The Interface Structure of Thin Liquid Films of Hydride Functional Siloxanes

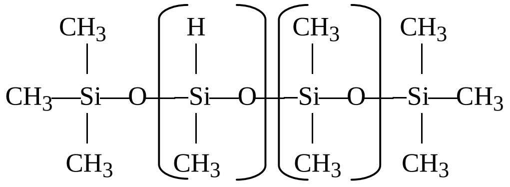
G. Evmenenko, C.-J. Yu, J. Kmetko, P. Dutta
Northwestern University, Evanston, IL, U.S.A.

Introduction

The field of confined liquids has been of considerable interest in the last 10 years, both from a theoretical point of view and because of its practical importance. Confinement complicates the physics of liquids, and the static and dynamic changes of microstructures at interfaces may drastically alter the behavior of simple liquids, polymers, and biological molecules near the surface or in thin films [1-5]. In our former work [6], evidence of molecular layering at the solid-liquid interface induced by geometrical confinement by a hard wall was obtained for thin films of lowest-molecular-weight polydimethylsiloxane (PDMS). Increasing the molecular weight of the samples led to the suppression of density oscillations and to a flatlike conformation of PDMS molecules absorbed on a solid surface. In this study, we used x-ray reflectivity (XRR) to study molecular ordering in thin films of polyfunctional poly(methylhydro-dimethyl)siloxane (PMDMS) copolymers with varying fractions of Si-H groups [7]. The presence of hydrogen influenced the reactivity of such hydride functional siloxanes and significantly change the structure in the interfacial region between the liquid film and the polished silicon wafer.

Methods and Materials

The PMDMS copolymers with different fractions of MeHSiO groups are a commercial product of Gelest Co., Inc., and were used as received. The chemical structure of PMDMS molecules is presented in Fig. 1. The molecular weight M_w of the samples was 2000 g/mol and the mol % of MeHSiO groups was 6-7% (HMS-071), 15-18% (HMS-151), and 25-30% (HMS-301). The substrates ($3 \times 1 \times 0.1$ in.), silicon(100) with native oxide, were purchased from Semiconductor Processing, Inc. We spread thin films by making dilute solutions of PMDMS in hexane (1.3, 2.6 and 3.9 mL/L), dipping the substrates in the solutions, and withdrawing them at constant speed of 1.5 mm/s to get uniform film thickness. In order to study the effect of surface hydrophobicity on the electron density profile of liquid films, some silicon wafers were covered by monolayers that served as hydrophobic surfaces with CH_3 end groups. XRR studies were performed at Sector 10 (MR-CAT) of the APS and at beamline X23B of the National Synchrotron Light Source by using a four-circle Huber diffractometer in the specular reflection mode (i.e., incident angle was equal to exit angle). X-rays of energy $E = 11.0$ keV ($\lambda = 1.127$ Å) at MR-CAT and $E = 10.0$ keV ($\lambda = 1.240$ Å) at X23B were used for all measurements. The beam size was 0.30-0.35 mm vertically and 1.1-2.0 mm horizontally. The samples were kept under slight overpressure of helium during the measurements to reduce background scattering from the ambient gas and radiation damage. The experiments were performed at room temperature. The off-specular background was measured and subtracted from the specular counts.



$$CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-O-\left(\overset{H}{\underset{CH_3}{Si}}-O\right)-\left(\overset{CH_3}{\underset{CH_3}{Si}}-O\right)-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$$

FIG. 1. Schematic representation of the chemical structure of PMDMS molecules.

Results and Discussion

We compared film structures of different PMDMS samples that were about 30-, 50-, and 70-Å thick. Normalized reflectivity data (R/R_F) were fitted by using the Gaussian-step model [8], which assumes the film consists of a silicon substrate and layers of different electron densities ρ_i with Gaussian broadened interfaces σ_i:

$$\frac{R(q_z)}{R_F(q_z)} = \left| \sum_{i=0}^{N} \frac{(\rho_i - \rho_{i+1})}{\rho_0} e^{-iq_z D_i} \; e^{-q_z^2 \sigma_{i+1}^2 / 2} \right|^2 ,$$

where:

$N =$ number of layers,
$\rho_0 =$ electron density of the substrate ($= \rho_{Si}$),
$D_i = \sum_{j=1}^{i} T_j$ = distance from the substrate surface to the i^{th} interface, and
$T_i =$ thickness of the i^{th} layer.

This model was used to fit the reflectivity data. The fitting parameters were the thickness of each layer, the electron density of each layer, and the rms width of each interface. The fits were performed by using only data for which $q > 2q_c$. The fitting procedure was as follows. First we tried to fit with a two-layer Gaussian-step model: silicon oxide layer and liquid layer. Then, if we could not find a satisfactory fit, we added one more layer with its structural parameters, and so on. Successive data fits were obtained by using a four-layer model (for films 28- to 31-Å thick) and a five-layer model (for films 49- to 55-Å thick and 65- to 80-Å thick). The corresponding electron density profiles for HMS-071 and HMS-301 samples of different thicknesses that were obtained from these fits are presented in Fig. 2.

From an analysis of Fig. 2, we can make the following conclusion: The changes in the electron density profile depend highly on the film thickness; the profile is essentially changed with increasing film thickness, and the low-density region increases both in size and in the amplitude of density dip. What will happen if we reduce the interaction between liquid molecules and the substrate surface? In Fig. 3, the electron density profiles for HMS-151 films on Si and hydrophobic substrates are shown for comparison. The PMDMS films have only a small density dip near the hydrophobic surface.

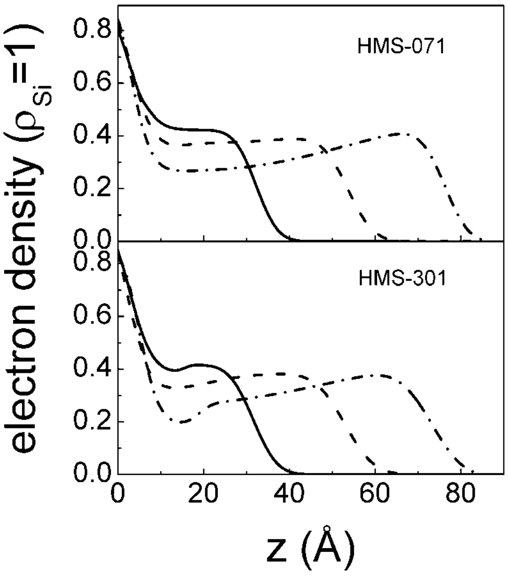


FIG. 2. Electron density profiles for HMS-071 and HMS-301 liquid films of different thickness. Zero of the x-axis is at the center of the film-substrate interface.

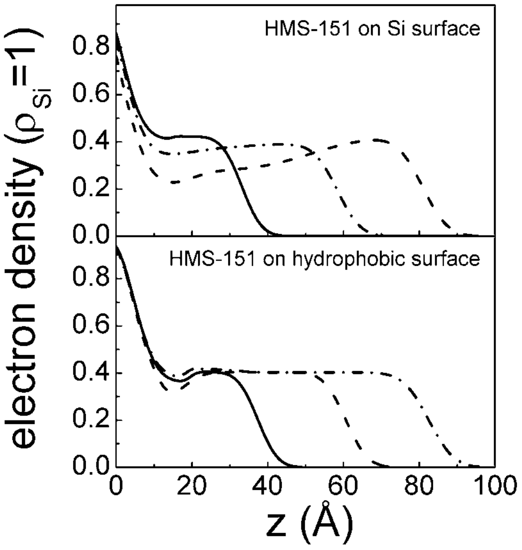


FIG. 3. Electron density profiles obtained from the XRR data for HMS-151 liquid films deposited on Si or hydrophobic substrates. Zero of the x-axis is at the center of the hydrophobic monolayer-Si substrate interface.

To obtain evidence of strong interactions of PMDMS molecules with Si surface, we tried to clean wafers after depositing the liquid films. We repeatedly sonicated wafers in hexane, acetone, and methanol before XRR measurements. For comparison, we repeated the procedure by using liquid films of PDMS of the same molecular weight. Such a cleaning procedure completely removes the PDMS film from the substrate; however, for PMDMS molecules, the presence of ~6- to 9-Å films was observed. On the other hand, for the PMDMS films on silicon wafers covered by hydrophobic monolayers, the cleaning procedure just described removes the polymer film from the substrate because the interaction between the hydrophobic substrate surface and PMDMS molecules is practically negligible.

As was shown for PDMS thin films, the interaction of the polar component of the PDMS-molecule, Si-O group leads to the formation of a stable physical bond between molecules and the hydroxylated surface of the Si substrate. In our case, in addition to the physical bonding by the Si-O groups for PMDMS molecules with the substrate surface, the stronger interaction between liquid molecules and the surface OH groups was observed. This was a result of adsorption of PMDMS molecules by breaking the Si-H bonds and sticking the PMDMS molecules on the unsaturated dangling bonds of the surface.

So, density anomalies in thin liquid films of hydride functional PMDMS on Si substrate can be related to the stronger interaction of the PMDMS molecules with the substrate surface by means of Si-O-Si bonds. At this moment, there is no satisfactory theory on this effect. In our opinion, the surface-induced segmental ordering in a restricted geometry under the specific interactions imposed by the interface is the main factor determining the thickness-dependent behavior of electron density profiles for the PMDMS liquid films.

Acknowledgments

This work was supported by the U.S. National Science Foundation under Grant No. DMR-9978597. Use of the APS was supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38. Work performed at MR-CAT is supported in part by funding from DOE under Grant No. DEFG0200ER45811.

References

[1] J. C. Henniker, Rev. Mod. Phys. **21**, 322 (1949).

[2] “Polymers in confined environments,” in *Advances in Polymer Science* series, edited by S. Granick (Springer, New York, NY, 1999), Vol. 138.

[3] “Biopolymers at interfaces,” in *Surfactant Science* series, edited by M. Malmsten (Marcel Dekker, New York, NY, 1998), Vol. 75.

[4] *Proc. of International Workshop on Dynamics in Confinement*, edited by B. Frick, R. Zorn, and H. Büttner, EDP Sciences, Les Ulis, published in J. Phys. IV (France) **10** (2000).

[5] J. Penfold, Rep. Prog. Phys. **64**, 777 (2001).

[6] G. Evmenenko, J. Kmetko, S. W. Dugan, and P. Dutta, Langmuir **17**, 4021 (2001).

[7] G. Evmenenko, C.-J. Yu, J. Kmetko, and P. Dutta, Langmuir **18**, 5468 (2002).

[8] T. M. Tidswell, B. M. Ocko, P. S. Pershan, S. R. Wasserman, G. M. Whitesides, and J. D. Axe, Phys. Rev. B **41**, 1111 (1990).