

Wetting films on chemically modified surfaces: An x-ray study

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The wetting of silicon wafers and silicon wafers coated with alkylsiloxane monolayers by saturated vapors of cyclohexane and methanol were studied using x-ray specular reflection. Differentially heating the substrate surface relative to the temperature of a liquid reservoir was used to probe the disjoining pressure as a function of the film thickness and surface chemistry. Uncoated silicon wafers wet completely. The variations in film thickness with ΔT are explained exclusively in terms of the nonretarded van der Waals forces for films 10–120 Å thick. Wafers coated with methyl terminated alkylsiloxane monolayers wet incompletely, with a microscopic film 1–3 Å thick adsorbing on the surface. Changing the alkylsiloxane terminal group from $-\text{CH}_3$ to $-\text{CH}_2\text{OH}$ converts the surface from incompletely to completely wet. Surfaces coated with partial monolayers of methyl terminated alkylsiloxane of greater than 50% coverage are incompletely wet by cyclohexane, with the monolayers “swelling” to a thickness close to that of fully extended alkane chains through incorporation of cyclohexane into the film structure. The data are consistent with a first-order transition to complete wetting upon reduction of the alkylsiloxane coverage below approximately 50%. The importance of the surface atomic layer in the promotion or suppression of complete wetting is explained in the context of van der Waals forces.

I. INTRODUCTION

A solid surface in contact with a vapor in coexistence with its liquid can be classified as completely or incompletely wet, depending on whether the surface adsorbed liquid film is macroscopically thick or microscopically thin (where “macroscopic” refers to micrometer or greater length scales and “microscopic” to atomic length scales).¹ Despite the dramatic contrast between these macroscopic manifestations, the variations in surface energetics that give rise to these different wetting properties are subtle and are controlled by the interplay of long- and short-range forces. While long-range forces depend on the chemical and structural nature of the substrate region that typically extends tens of angstroms or more from the surface, short-range forces are dominated by the chemistry and structure of a region within, at most, a few atomic layers of the surface.^{2–4} In addition, competition between long-range forces originating from different layers of a composite substrate can result in a net force that is functionally equivalent to one that has a short-range component.^{2,3} Several extensive reviews of wetting and surface forces are available in the literature.^{5–10}

The disjoining pressure,⁸ $\Pi(l)$ provides a convenient formalism for discussions of wetting. By definition

$$\Pi(l) = - \frac{dG^\sigma(l)}{dl}, \quad (1)$$

where $G^\sigma(l)$ is the excess a real free energy density of an adsorbed film of thickness l . Phenomenologically, the

disjoining pressure is the thermodynamic force per unit area between the free surface of the wetting film and the adsorbing substrate. In an isothermal system in which the film is in thermodynamic equilibrium with the vapor, the free surface of the wetting film is fixed at a position z , where $\Pi(z)=0$ and $d\Pi(z)/dz < 0$; nonzero values of $\Pi(l)$ describe the restoring forces for surfaces that deviate from the equilibrium condition. This condition for equilibrium corresponds to a minimum of the surface excess free energy.⁸

The most commonly used probe of wetting phenomena is the measurement of the angle that the edge of a macroscopic liquid drop makes with a homogeneous flat surface at equilibrium.^{6,11} This “contact angle” θ is related to the interfacial energies by Young’s equation:¹²

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos(\theta), \quad (2)$$

where γ is the interface areal free energy density (interfacial tension) and s , l , and v refer to the solid, liquid, and vapor, respectively. The sensitivity of contact-angle measurements to chemical changes of a fraction of a monolayer demonstrate the extreme surface sensitivity of wetting phenomena.^{6,13,14} The interpretation of contact-angle measurements, however, is greatly complicated by surface roughness, microscopically thin adsorbed films, reactive surface functionality, and chemical heterogeneity, which can introduce hysteresis into the measurement of advancing and receding contact angles.^{6,11} Although contact-angle measurements are sensitive to the presence of thin physisorbed films,¹⁵ extraction of the adsorbed

film characteristics from contact-angle measurements is difficult. Additionally, contact-angle measurements do not probe the disjoining pressure as a function of the distance from the solid surface. Indeed, the disjoining pressure formalism does not describe the translationally inhomogeneous case of macroscopic liquid droplets coexisting with a microscopically thin film.

Other techniques have been used to probe wetting transitions and the nature of the surface forces more directly. Krim, Dash, and Suzanne¹⁶ used a high-frequency microbalance to study the wetting of cryogenic gases on gold substrates. These gases were found to incompletely wet gold below the adsorbate triple point and completely wet above the triple point. For $T > T_{\text{triple}}$ the variation of the wetting film thickness with gas vapor pressure displayed the functional form expected for nonretarded van der Waals forces. Measurements of the surface excess heat capacity upon surface melting of thick films of solid argon on graphite (liquid argon "wetting" solid argon) confirmed the suitability of van der Waals forces to explain forces acting on length scales of tens of angstroms.¹⁷ Grazing incidence diffraction of x rays and neutron diffraction have also been used to study surface melting by direct observation of the structure factor of the surface layers.^{18–20}

Blake²¹ used ellipsometry to measure the thickness of an *n*-alkane film between a bubble and the surface of alumina. Completely wetting surface films thicker than approximately 300 Å were described using retarded van der Waals forces. Similar studies of tetradecane on quartz found that wetting films of thickness 30–120 Å were best described by a nonretarded van der Waals force.^{22,23} The adsorption of octamethylcyclotetrasiloxane on mica exhibited layering of the first two monolayers.²⁴ This layering highlights the inadequacy of the van der Waals description of surface forces for films of approximately molecular thickness.^{8,9} A more complete review of similar experiments is given by Derjaguin, Churaev, and Muller in Ref. 8.

While it is difficult to "tune" surface forces directly, a similar effect can be achieved through the use of substrates with surface adsorbed films as outlined below. Theoretical studies have indicated that by careful choice of substrate and surface film, it may be possible to access a variety of previous unobserved wetting phenomena.^{2,3} Organic monolayers are increasingly utilized in this capacity. The wetting of the surface of silylated capillary tubes by phase-separated binary liquids was studied by both capillary rise and ellipsometry.^{4,25,26} After judicious choice of the liquids and substrates, heavily silylated surfaces were found to undergo a first-order transition from incomplete to complete wetting with changes in temperature. The transition temperatures were correlated with the silane coverage. Due to the complex interactions of the substrate, liquids, and interfaces with each other, the forces acting in these systems are difficult to interpret. Different wetting regimes have also been studied using optical and x-ray techniques to probe the thickness and shape of wetting films of nonvolatile liquids spreading on solid substrates with various surface chemistries.^{27–30} The thickness of the precursor film of the advancing drop

is strongly dependent on the substrate structure within a few angstroms of the substrate surface.

In the investigation reported here, x-ray specular reflection was used to study the wetting of organic liquids on silicon substrates coated with self-assembled alkylsiloxane monolayers having various termination moieties. X-ray specular reflectivity has been used to study liquid wetting films in only a few cases to date.^{29,31–33} This technique provides direct characterization of the structure and thickness of the adsorbed film and the solid substrate. The utility of alkylsiloxane monolayer surfaces for wetting studies arises from their ease of formation, robustness, and uniformity. These properties have stimulated their use in several wetting studies.^{13,14,28–30} In addition, it is possible to "engineer" the chemistry of the precursor molecules so that different chemical species are introduced into the monolayer at specific locations in a well-controlled fashion.^{14,34} Recent x-ray studies of alkylsiloxane monolayers have revealed that complete monolayers have low concentrations of gauche bonds^{35,36} and that the alkyl chains are oriented almost vertical to the surface.³⁷ The monolayers are quite uniform and the molecular chains are tightly packed with liquidlike in-plane order characterized by a 45-Å correlation length.^{37,38} In the present study we investigated the wetting properties of "bare" silicon (silicon with ~15-Å-thick native silicon oxide films) and chemically modified silicon surfaces. The bare substrate wetting properties were altered using chemisorbed alkylsiloxane monolayers with methyl ($-\text{CH}_3$), vinyl ($-\text{CH}=\text{CH}_2$), and alcohol ($-\text{CH}_2\text{OH}$) terminations. In addition, the wetting of partial alkylsiloxane films were also studied. The siloxane head groups of these films are more loosely packed than the fully formed films.^{37,38} The alkylsiloxane chains possess a mean molecular tilt so that the films are thinner than the complete monolayers but have a similar electron density.³⁷ The form of the disjoining pressure curve was investigated for surfaces that were completely wet by differentially heating the substrate relative to the temperature of a liquid reservoir of the adsorbate in the sample chamber. This technique was used to thin the adsorbed films in a controlled manner.

II. PREPARATION OF MONOLAYERS

Uncoated silicon wafers (Semiconductor Processing Co., Boston, MA) were cleaned in a strongly oxidizing solution immediately prior to use, as outlined in Ref. 33. Previous studies^{33,37} have shown that these wafers are coated with a native silicon-oxide film about 15 Å thick, the surface of which has a rms roughness of about 2.5–3.5 Å.

All methyl terminated 18 carbon chain alkylsiloxane samples [$-\text{O}_{1.5}\text{Si}-(\text{CH}_2)_{17}\text{CH}_3$, complete and partial monolayers] were prepared by the same method as described in Ref. 38. An eight-carbon chain alkylsiloxane monolayer was prepared by a similar method.³⁵ The vinyl terminated monolayers [$-\text{O}_{1.5}\text{Si}-(\text{CH}_2)_{15}\text{CH}=\text{CH}_2$] were prepared following the method of Ref. 14. These samples, which are sensitive to room light,³⁹ were stored in the dark and generally used within 24 hours of

TABLE I. Ellipsometric thicknesses and the advancing (*a*) and receding (*r*) contact angles of water, hexadecane (HD), and cyclohexane (C₆H₁₂) for typical samples reported in this study. Typical contact angle errors at $\pm 2^\circ$. For contact angles $\lesssim 10^\circ$, however, the error is approximately the size of the measured angle. The last two entries in the table refer to incomplete monolayers where the parenthetical values refer to an x-ray estimate of the surface coverage. "Bare" silicon wafers were wet by all three liquids. The asterisk denotes samples not measured.

Sample	<i>l</i> (Å)	Contact angle (deg)					
		H ₂ O (<i>a</i>)	H ₂ O (<i>r</i>)	HD (<i>a</i>)	HD (<i>r</i>)	C ₆ H ₁₂ (<i>a</i>)	C ₆ H ₁₂ (<i>r</i>)
(CH ₂) ₁₇ CH ₃	27.5	112	104	45	44	30	30
(CH ₂) ₁₅ CH=CH ₂	26.3	101	92	39	38	*	*
(CH ₂) ₁₇ OH	23.5	54	47	9	0	7	0
(CH ₂) ₁₇ CH ₃ (33%)	8.0	82	66	36	0	11	0
(CH ₂) ₁₇ CH ₃ (45%)	11.9	93	75	44	37	17	0

formation. Hydroboration of vinyl terminated monolayers was used to produce alkylsiloxane monolayers with an alcohol termination [$-\text{O}_{1.5}\text{Si}-(\text{CH}_2)_{16}\text{CH}_2\text{OH}$].¹⁴

Preliminary analysis of the coated surfaces was carried out using ellipsometry and contact-angle measurements. Table I lists the ellipsometrically determined monolayer thicknesses and contact angles for water, hexadecane, and cyclohexane droplets on the substrates used in this study. The tabulated properties of the monolayers were similar to those found in previous studies.^{35,37,38} Only small variations between samples were detected for the full monolayers; incomplete monolayers, however, were much more inhomogeneous, with larger intersample and intrasample variations.³⁸

III. X-RAY MEASUREMENTS

X-ray specular reflectivity is sensitive to the density profile along the direction normal to the surface. For sufficiently smooth interfaces with low-atomic-weight materials, the reflectivity is described by the equations

$$R(q_z) = R_F(q_z) |\Phi(q_z)|^2 \quad (3)$$

and

$$\Phi(q_z) = \int \frac{1}{\rho_\infty} \frac{d\langle\rho\rangle}{dz} e^{iq_z z} dz, \quad (4)$$

where R_F is the Fresnel reflectivity from a sharp smooth interface, $q_z \approx (4\pi/\lambda)\sin(\theta)$, θ is the angle the incident beam makes to the surface, $d\langle\rho\rangle/dz$ is the derivative of the electron-density profile averaged over the in-plane coherence length of the x rays, and ρ_∞ is the electron density of the semi-infinite bulk.³⁷ This form is valid for angles larger than approximately twice the critical angle.

The data were analyzed by choosing a model form for the electron density along the surface normal and fitting the square of the analytical Fourier transform of this model [$|\Phi(q_z)|^2$] to the Fresnel normalized reflectivity (R/R_F). Typical interfaces between surface layers were assumed to have a Gaussian form for $d\langle\rho\rangle/dz$, i.e., $\langle\rho(z)\rangle$ has an error function form.³⁷ A one-layer (two-interface) model was used to describe the approximately 15-Å-thick native oxide film present on all silicon wafers

studied. Alkylsiloxane coated silicon wafers were described by a three-interface model.^{33,37} Excellent agreement between the data and the model were obtained when $d\langle\rho\rangle/dz$ for the silicon oxide-hydrocarbon interface was modeled by two Gaussians of equal area separated by one Gaussian width and the other interfaces were represented by single Gaussians. Wetting layers were modeled by the inclusion of an additional interface associated with the liquid-vapor surface, for which $d\langle\rho\rangle/dz$ was again assumed to have a Gaussian shape. For films thicker than approximately 50 Å, a Gaussian distribution for the liquid film thickness was included in the fitting form. For all samples reported here the rms width of this Gaussian was always less than 5% of the film thickness.

Measurements were performed on the AT&T beam line X16B at the National Synchrotron Light Source (NSLS) and at the rotating-anode x-ray source of the Harvard Materials Research Laboratory. At NSLS the wavelength used was 1.691 Å. The beam line was equipped with a bent mirror focusing in the vertical plane, and an asymmetrically cut Ge(111) crystal monochromator which was bent to focus in the horizontal plane. The spectrometer was configured with the scattering plane vertical and with the surface normal of the sample pointing down. The incident beam size was fixed using slits of dimension 1.0 mm wide by 0.05 mm high, positioned approximately 300 mm before the sample. These dimensions restricted the beam to fall wholly onto the samples for all angles except those much smaller than the critical angle. The detector arm slits were 4.0 mm wide by 1.0 mm high on an arm 660 mm long, giving an in-plane transverse resolution of about $(7 \times 10^{-4})q_z \text{ Å}^{-1}$. Small-angle reflectivity measurements were made using attenuators to avoid saturating the detector. With this arrangement a dynamic range of about 10^9 was obtained.

The rotating-anode measurements were carried out using 1.5405-Å Cu $K\alpha_1$ radiation selected using a Ge(111) monochromator crystal. The spectrometer was configured with both the scattering plane and the sample surface normal in the horizontal plane. The beam incident on the sample was defined by a slit positioned approximately 200 mm before the sample with dimensions 3 mm high by 0.05 mm wide for incident angles less than

about 1° and 3 mm high by 0.2 mm side for larger incident angles. The detector slit was approximately 500 mm from the sample with an aperture of 6 mm high by 1 mm wide. A dynamic range of 10^6 permitted measurement of hydrocarbon film thicknesses for films ≥ 8 Å.

The x-ray cell consisted of a two-stage temperature-controlled chamber with a gold-coated inner cell maintained at a temperature of 303 K (typical control: fluctuations < 1 mK/h, drift < 5 mK/10 h). The samples were mounted in the x-ray cell with the unpolished side against a thermoelectric device and supported 3 cm above a reservoir of approximately 5 cm³ of liquid cyclohexane or methanol which was in thermal contact with the cell walls. The cell was flushed with helium before sealing. After sealing, the organic vapor saturated the cell atmosphere, wetting the substrate by vapor transport from the liquid reservoir. The wetting film thickness was varied by differentially heating the substrate relative to the liquid reservoir by passing a current through the thermoelectric device. Typical substrate-reservoir differential temperatures ranged between 0 K (> 100 Å film) and ≈ 0.7 K (≈ 15 Å film).

Alkylsiloxane monolayers are noticeably damaged by x-ray exposures greater than approximately 10^{12}

photons/mm² (Refs. 37 and 38) as detected through changes in x-ray scattering and the more sensitive contact angle and breath test results. Therefore most x-ray data on the wetting of alkylsiloxane coated substrates were collected using a rotating-anode source, for which exposures of several days were found to produce no x-ray damage observable by either contact-angle measurements or the breath test. One methyl terminated alkylsiloxane sample [Figs. 1(c) and 1(d)] was measured at the synchrotron using an attenuated beam to limit the total exposure to $\sim 10^{11}$ photons/mm², which is below the threshold for radiation damage evident in contact-angle measurements and the breath test. The wetting of bare silicon substrates reported here include some results obtained after prolonged exposure to synchrotron radiation. These results were checked with fresh wafers at the rotating anode and found to be independent of accumulated dose (see below).

IV. RESULTS

A. Complete wetting of uncoated silicon

Figure 1(a) shows the Fresnel normalized x-ray specular reflectivity profile for a dry "bare" silicon substrate. All the data shown in Figs. 1(a)–1(d) were collected at the synchrotron. By comparison, the data shown in Figs. 1(e) and 1(f) were taken using a rotating anode and consequently have a much more restricted dynamic range.⁴⁰ The solid line in Fig. 1(a) represents a two-interface model of the substrate with a silicon oxide layer thickness of 15.8 ± 0.6 Å and a silicon oxide-vapor interface rms width of 4.1 ± 0.2 Å.

On placing this sample in a saturated atmosphere of cyclohexane, the reflectivity profile develops oscillations due to the interference between the reflections from the SiO₂-cyclohexane and the cyclohexane-vapor interfaces [Fig. 1(b)]. These data were modeled by a three-interface model using the parameters of the dry substrate listed above and the bulk density of liquid cyclohexane. The cyclohexane film thickness was determined to be 128 ± 2 Å. The roughness of the liquid-vapor interface and measurements of the diffuse scattering from this and other films on bare silicon substrates are discussed in a previous paper.^{33,41}

Formally, complete wetting requires that the thickness of the wetting film increases without limit as the system approaches coexistence between bulk liquid and vapor; however, experimental factors precluded realization of infinitely thick films in our system. For bare silicon samples, cyclohexane film thicknesses at bulk liquid-vapor coexistence ranged from 100 to 400 Å. Furthermore, films thicker than ~ 150 Å showed large uncontrolled drifts in thickness with time, while films of thickness 100–150 Å were stable to approximately 10 Å over a period of a day or more. A crude calculation of the thinning expected due to gravity using nonretarded van der Waals interactions predicts a maximum film thickness of approximately 350 Å, which is considerably thicker than we measured for most films. We attribute the additional thinning to small temperature variation and offsets be-

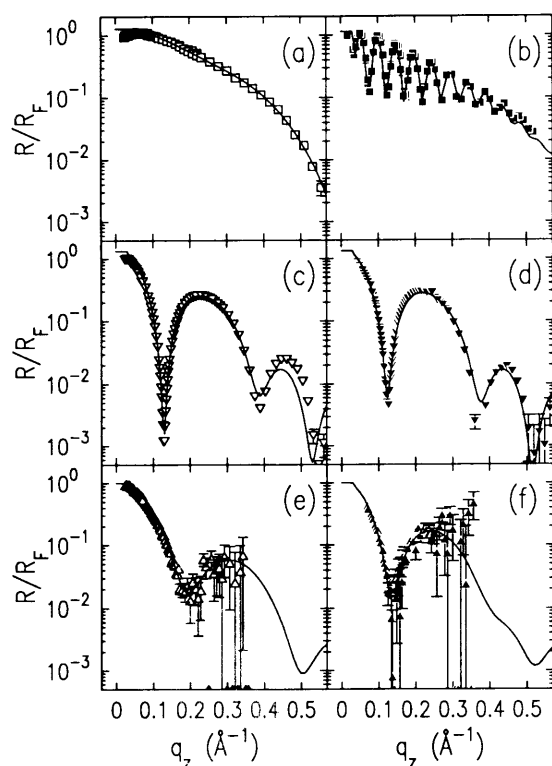


FIG. 1. Specular reflectivity scans from different samples: (a) and (b) show a "bare" silicon substrate dry (a) and in a saturated cyclohexane atmosphere (b); (c) and (d) show a full monolayer of methyl terminated alkylsiloxane molecules dry (c) and in a saturated cyclohexane atmosphere (d); (e) and (f) show a partial monolayer of methyl terminated alkylsiloxane molecules dry (e) and in a saturated cyclohexane atmosphere (f). All the data, except those shown in (e) and (f), were measured using a synchrotron x-ray source, with (e) and (f) measured using a rotating-anode source.

tween the sample and the liquid reservoir. Thus we assert that films with thicknesses over 100 Å are indicative of complete wetting in the absence of gravity and with improved temperature control.

For an isothermal system consisting of a substrate with a uniform adsorbed film of thickness l in equilibrium with vapor, the excess free energy per unit area of the film is given by

$$G^{\sigma}(l) = \gamma_{lv} + \gamma_{sl} - \gamma_{sv} + F(l), \quad (5)$$

where $F(l)$ is the thickness-dependent part of the excess free energy of the liquid film and the γ terms are the surface tensions for interfaces between the semi-infinite media denoted by the subscripts. $G^{\sigma}(l)$ is related to the disjoining pressure by Eq. (1), which leads to $\Pi(l) = -dF(l)/dl$. If we neglect entropic effects associated with the suppression of thermal fluctuations of the liquid-vapor interface due to the proximity of the solid substrate, the function $F(l)$ can be replaced by $F_0(l)$, whose l dependence is determined exclusively by the energetics of adsorbate-substrate and adsorbate-adsorbate interactions. Entropic effects are small for the film thicknesses of primary interest² and have the same dependence on the film thickness as the adsorbate-substrate interactions at large l .⁴² Ignoring entropic effects yields $\Pi(l) = \Pi_0(l) = -\partial F_0(l)/\partial l$ for an isothermal system.

Three possible forms for $\Pi_0(l)$ are shown in Fig. 2. The equilibrium thickness of a wetting film corresponds to the condition that $\Pi_0(l) = 0$ and $d\Pi_0/dl < 0$ (minimum of surface free energy). Curve 1 represents complete wetting since $\Pi_0(l = \infty) = 0$. For curve 2, the free-energy density has two local minima and the global minimum is distinguished by comparison of the areas A_1 and A_2 ; for $A_1 < A_2$, the global minimum is at $l = \infty$, which corresponds to complete wetting. Varying the ratio A_1/A_2 along a thermodynamic trajectory can result in a "thick-thin" film thickness transition across a "prewetting line."^{6,43} The existence of such a prewetting line is dependent on the exact form of the disjoining pressure at both short and long distances from the surface (i.e., on both short- and long-range forces). As depicted in Fig. 2, $A_1 > A_2$ and the surface is incompletely wet, with the

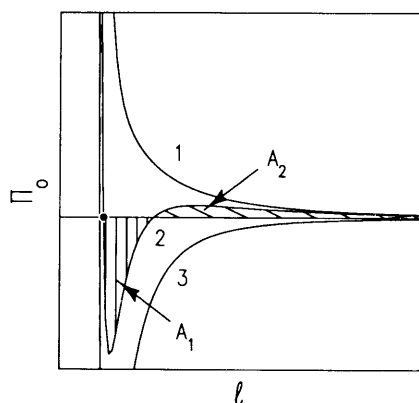


FIG. 2. Three typical model disjoining pressure curves. Curve 1 corresponds to complete wetting, curves 2 and 3 to incomplete wetting. See the text for details.

equilibrium liquid film thickness represented by the position of the dot. Curve 3 represents incomplete wetting in the case of a homogeneous substrate with a net repulsive adsorbate-substrate interaction.

Considering only van der Waals interactions between the adsorbed molecules and a uniform substrate over length scales for which the forces are not retarded ($\lesssim 300$ Å for the solvents employed), the disjoining pressure has the form $\Pi_0(l) = A_{\text{eff}}/(6\pi l^3)$,⁸ where $A_{\text{eff}} = A_{ij} - A_{ii}$, i represents the adsorbate, j denotes the substrate, and A_{ij} and A_{ii} represent the Hamaker constants for the substrate-adsorbate and adsorbate-adsorbate interactions, respectively. A van der Waals interaction energy between two molecules of the form $\epsilon(r) = -\alpha_{ij}/r_{ij}^6$ is assumed. We employ the approximations that van der Waals forces are additive^{9,10} and that $\alpha_{ij} \approx \sqrt{\alpha_i \alpha_j}$. Finally, the definition for the Hamaker constant $A_{ij} = \pi^2 n_i n_j \alpha_{ij}$, where $n_{i,j}$ is the molecular density, is utilized. Given these assumptions, the dissimilar Hamaker constant is $A_{ij} = \sqrt{A_{ii} A_{jj}}$. In practice, these approximations frequently are somewhat inaccurate^{8,10,44} and inconsistencies exist between Hamaker constants quoted in the literature.⁴⁵ The Hamaker approach, however, does describe the qualitative features observed in this study.

For the case where $A_{\text{eff}} > 0$, the disjoining pressure has a form similar to curve 1 in Fig. 2 and therefore corresponds to complete wetting. Alternatively, if $A_{\text{eff}} < 0$ and the effect of a hard-core repulsion is included, the disjoining pressure is similar to curve 3. The global minimum in F_0 corresponds to an atomically thin film. More complex disjoining pressure functions, like that shown as curve 2 in Fig. 2, can arise if forces other than van der Waals forces are present or when the substrate is heterogeneous along the surface normal (see below).

One method of probing the dependence of the disjoining pressure on the distance from the substrate surface is to measure the film thickness as a temperature differential ΔT is introduced between the substrate and the reservoir of bulk liquid adsorbate. Figures 3(a) and 3(b) show the measured dependence of the film thickness l on ΔT for a bare silicon substrate in contact with saturated atmospheres of cyclohexane and methanol, respectively. With the introduction of a temperature differential, the thickness-dependent part of the excess free energy of the adsorbed liquid film is given by

$$F(l) = F_0(l) + \Delta\mu n_i, \quad (6)$$

where $\Delta\mu$ is the chemical potential difference between liquid and vapor ΔT off the liquid-vapor coexistence line.⁴⁶ The term proportional to $\Delta\mu$ represents the energy cost (per unit area) associated with forming a liquid layer of thickness l at a temperature ΔT off the liquid-vapor coexistence line. The disjoining pressure is given by

$$\Pi \approx \Pi_0 - n_i \left[\frac{\partial \Delta\mu}{\partial T} \right]_p \Delta T. \quad (7)$$

Throughout we use the approximation $(\partial \Delta\mu / \partial T)_p \approx q/T$, where q is the latent heat of vaporization per

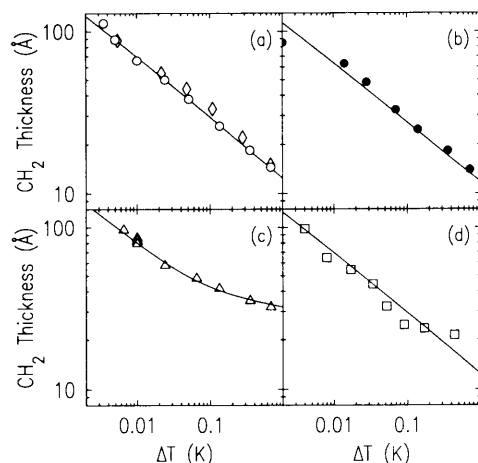


FIG. 3. The thickness of the wetting films on variously treated substrates as a function of differential temperature ΔT : (a) cyclohexane on "bare" silicon (\circ and \diamond); (b) methanol on bare silicon; (c) cyclohexane on an alcohol terminated alkylsiloxane sample; (d) cyclohexane on a partial monolayer of methyl terminated alkylsiloxane molecules. All the data were collected using a rotating anode source except for synchrotron data shown as \diamond in (a). The solid lines depict the results of calculations of $l(\Delta T)$ for van der Waals interactions between the adsorbate and the composite substrates, as discussed in the text.

molecule ($q \approx 5.4 \times 10^{-13}$ erg for cyclohexane) and we assume that the temperature gradient occurs in the vapor.

Introducing a temperature differential changes the condition for the equilibrium film thickness from $\Pi(l) = \Pi_0(l) = 0$ at liquid-vapor coexistence to $\Pi_0(l) = n_l q \Delta T / T$. Considering only nonretarded van der Waals interactions (in the Hamaker formalism), the film thickness for a uniform substrate scales as $l \propto (\Delta T)^{-\kappa}$ with $\kappa = 0.333$. Inspection of Figs. 3(a) and 3(b), however, reveals that the $l(\Delta T)$ are well described by a line with $\kappa = 0.40 \pm 0.03$, inconsistent with the simple theory. The crucial feature missing from this simple model is the inclusion of the silicon oxide layer, which has a substantially different Hamaker constant from that of silicon

(Ref. 45 and Table II). Inclusion of a substrate surface layer in the Hamaker formalism yields an effective adsorbate-substrate Hamaker "constant" with an l dependence:

$$A_{\text{eff}}(l) = (A_{FL} - A_{LL}) + (A_{SL} - A_{FL})(1 + d/l)^{-3}, \quad (8)$$

where L denotes the liquid film, S the substrate, and F the solid surface film of thickness d . The solid line shown in the Fig. 3(a) represents the results of a fit which assumes a two-layer model and uses the thickness of the silicon oxide film extracted from reflectivity measurements. The Hamaker constants obtained from this fit (using the cyclohexane Hamaker constant quoted in the literature⁴⁵) are listed in Table II. These empirical values for silicon and silicon oxide are comparable to the values quoted in the literature.⁴⁵ The thickness dependence of a methanol film adsorbed on a bare silicon substrate is depicted in Fig. 3(b). The solid line was calculated using the parameters extracted from the cyclohexane fits and the Hamaker constant for methanol as calculated directly from the methanol dielectric constant.⁴⁷

To summarize, neglecting temperature offsets less than approximately 5 mK, the change of the film thickness with ΔT is described by nonretarded van der Waals interactions when the heterogeneity of the substrate along the surface-normal direction is considered. We have interpreted this as evidence that bare silicon substrates are completely wet by cyclohexane and methanol, in agreement with contact-angle measurements.

B. Coated wafers: Modification of wetting properties

Generally, the presence of a thin film F of thickness d at a solid surface S introduces several interesting wetting phenomena. Using Eqs. (1) and (8) and expanding Π_0 in powers of (d/l) yields

$$\Pi_0(l) = \frac{H_3}{l^3} + \frac{H_4}{l^4} + O(l^{-5}), \quad (9)$$

where $H_3 \sim A_{SL} - A_{LL}$ and $H_4 \sim -d(A_{SL} - A_{FL})$. A similar form is obtained in a Landau expansion for the

TABLE II. The surface tensions and Hamaker constants for several surfaces and liquids. The surface-tension values for liquids were obtained from Ref. 54. The surface-tension values for the solids were extracted from measurements of the cyclohexane and hexadecane contact angles through application of Eq. (2) using the liquid surface-tension values listed. The interaction Hamaker constants are calculated from the tabulated A_{ii} using the relation $A_{ij} \approx \sqrt{A_{ii} A_{jj}}$. Unless otherwise noted, the literature values of the Hamaker constants were obtained from Ref. 45.

Material	γ erg cm ⁻²	$A_{ii} \times 10^{13}$ erg (literature)	$A_{ii} \times 10^{13}$ erg (Expt.)
c-Si		22–26	40 ± 15
a-SiO ₂		4–19	13 ± 4
—(CH ₂) _n CH ₃	21 ± 2		< 4.6 ^a
—(CH ₂) _{n-1} CH=CH ₂	22 ± 2		< 4.6 ^a
Cyclohexane	25.5	4.6	
Methanol	22.6	3.2 ^b	

^a The upper limit is set by the fact that the surfaces were not wet by cyclohexane, and therefore must have a higher surface energy.

^b Calculated from the static dielectric constant using the approximations of Ref. 47.

substrate and liquid interactions. In general the wetting properties depend on the magnitude and sign of H_3 , H_4 , etc.² For example, if H_3 and H_4 are both positive (i.e., $A_{FL} > A_{SL} > A_{LL}$) the wetting is complete; however, if H_3 is positive and H_4 negative (i.e., $A_{SL} > A_{FL} > A_{LL}$), the surface is either incompletely or completely wet, depending on the precise value of H_3/H_4 ; in this section we examine the effect upon wetting of changing H_4 through controlled modification of the substrate surface chemistry.

Figure 1(c) shows the x-ray reflectivity profile of a silicon wafer coated with a "complete" monolayer of methyl terminated alkylsiloxane molecules in the absence of cyclohexane. These reflectivity data are typical of high-quality alkylsiloxane monolayers.^{37,38} The solid line depicts the results of a fit to the reflectivity data utilizing the functional form described earlier. From this model the alkylsiloxane monolayer thickness⁴⁸ of 22.2 ± 1.0 Å is extracted.

Placing this sample in a saturated atmosphere of cyclohexane resulted in the x-ray reflectivity data shown in Fig. 1(d). Unlike the bare silicon wafer, the differences between the reflectivities for the "wet" and "dry" environments are very slight. Interpreting these slight differences as due to adsorption of a layer of cyclohexane, we find the adsorbed layer is only 1.0 ± 0.3 Å thick. Other similar alkylsiloxane monolayers (not shown) also had adsorbed films between 1 and 3 Å thick. The possibility that some cyclohexane has been adsorbed into the interior of the alkane chain region and the reflectivity differences are the result of a slight "swelling" of the alkylsiloxane monolayer cannot be excluded. In either case, the absence of a thick cyclohexane film clearly indicates incomplete wetting, as predicted by contact-angle measurements (Table I).

The simplest extension of the model describing wetting in terms of van de Waals interactions rests on the assumption that the Hamaker constant of the predominantly $-\text{CH}_2-$ alkylsiloxane film is equal to that of cyclohexane after scaling by the relative number densities of these two materials since $A_{ij} \sim n_i n_j$. In contrast with the observed incomplete wetting, this simple model of the adsorbate-substrate interaction predicts complete wetting since $n_{\text{alkylsiloxane}} > n_{\text{cyclohexane}}$. The essential element absent from this model is the different polarizability of the $-\text{CH}_3$ methyl termination and the $[-(\text{CH}_2)_n-]$ methylene groups. As the following discussion indicates, slight differences in these polarizabilities can profoundly modify the wetting characteristics of the substrate.

Here the wetting of $-\text{CH}_3$ terminated alkylsiloxane/ SiO_2/Si substrates is interpreted exclusively in terms of van der Waals interactions between the adsorbate and different layers of the composite substrate using the formalism of Eq. (8). (In addition to the entropic effects mentioned above, the molecular hard-core repulsion present at very small distances is also neglected.) Consider the two models of the disjoining pressure shown in Figs. 4(a) and 4(b) for different composite substrates (note that the $z=0$ origin corresponds to the silicon oxide surface and not the alkylsiloxane monolayer surface).

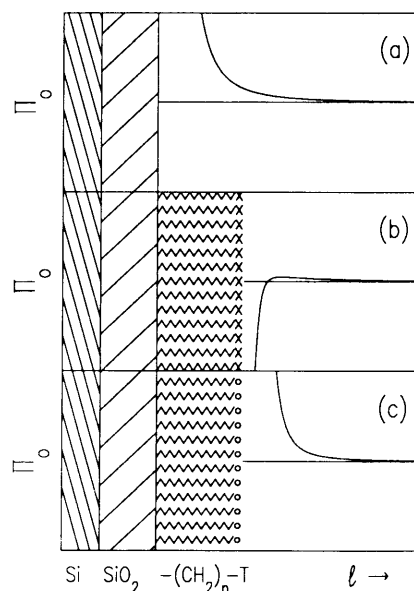


FIG. 4. Schematic of the surface structures for three surfaces together with model disjoining pressure curves for these surfaces: (a) the silicon-silicon oxide surface; (b) the same surface coated with a monolayer of alkylsiloxane with a methyl termination ($T = -\text{CH}_3$); (c) a similar surface where the terminal methyl group has been replaced by an alcohol group ($T = -\text{CH}_2\text{OH}$). (a) and (c) correspond to complete wetting [$\Pi_0(\infty) = 0$], whereas (b) corresponds to incomplete wetting. The form of $\Pi_0(z)$ was calculated using the experimentally determined Hamaker constants and those from Ref. 45 (see text for details).

Curves (a) and (b) represent the bare silicon sample and a possible model of the methyl terminated alkylsiloxane monolayer, respectively. Curve (a) was calculated using the Hamaker constants extracted earlier. Curve (b) uses the same values for the substrate, but treats the monolayer as follows. The Hamaker constant for the alkane interior of the monolayer is that of cyclohexane after scaling by the alkylsiloxane-cyclohexane density ratio. The terminal methyl group is assigned a Hamaker constant that is 5% less than the cyclohexane Hamaker constant (approximately 10% less than the monolayer alkane interior Hamaker constant) and a thickness of 3 Å. This value for the methyl moiety Hamaker constant is comparable to that extracted from the variation of Hamaker constants for bulk n alkanes as a function of chain length.⁹ Additional support for this description is provided by wetting studies of mixed monolayers of alkanethiols of different chain length on gold. The interfacial tension of the mixed monolayers is greater than that of the pure monolayers due to the significant number of methylene groups exposed to the liquid by the mixed monolayers.⁴⁹ Using these parameters, integration of curve (b) indicates that the area $A_1 > A_2$, corresponding to incomplete wetting. Note that although all the substrate-layer-adsorbate interactions are represented by attractive, long-range van der Waals forces, the net effect of competition between adsorbate-adsorbate and substrate-adsorbate interactions has a short-range effect

which results in a negative disjoining pressure at short distances inhibiting complete wetting. Inclusion of the neglected hard-core repulsive forces or other very-short-range forces will alter the exact form of the disjoining pressure, particularly at very short length scales where the disjoining pressure will have a shape similar to curve 2 of Fig. 2. So long as $A_1 > A_2$, the wetting remains incomplete.

A surface with very different wetting properties was prepared by hydroboration of a vinyl terminated alkylsiloxane monolayer to create an alcohol terminated sample ($-\text{CH}_2\text{OH}$). Both contact angle and x-ray reflectivity data indicate cyclohexane completely wets the alcohol terminated surface. (By contrast, the vinyl terminated monolayer precursor was incompletely wet; an adsorbed film of 3.0 ± 0.5 Å formed on the surface.⁵⁰) At coexistence ($\Delta T = 0$), the total hydrocarbon thickness on the alcohol terminated sample (alkylsiloxane + cyclohexane) is ≈ 140 Å. A plot of the total hydrocarbon film thickness as a function of differential temperature is shown in Fig. 3(c). For small ΔT (thick films) the slope is similar to that measured for bare silicon [see Fig. 3(a)]. For $\Delta T \gtrsim 0.02$ K (total hydrocarbon thickness $\lesssim 50$ Å), however, the film thickness decreases more slowly with ΔT since the surface attraction is then dominated by the terminal alcohol moiety. The solid line in Fig. 3(c) is the result of a fit for Π_0 using the same model that describes the methyl terminated substrates, with the Hamaker constant associated with the methyl group replaced by an adjustable Hamaker constant representing the alcohol termination. This effective Hamaker constant for the alcohol termination is approximately 8×10^{-13} erg as determined from the fit. Figure 4(c) depicts the calculated Π_0 .

In summary, the effect of substrate surface chemistry upon wetting has been investigated. Specifically, altering the substrate surface chemistry from a methyl termination to an alcohol termination changed the wetting from incomplete to complete. This effect is interpreted in terms of a net interaction consisting of the sum of exclusively nonretarded van der Waals interactions between the adsorbate and different layers of the composite substrate.

C. Incomplete alkylsiloxane films

We attempted to change the wetting properties of surfaces continuously through the use of methyl terminated alkylsiloxane partial monolayers. Previous studies^{37,38} have shown that the thicknesses of partial monolayers decrease with increasing molecular area, while the electron density of the alkane films remains essentially the same as that of fully formed monolayers. Notably, these results indicate that partial monolayers do *not* form islanded structures. The results of cyclohexane contact angle measurements for a series of incomplete monolayers are shown in Fig. 5. For all partial monolayers with ellipsometrically determined thicknesses greater than about 7 Å, the advancing contact angles are nonzero. The receding contact angles, however, are consistently nonzero only for alkylsiloxane films with thicknesses greater than approxi-

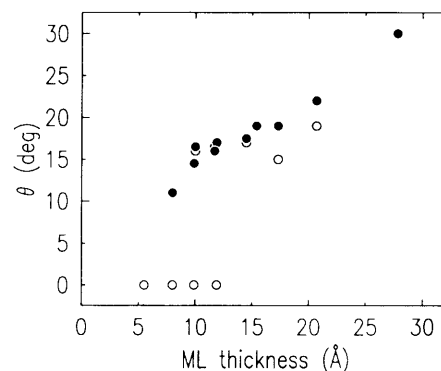


FIG. 5. The contact angle of cyclohexane on partial coverage 18 carbon chain alkylsiloxane surfaces. The advancing contact angles are shown as closed circles, receding by open circles. The film thicknesses ("ML thickness") were measured by ellipsometry, which typically overestimates the thickness of the film by approximately 5 Å as compared to the x-ray determined length (Ref. 38). The contact-angle measurement uncertainty is approximately $\pm 2^\circ$ for $\theta > 10^\circ$ and approximately $\pm 10^\circ$ for smaller angles. When only the advancing angle is shown, the receding contact angle was indistinguishable (within experimental uncertainty).

mately 15 Å. Individual alkylsiloxane films of thickness 10–15 Å, while having nonzero advancing contact angle, can have either zero or nonzero receding contact angle. These receding contact-angle variations result from a lack of complete control during the production of partial monolayers.

The x-ray determined total hydrocarbon film thickness of partial monolayers in contact with a saturated vapor of cyclohexane with $\Delta T = 0$ is shown in Fig. 6. An example of the change to the x-ray reflectivity profile of an incompletely wet partial monolayer on immersion in a saturated vapor of cyclohexane is given in Figs. 1(e) and 1(f). Alkylsiloxane films more than 30–50% complete are incompletely wet. For these alkylsiloxane coverages the total hydrocarbon film thickness (as determined from the position of the first interference minima in the reflectivity data) is essentially independent of alkylsiloxane coverage and comparable to the thickness of a complete alkylsiloxane monolayer. These observations coupled with the insensitivity of the total hydrocarbon film thickness to applied temperature differentials (see below) suggest that cyclohexane is incorporated into the loosely packed alkylsiloxane monolayers resulting in swelling of the monolayers. Although the swelling of hydrocarbon monolayers has been inferred in several previous studies of the contact-angle behavior of self-assembled monolayer surfaces,^{51,52} and the change in surface tension of hydrocarbons in contact with surfactant monolayers on water,⁵³ we believe this is the first direct evidence of this phenomenon. The absence of significant variation of the total hydrocarbon film thickness with alkylsiloxane coverage implies the zero of the disjoining pressure is largely independent of alkylsiloxane coverage for coverages $> 50\%$. Consequently, the disjoining pressure is expected to resemble curve 2 in Fig. 2 with $A_1 > A_2$. Unfor-

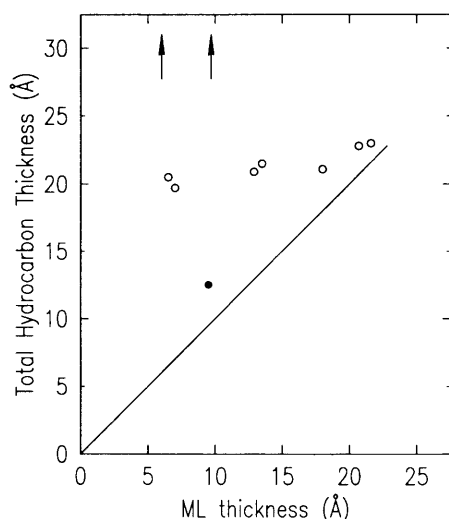


FIG. 6. The total hydrocarbon film thickness of cyclohexane wetted partial alkylsiloxane monolayers plotted against the x-ray determined thicknesses of the dry alkylsiloxane films ("ML thickness"). The open circles are 18 carbon chain alkylsiloxane films. The closed circle is a complete 8 carbon chain alkylsiloxane sample. Surfaces with no adsorbed cyclohexane film would fall on the solid line. The arrows indicate the thickness of alkylsiloxane monolayers which are completely wet (hydrocarbon film thickness > 100 Å).

tunately, the dynamic range of the data did not permit extraction of other structural features of the surface films (e.g., electron densities, interface widths).

For films with approximately 30–50% coverage, the monolayers were found to swell in a similar fashion to the more complete monolayers or wet completely by the cyclohexane. Alkylsiloxane monolayers with coverage less than approximately 30% were completely wet, although these samples were difficult to characterize when dry. For the completely wet monolayers the adsorbed film thickness was approximately 100 Å. Although our measurements were not exhaustive, we found that the films fell into only the two groups mentioned above, with no films of thickness 30–80 Å. These results are consistent with a first-order (discontinuous) transition between incomplete and complete wetting upon surface modification.² Uncontrolled variations in the formation of the incomplete alkylsiloxane monolayers precludes determination of the alkylsiloxane coverage at the transition to better than ~20%.

Differentially heating a completely wet, partial alkylsiloxane monolayer yields the $l(\Delta T)$ data shown in Fig. 3(d). The dependence of l on ΔT is intermediate between that of the bare silicon and the alcohol terminated alkylsiloxane samples. [For comparison, the solid line in Fig. 3(d) is the same as the line shown in Fig. 3(a) for bare silicon wet by cyclohexane.] For thick films the reduction of film thickness with increasing temperature differential is dominated by the long-range silicon and silicon oxide interactions, and has a dependence on the differential

temperature that is similar to that of bare silicon or alcohol terminated samples; at higher differential temperatures the film thins more slowly than the bare silicon. The disjoining pressure in this region is dominated by details of the interactions near the surface. Although the scatter of the data is large, the deviations away from the line representing the wetting of bare silicon are significant only for films with thickness $\lesssim 25$ Å, close to the complete monolayer thickness. Temperature variations on samples which were only *incompletely* wet showed a very slow variation of film thickness with differential temperature. Specifically, a differential temperature of approximately 0.7 K applied to an incompletely wet alkylsiloxane monolayer with 50% coverage reduced the total hydrocarbon thickness by about 1 Å, again demonstrating the strong forces present very close to the surface.

V. CONCLUSIONS

Experiments in which the wetting of silicon wafers and silicon wafers coated with alkylsiloxane monolayers by organic vapors studied by x-ray specular reflection have been described. Chemical changes to alkylsiloxane monolayer and variations in coverage for submonolayer coatings have been used to alter the wetting properties of the surfaces in a controlled fashion. For complete wetting substrates, the data are described well by invoking nonretarded van der Waals substrate-adsorbate interactions for length scales between approximately 10–120 Å. van der Waals interactions are also used to describe incompletely wetting surfaces in a qualitative fashion; quantitative analysis of the thickness of these films would require knowledge of the short-range interactions. The magnitudes of the substrate-adsorbate van der Waals interactions for complete wetting samples are consistent with values previously reported in the literature.⁴⁵ The dramatic difference between complete and incomplete wetting for substrates with slightly different surface chemistry is explained by the inclusion of van der Waals forces associated with very thin surface layers (typical thickness ~ 2 Å). It is demonstrated that the competition between van der Waals interactions associated with different layers in a composite substrate-adsorbate can result in a net substrate interaction with an effectively short-range component.

Finally, we note that alkylsiloxane and similar organic films could be used to explore other wetting phenomena. Surfaces with disjoining pressures similar to curve 2 of Fig. 2, but which have a local minimum near the surface that is *not* the global minimum, may undergo a "thick-thin" transition on application of a ΔT .^{2,3} The possibility also exists for a continuous wetting transition in a system with a substrate which favors incomplete wetting coated with a film which promotes complete wetting.^{2,3}

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¹Note that this definition is somewhat different than that used by the surface chemistry community, where complete and incomplete wetting refer to whether or not a film is continuous, no matter how thick the film.

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