than a gas/solid and a solid, the motion of the liquid entrained by the crystal oscillation is damped and decays within a penetration depth $\delta=\sqrt{(2\eta/\omega\rho)}$ of the interface [2,3]. Here ω is the angular frequency and η and ρ are the dynamic viscosity and the density of the fluid. The Kanazawa and Gordon equation then describes both a frequency shift and a damping of the crystal resonance proportional to the square root of the viscosity-density product of the liquid. The Sauerbrey equation can be applied for attachment of mass to a solid surface from the liquid phase.

It is recognized in the literature that surface roughness can enhance the response of an acoustic wave sensor [4,5]. A number of models have been proposed for this effect, including Martin *et al*'s suggestion of a trapped mass of liquid acting as a rigid mass load [6,7] in addition to the Kanazawa and Gordon liquid response. Further, Theisen *et al.* [8] have suggested that for a TSM device the contact angle on a rough surface can lead to trapped gas and hence a trapped mass response dependent on the hydrophobicity of the surface. Thompson *et al.* [9-11] have suggested that interfacial slip may occur so that a contact angle dependent response might exist even on a smooth surface. Ellis *et. al.* [12] have provided a predictive model showing how the equilibrium contact angle on a QCM surface might lead to interfacial slip. Recently, McHale and Newton [13] have shown how a hydrodynamic slip boundary condition can provide a theoretical basis for either a trapped mass response or an interfacial slip response.

In this work we have investigated the effect on the resonant frequency of a QCM of systematically patterning layers of SU-8 photo-resist on the QCM crystal and of a subsequent chemical coating to produce hydrophobic, tending to super-hydrophobic, surfaces.

2. Experimental

SU-8 is an epoxy based negative photo-resist that can be used to fabricate thick patterns with smooth walls and which is strong, stiff and chemically resistant after processing. The properties of SU-8 also make it suitable for making super-hydrophobic surfaces in the form of arrays of pillars. Super-hydrophobic surfaces are hydrophobic surfaces with high surface roughness and/or high aspect ratio surface texture. The combination of hydrophobic surface chemistry and surface roughness/texture can reduce interaction between water and the surface and so allow drops to roll off surfaces that are slightly inclined [14,15]. In a recent article Hossenlopp *et al.* [16] have demonstrated that SU-8 has suitable properties for applications as a wave-guide material for shear-horizontal surface acoustic wave devices (SH-SAW) by depositing flat layers of SU-8 on a QCM. In recent work [17], we have reported a technique that allows routine patterning of SU-8 on commercially available 5 MHz quartz crystals (Maxtek), with gold electrodes; note that the main difficulty in fabrication of SU-8 in this way comes from the reflective gold electrode on the QCM. Fig. 1 shows typical electron microscope images of the patterned surfaces. The resonant frequency of the QCM was measured at each stage by mounting it in a Maxtek CHC-100C sample holder and recording the spectrum using an Agilent 8712ET network analyser over the frequency range 4.8 to 5.4 MHz. The CHC-100C sample holder was filled with 0.8 ml for each test solution, which corresponded to a depth of 3 mm; this ensured that the height was much greater than the penetration depth of the acoustic wave into the liquid. The contact angle was measured for drops, of volumes in the range 3–6 μl, for the different solutions and on the different surfaces using a Krüss DSA10 contact angle meter.

The pillar size was chosen to be 5 μm diameter with a centre-centre separation of 10 μm and with heights from 3 μm to 10 μm; equivalent thickness flat layers of SU-8 were also investigated. Solutions of 3350 molecular weight Poly (ethylene glycol) (PEG) were produced giving zero, 0.02, 0.04, 0.06 .0.8, 0.10, 0.12 and 0.14 mol and having viscosities from 678 mPa s to 20000 mPa s. For each solution the crystals were fully immersed and the resonance spectra captured. The crystals were then cleaned sufficiently to allow the resonant frequency to return to the initial value. Following testing, the surfaces were coated with a thin layer of hydrophobising chemical originally designed for waterproofing breathable fabrics (Grangers Extreme Wash In) and the test solutions repeated.

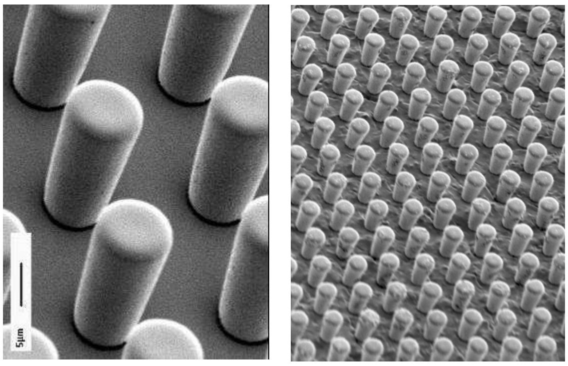

Fig. 1. Electron microscope images of typical SU-8 patterns on the quartz crystal microbalance.

3. Results and Discussion

In Fig. 2 we show the contact angle on flat SU-8 surfaces compared to the contact angle on the patterned surfaces for different solutions of PEG on 3 μm (open diamonds) and 10 μm (open squares) tall patterns; the trend lines have been included only as a guide to the eye. The pure water provides the highest contact angles and the highest molar PEG solution provides the lowest contact angles. Pure water on the 3 μm tall patterns shows a contact angle of 80^{o} and this increases to 101^{o} for the 10 μm tall patterns clearly demonstrating the effect of surface patterning. The solid symbols represent the contact angles for the same surfaces treated with the hydrophobic treatment, which now give a contact angle for water of 120^{o} for the 3 μm tall patterns and 146^{o} for the 10 μm

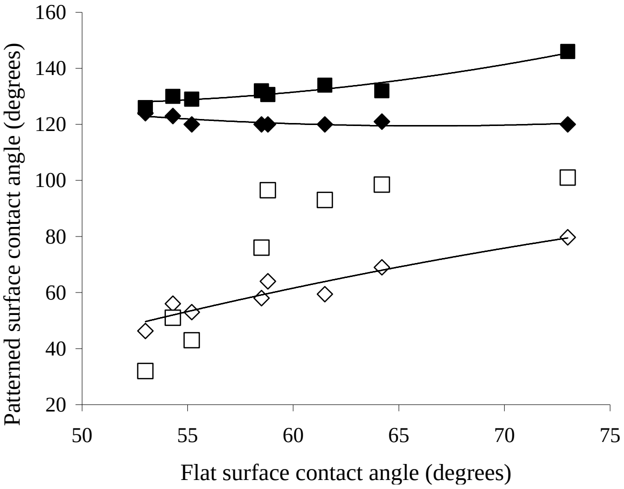

Fig. 2. Contact angles for different concentrations of PEG on smooth and patterned surfaces without hydrophobic coating; 3 μm tall (open diamonds) and 10 μm tall (open squares) and with hydrophobic coating 3 μm tall (solid diamonds) and 10 μm tall (solid squares).

patterns. The trends observed in this data are consistent with what is expected from a Cassie-Baxter form of superhydrophobicity [15].

In Fig. 3 we show the decrease in resonant frequency of the QCM for the 3 μm thick flat layer (open diamonds) and 3 μm high pillars (open triangles), both without hydrophobisation, as a function of the square root of the density-viscosity product of the different solutions of PEG. Note that in this format the pure water is on the extreme left and the highest molar PEG solution to the extreme right. The flat surfaces show a trend consistent with the Kanazawa and Gordon model; the 3 μm tall patterns show a more significant frequency change, but still with the same general trend. This indicates that the effect of the structure is more complex than a simple mass response as the pillars have less mass than the flat layers but produce a greater fall in frequency. The solid symbols show the effect of the hydrophobic treatment on the 3 μm flat (solid diamonds) surfaces and the 3 μm tall patterns (solid triangles). Neither set of data show any significant difference compared to without the hydrophobic treatment.

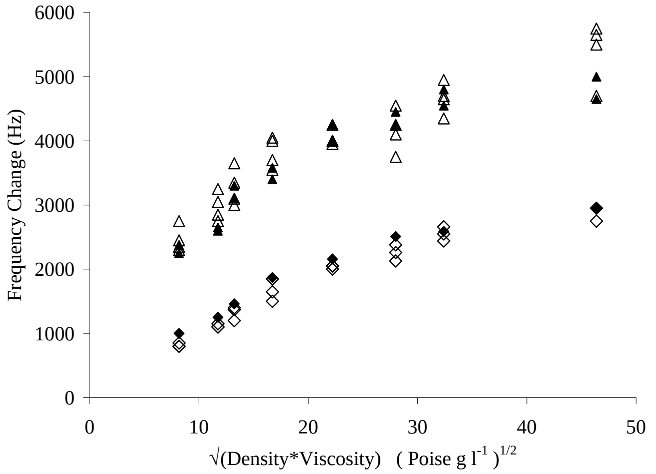

Fig. 3. Change in resonant frequency as a function of the square root of the density-viscosity product for 3 μm thick flat surfaces without hydrophobic treatment (open diamonds), 3 μm thick flat surfaces with hydrophobic treatment (solid diamonds), 3 μm tall patterns without hydrophobic treatment (open triangles) and 3 μm tall patterns with hydrophobic treatment (solid triangles).

Above 3 μm the effect of hydrophobisation of the patterns becomes more significant; data for 5 μm tall patterns is shown in Fig. 4. The open diamonds show the frequency changes for the patterns without hydrophobic treatment with the characteristic increasing frequency change (decrease) with increasing density-viscosity product and showing around twice the magnitude of that for the 3 μm tall structures. The solid diamonds show the effect of the hydrophobic coating is to produce a smaller frequency change than the equivalent untreated surfaces; hyrophobising this patterned surface therefore reduces the magnitude of the frequency decrease. This would be

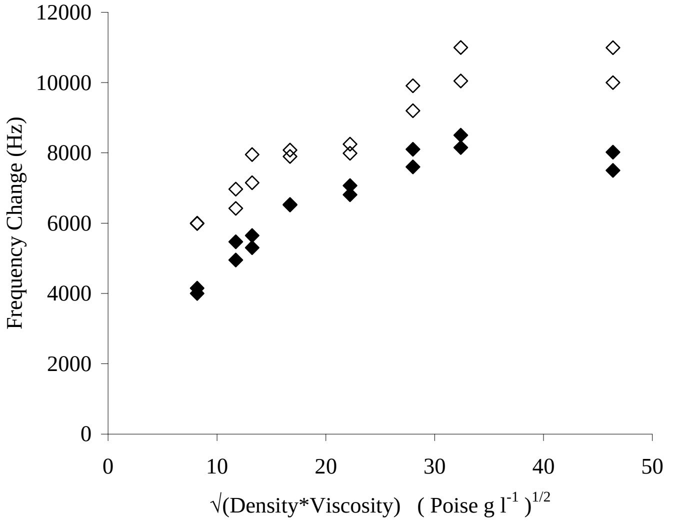

Fig. 4. Change in resonant frequency as a function of the square root of the density-viscosity product for 5 μm tall patterns without hydrophobic treatment (open diamonds) and 5 μm tall patterns with hydrophobic treatment (solid diamonds).

consistent with there being less penetration of the liquid into the patterns as would be expected for a super-hydrophobic surface obeying a Cassie-Baxter mechanism.

The most dramatic changes have been observed for the 10 μm tall structures however the data shows some scatter and, for the hydrophobic treated structures the patterns start to be removed with the cycling of the water/PEG solutions. In Fig. 5 the open triangles are the data for a 10 μm thick flat layer giving the characteristic Kanazawa and Gordon trend. The open squares represent the data for three samples having 10 μm tall patterns. Although these taller structures are much harder to fabricate with reliable patterns across the whole crystal surface, the trend described in this data is clear and contrary to the data for the smaller structures. All these tall patterns show a larger frequency shift for water than for the PEG solutions. Contact angle measurements (Fig. 2) show that in this range of heights the pattern is having a significant effect on the apparent hydrophobicity of the surface. The solid diamonds shows data for two water/PEG cycles on the same 10 μm tall structure, but after it had been coated with the hydrophobic treatment. Initially, the effect was dramatic with a much reduced frequency shift, which was also lower than that for the 10 μm flat layer (solid diamonds closest to the square root of the density-viscosity product axis). However on the subsequent cycle the effect was to give a response which was much larger and may be an indication of damage to the structures and/or the hydrophobic coating.

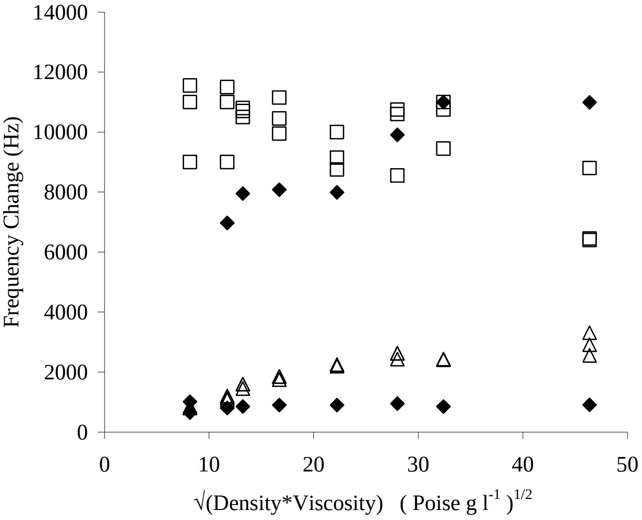

Fig. 5. Change in resonant frequency as a function of the square root of the density-viscosity product for 10 μm thick flat surfaces without hydrophobic treatment (open triangles), 10 μm tall patterns without hydrophobic treatment (open squares) and 10 μm tall patterns with hydrophobic treatment (solid diamonds).

4. Conclusion

In this work we have presented data showing the effect of patterning layers of SU-8 photoresist on a quartz crystal microbalance and subsequent chemical treatment to increase their hydrophobicity. Flat layers of SU-8 have shown a typical Kanazawa and Gordon like response to changes in the density viscosity product of covering liquid. Patterns with 5 μm diameter pillars separated by 10 μm with heights of 3 μm have also shown this type of response, but with a larger frequency shift even though there is less mass associated with the layers. The effect on the frequency shift of chemical hydrophobic treatment has been negligible on both these surfaces. Patterns with 5 μm diameter pillars separated by 10 μm with heights 5 μm have almost doubled the frequency shift of the 3 μm tall structures; the effect of the hydrophobic treatment has been shown to be to reduce this frequency decrease compared to the equivalent untreated structures. The most striking results were observed for the 10 μm tall structures, which tended to super-hydrophobic behaviour with the chemical treatment and which showed an opposite trend in the quartz crystal frequency change.

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