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Specular X-ray reflectivity analysis of adhesion interface-dependent density profiles in nanometer-scale siloxane-based liquid films

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Abstract

Nanometer-scale thick liquid films of poly(methylhydro-dimethyl)siloxane copolymer (PMDMS) deposited on hydrophilic and hydrophobic solid organic films have been studied using synchrotron X-ray specular reflectivity (XRR). The physico-chemical properties of liquid PMDMS at the interfacial level are controlled by the nature of the solid surface. Detailed analysis of the XRR-data revealed the formation of a low-density region in the liquid PMDMS film in the vicinity of the hydrophobic surface, whereas a densely packed molecular layer is formed at the liquid PMDMS-hydrophilic substrate interface. Non-covalent polymer chains are 'frozen' at the solid–liquid interfaces in the confined liquid films and interactions with the substrate surfaces (i.e. hydrogen bonding) are responsible for distinctly different density profiles.

Keywords: Specular X-ray reflectivity; Thin liquid films; Solid/liquid interface

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1. Introduction

Many properties of polymer-based liquid materials, including composites, lubricant films, and adhesives, are regulated by the interactions of polymer chains with solid surfaces. Surface force measurements [1–4] and theoretical studies [5–11] indicate that molecular packing is strongly perturbed in the interface regions with respect to the bulk. For instance, physisorbed perfluoropolyether polymers have an extended, flat conformation at the surface of silicon wafers [12]. Monte Carlo simulations of a polymer melt of short, non-entangled chains embedded between two impenetrable walls show a surface induced orientation of the chains parallel to the wall [13]. Chain conformation distortions parallel and perpendicular to the surface of polystyrene films spin-coated onto glass substrates were observed by diffuse neutron scattering [14]. Direct evidence of molecular layering and a flat-like molecular conformation was recently obtained by us for thin liquid films of polydimethylsiloxane (PDMS) absorbed on solid silicon substrates [15]. Synchrotron X-ray reflectivity measurements show that the region adjacent to the silicon substrate (i) is highly sensitive to the molecular shape of non-polar van der Waals liquids, and (ii) has a lower density in the case of more complex molecules [16].

Recently we have demonstrated this effect for thin liquid films of poly(methylhydro-dimethyl)siloxane copolymers (PMDMS; Fig. 1) adsorbed on polished silicon wafers with a native oxide layer [17]. Reduction of orientational freedom of polymer chains, in combination with specific non-covalent interactions of the fluid with the substrate surface, results in the formation of a low-density region in the vicinity of the substrate. The amplitude of this density dip depends on the percentage of Si–H groups in PMDMS with the greatest density deficiency for molecules with the largest number of Si–H moeities. Furthermore a significant effect of the organic solid film on the density profile of PMDMS was found [17].

A reduction of electron density near the native oxide layer of silicon was also observed by X-ray reflectivity for spin-coated polystyrene films [18]. Partial grafting of polystyrene chains to the substrate may change the polymer conformation near the silicon–polymer interface. On the other hand, a density increase in the vicinity of $(SiO_2)_x$

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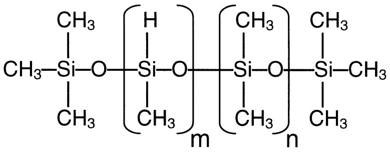

Fig. 1. Chemical structure of poly(methylhydro-dimethyl)siloxane (PMDMS).

surfaces was observed for 20–80 nm thick films of spin-casted poly(methylmethacrylate) (PMMA) [19]. Acid–base interactions of PMMA with the hydrophilic $(SiO_2)_x$ surface were proposed as the driving force for this interfacial density enhancement. It is clear that the complex surface behavior of polymers in confined systems (i.e. thin films) and factors governing non-covalent interactions at solid–liquid interfaces are still poorly understood. This is due to the interplay of many different factors such as (i) confinement and related molecular mobility, (ii) chain 'stiffness', and (iii) non-covalent interfacial interactions. Many intriguing fundamental issues remain. How and to what extent does a solid surface interact with and influence the physical properties of a liquid at the nano- and even at the microscale level? Such solid–liquid interactions are expected to play a key-role in the design and performance of nano- and microfluidic devices [20], whereas the formation of transparent polymers with well-defined regions of different electron densities may open a window of opportunities for the formation of novel 'all-organic' photonic devices [21–25]. Device components having weak polymer/oxide boundary layers are expected to have limited lifetimes. Modification of oxide surfaces that covers the vast majority of engineering materials using silane adhesion promoters may significantly improve device performance [26–28]; however, little is known about the nature of interfaces formed by the presence of siloxane-based adhesion layers. Obviously, much more experimental and theoretical work is needed to obtain a complete structural understanding of such systems.

In the present work, we report the surface-dependent structural behavior of thin liquid films (24–66 Å) of PMDMS dip coated from polymer/hexane solutions on solid organic films. Amino-*n*-propyl and *n*-Octyl siloxane-based films (**1**, **2**) were used to form chemically distinctly different hydrophobic and hydrophilic adhesion layers covalently bound to the native oxide layer of flat silicon substrates.

2. Experimental

2.1. Materials

3-Amino-*n*-propyltrimethoxysilane ($H_2N(CH_2)_3$-$Si(OCH_3)_3$) (**1**), *n*-octyltrichlorosilane ($CH_3(CH_2)_7SiCl_3$) (**2**), and PMDMS copolymer with 15–18% mole% fraction of MeHSiO groups (HMS-151) and a molecular weight M_w of 1600–2400 g/mol were purchased from Gelest Co., Inc. Compounds **1** and **2** were vacuum distilled prior to use. The chemical structure of PMDMS is presented in Fig. 1. Polished silicon (100) substrates ($3'' \times 1'' \times 0.1''$) with a native oxide layer of ~10 Å thickness and a surface roughness $\sigma \sim 3$ Å (by XRR), were purchased from Semiconductor Processing, Inc.

2.2. Methods

Silicon wafers were cleaned by immersion in a freshly prepared 'piranha' solution (conc. H_2SO_4/H_2O_2 30% = 7:3 v/v) at 80 °C for at least 45 min. This solution is a very strong oxidizing agent and should be handled carefully. After cooling to room temperature, the substrates were rinsed repeatedly with de-ionized (DI) water and subjected to an RCA-type cleaning procedure (H_2O/H_2O_2 30%/NH_4OH 5:1:1 v/v/v; sonicated at room temperature for at least 45 min). The wafers were then rinsed with DI water and dried in an oven overnight at 115 °C. The water used in all cleaning procedures was purified to a resistivity of 18 MΩ cm with a Barnstead E-Pure water purification system. All substrate functionalization reactions were carried out under inert atmosphere in nitrogen filled glove box or using standard Schlenk techniques. Heptane, pentane and toluene were dried over sodium, distilled, and degassed before use.

Freshly cleaned silicon wafers were functionalized with oligomeric self-assembled (moderately) hydrophobic and hydrophilic films by immersion into toluene and heptane solutions (2 mM) of 3-amino-*n*-propyltrimethoxysilane (**1**) and *n*-octyltrichlorosilane (**2**), respectively. Film thickness and surface morphology can be varied with trichloro- and trimethoxysilanes using prolonged reaction times and/or by addition of traces of water to the reaction solutions [29–33]. The XRR-derived surface roughness of the used organic films, $\sigma_{\text{film-air}}$ for **1** (~5 Å) and **2** (~3.5 Å) is comparable. Surface polarity was determined by advancing aqueous contact angle measurements—the wettability of silicon, **1**, and **2**-based surfaces varies from <25°, ~55° to ~110°, respectively. Many factors may play a role in molecular ordering induction, the large contact angle difference between silicon, **1**, and **2** may make the surface polarity one of the dominant factors in comparing the series of solid–liquid interfaces reported here. The organic films (**1**, **2**) and native oxide layer of silicon wafers are amorphous and may be viewed as 'structureless' walls.

Ultrasonic treatment of substrates in acetone for 10 min was used before deposition of the liquid films. Thin liquid PMDMS films were prepared by dipping the functionalized silicon substrates into diluted PMDMS/hexane solutions (1.3–3.9 ml/l) and withdrawing them at constant speed to ensure uniform PMDMS film thickness. The thickness of the PMDMS films ranges from 24 to 80 Å and can be controlled by varying dipping solution concentration and substrate withdrawal speed. The XRR-derived PMDMS surface roughness, $\sigma_{\text{film-air}} \sim 4$ Å is similar to the roughness of the adhesion layers (**1**, **2**) and does not seem to depend on the liquid film thickness.

XRR studies were performed at Sector 10 (MRCAT) of the Advanced Photon Source and at beam line X23B of the National Synchrotron Light Source using a four-circle Huber diffractometer in the specular reflection mode (i.e. incident angle θ was equal to exit angle). The reflected intensity was measured as a function of the scattering vector component $q_z = (4\pi/\lambda)\sin\theta$, perpendicular to the reflecting surface. X-rays of energy $E = 11.0$ keV ($\lambda = 1.127$ Å) at MRCAT 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 the 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.

3. Results and discussion

Information about the microstructure of liquids near surfaces and in thin films can be obtained by X-ray reflectivity measurements, which provide electron density profiles normal to the surface [34–36]. These measurements show that the region of a liquid film adjacent to a substrate is highly sensitive to the shape of the molecules of the liquid and to the interaction between the molecules of the liquid and the substrate surface [15–19]. Possible structural changes in the interfacial regions of the liquid PMDMS films can be related to configurational reorientation of polymer chains near the solid organic film and to specific non-covalent interactions between the liquid polymer and the surface of the solid film.

Figs. 2 and 3 show normalized reflectivity data (R/R_F) for 22–23 Å thick 3-amino-*n*-propylsiloxane-based films (**1**) with 24 and 46 Å thick liquid PMDMS films dip coated on their surface, respectively. A Gaussian-step model was used to fit the reflectivity data, assuming that the Si/SiO$_2$/**1**/PMDMS stack structure consists of a silicon substrate and three relatively thin layers of different electron densities, ρ_i, with Gaussian broadened interfaces, σ_i. The fitting parameters included the thickness and the electron density of the individual layers, and the root-mean-square width of each interface. Modeling was performed using only data for which the Born approximation is valid ($q_z > 2q_c$). A detailed description of XRR data analysis and models can be found elsewhere [17,34–41]. The applied fitting procedures involved the following steps. The XRR data for hydrophilic substrates was fitted with a 2-layer Gaussian-step model having (i) a native silicon oxide layer with a constant density of $\rho_{\text{SiO}_2} = 0.68$ e Å^{-3} and (ii) the covalently bound organic film (**1**). Figs. 2 and 3 illustrate representative fits (solid lines labeled '1') with the corresponding electron density profiles obtained from these fits presented in the insets. Subsequently, we added a uniform liquid layer with its structural parameters to our model, and fitted the XRR data for the liquid films deposited on the hydrophilic surfaces. The electron density profile for the region of the robust hydrophilic films was assumed to be (nearly) identical to that obtained for the hydrophilic

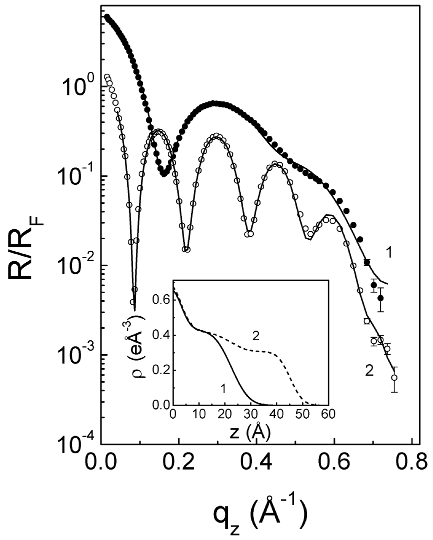

Fig. 2. X-ray reflectivity data for a hydrophilic substrate (1) and for a PMDMS liquid film dip coated on such a hydrophilic substrate (2). The films were absorbed from 1.3 ml/l solutions of PMDMS in hexane. Solid lines—best fits using a variable electron density within the film. Corresponding electron density profiles are shown in the inset.

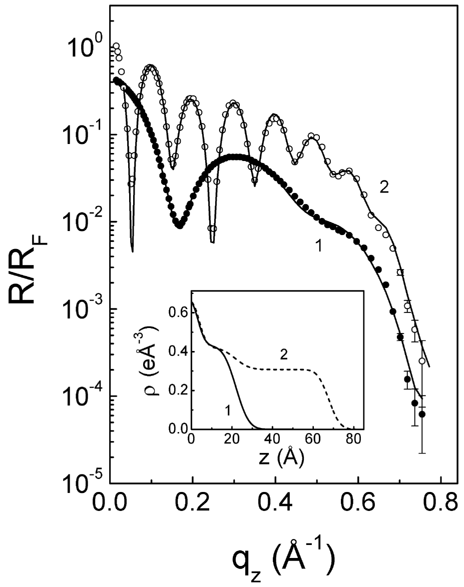

Fig. 3. X-ray reflectivity data for a hydrophilic substrate (1) and for a PMDMS liquid film dip coated on such a hydrophilic substrate (2). The films were absorbed from 2.6 ml/l solutions of PMDMS in hexane. Solid lines—best fits using a variable electron density within the film. Corresponding electron density profiles are shown in the inset.

substrates without the liquid layer in order to reduce the number of various fitting parameters.

Models based on the liquid PMDMS film with a uniform density did not give good fits, indicating that the PMDMS layer has a complicated electron density profile. Indeed, models with an additional interfacial region provided excellent fits to the XRR-derived experimental data. The solid lines labeled ‘2’ in Figs. 2 and 3 illustrate fits for the Si/SiO$_2$/**1**/PMDMS stack structure obtained by the data analysis process described above. The corresponding electron density profiles for **1**/PMDMS samples of different thickness obtained from these fits are presented in the insets. Interestingly, liquid PMDMS films have a ‘transition’ region of ~ 10 Å between the hydrophilic surface and liquid. The electron density of the latter becomes 0.31 e Å^{-3}, which is approximately equal to the calculated electron density for PMDMS from its elemental composition and density. Such interfacial behavior is typical for systems with strong interactions between deposited molecules and substrate surface (for example, see XRR data for covalently bound self-assembled organic films adhered to hydrophilic substrates) [42].

One of the important fundamental properties of polysiloxanes such as PMDMS is the highly pronounced inherent conformational flexibility of the main-chain backbone [43]. The Si–O–Si bond angles can vary between 135 and 180° affording an unusually high mobility of segments and even entire molecules. Non-covalent interactions and hydrogen bonding of PMDMS molecules with terminal NH$_2$-surface groups of **1** may drive the arrangements and conformation of the polymer chains at the solid–liquid interface. The polymer backbones align parallel to the surface and increase the monomer density near the liquid/substrate interface as observed by XRR measurements (insets of Figs. 2 and 3) in order to maximize possible Si–O···H–N interactions.

What will happen if we alter the interfacial interactions by changing the adhesion layer? A similar dip coating procedure was applied for the deposition of PMDMS films on silicon substrates functionalized with *n*-octylsiloxane based films (**2**). Fig. 4 shows normalized reflectivity data (R/R_F) from a typical scan of a liquid PMDMS film of ~ 20 Å thick deposited on a hydrophobic film (**2**). The corresponding Patterson functions $P(z)$ are shown in the inset of Fig. 4 [15,17]. The large primary maximum of curve 1 is due to the silicon substrate–hydrophobic film and hydrophobic film–gas interfaces—its position indicates the film thickness. This maximum is also present in Patterson functions of PMDMS liquid films dip coated on **2** (smaller maximum of curve 2). The large primary maximum of curve 2 corresponds to the overall film thickness (= film **2** + PMDMS layer).

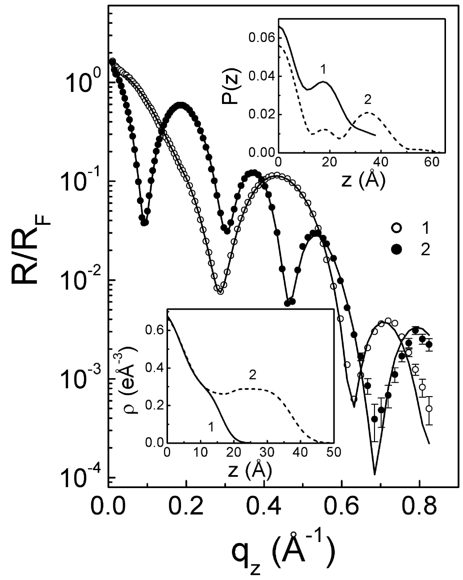

Fig. 4. X-ray reflectivity data for a hydrophobic substrate (1) and for a PMDMS liquid film deposited on hydrophobic substrate (2). The films were absorbed from 1.3 ml/l solutions of PMDMS in hexane. Solid lines—best fits that give corresponding electron density profiles shown in the inset. In the second inset Patterson functions from the observed XRR data are presented.

Similar X-ray reflectivity data were obtained for thicker PMDMS films. The XRR data was fitted using the model described above. The obtained electron density profiles for the liquid PMDMS films deposited on the hydrophobic surfaces are presented in Fig. 5 (from Ref. [17]). There is a striking difference between the electron density profiles of liquid PMDMS films on solid hydrophilic (**1**) and hydrophobic (**2**) films. In sharp contrast to the **1**/PMDMS system, the liquid PMDMS films have a reduced electron density near the hydrophobic surface (**2**). This noticeable density dip is similar to electron density profiles observed for non-polar *n*-hexane and perfluorohexane films on bare Si

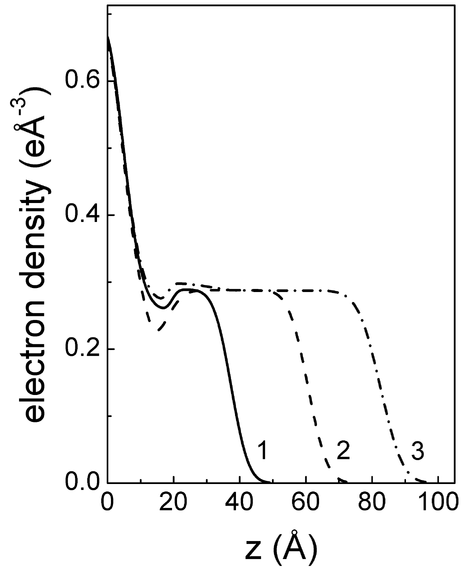

Fig. 5. Electron density profiles obtained from the XRR data for liquid PMDMS films of different thickness deposited on hydrophobic substrates [17]: (1) absorbed from 1.3 ml/l solution of PMDMS in hexane, (2) from 2.6 ml/l, (3) from 3.9 ml/l. The origin of the *x*-axis is at the center of the hydrophobic layer—substrate interface.

substrates [16]. The estimated unperturbed mean-square radius of gyration for the PMDMS molecules is about 11.3 Å [15]. Comparing this value with the electron density profiles presented in Fig. 4, we can conclude that the thickness of surface-sensitive region for PMDMS films equals approximately twice the radius of gyration for these molecules (~22 Å). Liquid PDMS films (lacking Si–H moieties, molecular weight M_w of 2000 g/mol) coated on hydrophobic surfaces exhibit similar density dips as observed for PMDMS films dip coated on hydrophobic substrates. In contrast, density profiles of thin liquid PMDMS films adsorbed on polished silicon wafers with a native oxide layer exhibit an interfacial density dip, which is affected by the PMDMS film thickness and the amplitude of the density dip is a function of the number of Si–H groups—the interfacial density decreases with an increasing number of Si–H groups.

As expected, the PMDMS film properties close to the walls substantially deviate from the bulk behavior. Generally, such deviations should depend on polymer–substrate interactions, film deposition methods and various other parameters, such as film thickness, pressure or temperature. Moreover, thin films undergo a transition from liquid-like to a solid-like behavior below a critical thickness corresponding to several molecular layers of the liquid [44–47]. We believe that at the liquid PMDMS–hydrophobic interface an interplay of energetic (interactions between polymer chains and surface based on van der Waals forces) and entropic (the reduction of orientational freedom due to the presence of an impenetrable wall) leads to a depletion of the chains near the wall. In other words, the PMDMS molecules prefer to stay away from an interface and form a low-density region if the interface limits the number of accessible molecular configurations (Fig. 5). Our observations are in full agreement with theoretical studies suggesting that the crossover from the substrate to the bulk behavior for short polymer chains extends over a zone of size of about $2R_g$ next to the interface (when only excluded volume interactions are taken into account) [13]. Experimental results on polystyrene thin films spin-coated on glass substrates show that distortions of the chain conformation starts to increase for films with a film thickness smaller than six times the radius of gyration in the bulk [14]. On the other hand, long-range surface-induced effects on the polymer dynamics are observed for polystyrene films on oxide-covered silicon at distances up to 10 times the radius of gyration [48]. An NMR study of PDMS liquid films shows that even in the absence of specific interactions, non-absorbing surfaces modify the free polymer chain dynamics [49]. The uniaxial chain segment ordering appears over an essentially wider range of film thicknesses for films of lower molecular weight (for example, the surface induced order is still observable for PDMS films with $M_w = 1.6 \times 10^4$ and $30R_g$ thickness). Competition between the gain in interaction energy and the loss of configurational entropy in liquid–solid interface of thin polymer films may play an important role. Chain stiffness disparity may also contribute to the entropy-driven segmental reorientation and adhesion of polymer chains in the liquid–solid interfacial region [50,51].

It should be emphasized that the surface roughness is an important factor in the surface induced density variations of a liquid. No density anomaly was observed by XRR measurements for PMDMS films (~30 Å thick) deposited on relatively rough hydrophobic films with a root-mean-square width of 10–20 Å. We only observed so-called conformal or correlated roughness effects [52], that are typical for thin liquid films behaving like frozen liquids: PMDMS uniformly covers such a coarse substrate surface and follows the surface morphology.

4. Conclusions

Thin liquid PMDMS films deposited on smooth organic (hydrophilic and hydrophobic) surfaces exhibit surface controlled density profiles at the liquid PMDMS/substrate interfaces, whereas no remarkable features were observed at the PMDMS/air interfaces. A balance of confinement-restricted segmental ordering, non-covalent interactions such as hydrogen bonding between substrate surface and molecules at the surface of the liquid is likely to determine the electron density in thin polymer films in the vicinity of substrates of different hydrophobicity having chemically different surface moieties (i.e. $-NH_2$ vs. $-CH_3$). Interfacial interactions are apparently highly dependent on the used organic coating of the silicon substrate perhaps allowing formation of liquid polysiloxane based films with graded interfacial interactions and tuneable density profiles.

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