Nanotribological characterization of fluoropolymer thin films for biomedical micro/nanoelectromechanical system applications

Kang Kug Lee and Bharat Bhushan
Nanotribology Laboratory for Information Storage and MEMS/NEMS, The Ohio State University, 650 Ackerman Road, Suite 255, Columbus, Ohio 43202

Derek Hansford
Biomedical Engineering Center, The Ohio State University, Columbus, Ohio 43210

(Received 14 October 2004; accepted 13 December 2004; published 24 June 2005)

A vapor phase deposition system was designed to coat uniform, conformal and ultrathin coatings of fluoropolymer and fluorosilane thin films inside silicon nanochannels. Surface modifications using vapor phase deposition become increasingly important for biomedical micro/nanoelectromechanical system (BioMEMS/NEMS) applications and have advantages over liquid phase deposition since the vapor can permeate more efficiently into silicon nanochannels. In this article, we explore the use of vapor phase deposition to deposit ultrathin films of two fluoropolymers and a fluorosilane, identifying deposition parameters to optimize the process. The films are desirable to control the hydrophobicity of the surface and reduce or prevent undesired protein adsorption or cell interactions, which may cause detrimental effects to the performance of most BioMEMS/NEMS devices. The films were characterized by means of a contact angle analyzer for hydrophobicity and an ellipsometer for film thickness. Atomic force microscopy was used extensively to collect surface images, adhesive and frictional properties of these films, all of which play a very important role in characterizing uniform, conformal and ultrathin films on the surface. © 2005 American Vacuum Society. [DOI: 10.1116/1.1861939]

I. INTRODUCTION

Biomedical micro/nanoelectromechanical systems (BioMEMS/NEMS)1 have the potential to revolutionize medical diagnostics and biological experimental processes. BioMEMS/NEMS devices have become the logical approach to satisfy the requirements for cost efficient medical devices that are capable of analyzing, filtering, and manipulating minute volumes. The utilization of the microfabrication technology has produced such MEMS/NEMS-based instrumentation as flow cytometers, biological assays, and nano-filters.2,3 Several applications have been proposed based on silicon, glass, or polymer nanochannels (conduits with one minimum dimension <100 nm), including cell immunosolation chambers, protecting biosensors from fouling, DNA separation devices, and entropic barriers for molecular separations.3 For gas-based separations based on nanochannels, having hydrophobic surfaces provides several advantages, including low fouling and higher gas transport rates.

One application of nanochannel membranes is the microencapsulation of cells or other biological tissues for the transplantation of cells for biological function replacement. A schematic diagram of the microfabricated biocapsule is shown in Fig. 1(a), showing the exclusion of immune molecules (with sizes of ≥15 nm) while allowing the passage of insulin and nutrients (sizes of ≤6 nm). As shown in Fig. 1(b), the biocapsule consists of two separate microfabricated membranes bonded together with the desired cells contained within the cavities. In order to fabricate a membrane with highly defined channels, it was necessary to develop a robust protocol that could use standard microfabrication processes.3–5

The fabrication of nanochannels can be accomplished through several routes. Direct writing of nanostructures using e-beam lithography provides high fidelity features, but requires serial processing and is thus a slow process. The use of a sacrificial layer allows the direct control of nanochannel dimensions so long as there exists a method for removing the sacrificial layer with absolute selectivity to the structural layers. A materials system with such selectivity is the silicon/silicon oxide system used widely in the microfabrication of MEMS devices. The use of sidewall deposition of the sacrificial layer and subsequent etching allows for the fabrication of high density nanochannels for biomedical applications.2,3 Figure 2 shows micrographs for a 25 nm channel and a 50 nm channel in silicon membranes fabricated using such a technique.

The surface modification6–9 of interior surfaces of nanochannels presents many problems. Transport of reactive species, self-limiting reactions, uniform distribution of reactants, and complete coverage of surfaces are several limitations of most techniques, including liquid phase deposition. The use of low-pressure vapor phase deposition allows many of these limitations to be overcome.8

The objective of this study was first to construct a vapor phase deposition system capable of accommodating 100 mm (4 in.) silicon wafers or an array of silicon chips with microfabricated nanochannels. Films of two fluoropolymers (CY-TOP™ and Fluorinert™) and a fluorosilane [Pentafluorophenyltrichlorosilane (PFTCS) and TOP™] were deposited in the vapour phase. The second objective was to test the hydrophobic characteristics of these films for applications in microencapsulation systems. Several experiments were performed to identify deposition parameters to optimize the process. The films are desirable to control the hydrophobicity of the surface and reduce or prevent undesired protein adsorption or cell interactions, which may cause detrimental effects to the performance of most BioMEMS/NEMS devices. The films were characterized by means of a contact angle analyzer for hydrophobicity and an ellipsometer for film thickness.
Nytriethoxysilane (PFPTES) were deposited onto silicon surfaces to study the deposition parameters and identify an optimized deposition protocol. Modified silicon surfaces were characterized using several techniques—static contact angle, ellipsometer and atomic force microscopy (AFM). We will particularly focus on the vapor deposition conditions and nanotribological behavior of the hydrophobic polymer thin films. The surface images and frictional properties of three different types of thin films were examined using AFM.

II. EXPERIMENTAL DETAILS

A. Materials and experimental procedures

Test grade silicon wafers (p-type, (100) orientation) were prepared as substrates in this study. Two kinds of fluoropolymer chemicals, CYTOP™ (CTL-107M, solute and CT-SOLV100, solvent, Asahi Glass, Charlotte, NC) and Fluorinert™ (SJ040715C, FC722, solute and FC72, solvent, 3M, Seoul, Korea) were used as precursors for the vapor phase deposition. A fluoroisilane, (PFPTES, 97%, No. SJP6716.7, ABCR GmbH & Co. KG, Karlsruhe, Germany) was also used as a precursor for the vapor phase deposition. Figure 3 schematically shows the chemical structures of the chemicals deposited on silicon surfaces in this study. Their typical properties are summarized in Table I.

The silicon wafers were first cut into 15 mm × 15 mm rectangular shapes for the experiment. All wafers were cleaned by immersion in Piranha solution (a mixture of 3:1 v/v 98% sulfuric acid: 30% hydrogen peroxide) at 90 °C for 30 min followed by a triple rinse in de-ionized water. The wafers were then immersed in 49% HF solution for 10 min to remove the native oxide followed by another triple rinse with de-ionized water and dried with high-pressure high-purity nitrogen gas as depicted in Fig. 4. The wet cleaned silicon wafers were placed in a vacuum chamber as shown in Fig. 5. Nitrogen from the gas cylinder was passed through a glass tube connected with glass source cup, passed through the chamber and flowed over the silicon substrates inside the chamber. Chemicals were vaporized in the glass source cup using a heating tape. The chemical vapors were picked up by the carrier nitrogen and deposited on the silicon surface to form thin polymer films inside the vacuum chamber.

B. Vapor phase deposition system

A schematic diagram of the apparatus for vapor phase deposition is shown in Fig. 5. The system consists mainly of
three parts: a vacuum chamber, a glass source cup and a glass tube and a nitrogen gas flow system. The vapor phase deposition process was carried out in a vacuum chamber/VWR model 1400E, 110 V, 50/60 Hz, 550 W. The valves and fittings from Swagelok/No. SS-42S4, SS-400-3 and SS-400-9 were used as connectors between Teflon tubings. All Teflon tubings for the system were from Fisher/No. 14-176-179, 890FEP. The glass tube and the glass source cup were designed for this system with input and output port valve plugs and O rings for sealing. The glass tube and the glass source cup were connected using a clip and O ring for sealing. These features provide a convenient way to fill chemicals by separating the glass tube from the glass source cup. A heating tape used for heating the glass source cup, glass tube and Teflon line was a FluidX model/BHBSAT101002, Salt Lake City. The chemicals were put into the glass source cup, which was maintained at constant temperature during processing by a heating tape. The final major component in this system is the nitrogen carrier gas system. Ultrahigh-purity nitrogen gas was dispensed from the gas cylinder using a pressure regulator before it was delivered to the glass tube and source cup. The nitrogen gas could either be introduced into the by-pass line or the direct flow line over the glass source cup. The by-pass line was used before and after the deposition process to purge the chamber, and the direct flow line was used during the deposition processes. After the samples were loaded, nitrogen gas was used to purge the chamber of moisture for about 5 min. Following this purge step, the deposition process for the CYTOP™ and Fluorinert™ consisted of a vapor injection into the chamber until a pressure of 200 Torr was achieved, at which point the vacuum line and carrier gas line were closed. For the PFPTES deposition, a steady-state chamber pressure of 200 Torr was achieved by flow control of the carrier nitrogen gas and the vacuum line. The carrier gas helps to remove excess, unreacted chemicals. The deposition process was followed by an annealing step for 20 min. Once the deposition process was completed, the inlet/outlet valves were closed to isolate the glass tube and pump down the chamber. After the deposition was completed, typically 50 min, the by-pass carrier gas line was opened, introducing pure nitrogen gas into the vacuum chamber to complete the removal of by-products and nonreacted chemicals. Finally, the samples were removed from the vacuum chamber and transferred into a vacuum desiccator until characterization.

![Flow chart of procedure for vapor phase deposition](image1)

![Schematic diagram of the apparatus for vapor phase deposition of polymer thin films](image2)

<table>
<thead>
<tr>
<th>Properties</th>
<th>CYTOP™</th>
<th>Fluorinert™</th>
<th>PFPTES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>...</td>
<td>340</td>
<td>330.33</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>2.03</td>
<td>1.68</td>
<td>1.24</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>97–102</td>
<td>56</td>
<td>130</td>
</tr>
<tr>
<td>Vapor pressure (Torr)</td>
<td>42–46</td>
<td>232</td>
<td>...</td>
</tr>
<tr>
<td>Glass transition temperature (°C)</td>
<td>108</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Surface tension (dynes/cm²)</td>
<td>19</td>
<td>12</td>
<td>...</td>
</tr>
<tr>
<td>Water adsorption (%)</td>
<td>&lt;0.01%</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Durometer hardness</td>
<td>HDD78</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Thermal conductivity (W/mK)</td>
<td>0.11</td>
<td>0.057</td>
<td>...</td>
</tr>
<tr>
<td>Coefficient of expansion (°C)</td>
<td>7.4×10⁻⁵</td>
<td>1.6×10⁻³</td>
<td>...</td>
</tr>
</tbody>
</table>

Table 1: Properties of CYTOP™, Fluorinert™ and Pentafluorophenyltriethoxysilane (PFPTES).
C. Analytical methods

In this study, static contact angles with high purity deionized water (18.2 MΩ cm) were measured in air by a sessile-drop method using a contact angle goniometer (Model 100, Rame-Hart Inc., Mountain Lakes, NJ) in order to determine the hydrophobicity of the modified surfaces. Deionized water (5 μL) was applied on the sample surfaces using a micropipette. Three contact angle measurements were taken on each sample. This was repeated for a total of two samples. Reported measurements are averages of the measurements on two samples.

The thickness of the polymer film was measured on a Gaertner L116SF ellipsometer, which was equipped with a He–Ne laser (632.8 nm) set at an incident angle of 70° to maximize the sensitivity in the range close to the Brewster angle of the films. The refractive indices of 1.34 and 1.36 were assumed for CYTOP™ and Fluorinert™ thin films, respectively. A value of 1.34 was estimated for PFPTES thin films. Over ten replicate measurements were carried out for each specimen. The effective thickness is the difference between the thickness of modified and unmodified silicon.

The nanotribological behavior of the polymer thin films was characterized on a commercial AFM system (Digital Instrument, Santa Barbara, CA). Square pyramidal Si₃N₄ tips with a nominal 30–50 nm radius mounted on gold-coated triangular Si₃N₄ cantilevers with spring constants of 0.58 N/m were used. By measuring the friction force as a function of normal load, an average value of the coefficient of friction was obtained. To obtain the adhesive force between the AFM tip and the film surface, the force-distance curve was recorded and the pull-off force reckoned as the adhesive force. The adhesive forces were also calculated from the horizontal intercept of friction versus normal load curves at a zero value of friction force. The AFM images were obtained under ambient conditions and all the scans were 1 μm in size.

A microtriboapparatus (Tetra Inc., Ilmenau, Germany) was used to measure the adhesive force between the silicon and the film surfaces. This apparatus has the following advantages: it can deliver velocity higher than that in AFM; a large radius or flat specimen can be used to reduce the contact stress; and MEMS/NEMS components can be directly mounted on this machine for tribological tests.

III. RESULTS AND DISCUSSION

A. Static contact angle, thickness, and roughness variation of vapor phase deposited films

The static contact angle, thickness and roughness variation of three kinds of films were plotted as a function of pressure, processing time and temperature in Fig. 6. The contact angle analysis is a simple, but a very powerful method for measuring the changes of surfaces at the monolayer level. In order to optimize the vapor phase deposition conditions, the static contact angles were measured after the film deposition as a function of pressure, processing time and temperature. The deposited film with the highest contact angles and lowest standard deviations determined the optimum process conditions. Pre-process conditions were designed before optimizing process conditions. A two-step vapor phase deposi-
tion process was applied in this study; first, samples were left in a vacuum chamber at its base pressure, and then, the samples were annealed at a higher pressure induced by nitrogen gas filling in the same chamber and at the same temperature. The first deposition process was carried out for 20 min and the second annealing process was also performed for 20 min to find the optimum temperature, 140 °C, as shown in Fig. 6. At 140 °C, the optimum pressure 200 Torr was also determined by the measurements of contact angles as shown. The length of processing time 20 min was also determined using contact angle measurement under the temperature and pressure obtained from the above. The optimized vapor deposited surfaces showed an increase in contact angle (contact angle ~85°) as compared to the wet cleaned silicon surface (contact angle ~68°). From the observations above, it can be concluded that the surface modified by the fluoropolymer films has a higher water contact angle than the silicon surfaces. The surface wettability was considerably modified to hydrophobic by the vapor phase deposition.

As expected, the results showed the film thickness of CYTOP™ and Fluorinert™ on silicon was increased as a function of processing time and temperature. The film thickness of the PFPTES on silicon was not affected by pressure, annealing time and temperature. This is because the film was coated as a monolayer. As can be seen in Fig. 6, the decrease in rms roughness for the vapor phase deposited films was found as compared to the wet cleaned silicon surface, which suggests that the coatings decrease the surface roughness. The native oxide on silicon is chemically more heterogeneous, and the capillary formation may not be uniform during scanning. This could affect AFM topography measurements because of heterogeneous adhesive forces due to the capillary effect. The capillary formation may be more uniform for the vapor phase deposited samples, explaining the reduced rms roughness for the samples. The rms roughness values of the CYTOP™ were decreased as a function of temperature, while those of Fluorinert™ and PFPTES remained relatively constant with temperature.

**B. Frictional properties of vapor phase deposited films**

Figure 7(a) shows gray-scale images of surface height and friction force captured simultaneously of wet cleaned silicon, CYTOP™, Fluorinert™ and PFPTES on silicon over a region of 1 μm × 1 μm by contact mode AFM. The topography of silicon surface appears to be heterogeneous. The roughness values decreased with film deposition. The friction force maps in Fig. 7(a) clearly show the reduction in friction force for the CYTOP™, Fluorinert™ and PFPTES on silicon as more uniform contrast, compared with the wet cleaned silicon. For all the surfaces, a good correlation between the surface height and the corresponding friction force images was observed.

To investigate the frictional properties of the vapor phase deposited films on silicon, the friction force versus normal load curves were measured by making friction measurements...
at increasing normal loads. The representative results of wet cleaned silicon, CYTOP™, Fluorinert™ and PFPTES on silicon are shown in Fig. 7(b). An approximately linear response of all the four samples is observed in the load range. The friction force of the CYTOP™, Fluorinert™ and PFPTES films on silicon is consistently smaller than that for wet cleaned silicon. The nonzero value of the friction signal at zero external loads is due to the adhesive forces. It is well known that the following relationship exists between the friction force $F$ and external normal load $W$:

$$F = \mu (W + W_a),$$  

(1)

where $\mu$ is the coefficient of friction and $W_a$ is the adhesive force. Based on this equation and the data in Fig. 7(b), we can calculate the $\mu$ and $W_a$ values. Since the coefficient of friction was affected by the vapor phase deposition, the vapor phase deposited films on silicon showed an improvement in coefficient of friction as compared to the silicon substrate. The coefficients of friction of wet cleaned silicon, CYTOP™, Fluorinert™ and PFPTES are 0.06, 0.055, 0.056 and 0.059, respectively. Based on Eq. (1), the adhesive force values are obtained from the horizontal intercepts of the friction force versus normal load curves at a zero value of friction force. The average values and standard deviation of the static contact angles, adhesive forces and coefficients of friction measured by contact mode AFM are presented in Fig. 8.

Corresponding surface height and friction maps are also shown in Fig. 7(a). It shows that vapor deposited films can reduce the adhesive and frictional forces of silicon. In particular, CYTOP™ and Fluorinert™ exhibit lower adhesive and frictional forces than the silicon substrate. It means that these fluoropolymer films can be used as effective lubricants or barriers for micro/nanodevices fabricated from silicon. In the third diagram of Fig. 8, adhesive force values of wet cleaned silicon, CYTOP™, Fluorinert™ and PFPTES are 78, 50, 55, and 67 nN, respectively. The adhesive forces of these samples were also measured by force calibration method. In this technique, the tip is brought into contact with the sample and the maximum force, needed to pull the tip and sample apart, is measured. The adhesive forces of wet cleaned silicon, CYTOP™, Fluorinert™ and PFPTES were also measured by the microtriboapparatus and the measured adhesive forces were summarized in the last diagram of Fig. 8. The adhesive force values are 670, 622, 483, and 545, respectively. It shows that the presence of fluoropolymer films reduces the adhesive force of silicon, whereas Fluorinert™ film has the lowest adhesive force. Differences of the data between the different techniques are due to differences in the tip material, shape and scale of the microtriboapparatus compared to the AFM. In the nanochannel system, it is critical to obtain hydrophobic, uniform and conformal ultrathin films deposited inside the nanochannels. The hydrophobic polymer films have lower adhesive and frictional forces than the silicon substrate in this article. Characterization of the static contact angle, frictional forces, and adhesion forces of the vapor deposited films demonstrates the usefulness of this process for these applications.

IV. CONCLUSIONS

A vapor phase deposition chamber able to accommodate 100 mm silicon wafers or an array of silicon chips with microfabricated nanochannels was designed to coat uniform, conformal and ultrathin polymer thin films on the silicon surfaces. The deposition of these films on silicon surfaces is important for the development of useful biomedical nanodevices. This work focuses on the development and characterization of vapor phase deposited polymer thin films on sili-
con surfaces to achieve controlled surface wettability, roughness and adhesion. The surface properties of all the films on silicon were dominantly governed by deposition temperature and annealing time but there is little effect due to chamber pressure. Increase in static contact angle was observed for CYTOP™, Fluorinert™ and PFPTES films as compared to silicon. The static contact angles of the Fluorinert™ films were higher than those of CYTOP™ films with pressure, annealing time and temperature. The thickness of the CYTOP™ and Fluorinert™ films was increased with annealing time and temperature. While the CYTOP™ and Fluorinert™ were deposited as multilayer film on silicon, the PFPTES was deposited as monolayer with the silane reaction controlling the processing conditions. In the nanochannel system, coating on a monolayer level is favored due to the nanochannel dimensions. The rms roughness values and the standard deviation of the values of CYTOP™ films on silicon were decreased as a function of temperature. Reduction in coefficient of friction was found for CYTOP™, Fluorinert™ and PFPTES films as compared to the substrates. Reduction in adhesive force was also found for the all three films on silicon substrate.

ACKNOWLEDGMENTS

Financial support for this work was provided by the National Science Foundation (Contract No. ECS-0301056). The content of this information does not necessarily reflect the position or policy of the Government and no official endorsement should be inferred. The authors would like to thank Dr. Toshi Kasai and Nikhil Tambe of the Nanotribology Laboratory for Information Storage and MEMS/NEMS (NLIM) for many helpful discussions in AFM measurements. The authors also thank Dr. Guohua Wei and Dr. Zhenhua Tao of NLIM for many helpful discussions in organizing and preparing figures for the article. Special thanks to Zachary Burton of NLIM for measuring adhesion data using the microtriboapparatus.