Reliability of Self-Assembled Hydrophobic Coatings: Chemical Resistance and Mechanical Durability

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ABSTRACT

We report on hydrophobic self-assembled nano-scale coatings with improved chemical and mechanical stability on both Al and Si substrates. These improvements were obtained by using a new molecular deposition method[1] known as MVD™, which combines and integrates the vapor deposition process of self-assembled monolayers with various surface preparation techniques and adhesion layers. The packaging density and therefore durability of the SAM coatings can be increased by using an in-situ adhesion layer deposited as an intermediary layer in a dual-layer process sequence. We present data on the chemical stability of the composite MVD layers in immersion to liquids frequently used in biochemistry and spectroscopy applications. The measured mechanical stability of a hydrophobic FDTS films was superior to perfluorinated DLC coatings as tested using standard wipe tests.

Keywords: self-assembled monolayers, SAM, hydrophobic, MVD, molecular vapor deposition, durability, chemical stability, adhesion layers

1. INTRODUCTION

The functionality and performance of many MEMS devices is closely coupled to the control of the microstructure’s surface properties. MEMS, microfluidics, micro-plates, ink-jet heads, and other micro devices all benefit from low surface energy hydrophobic coatings, which enhance their performance. Engineering of these nano-surfaces is typically achieved by the application of a self-assembled monolayer (SAMs) with the desired functional properties. However, the chemical and mechanical stability of these nano-scale films has been a major obstacle inhibiting the commercialization of SAMs. Conventional SAM coatings are known to degrade upon immersion in different liquids[2] while devices which operate in contact with different liquids are frequently subjected to harsh chemical environments. For example, organic SAM coatings used on ink-jet heads have to survive long-term exposure to various solvent-based inks and to withstand dry and wet wiping.

In this paper, we present results of organic coatings with improved chemical and mechanical stability based on conventional SAM precursors but with an addition of a special surface modification layer deposited in-situ. This “adhesion” layer increases the density of the bonding sites, which in turn, enhances the density of the functional layer grown on top.

2. EXPERIMENTAL

FDTS (heptadecafluoro-1,1,2,2-tetrahydrodecyltrichlorosilane) and FOTS (tridecafluoro-1,1,2,2-tetrahydrooctyltrichlorosilane) coatings were deposited using liquid precursors (provided by Gelest Inc.) in the MVD100 vapor deposition system manufactured by Applied MicroStructures. The MVD (Molecular Vapor Deposition) method used has been previously described [3,4]. Surface cleaning and hydroxylation of the substrates were performed in-situ in an oxygen atmosphere using a remote RF plasma. Adhesion layers and FDTS films were grown sequentially without exposure of the substrate to ambient air. All samples were baked after deposition using a hot plate at 110°C for 30 min. Both de-ionized water and 1X PBS (Phosphate Buffered Saline) 0.5% Triton X-100 solution was used for contact angle measurements. The later test liquid allowed for measurements more sensitive to small changes in the surface properties. Mechanical durability of the films was evaluated using a dry wipe test method and an HP-990 Maintenance Blades Tester.
3. RESULTS AND DISCUSSION

Chemical stability of the SAM layers depends on the reactivity of the organic molecules to the surrounding liquid and on the density and defects of the coating. Perfluorinated organosilanes are chemically inert thus not reacting with a wide range of liquids used in life science and printing applications. However, it is generally difficult to achieve a pin-hole-free layer due to the incomplete packing of the SAM film. For example, the delamination of a SAM film immersed in water is attributed to the penetration of polar molecules through the SAM film to the surface attachment points.

In this work, an adhesion layer is used to increase bonding sites density and to allow the formation of closely packed molecules. As a result, we can see improved stability of MVD coatings to polar solutions and other liquids, as shown in Fig 1. Such improvement caused by using adhesion layers is much more pronounced for FOTS layer, since FDTS is more stable than FOTS by itself.

This effect has been verified for other substrate materials and immersion liquids. Fig. 2 presents in improvement in the stability data of FDTS layer deposited on Al. Series of liquids commonly used in spectroscopy and biosciences have been used for the study. The contact angle was measured using a solution of 1X PBS 0.5% Triton X-100 rather than DI water to enhance sensitivity to small changes in hydrophobicity. As one can see, hydrophobic properties remain unchanged in quite long immersion (24 hours) in different liquids, some of them even with ultrasonic treatment.

The improved mechanical stability of the hydrophobic FDTS film on Si demonstrated in Fig. 3. The SAM film grown using the MVD method is compared to a perfluorinated-DLC (Dimond-Like-Carbon) layer deposited using conventional PECVD technology. A dry wipe test is performed on both films using an HP-990 Maintenance Blades tester. The results show excellent long-term mechanical stability of the FDTS film in the repetitive harsh environment of intense mechanical impact.

![Fig. 1 DI-water immersion stability of FDTS and FOTS on Si with and without adhesion layer, room temperature.](image)

![Fig. 2. Chemical stability of FDTS SAM deposited on Al substrate](image)

![Fig. 3. Stability of the hydrophobic FDTS coating measured in a dry wipe test (1xPBS solvent contact angle)](image)
normal load feedback control loop and gives greatly improved load application. The
displacement sensor, $D_z$, monitors the surface profile of the sample under a constant load, this
being a very useful method of measuring the penetration depth during a scratching operation
and the residual depth after a scratch test has been completed. The displacement sensor, $F_N$,
measures the deflection of the double cantilever beam and consists of a linear voltage differential
transformer (LVDT). An adjustable feedback system allows the applied load to be maintained
at the desired value. The sample is mounted on a friction table, which permits frictional variations
to be characterized during a scratch test.

![Fig. 4 Schematics of nanoscratch tester](image)

<table>
<thead>
<tr>
<th>Load Type</th>
<th>Progressive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Load</td>
<td>0.5 mN</td>
</tr>
<tr>
<td>Final Load</td>
<td>25 mN</td>
</tr>
<tr>
<td>Loading Rate</td>
<td>24.5 mN/min</td>
</tr>
<tr>
<td>Scratch Length</td>
<td>1.0 mm</td>
</tr>
<tr>
<td>Speed</td>
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<tr>
<td>Scanning Load</td>
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<tr>
<td>Cantilever</td>
<td>ST-020</td>
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<tr>
<td>Indenter</td>
<td>Rockwell 2 µm</td>
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<tr>
<td></td>
<td>Diamond 039390/90</td>
</tr>
</tbody>
</table>

Table 1. Nanoscratch test settings

The following table show, for each sample, the critical force $L_C$ at which damage of the coating
occurs. It is evident from the results that composite multi-layer with 80 nm total thickness is more durable than other 2 films.

<table>
<thead>
<tr>
<th>Layer type</th>
<th>1st Defect [mN]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single layer (FDTS)</td>
<td>0.50 ± 0.00</td>
</tr>
<tr>
<td>Composite multi-layer (20 nm total thickness)</td>
<td>0.50 ± 0.00</td>
</tr>
<tr>
<td>Composite multi-layer (80 nm total thickness)</td>
<td>1.17 ± 0.12</td>
</tr>
</tbody>
</table>

Table. 2 Results of durability obtained using nanoscratch test

**SUMMARY**

Stability of hydrophobic films can be significantly improved using MVD technology of composite layers. This work demonstrated excellent chemical resistance of FDTS layers in immersion to difference liquids and good mechanical durability under strong mechanical impact of dry blade wiping. We associate this improvement with increased packing density of molecules due to introduction of additional bonding sites for attachment by in-situ deposited adhesion layers.

**REFERENCES**

[1] Molecular Vapor Deposition (MVD) is a trademark of Applied MicroStructures, Inc