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## **Postprint Version**

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

C.R. Evans, G. McHale, N.J. Shirtcliffe, S. M. Stanley and M.I. Newton\*

School of Biomedical and Natural Sciences,  
The Nottingham Trent University,  
Clifton Lane,  
Nottingham NG11 8NS, UK

### **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  $\mu\text{m}$  diameter pillars spaced every 10  $\mu\text{m}$  have been fabricated with heights of 3  $\mu\text{m}$ , 5  $\mu\text{m}$  and 10 $\mu\text{m}$  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

Corresponding author e-mail [michael.newton@ntu.ac.uk](mailto:michael.newton@ntu.ac.uk)

## 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  $\omega$  is the angular frequency and  $\eta$  and  $\rho$  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.

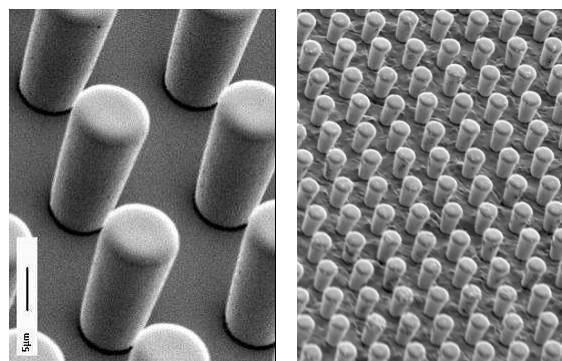
In this work we have investigated the effect on the resonant frequency of a QCM of systematically patterning layers of SU-8 photo-resist on the QCM crystal and of a subsequent chemical coating to produce hydrophobic, tending to super-hydrophobic, surfaces.

## 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  $\mu\text{l}$ , for the different solutions and on the different surfaces using a Krüss DSA10 contact angle meter.

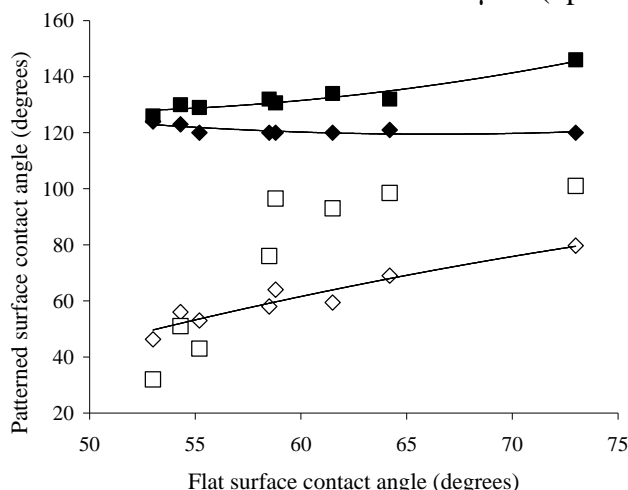
The pillar size was chosen to be 5  $\mu\text{m}$  diameter with a centre-centre separation of 10  $\mu\text{m}$  and with heights from 3  $\mu\text{m}$  to 10  $\mu\text{m}$ ; equivalent thickness flat layers of SU-8 were also investigated. Solutions of 3350 molecular weight Poly (ethylene glycol) (PEG) were produced giving zero, 0.02, 0.04, 0.06, 0.08, 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

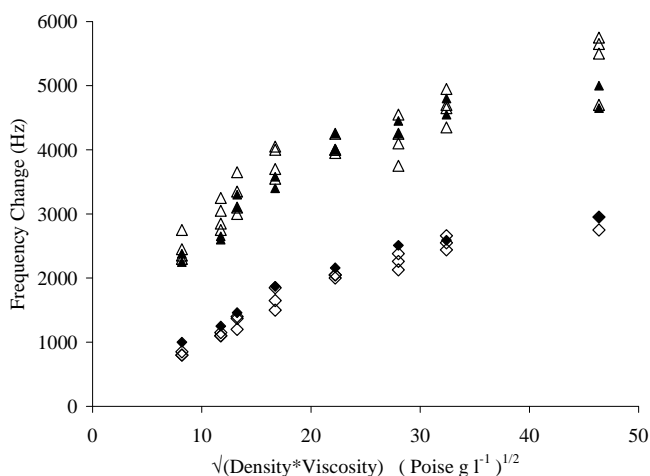
In Fig. 2 we show the contact angle on flat SU-8 surfaces compared to the contact angle on the patterned surfaces for different solutions of PEG on 3  $\mu\text{m}$  (open diamonds) and 10  $\mu\text{m}$  (open squares) tall patterns; the trend lines have been included only as a guide to the eye. The pure water provides the highest contact angles and the highest molar PEG solution provides the lowest contact angles. Pure water on the 3  $\mu\text{m}$  tall patterns shows a contact angle of 80° and this increases to 101° for the 10  $\mu\text{m}$  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° for the 3  $\mu\text{m}$  tall patterns and 146° for the 10  $\mu\text{m}$



**Fig. 2.** Contact angles for different concentrations of PEG on smooth and patterned surfaces without hydrophobic coating; 3  $\mu\text{m}$  tall (open diamonds) and 10  $\mu\text{m}$  tall (open squares) and with hydrophobic coating 3  $\mu\text{m}$  tall (solid diamonds) and 10  $\mu\text{m}$  tall (solid squares).

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

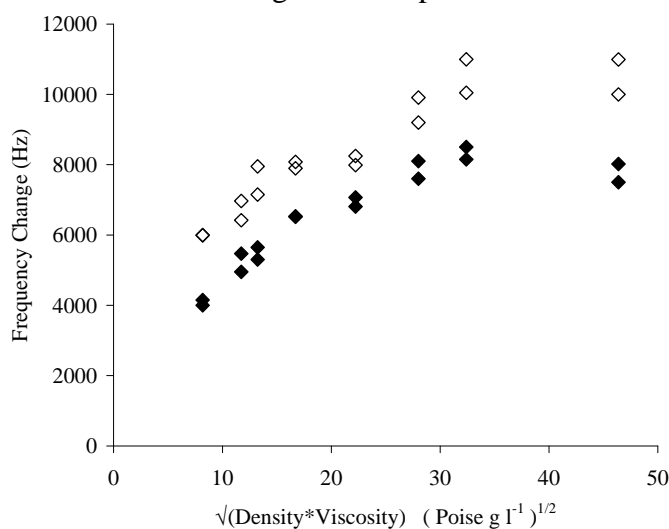
In Fig. 3 we show the decrease in resonant frequency of the QCM for the 3  $\mu\text{m}$  thick flat layer (open diamonds) and 3  $\mu\text{m}$  high pillars (open triangles), both without hydrophobisation, as a function of the square root of the density-viscosity product of the different solutions of 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  $\mu\text{m}$  tall patterns show a more significant frequency change, but still with the same general trend. This indicates that the effect of the



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

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  $\mu\text{m}$  flat (solid diamonds) surfaces and the 3  $\mu\text{m}$  tall patterns (solid triangles). Neither set of data show any significant difference compared to without the hydrophobic treatment.

Above 3  $\mu\text{m}$  the effect of hydrophobisation of the patterns becomes more significant; data for 5  $\mu\text{m}$  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  $\mu\text{m}$  tall structures. The solid diamonds show the effect of the hydrophobic coating is to produce a smaller frequency change than the equivalent untreated surfaces; hydrophobising this patterned surface therefore reduces the magnitude of the frequency decrease. This would be

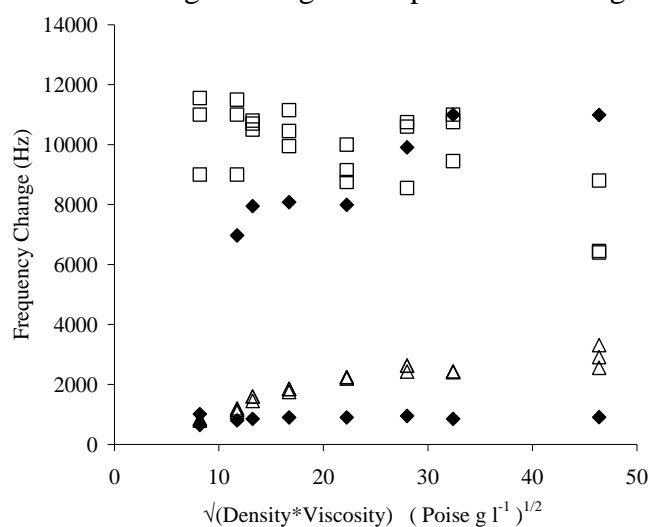


**Fig. 4.** Change in resonant frequency as a function of the square root of the density-viscosity product for 5  $\mu\text{m}$  tall patterns without hydrophobic treatment (open diamonds) and 5  $\mu\text{m}$  tall patterns with hydrophobic treatment (solid diamonds).

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  $\mu\text{m}$  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  $\mu\text{m}$  thick flat layer giving the characteristic Kanazawa and Gordon trend. The open squares represent the data for three samples having 10  $\mu\text{m}$  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  $\mu\text{m}$  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  $\mu\text{m}$  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  $\mu\text{m}$  thick flat surfaces without hydrophobic treatment (open triangles), 10  $\mu\text{m}$  tall patterns without hydrophobic treatment (open squares) and 10  $\mu\text{m}$  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  $\mu\text{m}$  diameter pillars separated by 10  $\mu\text{m}$  with heights of 3  $\mu\text{m}$  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  $\mu\text{m}$  diameter pillars separated by 10  $\mu\text{m}$  with heights 5  $\mu\text{m}$  have almost doubled the frequency shift of the 3  $\mu\text{m}$  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  $\mu\text{m}$  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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## References

- [1] G.Z. Sauerbrey, Verwendung von Schwingquarsen zur Wängung dünner Schichten und zur Mikrowängung. *Z. Phys.* 155 (1959) 206-222.
- [2] S. Bruckenstein and M. Shay, Experimental aspects of use of the quartz crystal microbalance in solution. *Electrochim. Acta* 30 (1985) 1295-1300.
- [3] K.K. Kanazawa and G.J. Gordon, Frequency of a quartz microbalance in contact with a liquid. *Anal. Chem.* 57 (1985) 1770-1771.
- [4] R. Schumacher, G. Borges and K.K. Kanazawa, The quartz crystal microbalance – A sensitive tool to probe surface reconstructions on gold electrodes in liquid. *Surf. Sci.* 163 (1985) L621-L626.
- [5] R. Schumacher, J.G. Gordon and O. Melroy, Observation of morphological relaxation of copper and silver electrodes in solution using a quartz microbalance. *J. Electroanal. Chem.* 216 (1987) 127-135.
- [6] S.J. Martin, G.C. Frye, A.J. Ricco and S.D. Senturia, Effect of surface roughness on the response of thickness shear mode resonators in liquids. *Anal. Chem.* 65 (1993) 2910-2922.
- [7] S.J. Martin, Interactions of acoustic waves and thin films and interfaces: Closing Remarks. *Faraday Discuss.* 107 (1997) 463-476.
- [8] L.A. Theisen, S.J. Martin and A.R. Hillmann, A model for the quartz crystal microbalance frequency response to wetting characteristics of corrugated surfaces. *Anal. Chem.* 76 (2004) 796-804.
- [9] M. Thompson, A.L. Kipling, W.C. Duncan-Hewitt, L.V. Rajakovic and B.A. Cavic-Vlasak, Thickness shear mode acoustic wave sensors in the liquid phase – A review. *Analyst* 116 (1991) 881-890.
- [10] M.S. Yang and M. Thompson, Surface morphology and the response of the thickness shear mode acoustic wave sensor in liquids. *Langmuir* 9 (1993) 1990-1994.
- [11] M.S. Yang, M. Thompson and W.C. Duncan-Hewitt, Interfacial properties and their response of the thickness shear mode acoustic wave sensor in liquids. *Langmuir* 9 (1993) 802-811.
- [12] J.G. Ellis, G. McHale, G.L. Hayward and M. Thompson, Contact angle-based predictive model for slip at the solid-liquid interface of a transverse-shear mode acoustic wave device. *J. Appl. Phys.* 94 (2003) 6201-6207.
- [13] G. McHale and M.I. Newton, Surface roughness and interfacial slip boundary condition for quartz crystal microbalances. *J. Appl. Phys.* 95 (2004) 373-380.
- [14] T. Onda, S. Shibuichi, N. Satoh and K. Tsujii, Super-water-repellent fractal surfaces. *Langmuir*, 12 (1996) 2125-2127.
- [15] G. McHale, M.I. Newton and N.J. Shirtcliffe, Super-hydrophobic and super-wetting surfaces: Analytical potential? *Analyst* 129 (2004) 284-287.
- [16] J. Hossenlopp, L. Jiang, R. Cernosek and F. Josse, Characterization of Epoxy Resin (SU-8) film under thickness shear mode (TSM) resonator under various conditions. *J. Polym. Sci. B: Polym. Phys.* 42 (2004) 2373-2384.
- [17] N.J. Shirtcliffe, S. Aqil, C. Evans, G. McHale, M.I. Newton, C.C. Perry and P. Roach, The use of high aspect ratio photoresist (SU8) for super-hydrophobic pattern prototyping. *J. Micromech. Microeng.* 14 (2004) 1384-1389.