The Study of Interaction of Superhydrophobic (SH) Materials with Fluids using TSM sensors

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Abstract— Recent progress in nanotechnology has lead to development of novel materials with very unique superhydrophobic (SH) properties. In this paper we study the Thickness-Shear Mode (TSM) sensing technique as a potential measurement tool for characterization of SH properties of materials. The TSM sensors, coated with different SH thin films were capable to differentiate between a range of the SH properties of those films though the contact angle of those films, measured with optical techniques, have shown similar values. Also, the TSM sensors, coated with some of those SH films, exhibited almost zero attenuation and very small frequency shift when loaded with deionized water, which indicated a presence of significant slip in the mechanical interfacial boundary conditions. The observed sensitivity of the TSM technique to nanoscale-level structural features of SH films suggests that TSM sensing technology may provide more sensitive means for measurements and characterization of superhydrophobicity in comparison to the existing SH measurement techniques.

I. INTRODUCTION

Recent progress in nanotechnology has lead to development of new materials with very unique superhydrophobic (SH) properties [1-4]. SH materials have already enabled many novel applications in biotechnology, and the chemical, automotive and environmental industries as well they have opened new exciting possibilities of creating of new devices based on MEMS/NMES technologies; for example, self-propelled micro-fluidic systems. Further progress in synthesis and fabrication of SH materials depends strongly on the availability of precise measurement tools capable of interrogating SH features at the level where SH originates, i.e. at the nanoscale level. The TSM technique, due to its inherent features of nanoscale-level interrogation mechanisms, is a possible candidate for that task and may provide the base for novel SH measurement tools.

The purpose of this investigation is to evaluate Thickness-Shear Mode (TSM) sensing technique for the study of interfacial interaction of SH surfaces with deionized (DI) water loading and to correlate the TSM response with micro-nano-scopic features of SH surfaces. For many years acoustic wave devices, especially thickness-shear mode (TSM), have been used for characterization of broad range of interfacial processes [5, 6]. In the late 1950s, Sauerbrey investigated thin solid films and developed a relationship correlating the TSM resonant frequency shift to the surface mass density during deposition process. In the 1980s Kanazawa and Golden applied TSM technique for studying liquid media and correlated the resonant frequency shift with viscosity and density of the Newtonian liquid [7]. After that, several authors applied and tuned those concepts in variety of theoretical problems and experimental conditions proposing applications in the areas of surface physics and chemistry, biology, medicine, etc. [8, 9]. Despite the clear successes of these theories, there have been many reports about discrepancies between the theoretical and experimental data [2]. While most observations showed larger response of the TSM sensors than the theoretical expectations, which were related to surface roughness [2], Thompson et al. [1], reported smaller response of the TSM sensors than predicted by the theory when the surface of the TSM sensors were coated with hydrophobic films. In order to explain these discrepancies he postulated a slip at the interface between a TSM transducer and the liquid media. Following Thompson’s work, several other researchers have attacked the problem of slip-no-slip boundary conditions and proposed a novel their formulation [10, 11]. However, the experimental data and verification of the postulate of discontinuity of mechanical displacement and force at the interface of solid-liquid phase have been very limited and not comprehensive, and in many
Table 1 Physical properties of SH-films deposited on TSM sensors.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Film</th>
<th>Surface treatment</th>
<th>Contact angle</th>
<th>*DI Water drop on TSM sensors</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Gold</td>
<td>No treatment</td>
<td>80 °</td>
<td>TSM</td>
</tr>
<tr>
<td>2</td>
<td>SH (TFPTMOS)</td>
<td>(trifluoropropyltrimethoxysilane)</td>
<td>No treatment</td>
<td>140 °</td>
</tr>
<tr>
<td>3</td>
<td>SH + Chem. (HMDS)</td>
<td>Enhance hydrophobicity by providing methyl groups on the surface.</td>
<td>155 °</td>
<td>~600 nm</td>
</tr>
<tr>
<td>4A</td>
<td>SH + Chem. + NP</td>
<td>NP: silica nano particles increase the surface roughness &amp; geometrical SH mechanism.</td>
<td>155 °</td>
<td>~600 nm</td>
</tr>
<tr>
<td>4B</td>
<td>SH + Chem. + NP + UV</td>
<td>UV light treatment removes superhydrophobicity from the surface.</td>
<td>90 °</td>
<td>~600 nm</td>
</tr>
</tbody>
</table>

* These pictures shows the behavior of water droplet on prepared SH surfaces, however the whole area of SH surface was covered by 4 mm thickness of DI water layer during the measurements.

cases even being non-conclusive.

Recently, the development of novel superhydrophobic (SH) surfaces with unique characteristics has provided a new impetus to investigate the slip/no-slip boundary conditions. The typical characteristics of SH surfaces are its geometrical micro-scale roughness and a high contact angle (angle between the plane of the surface and the tangent to the surface of a droplet on it) \( \theta \), usually with \( \theta > 140^\circ \) [12-15].

In this study, the main goals are focused on evaluation of the thickness-shear mode (TSM) sensing technique for the study of interaction of SH surfaces with Newtonian liquid loading; correlation the TSM response with macro- and nano-scopic features of SH surfaces, and development of heuristic models explaining those interactions. The follow-up publications will address, in depth, mechanical (slip/non-slip) boundary conditions as well will propose quantitative models of TSM-SH-fluid phase interface.

II. EXPERIMENT

A. Sample Preparation

Four quartz crystal TSM sensors with 10 MHz fundamental resonant frequency were used to prepare five samples for the overall experiments. Sample No. 1 was a bare TSM sensor without any surface treatment on the gold electrode surface. The gold surface of No. 1 is neutrally wetting with a contact angle of about 80°. The No. 2 TSM sensor was coated with TFPTMOS (trifluoropropyltrimethoxysilane) as SH surface with the low surface free energy [13]. The thickness of TFPTMOS film was about 510 nm with 140° contact angle. This high contact angle shows the SH characteristic of the surface. The No. 3 sensor was the same as sample No. 2 with additional post liquid HMDS (hexamethyldisilizane) treatment of the TFPTMOS surface. The HMDS treatment enhances the hydrophobicity by providing more CH₃-pendent groups on the surface. The thickness was 510 nm and the contact angle was 155°. The No. 4A sensor was prepared with silica nano particles mixed in TFPTMOS to increase the surface roughness in nano-scale, and then the surface was treated with liquid HMDS, like sample No. 2. The thickness of sample 4A was slightly higher at 600 nm, but the contact angle remained at 155°. After the DI water loading measurements on Sample No. 4A, the surface of sample No. 4A was treated with ultra violet (UV) light to remove the super hydrophobicity from the surface. This was labeled as a sample No. 4B. Sample No. 4B has the same surface morphology as 4A while there is less hydrophobicity on the surface. All the SH samples were prepared and coated at Dr.
C. Jeffery Brinker’s laboratory at University of New Mexico. (Table 1 shows the physical properties of each sample).

B. Measurement system

A network analyzer based measurement system (shown in figure 1) was used to monitor the response of the TSM sensors loading with DI water. All the measurements were performed in an air flow controlled chemical hood, at room temperature (approximately 25 °C ± 0.1 °C). The whole surface of the sensor was covered by 200 µl (about 4 mm thickness) of DI water and the frequency responses (S21: forward transmission parameters) were measured at each harmonics (1st, 3rd, 5th, and 7th) of the water covered surface relative to the dry surface. The key measured parameters were the changes in resonant frequency (Δf) and attenuation (Δα) of the sensor.

III. RESULTS AND DISCUSSIONS

A. AFM Images and Roughness Analysis

Atomic Force Microscope (AFM) images of the surface of the entire sample were obtained in 3 µm x 3 µm scale to see the surface morphology. Tapping mode was used for imaging, and the diameter of the tip of AFM was 10 nm. The surface area of each sample was obtained by “roughness analysis” in the AFM. Image (a) in figure 2 is the AFM image of the surface of the No. 1, the TSM sensor. This image shows the actual surface morphology of a gold electrode on the TSM sensor. The measured surface area was 9.034 µm², and the surface is relatively smooth. Image (b) is the surface of sample No. 2, TSM with the SH film (TFPTMOS). There are many hills and valleys (uneven and rough) on the surface of sample No. 2. These hills and valleys are typical characteristic of SH surfaces to provide less surface area that directly contacts with water on it and also small surface free energy for water droplets to bead easily with high contact angle. The surface area of sample No. 2 was 10.575 µm² an increase in area of 18%. This increased surface area indirectly reveals the increased surface roughness. Image (c) shows the surface of sample No. 3 that the chemically (with liquid HDMS) treated surface of SH film coated TSM sensor. From the roughness analysis, it was shown that the surface area also increased (from 10.575 to 12.887 µm²) due to the chemically provided pendent methyl (CH₃) groups on the SH surface. Finally, image (d) shows the surface of sample No. 4A, TSM sensor coated with chemically (HMDS) treated silica nano-particle mixed TFPTMOS SH films. Basically presence of mixed nano-particles provide nano-scale roughness on the surface of the SH films and enhances the geometrical SH mechanisms on the surface. This can be seen from the slight increase in the surface area. The surface area was increased from 12.887 (sample No. 3) to 13.177 µm² (sample No. 4A). Therefore, each steps increased the SH characteristic on the surface of SH films and this was shown in the increases in the contact angle and Table 2 shows a summary of the roughness analysis of SH films on each sample by AFM.

B. Response of SH Film coated TSM sensors to DI water Loading

Each sample was mounted on a custom designed TSM sensor holder (see picture (b) in Figure 1) and this holder...
Table 2. Roughness Analysis of SH films on TSM sensors

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Area ((\mu m^2))</th>
<th>(^1)Surface Area Difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Bare TSM</td>
<td>9.034</td>
<td>0.377</td>
</tr>
<tr>
<td>2. TSM + SH</td>
<td>10.575</td>
<td>17.504</td>
</tr>
<tr>
<td>3. TSM + SH + Chem.</td>
<td>12.887</td>
<td>43.191</td>
</tr>
<tr>
<td>4A. TSM + SH + Chem. + NP</td>
<td>13.177</td>
<td>46.406</td>
</tr>
</tbody>
</table>

\(^1\)Original Area = 9 \(\mu m^2\)

was connected to the network analyzer based measurement system (see picture (a) in Figure 1). At the fundamental and 3rd harmonics (about 10 MHz and 30 MHz), the changes in the resonant frequency of bare TSM sensor (sample No. 1), sample No. 2, and No. 3 were similar with approximately 2 ~ 3 kHz changes at 1st harmonic and 5 ~ 6 kHz at 3rd harmonic while \(\Delta f\) of sample No. 4A showed relatively smaller changes in the resonant frequency with only 300 Hz and 800 Hz for 1st and 3rd harmonics. However, at 5th and 7th harmonics (50 MHz and 70 MHz), \(\Delta f\) of No. 2 and 3 are greater than \(\Delta f\) of sample No. 1 while \(\Delta f\) of sample No. 4A showed, again, smaller changes (see table No. 3 for details).

For the changes in the attenuation (\(\Delta \alpha\)), it seems that always the \(\Delta \alpha\) of sample No. 1 is greater than the others except at 3rd harmonic and as the harmonic increases the \(\Delta \alpha\) of sample No. 2, 3, and 4A are reduced and finally shows almost no changes (see table 4 for details).

Three obvious phenomena can be extracted from the graphs (a) and (b) in Figure 3:

- (1) Sample No. 4A always shows smaller \(\Delta f\) and \(\Delta \alpha\) than the other samples in all harmonics
- (2) At higher harmonics, such as 5th and 7th, \(\Delta f\) of sample No. 2 and 3 are greater than No. 1 while \(\Delta f\) of sample No. 4A is still smaller than No. 1
- (3) \(\Delta \alpha\) seems to be getting smaller as the harmonics increases in all samples

These can be explained based on the hypothesis that although the contact angle of water layer on the SH surface are similar, actual penetration depth of the floating (covering) water layer into the valleys of SH surface are dependent on the conditions (surface wettability) of the SH surface and this can be observed from the monitoring of TSM responses. The contact angle of water droplet on the surface of sample 2, 3, and 4A are similar with approximately 150° (see the table 1), but the response of TSM sensors to DI water loading of each SH sample are different and it is also dependent on the harmonics.

Figure 4 depicts a schematic showing the penetration of acoustic waves into the water layer. As the harmonics increases the penetration depth (\(\delta\)) of the acoustic waves in the water decreases. At lower harmonics, such as 1st and 3rd, the penetration depth (\(\delta\)) of shear acoustic waves are greater than the actual height of the hills and valleys of the SH surface so the viscous loading effect is dominant and results are similar for each sample. However, at higher harmonics,
such as 5th and 7th harmonics, the penetration depth of acoustic shear waves are similar to the height of the hills and valleys of the SH surfaces and the mass loading effect is greater than the viscous loading effect. This shows larger $\Delta f$ response on the sample No. 2 and 3 compare with No. 1. Since the penetration depth of water layer into the hills and valleys of sample No. 4A is smaller than sample No. 2 and 3, the mass loading effect will be smaller than No. 2 and 3 and, due to the smaller surface contact area between SH films and water layer, viscous effect will be also smaller than the other samples, such as sample No. 1, 2, and 3. Both the transmission line model [16] and Kanazawa model [7] assume continuity of mechanical shear stress and particle velocity so it is hard to explain the behaviors of sample No. 4A. Therefore this reduced response of sample No. 4A may explain the existence of slip boundary conditions at the boundary between SH surfaces and DI water.

C. Response of UV Treated SH Film coated TSM sensors to DI water Loading

After the experiments with DI water loading on the 4A, the SH surface of sample 4A was treated with ultraviolet (UV) light for about 30 minutes to remove the SH characteristic from the surface. This UV treatment does not change the surface morphology; rather it only breaks the chemically bonded CH$_3$ and CF$_3$ groups from the surface and provides less chemically hydrophobicity. The UV treated sample was labeled as a sample No. 4B. The contact angle on this 4B surface was approximately 90° (see table 1 in the appendix). Again, the closer to one of before $\Delta f$ and $\Delta \alpha$ of sample No. 4B were monitored and compared with before UV treatment (sample No. 4A) and bare TSM (sample No. 1). From the graphs (a) and (b) in Figure 5, it seems that the $\Delta f$ and $\Delta \alpha$ of UV treated sample (sample No. 4B) response to DI water loading is similar with one of bare TSM (sample No. 1) and $\Delta \alpha$ of UV treated sample (sample No. 4B) were similar to sample No. 1. Especially at higher harmonics, $\Delta \alpha$ of UV treated sample responses to DI water loading are getting approach UV treated surface (sample No. 4A).

Again, Figure 6 shows the hypothetical cross-section of DI water and uneven surface of films as DI water penetrates
into hills and valleys textured surface. Solid line indicates DI water sitting with high contact angle on before UV treated SH surface (sample No. 4A) and dotted line indicates DI water sitting with relatively low contact angle on after UV treated surface (sample No. 4B). The penetration depth of DI water on before UV treated SH surface and on after UV treated surface are different because of the different surface wettability. The penetration depth of DI water on after UV treated surface is larger than the other with small contact angle. This trapped DI water in uneven surface contributes more mass loading effect than viscous loading effect and this governing mass loading effect increase the Δƒ to similar to the one of bare TSM (sample No. 1).

IV. SUMMARY AND CONCLUSIONS

Five different SH films were characterized with three methods: (1) acoustic response of TSM sensors coated with SH film to DI water loading, (2) nano-scale SH surface morphology by AFM method, and (3) SH contact angle of DI water droplet by optical method. The SH surfaces were fabricated with five different processes. The AFM data representing the surface topography showed different results for each film. The differences in those data were next supported by TSM results which also showed the significant differences between those films. However, the optical data, based on the measurement of the contact angle, were not to be able to show dissimilarity. Specifically, the three SH films, fabricated with nanoparticles and dedicated chemical treatment showed the same measured contact angle; the optical method was capable of only measuring the difference between less hydrophobic (sample No. 1 and No. 4B) and more hydrophobic (sample No. 2, 3 and 4A). Typically the contact angle on less hydrophobic surfaces was approximately 80 ~ 90° while on more hydrophobic surfaces it was close to 150°.

Thus, though the contact angles of DI water droplet are similar on all SH films (sample No. 2, 3, and 4A), but acoustic method using TSM sensors clearly exhibited different responses in each samples. It is interestingly to notice that the TSM responses were dependent on the harmonic frequency. One of the SH films, sample No. 4A showed almost zero attenuation and very small frequency shift under DI water loading.

Ongoing work is focused on the development of quantitative models explaining interaction of TSM-SH sensors with fluidic media and providing feedback information leading to synthesis and fabrication high performance SH materials.

REFERENCES