Durable Anti-Stiction Coatings by Molecular Vapor Deposition (MVD)

Boris Kobrin[a], Jeff Chinn[a], and Robert W. Ashurst[b]

[a] Applied Microstructures, Inc., 4425 Fortran Drive, San Jose, CA 95134, info@appliedmst.com
[b] Department of Chemical Engineering, Auburn University, Auburn, Al 36849, ashurwr@eng.auburn.edu

ABSTRACT

This paper reports on the results of an improved surface modification method called Molecular Vapor Deposition (MVD)[1]. MVD allows for the creation of molecular organic coatings which are denser and more durable than those obtained by current liquid or vapor-phase methods. This improvement has been achieved using a "sequential" or "layered" vapor deposition scheme of two different molecular films. The first molecular coating is a "seed" or adhesion promoter layer which is used to increase the binding sites for the subsequent functional molecular layer. The resulting surface coatings were observed to have improved stability to immersion applications, higher temperature stability and overall improved durability as a result of the increased surface coverage when compared to standard self-assembled monolayers (SAMs). These new film capabilities will have significant importance in improving the functionality and reliability of many micro- and nano-scale devices. The sequential approach with the seed layer has also been used to deposit molecular coatings on a variety of substrate materials (such as polymers, plastics and metals) which normally do not allow high quality surface coatings.

Keywords: self-assembled monolayer, anti-stiction coating, Molecular Vapor Deposition, MVD, MEMS

1. INTRODUCTION

Self-assembled monolayer (SAM) coatings have been a common technique employed in MEMS, optics, and life science applications for the modification of surfaces. However, there have been several commercialization hurdles which have stymied the widespread adoption of this technology. One major hurdle is the development of a production worthy, repeatable application technique. The application of these films in manufacturing is extremely difficult due to particulation problems caused by the high sensitivity of the reaction to environmental humidity[2]. For MEMS devices, reliability is often improved by the application of an anti-stiction layer. However, the use of solution-based films has been limited by the quality, scalability, and reproducibility of the films that are produced by elaborate wet processing. More recently, a variety of monolayer systems including self-assembled monolayers (SAMs) have been deposited in the vapor phase in an effort to further improve the performance of the MEMS devices and to eliminate in-use stiction[3,4]. The vapor-phase deposition processes of these anti-stiction films have been shown to produce higher quality films and appear to be an attractive in MEMS manufacturing.

Another technical obstacle to a wider acceptance of SAMs has been the lack of chemical stability of the coatings in certain critical environments. For example, SAM coatings usually cannot withstand liquid immersion applications for long periods of time. The coatings have been observed to detach[5] from the target surface. This phenomenon has been attributed to polar molecules penetrating through the film and breaking the surface attachment bond. Additionally, some SAM coatings do not survive thermal environments necessary in backend manufacturing processes (e.g. die attach, wire bonding, soldering, etc.) where temperatures may exceed 250°C, even though the elevated temperature may last for very short periods of time.

In this paper, the development of new SAM coatings using a "sequential" vapor technique which can be deposited on almost any substrate material and withstand harsh environments is reported. This improvement has been achieved using a sequential or "layered" vapor deposition scheme[6] of two different molecular films. In this multi-step process, an initial "seed" or adhesion promoter layer is used to increase the binding sites for the subsequent functional SAM coating. Subsequently, the deposited SAM layer that forms is denser and is believed to be better attached to the surface depending on the substrate material. The resulting molecular coatings are observed to have improved stability to immersion applications, overall high temperature stability and improved durability as a result of the improved surface coverage when compared to standard self-assembled monolayers (SAMs).

2. EXPERIMENTAL

A schematic diagram of the MVD coating apparatus is shown on Fig. 1. The vapor deposition chamber is evacuated by a mechanical dry pump and can be purged with nitrogen. SAM precursors and catalytic agents are

delivered using a temperature controlled vapor delivery system which assures the accurate delivery of material during the reaction. A remote O_2 plasma treatment is used for substrate surface conditioning prior to the organic layer deposition. The process is programmable and executable by the controller. The chamber walls and the delivery lines are heated above room temperature to eliminate condensation of the reactants and residual vapor contamination. The reaction pressure can be controlled within a relatively wide range depending on the initial vapor pressure of the precursor used in the reaction but is typically maintained in the range of 0.1 to 50 Torr.

The following organo-chloro-silane chemistries were used for deposition of the anti-stiction coatings: tridecafluoro-1,1,2,2-tetrahydrooctyltrichlorosilane (FOTS) and heptadecafluoro-1,1,2,2-tetrahydrodecyltrichlorosilane (FDTS). The reaction was carried out using 18 MΩ-cm de-ionized water vapor as a catalytic agent. Both the precursors and catalytic agent, were degassed in vacuum prior to their use. The resulting FDTS and FOTS films were annealed after deposition at $120^{\circ}C$ for about 30 minutes. Here, only the use of trichloro-silane based precursors is reported, but methoxy-silanes, ethyloxy-silanes, thiols and other common SAM precursors have been successfully used with this technique.

Water, hexadecane and diiodomethane contact angles were measured on Si(100) wafers using a Rame-Hart-100 goniometer equipped with DROP-image software. The film composition was obtained by X-ray photoelectron spectroscopy (XPS) performed on an Omicron EAC-125 hemispherical energy analyzer with a DAR-400 X-Ray source. The excitation source was Mg (Kα) at 1253.6 eV and the XPS system has a base pressure of less than 3×10^{-9} Torr.
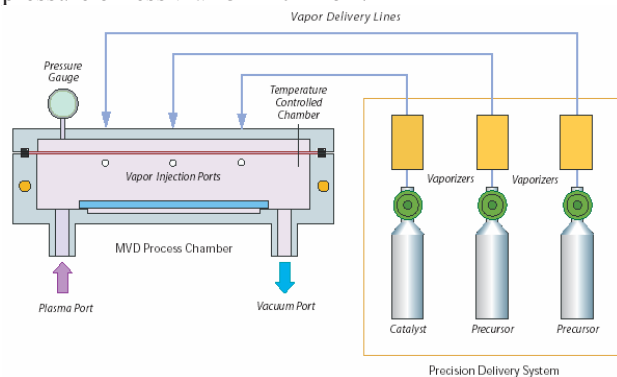

Fig. 1: Schematic of the MVD vapor deposition system

3. RESULTS AND DISCUSSION

In the case of a smooth, non-porous silica surface, it is generally accepted that there are 4-5 hydroxylated silanol sites present per nm^2 as compared to the theoretical limit[7] of 7.8 sites/nm^2. Thus, under standard deposition conditions, the surface coverage is limited by the surface binding sites, which are often less than ideal. In materials such as metals or polymers, there are often very few reactive sites and thus the surface coverage by a SAM coating is generally poor. Using a sequential vapor exposure method, an intermediate adhesion layer was created in order to increase the density of the reactive sites prior to the surface coating. As evidence of this increased surface coverage or film density, XPS analysis[8] shows that the ratio of total fluorine to the total silicon peaks for a FOTS SAM coating on a seed layer is approximately 15% higher than that of a liquid-phase or vapor-phase deposited film on a glass surface. This indicates an increase in density of the SAM coating in terms of molecular coverage. In Table-1, the improved contact angle of the sequential coating, using a diiodomethane test, is another independent verification of this increased surface coverage.

Coating Technique	VSAM	Sequential	Comments
Water Contact Angle	110	110	Polar + Hydrogen Bonding
Diiodomethane	84	94	Polar / No Hydrogen Bonding
Hexadecane	75	75	Non Polar / No Hydrogen Bonding

Table 1. Sessile drop contact angle analysis of an FOTS layer with and without seed layer as measured by different liquids.

Many different precursors can be used as a seed layer during a sequential deposition process. A typical seed layer is a in-situ vapor deposited silane containing layer prior to deposition of the SAM layer in the same chamber. In this work, an organo-silicon chloride was used as the seed layer. In our studies, the thickness of seed layer is important to increase in the starting hydroxyl (-OH) density. The –OH surface coverage can be measured by the water contact angle of the surface.
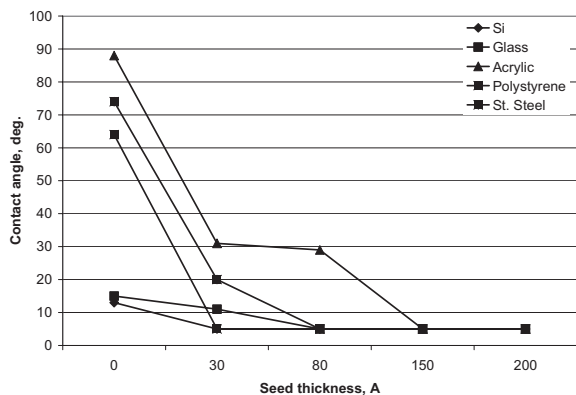
Fig. 2 Seed layer hydrophilicity (measured by water contact angle) on different materials as a function of thickness.

Fig. 3. Dependence of FDTS layer coverage (contact angle) on thickness of seed layer for different materials

Completely hydroxylated surfaces are hydrophilic (Fig. 2) in nature. For example, a hydroxylated Si wafer is very hydrophilic (<5 deg water contact angle). This can be achieved by exposing a clean silicon surface to an oxygen plasma. By vapor depositing an adhesion promoter layer, the silanol density can be increased. In the case of a stainless steel material, a seed layer of approximately 30Å is used to obtain to a completely hydrophilic surface as measured by the water contact angle. Glass and polystyrene materials were observed to be very hydrophilic with an ~80Å seed layer, and an acrylic required ~150Å of seed layer to have hydrophilic properties. These experiments also show that different materials require specific thickness of seed layer for complete coverage of organic layers. After having increased the silanol density with a seed deposition layer, the SAM precursor can be deposited, exploiting the maximum number of available surface binding sites.

Fig. 3 demonstrates the effectiveness of the seed layer in a different way. Using a baseline process of FDTS, and varying the thickness of the seed layer, it is observed that any chosen material can be made to have water contact angles comparable to FDTS deposition performed on a silicon substrate, approximately 110º. For instance, an 80Å seed layer results a complete coverage contact angle of FDTS on stainless steel. Alternately, the contact angle associated with complete FDTS coverage is not achieved until 150Å of the seed layer is deposited on glass and polystyrene while acrylic required nearly 400Å.
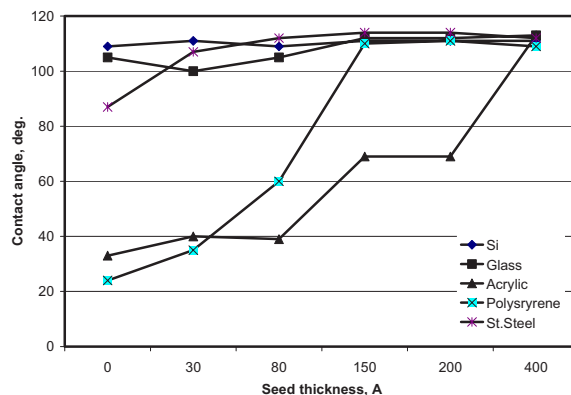
Sequential or "layered" coatings can also improve the SAM's stability to resist harsh environments, such as exposure to moist environments or in aqueous immersion applications. As an example, a standard vapor deposited SAM coating of FOTS on TiN typically exhibits a water contact angle of $\geq 120°$, which is indicative of full surface coverage. The stability of this coating in ambient air is excellent. However, upon immersion in water or other polar solvents, the film rapidly degrades over time as shown in Fig. 4. It is speculated that small polar molecules (e.g. water) can diffuse through the interstices of long chain surface coating and attack the covalent bonds which anchor the molecule to the surface. This phenomenon can be greatly reduced or even eliminated by the MVD method, using an intermediate sequential seed layer to increase the packing density. The stability and durability of the MVD coating is improved even after a prolonged (2 weeks) immersion in DI-water.
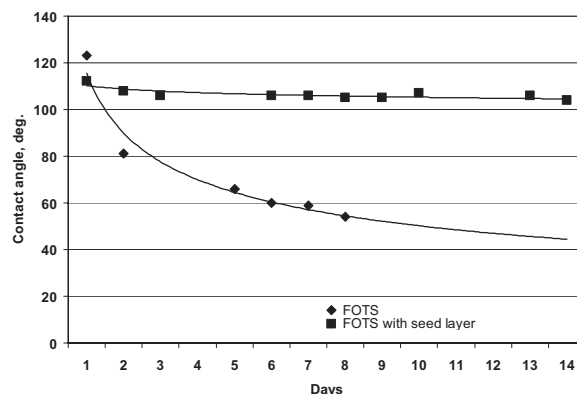

Fig. 4 FOTS coating stability in DI water (TiN substrate with and without seed layer)

The stability of MVD coatings in DI water has been investigated for the same set of materials: Si, glass, acrylic, polystyrene and stainless steel. Since polymers can not be annealed after the deposition, for consistency

of this study deposited films on Si, glass and stainless steel have not annealed.

The sequential coating also has greater thermal stability on various materials other than silicon, which is important in many MEMS/MOEMS devices. In Fig.5, an FOTS sequential coating on aluminum demonstrates its ability to retain contact angle under elevated temperatures (250°C).
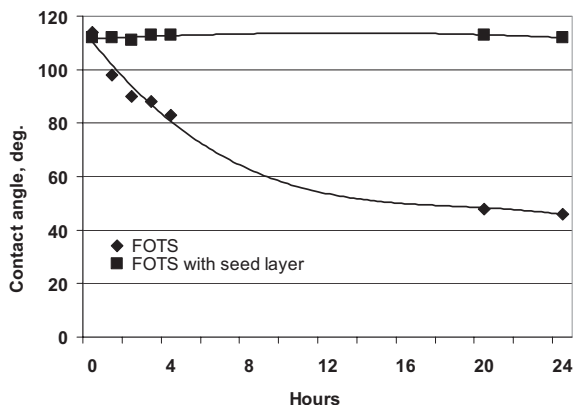

Fig. 5 FOTS coating thermal stability (Al substrate with and without seed layer)

MVD coating has been proven to be more abrasion resistant. Nano scratch tester experiments performed on a regular FDTS and MVD multi(5)-layer FDTS coating indicate that critical force for inducing coating damage is 2.34 times higher for MVD coating in comparison to the regular FDTS.

SUMMARY

The Molecular Vapor Deposition (MVD) technique using a sequential deposition approach allows for the synthesis of self-assembled coatings on a variety of new materials. Depending on the material to be coated, the native reactive surface site density may be low, which may be augmented by the deposition of a seed layer. This can be achieved using an organo-silane layer deposition which effectively increases the surface silanol density. Thus, a full coverage SAM coating can be realized on many different materials using a manufacturable and repeatable process. Additionally, the use of a seed layer allows for a more robust molecular film which is manifested by improved thermal and immersion stability compared to standard liquid based synthesis approaches.

References

[1] Molecular Vapor Deposition (MVD) is a trademark of Applied MicroStructures, Inc.
[2] W. R. Ashurst, C. Yau, C. Carraro, R. Maboudian, M. T. Dugger, "Dichlorodimethylsilane as an anti-stiction monolayer for MEMS: a comparison to the octadecyltrichlorosilane self-assembled monolayer", J. Microelectromechanical Systems, 10, 41-49, 2001.
[3] T. M. Mayer, M.P. de Boer, N.D. Shinn, P.J. Clews, "Chemical vapor deposition of fluoroalkylsilane monolayer films", J. Vac. Sci. Technol. (B), 18, 2433-2440, 2000.
[4] W. R. Ashurst, C. Carraro, R. Maboudian, W. Frey, "Wafer level anti-stiction coatings for MEMS", Sensors and Actuators (A), 104, 213-221, 2003.
[5] Thesis, Elizabeth Parker, UC-Berkeley, 2004. (eparker@kcp.com)
[6] Patent Pending, Applied MicroStructures, Inc.
[7] Lier, K.P., The Chemistry of Silica, John Wiley and Sons, New York, 1979
[8] Unpublished work: W.R. Ashurst – UC Berkeley (Currently at Auburn University)