

Growth Kinetics and Morphology of Self-Assembled Monolayers Formed by Contact Printing 7-Octenyltrichlorosilane and Octadecyltrichlorosilane on Si(100) Wafers

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Received March 2, 2004

The growth kinetics and morphologies of self-assembled monolayers deposited by contact printing 7-octenyltrichlorosilane (OCT) and octadecyltrichlorosilane (OTS) on Si(100) were studied by ellipsometry and atomic force microscopy. We found that, for both OCT and OTS, full monolayers could be obtained at room temperature after printing times of 120–180 s; the printing-based monolayer assembly processes follow apparent Langmuir adsorption kinetics, with the measured film growth rates increasing both with the ambient humidity and with concentration of the ink used to load the stamp. At a dew point of 10 °C and an ink concentration (in toluene) of 50 mM, the observed film growth rate constant is 0.05 s⁻¹. When the printing was carried out at a lower ambient humidity (dew points of 1–3 °C), the measured rates of assembly were approximately a factor of 2 slower. Increasing the deposition temperature from 25 to 45 °C under these conditions increased the film growth rate only slightly. The morphology of the films depends on the identity of the ink. Uniform, high-coverage films could be obtained readily from the eight-carbon chain length adsorbate OCT, provided that the stamp was not overloaded with the ink; for high concentrations outside of the optimal range, the surface presented significant numbers of adsorbed particles ascribed, in part, to siloxane polymers formed by hydrolysis of the ink on the stamp before printing. In marked contrast, for the 18-carbon adsorbate OTS, the printed films always consisted of a mixture of a uniform monolayer plus adsorbed polysiloxane particles. The different film morphologies seen for OCT and OTS are proposed to result from the different transfer efficiencies of the organotrichlorosilane relative to polysiloxane hydrolysis products formed during the printing process. These transfer efficiencies exhibit sensitivities related to the permeation of the poly(dimethylsiloxane) (PDMS) stamp by the silane reagents. Short-chain inks such as OCT evidently permeate the PDMS stamp more deeply than longer-chain inks such as OTS. This difference, and the different diffusion rates of ink vs oligomeric silane hydrolysis products, determines the film morphology obtained by contact printing. The mass transfer dynamics of the process thus yield surface layers derived from varying quantities of siloxane oligomers, which subsequently transfer to the substrate along with unhydrolyzed silane adsorbate during the printing step. The structural evolution of the contact-printed films so obtained is strikingly different from that of SAMs prepared by immersion.

Introduction

Self-assembled monolayers (SAMs)^{1–4} of organosiloxanes are of great interest for applications in materials fabrication because they provide a convenient route for functionalizing the surfaces of important (oxide-bearing) substrates such as Si and glass. Organosiloxane SAMs can be prepared on flat substrates from organotrichlorosilanes either by immersion^{1,2,4} or by soft lithographic techniques such as microcontact printing (μ CP) using poly(dimethylsiloxane) (PDMS) stamps.^{5,6} Indeed, the simplicity and patterning capability of μ CP has made this technique an attractive one for depositing SAMs.⁷

Depending on the choice of the organotrichlorosilane, SAMs patterned by μ CP can be used in thin film processing

either as passivating layers or as reactive layers for further chemical reactions. For example, SAMs formed by μ CP of octadecyltrichlorosilane (OTS) have been used as templates for the patterning of metals such as Cu, Pt, and Pd by chemical vapor deposition,^{8,9} for the patterning of polymers,^{10,11} and for the fabrication of organic light-emitting diodes.¹² SAMs in which the monomer possesses a terminal functional group can be chemically modified in subsequent steps to allow both directed modifications of interfacial properties and the further deposition of additional molecular constituents in a multilevel architecture.^{13,14} Procedures have been described, for example, in which the substrates are treated in an orthogonal fashion^{15,16} with multiple organotrichlorosilane reagents

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possessing different functional groups to create complex thin film structures presenting graded chemical properties.

Despite the considerable interest that exists in the deposition of patterned organosiloxane SAMs, little is known about the mechanism of film formation by μ CP.^{5,6} It is known that film formation by μ CP is affected by several process factors, including the amount of water present in the reaction environment,^{17–21} the temperature at which the printing is carried out,^{22–25} the type and cleanliness of the substrate,²⁶ the solvent used to prepare the ink,^{19,27} and most importantly the concentration of the adsorbate used to load the stamp.⁴ To date, little attention has been given to how these sensitivities influence the structure or morphology of contact-printed films. It is clear, however, that the assembly processes that occur in contact printing must be different in some measure from those involved in the formation of SAMs via immersion in solution. Consider, for example, the relative kinetics involved in each case: for OTS, printing yields high-coverage SAMs within several minutes whereas immersion can take hours to as much as a day to achieve the same result.

In contrast, many detailed studies have been made of the assembly process for organosiloxane SAMs formed by immersion. In particular, the amount of water present on the substrate is known to play an important role in the formation of high-quality films.^{17,18,28–32} Surface-bound water hydrolyzes the organotrichlorosilanes to organosilanol, which eventually cross-link and bind to the substrate.^{22,28,33} Too much water leads to undesired condensation of the alkyltrichlorosilane in solution, whereas too little leaves the substrates insufficiently hydrated to obtain well-organized SAMs with high surface coverage.^{17,18,28–30} It also has been reported that the water present on the substrate surface can be extracted by the immersion solvent and that the quality of the film formed depends strongly on the solubility of water in that solvent.¹⁹

During the preparation of SAMs by immersion, the presence of a thin film of water on the substrate surface

is thought to allow the organotrichlorosilane molecules to move freely, so that the film forms by a two-dimensional (2D) diffusion-limited aggregation process.^{22,31,32,35} Only the top layers of an adsorbed water layer (~ 15 Å of water exists on fully hydroxylated quartz at relative humidity of ~ 10 – 70% and 21 °C)³⁴ are believed to participate in the hydrolysis of the organotrichlorosilane.¹⁷ Data from IR and ellipsometry studies have shown that, at high concentrations of water, the surface coverage increases rapidly early in the film-formation process and that the growth kinetics deviate from a simple Langmuir adsorption model.²¹

Hoffmann et al. have reported rate constants for film formation from undecyltrichlorosilane, in which deposition was carried out by immersing the Si substrate in a 1 mM solution of the adsorbate in benzene.²¹ From in situ attenuated total reflectance experiments, they measured rate constants, k , of 0.28 and 0.67 M⁻¹ s⁻¹, when the concentration of water present in the reaction solution was 2.2 and 6.4 mM, respectively.

For the longer chain OTS, the rate constants for film growth by immersion have been measured using various analytical techniques under a variety of experimental conditions.^{21,27,38–40} Typically, values lying in a rather wide range of 0.2 to 5 M⁻¹ s⁻¹ have been reported by various researchers for OTS concentrations between 0.1 and 1 mM in hydrocarbon solvents. The water concentration dependence was not determined in these studies and, in this sense, the rate description is less than complete.

Atomic force microscopy (AFM) studies by Iimura³¹ and Kumar³² showed that partial films grown from n -alkyltrichlorosilanes on hydrated substrates exhibit large fractal-like domains, whereas films prepared on drier substrates present smaller domains with little branching. On hydrated substrates, secondary nuclei that are much smaller than the primary fractal-shaped domains are seen as well. These studies confirmed that the film growth is strongly accelerated on hydrated substrates. Similar results and conclusions were reported by Hoffmann et al., who investigated the effect of water in the incubation solution on the growth of films on silicon from OTS.^{20,21} Their AFM studies showed that the partial monolayer prepared at high concentrations of water consists of patches of large organosiloxane islands with jagged edges and smaller round nuclei. At low concentrations of water in the solution, the islands are smaller and longer immersion times are required to reach a surface coverage comparable to that seen for samples prepared in the presence of higher water concentrations.²⁰ The enhanced organizational ordering and surface coverage seen in the films prepared at higher water concentrations were suggested to result from the surface binding of OTS molecules that had hydrolyzed and partially condensed in the solution prior to adsorption.^{20,21}

The effect of deposition temperature on the growth and morphology of organosiloxane films prepared by immersion also has been studied.^{22–24,31,35–37} Brzoska et al.,^{22,36}

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for example, used contact angle measurements to determine an apparent critical temperature, T_c , for films prepared from *n*-alkyltrichlorosilanes ($\text{CH}_3(\text{CH}_2)_n\text{SiCl}_3$, where $n = 9, 11, 15, 17$, or 21) on Si/SiO_2 ; similarly, Parikh et al.²³ used ellipsometry, contact angle measurements, and IR data to determine T_c and the corresponding film structure for SAMs prepared from OTS. In both cases, the studies suggested that high-coverage, well-ordered monolayers could be formed only when the sample preparation is carried out below this critical temperature and that T_c increases with increasing chain length. There remains some disagreement as to the value of T_c for specific adsorbates (e.g., $\sim 28^\circ\text{C}$ for OTS^{22,23} vs 10°C reported by others³¹). Above T_c , the SAMs form a more disordered monolayer, and the observed mass coverage and the rate of the film growth are generally found to decrease as well.

The above summarized observations have been rationalized in the context of a Langmuir adsorption model for the monolayer formation process.^{22–24} This model has been extended further to incorporate into the adsorption/assembly process complex dynamics involving 2D surface gas, liquid, and solid phases.⁴ Microscopy studies show that, below T_c , the adsorbing *n*-alkyltrichlorosilane molecules initially form a dilute gaslike surface phase, which eventually transforms as the coverage increases into a denser solid phase; the structure present at intermediate coverages is one involving coexistence of gas and solid phases. Above T_c , the film formation process is similar except that it involves a coexistence of liquid and solid phases at the highest adsorbate coverages. We should note here that the true mechanism must be somewhat more complex than this simple thermochemical-kinetic model suggests. The adsorption/assembly process is not fully reversible owing to the hydrolysis of the organotrichlorosilane molecules and subsequent covalent cross-linking of the resulting organosilanol, a process that is accelerated at high temperatures and precludes the annealing of defects in adsorbed sheets of organosiloxanes.²³

As noted above, the structural consequences of assembling SAMs from solutions of OTS below T_c have been confirmed by *ex situ* AFM studies: the growing monolayer consists of high-coverage fractal islands surrounded by a low-coverage (gaslike) adsorbate phase.^{24,37} As the reaction temperature increases (but still held at a point below T_c), the island size decreases. Films prepared well above T_c appear smooth, a result suggesting that the adsorbates are present in a liquidlike phase. This behavior appears to be general: the growths of monolayers from OTS on either mica³⁵ or Si wafers,³² and of *n*-alkyltrichlorosilanes ($n = 16, 18$, or 22) on glass,³¹ all show similar trends. Interestingly, Sung et al. have shown that the microstructure of partial films grown from OTS can be altered by means of thermal annealing in the presence of a solvent.²⁵ They observed a quasi-reversible transition between a crystalline-like island phase ($T < T_c$) and a homogeneous (liquid) phase ($T > T_c$) without a significant loss of OTS via desorption into the solvent.

As noted above, many of the mechanistic aspects of the formation of organosiloxane SAMs by contact printing remain poorly understood. It is unclear whether the film growth process is one analogous to that responsible for film grown by immersion of a substrate into an adsorbate-containing solution. This study, which is intended to address this issue, was motivated by our desire to define experimental conditions for μCP that yield SAM resists on Si for applications in thin-film microfabrication. As a part of this effort, we studied the dependence of the film morphology on the concentration of water (humidity) present in the printing environment, the deposition

temperature, the concentration and molecular identity of the organotrichlorosilane ink, and the contact time. We chose two molecules for this study, OTS and 7-octenyltrichlorosilane (OCT), adsorbates that are useful in microfabrication as resists and reactive templates and that exhibit very different values of T_c in solution-based assembly. The results of this investigation present an interesting and somewhat unexpected picture of the mass-transfer processes that underlie contact printing using PDMS stamps and amphiphilic organotrichlorosilane inks.

Experimental Section

Octadecyltrichlorosilane (Aldrich) and 7-octenyltrichlorosilane (Gelest) were vacuum distilled and stored under nitrogen. Toluene (anhydrous grade) was obtained from Fisher and used as received. Toluene solutions (5–100 mM) of OTS and OCT were prepared in a glovebox immediately before use. B-doped, p-type Si(100) wafers (Silicon Sense, test grade, $1\text{--}25\ \Omega\ \text{cm}$) were cut into $\sim 1 \times 1\ \text{cm}^2$ pieces for film deposition studies. The wafers were cleaned in piranha solution (3:1 $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$) for 2 min, rinsed with deionized water, and dried in a stream of nitrogen. The wafers were then placed in a UV/ozone chamber for at least 15 min, rinsed with deionized water, and dried with nitrogen before use.

Contact printing was performed using a featureless poly(dimethylsiloxane) (PDMS) stamp coated with either OTS or OCT solutions. The stamps were loaded by dripping ink solutions from a pipet onto the stamp (the surface of the stamp was flooded with a volume of ink sufficient to completely wet it with a bulk liquid layer), which was mounted on a spinner. The stamp was spun at 3000 rpm for 30 s. For the OTS ink solutions, small particulates were found to form on the inside of the glass pipet used to deliver the solution onto the stamp. To minimize their transfer, the pipet was rinsed with toluene, dried in a stream of dry air, and flushed once with the OTS solution before inking the stamp. The stamp was dried for 30 s in a nitrogen stream and was manually placed in contact with a clean silicon substrate. The substrate was held at a constant temperature using a temperature-controlled platform.⁶ The printed wafers were rinsed with hexane, 2-propanol, and deionized water and finally dried in a stream of dry nitrogen.

Films were also deposited by immersion. Clean wafers were placed in toluene solutions of the appropriate alkyltrichlorosilane in a nitrogen-filled glovebox. The treated samples were rinsed successively with toluene and 2-propanol and then dried in a stream of nitrogen. After removal from the glovebox, the samples were rinsed again with 2-propanol and deionized water and dried in a nitrogen stream.

The relative humidity and temperature of the room and glovebox were monitored by means of a thermohygrometer (Fisher). The dew point was lower than the reaction temperature for all experiments. Ellipsometry measurements were performed on a Gaertner Scientific ellipsometer (model L116C) equipped with a He–Ne laser (632.8 nm) set at an angle of incidence of 70° . Before films were deposited, the substrate constants were calculated from replicate ellipsometric measurements made at 5–10 different locations. Ellipsometric measurements of the deposited film were determined similarly, and the mass coverage was calculated by assuming that the refractive index of the film was 1.5. AFM images were collected using a Digital Instruments Dimension 3100 scanning probe microscope. Images were recorded in the tapping mode with a silicon probe or with a silicon nitride probe in the contact mode, in both cases by applying the minimum force required to maintain feedback.

Results

Formation of SAMs from 7-Octenyltrichlorosilane (OCT) by Contact-Printing. Effect of Ink Concentration on Film Growth Kinetics. The deposition of films derived from OCT by contact printing was monitored by ellipsometry to determine the average thickness of the deposited layer over a range of stamp contact times (Figure 1a). The OCT concentration of the toluene solutions used to load the stamp was varied between 5 and 100 mM, and

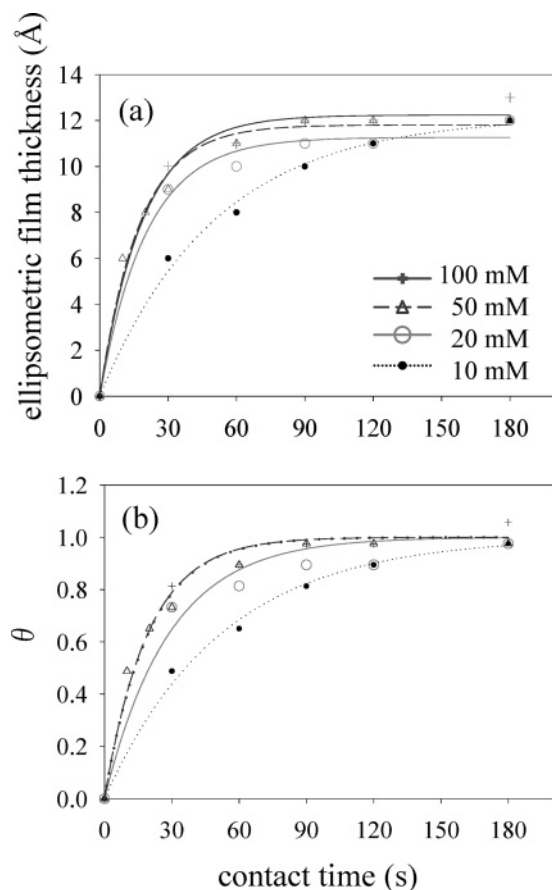


Figure 1. Ellipsometric thickness, as a function of printing time and ink concentration, of films deposited on Si(100) from toluene solutions of OCT by contact printing. The dew point was ~ 8 – 11 °C (“standard-humidity”) and the temperature was ~ 23 – 26 °C. The estimated standard deviations for the thickness measurements were ~ 1.5 Å. The curves show the fits of the data to eq 1; the derived values of the desorption rate constant k_{obs} were 0.02, 0.03, 0.05, and 0.05 s^{-1} at ink concentrations of 10, 20, 50, and 100 mM, respectively.

the printing times were varied between 10 and 180 s. The dew point of the ambient laboratory air was typically 8–10 °C and the temperature was 23–26 °C during a contact printing experiment.

For all ink concentrations studied (5–100 mM), the average thickness increased with the stamp–substrate contact time but reached a limiting value (for samples not grossly contaminated by aggregate multilayers, see below) of ~ 12.3 Å that corresponds closely to an OCT chain at full extension.¹⁴ For these films, we define a fraction of the surface covered with the organosilicon molecules (θ) is equal to the ellipsometrically determined thickness (d) divided by the thickness of a full monolayer, d_{m} .²⁷ Using this formalism, the time-dependent data show that the kinetics of the film formation can be described by a simple Langmuir model involving irreversible adsorption^{27,38} of the OCT. This rate law is given as

$$d = d_{\text{m}}\theta = d_{\text{m}}(1 - e^{-k_{\text{obs}}t}) \quad (1)$$

where k_{obs} is the observed deposition rate constant and t is the printing time.

The fits shown in Figure 1b were calculated using eq 1. The observed deposition rate constants, k_{obs} , derived from the fits were 0.02, 0.03, 0.05, and 0.05 s^{-1} at ink concentrations of 10, 20, 50, and 100 mM, respectively. The trends seen in the dependence of k_{obs} on the concen-

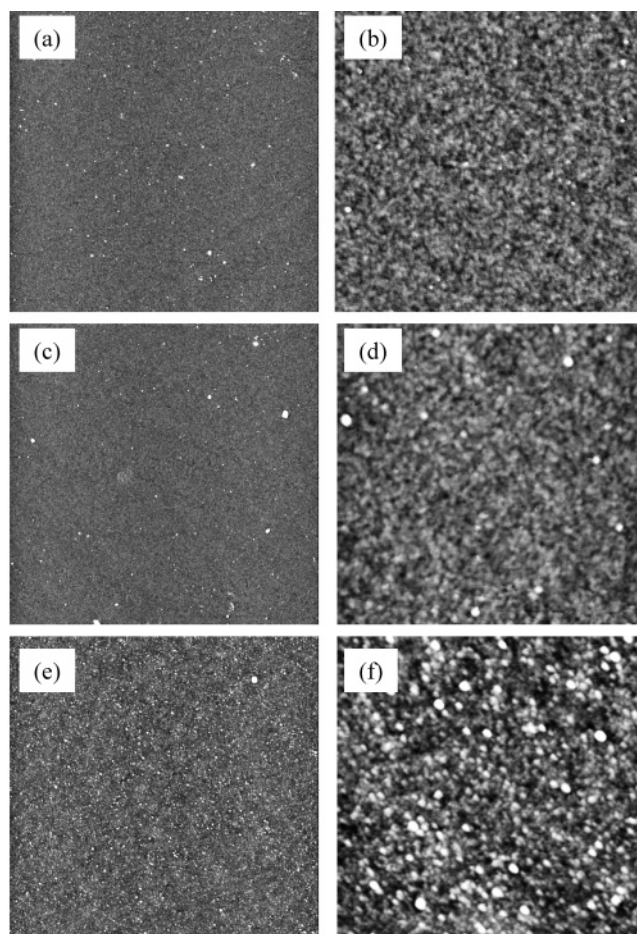


Figure 2. AFM images of films prepared by contact printing from a 5 mM OCT solution under the same conditions as for Figure 1. Printing times were 30 s for (a) and (b), 60 s for (c) and (d), and 120 s for (e) and (f). The images are $5 \times 5 \mu\text{m}$ scans (left) and $1 \times 1 \mu\text{m}$ scans (right). The vertical height is shown in gray scale from 0 (black) to 40 Å (white).

tration of OCT suggest that the higher concentration inks are more effective in saturating the stamp surface (or a near-surface boundary layer) with silane molecules, thus increasing the throwing power of the stamp.

Although the deposition rates increased with increasing ink concentration, the relationship found was not linear. Apparent fundamental rate constants, k , calculated by dividing k_{obs} by the silane concentration of the ink, were on the order of $1 \text{ M}^{-1} \text{ s}^{-1}$ but varied by a factor of 4 over the ink concentration range studied. This variance suggests that the inking procedure, and possibly the mass-transfer processes that underlie the printing process itself, influence the kinetics of the layer formation in a complex way. We return to this point later.

Effect of Ink Concentration on Film Morphology.

The structural evolution occurring during the growth of the OCT film was examined by AFM. Representative micrographs of the samples corresponding to the data presented in Figure 1 are shown in Figures 2–4.

AFM images of films prepared from a relatively low concentration OCT ink (5 mM) by stamping for 30 s showed a granular, low-amplitude background of height variations (ones differing markedly from the long period, ~ 2 Å roughness of the silicon substrate) and a low density of brighter (i.e., taller) round islands about 30 nm in diameter and 20–40 Å in height (parts a and b of Figure 2); the average thickness of this film (determined ellipsometrically) was ~ 4 Å. For a sample printed with a contact time

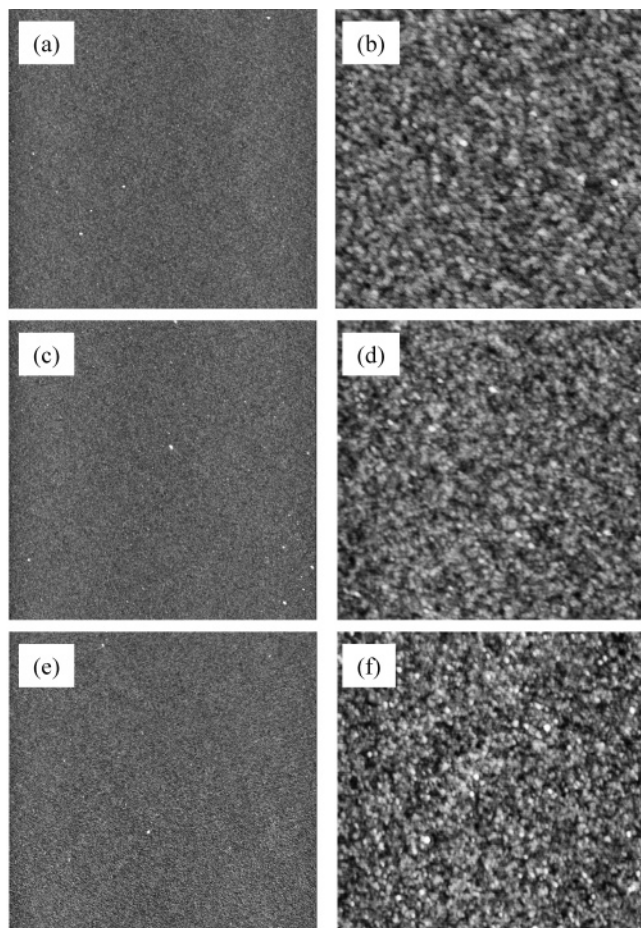


Figure 3. AFM images of films prepared by contact printing a 50 mM OCT solution under the same conditions as for Figure 1. Printing times were 30 s for (a) and (b), 60 s for (c) and (d), and 120 s for (e) and (f). The images are $5 \times 5 \mu\text{m}$ scans (left) and $1 \times 1 \mu\text{m}$ scans (right). The vertical height is shown in gray scale from 0 (black) to 40 Å (white).

of 60 s, the granular texture noted was somewhat coarser (parts c and d of Figure 2). After 120 s, the round islands were relatively common structural features (parts e and f of Figure 2). The round islands formed at this low ink concentration could not be removed either by extensive washing with solvents or by sonication.

The granular texture of the background of these samples is characteristic of a submonolayer coverage of OCT; we believe these round islands are most likely siloxane oligomers or polymers formed by hydrolysis of the ink (see below). That hydrolysis of OCT occurs is supported further by the observation that PDMS stamps exposed to high-concentration inks become cloudy over time.

Perhaps the most striking growth trend observed in our study was that the number of the strongly bound polysiloxane islands per unit area *decreased* with an increasing ink concentration. The samples prepared from a 50 mM ink, for example, had the characteristic granular texture of a growing OCT monolayer but were largely free of polysiloxane islands (Figure 3). For contact times between 30 and 120 s, as the film increases in thickness toward a limiting monolayer coverage of OCT, the AFM images indicated that the surface was remarkably smooth. The corrugation measured was only of the order of 10 Å, a value consistent with the organization of OCT into 2D domains. The AFM images suggested that some parts of the substrate remain incompletely covered by OCT, even for a 120 s contact time, although the ellipsometry data suggested that no significant film growth occurs after this

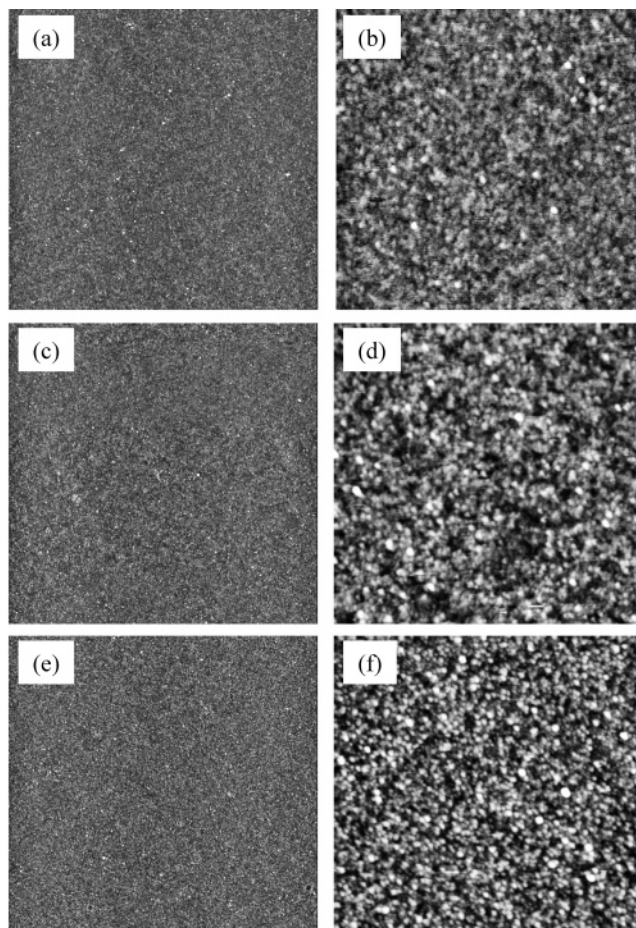


Figure 4. AFM images of films prepared by contact printing a 100 mM OCT solution under the same conditions as for Figure 1. Printing times were 30 s for (a) and (b), 60 s for (c) and (d), and 120 s for (e) and (f). The images are $5 \times 5 \mu\text{m}$ scans (left) and $1 \times 1 \mu\text{m}$ scans (right). The vertical height is shown in gray scale from 0 (black) to 40 Å (white).

point. After a contact time of 120 s, some polysiloxane islands were present, but they were both fewer in number and smaller in diameter ($\sim 20 \text{ nm}$) compared to those found for the 5 mM ink concentration.

The above-noted protective qualities of the 50 mM OCT ink appear to break down at higher ink concentrations, for which polysiloxane islands again became common features on the printed surfaces. For example, although the ellipsometrically determined thicknesses of samples printed using a 100 mM solution of OCT closely resembled those obtained using a 50 mM ink, the AFM images revealed the presence of a greater number of polysiloxane islands (Figure 4). The islands were about the same size as those seen on other samples (e.g., Figures 2 and 3).

This finding suggests that at specific concentrations the inks either passivate the sample toward the irreversible deposition of the polysiloxanes formed by the hydrolysis of the OCT or promote the formation of a SAM quickly enough to preclude the binding of polysiloxanes during the printing step. This point is discussed in greater detail below.

Effect of Humidity on Film Morphology. The AFM data reported above, which were obtained at an ambient dew point of 8–10 °C, suggested that the best SAMs were obtained when the PDMS stamp was inked with a 50 mM solution of OCT. It is instructive to compare those films to ones prepared at lower humidity using the same ink concentration. The ellipsometry data and the correspond-

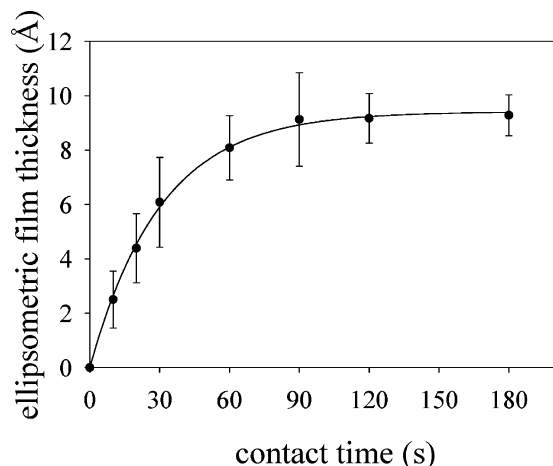


Figure 5. Ellipsometric thickness, as a function of printing time, of films deposited on Si(100) from a 50 mM toluene solution of OCT by contact printing. The dew point was $\sim 1\text{--}3\text{ }^{\circ}\text{C}$ ("low humidity") and the temperature was $\sim 22\text{--}24\text{ }^{\circ}\text{C}$. The curve shows the fit of the data to eq 1; the derived values of the limiting film thickness and desorption rate constant were $9.4\text{ }\text{\AA}$ and 0.03 s^{-1} , respectively.

ing fit based on eq 1 for such films are shown in Figure 5. For these samples, the dew point was held at $\sim 1\text{--}3\text{ }^{\circ}\text{C}$ and the ambient temperature was $\sim 22\text{--}24\text{ }^{\circ}\text{C}$ during the printing process. The film growth was markedly impacted, and the printed SAMs never reached the expected maximum thickness of $12.3\text{ }\text{\AA}$ for the contact times investigated here (Figure 5). Fitting the time dependence of the average thickness afforded values of $9.4\text{ }\text{\AA}$ for the maximum limiting thickness and 0.03 s^{-1} for the observed deposition rate constant, k_{obs} . The latter value is smaller than that of 0.05 s^{-1} obtained for the same concentration OCT ink printed under higher humidity conditions.

AFM images of the films printed at lower ambient humidity appeared similar to those shown in Figure 3 (data not shown). As before, contact printing led to a granular surface consisting of monolayer domains of the organosiloxane SAM. The films were relatively smooth, presenting a low density of polysiloxane islands (which were observed only in those samples subjected to longer contact times). In the early to intermediate stages of the deposition process (i.e., when the average thickness of the film is $\sim 6\text{ }\text{\AA}$), the SAM consisted of high-coverage (solidlike) domains surrounded by low-coverage areas, but the domain boundaries were not well-defined. The high-coverage domains packed more densely as the mass coverage increased at longer stamp contact times.

Growth Rate and Morphology of SAMs Formed by Immersion. For purposes of comparison, organosiloxane films were prepared by immersion in a 50 mM solution of OCT in toluene at room temperature. These experiments were conducted in a dry nitrogen atmosphere, thus excluding atmospheric moisture from the reaction environment. The time-varying mass coverages of the films were determined by ellipsometry, and these data and the fit to eq 1 are shown in Figure 6. The ellipsometry data show some scatter in the measured thicknesses, and the fit to the Langmuir model therefore carries a notable degree of uncertainty. Interestingly, the films did not reach the expected full monolayer thickness of $\sim 12\text{ }\text{\AA}$; instead, the thickness approached a limiting value of $\sim 7\text{ }\text{\AA}$. The best estimate of the deposition rate constant k_{obs} of $7 \times 10^{-4}\text{ s}^{-1}$ is much smaller (by at least 1–2 orders of magnitude) than the value obtained for films prepared by contact printing.

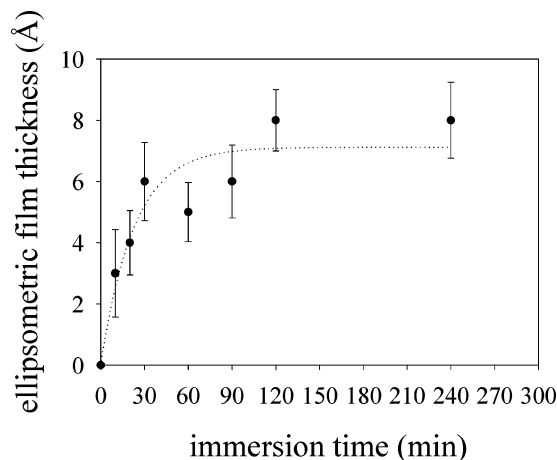


Figure 6. Ellipsometric thickness, as a function of immersion time, of films deposited on Si(100) by immersion in a 50 mM toluene solution of OCT. The dew point was $\sim 2\text{--}4\text{ }^{\circ}\text{C}$ and the temperature was $\sim 22\text{--}23\text{ }^{\circ}\text{C}$. The curve shows the fit of the data to eq 1; the derived values of the limiting film thickness and desorption rate constant were $7\text{ }\text{\AA}$ and $7 \times 10^{-4}\text{ s}^{-1}$, respectively.

Despite the slower deposition rate compared with contact printing, the structural outcomes were similar: AFM images of the films prepared by immersion showed a granular monolayer texture in conjunction with a small number of polysiloxane islands (data not shown).

Formation of Contact-Printed SAMs from Octadecyltrichlorosilane (OTS): Film Growth Kinetics. The formation of SAMs from the 8-carbon ink 7-octenyltrichlorosilane is of interest owing to the presence of the terminal C=C double bond, which serves as a reactive functional group for further chemistry. Because the 18-carbon molecule octadecyltrichlorosilane (OTS) is so widely used to prepare SAMs, we also investigated the growth kinetics and morphology of the films prepared by microcontact printing this ink.

Figure 7 shows the measured, time-varying thicknesses (and corresponding fits based on eq 1) for films prepared by contact printing at two different temperatures (25 and $45\text{ }^{\circ}\text{C}$) using a PDMS stamp inked with a 10 mM OTS solution. The dew points of the ambient atmosphere were $1\text{--}7\text{ }^{\circ}\text{C}$ for samples printed at $25\text{ }^{\circ}\text{C}$ and $4\text{--}5\text{ }^{\circ}\text{C}$ for those prepared at $45\text{ }^{\circ}\text{C}$. As expected, the films grew more rapidly at the higher printing temperature. The fits of the measured time-dependent thicknesses to eq 1 gave $26.2\text{ }\text{\AA}$ for the maximum film thickness (the correct value for OTS)¹⁴ and deposition rate constant k_{obs} of 0.009 and 0.016 s^{-1} at 25 and $45\text{ }^{\circ}\text{C}$, respectively. These deposition rate constants are within a factor of 2 to those measured for the contact printing of OCT under similar conditions.

Morphology of OTS Films Deposited by Contact Printing. AFM images of films prepared by contact printing using a 10 mM OTS ink solution at $25\text{ }^{\circ}\text{C}$ are shown in Figure 8 for stamp contact times varying between 30 and 180 s. (For these contact times, the ellipsometry data showed that the average thickness of the film increased from 5 to $21\text{ }\text{\AA}$.) The insets (Figure 8) show height profiles extracted from the indicated line scans (arrows). After a 30 s contact time, the film surface consisted of a relatively uniform low-coverage background layer on which was superposed a scattering of $\sim 9\text{ }\text{\AA}$ taller oval-shaped islands similar to those observed in the films prepared from OCT. After a 60 s contact (when the ellipsometrically determined thickness was $\sim 10\text{ }\text{\AA}$), small islands that were $\sim 14\text{ }\text{\AA}$ thick relative to the background were clearly visible in the AFM image. After a 90 s contact

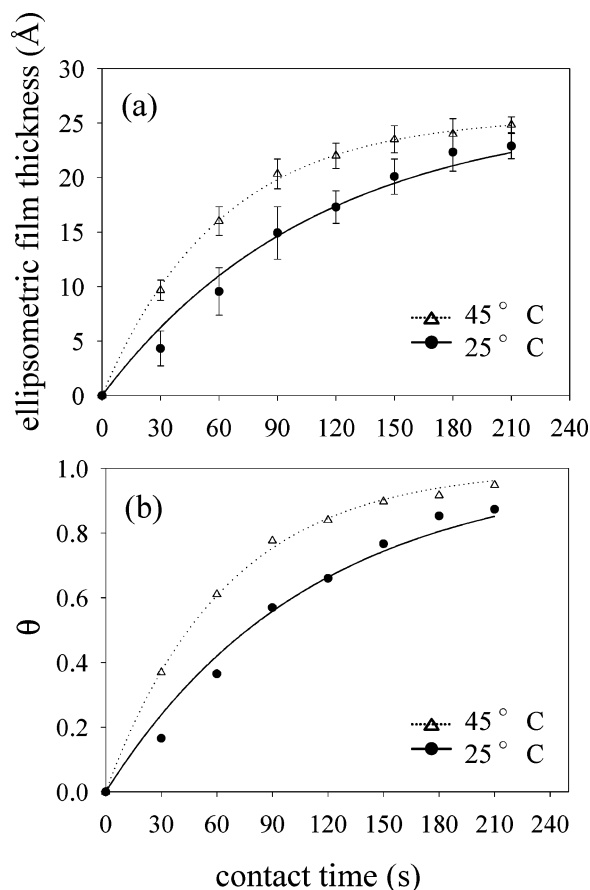


Figure 7. Ellipsometric thickness, as a function of printing time and temperature, for films deposited on Si(100) from a 10 mM toluene solution of OTS by contact printing. The printing temperature was at 25 °C (●) or 45 °C (Δ) and the dew point was ~ 1 –7 °C. The curves show the fit of the data to eq 1; the derived value of the limiting film thickness was 26.2 Å, and the desorption rate constants were $9 \times 10^{-3} \text{ s}^{-1}$ at 25 °C and $16 \times 10^{-3} \text{ s}^{-1}$ at 45 °C.

time, these taller islands were larger and more clearly defined (Figure 8c). The low-coverage background layer was ~ 10 Å thick relative to the substrate. After a 180 s contact time, the film was close to full coverage and a large fraction of the substrate was covered by the tall, high-coverage domains, although some low-coverage areas remained. The maximum height difference seen (~ 23 Å) corresponds well to the length of the OTS chain. Additional sample scans (data not shown) revealed that an increasing number of polymeric OTS domains were deposited for longer contact times and for this reason the studies were stopped at this point. We note that films printed using more concentrated OTS solutions also displayed a patchy high-coverage OTS domain structure, but further showed a greater number of cross-linked OTS polymer islands as well. These films also had a lower density of holes or gross low-coverage area defects when the film reached the limiting thickness.

Figure 9 shows AFM images of films printed at 45 °C using a 10 mM OTS ink. The film structure, which was very similar to that seen at 25 °C, consisted of low-coverage regions, high-coverage monolayer domains, and a number of strongly adherent polysiloxane islands. In early stages of the growth process, the film was relatively smooth: most of the features seen were less than 10 Å tall but a few are ~ 14 Å tall as judged by AFM. After a 60 s contact time, the 14 Å domains had become larger, but small round domains surrounding the larger patches were also observed. The various organosiloxane domains noted are

~ 15 Å taller than the low-contrast areas seen in the image. Some taller aggregates showed sharper branches (e.g., Figure 9b) similar to the fractal-shaped domains reported by others.^{20,21,31,32} The AFM image in Figure 9b, for example, was taken from a ~ 15 Å thick film, and its morphology correlates well with the one observed in the image presented in Figure 8c for a film of comparable mass coverage. The OTS islands seen in Figure 9b, however, appeared to be somewhat more distinct and larger than those seen in Figure 8c. At a 90 s contact time, when the average thickness of the film was ~ 20 Å, the fractal motif had become less distinct as more adsorbate molecules covered the substrate surface (Figure 9c). The height difference between the short and tall domains was ~ 9 Å at this point. By the time the average ellipsometrically determined thickness reached ~ 24 Å, the domains had coarsened and coalesced but defects and gaps clearly remained (Figure 9d).

The above studies were conducted with a 10 mM ink. Experiments conducted with more concentrated inks resulted in the formation of aggregates on the PDMS stamp before it could be brought into contact with the substrate, and less concentrated inks required long contact times to reach the same limiting thickness.

Discussion

Film Growth Rates and Limiting Coverages. Our studies suggest that the film growth rates, whether by μ CP or immersion (or from OCT or OTS), can be described reasonably well using the mechanistic assumptions embedded in Langmuir adsorption kinetics. The measured film growth rate constant by contact printing, k_{obs} , is about the same for OCT and OTS, provided that the ink concentration used to load the stamp, the relative humidity of the ambient atmosphere, and the temperature are similar.

We find that, for contact printing, k_{obs} is not linearly dependent on the concentration of the ink used to load the stamp. As a result, “fundamental rate constants” calculated by dividing k_{obs} by the concentration of ink are not in fact constant. The nonlinear dependence of k_{obs} on the concentration of the ink used to load the stamp most likely reflects the nonlinearities associated with the loading, washing, and drying of the stamp and with the diffusion of the ink into (and out of) a near-surface region of the stamp interior.

For OCT, our data confirm previous findings that the film growth rate increases with increasing amounts of water in the reaction environment, as can be seen from the following experiments, which were all conducted with 50 mM solutions of OCT. When film growth was conducted by contact printing in air with high relative humidity (dew points of 8–10 °C), the growth rate constant k_{obs} was $\sim 0.05 \text{ s}^{-1}$ and full monolayers ~ 12 Å thick were formed. In contrast, when films were prepared from OCT by contact printing under conditions of low relative humidity (dew points of 1–3 °C), the rate constant was slowed by about a factor of ~ 2 and the limiting thickness was only ~ 8 –9 Å. When films were grown by immersion under a dry inert atmosphere, the rate constant was nearly 2 orders of magnitude slower ($k_{\text{obs}} \sim 7 \times 10^{-4} \text{ s}^{-1}$) and the limiting thickness was only ~ 7 Å, even after long incubation times. The differences in rate constant and limiting film thickness confirm the hypothesis that insufficient water at the reaction interface leads to lower film growth rates and lower mass coverage.

The formation of incomplete monolayers under immersion conditions has been attributed by others to the critical

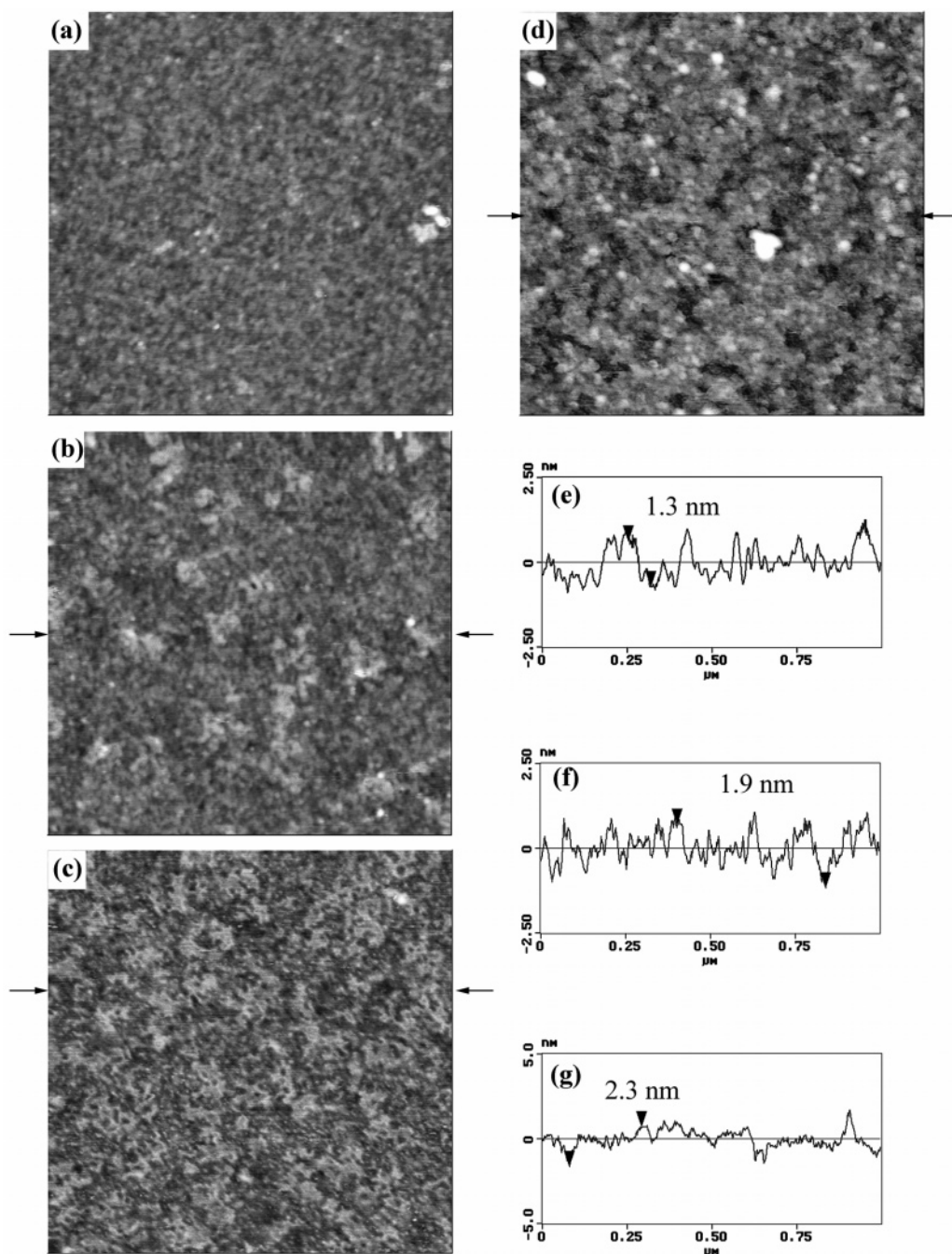


Figure 8. AFM images of films prepared by contact printing from 10 mM toluene solutions of OTS at 25 °C. For (a) the printing time was 30 s and the average film thickness was ~ 5 Å, for (b) 60 s and ~ 10 Å, for (c) 120 s and ~ 14 Å, for (d) 180 s and ~ 21 Å. All images are $1\ \mu\text{m} \times 1\ \mu\text{m}$ scans. Inset (e) shows the height profile taken between the arrows in (b); insets (f) and (g) show similar data for (c) and (d), respectively.

role that temperature plays in controlling the structure and packing density of organosiloxane SAMs.^{22–24} It has been suggested that the morphology of organosiloxane SAMs differs depending on whether growth occurs below or above a critical temperature, T_c , that is characteristic of the adsorbate. Below T_c , the assembly process proceeds to give densely packed SAMs with conformational states for the chains resembling those found in a crystal. Above T_c , the chains essentially “melt” and the resulting SAMs contain a significant fraction of conformational defects that limit the coverage of the adsorbate reached at equilibrium.

The films of OCT prepared by contact printing disagree with the predictions of the above studies. In air, with a

sufficiently high dew point, the SAMs prepared by microcontact printing from OCT at room temperature quickly reached the thickness expected for a full monolayer, despite being grown at a temperature that is well above its estimated value of T_c (which is probably as low as ~ 7 °C).²² We conclude that the temperature effect described above must not be the only factor that contributes to the coverage of the resulting film; also important must be the amount of water present in the reaction environment (as described above). Another factor that might promote the growth of full-monolayer films at temperatures above T_c is the flux of the adsorbate to the surface. For contact printing, the flux might be quite high if the transfer of species from the stamp to the substrate

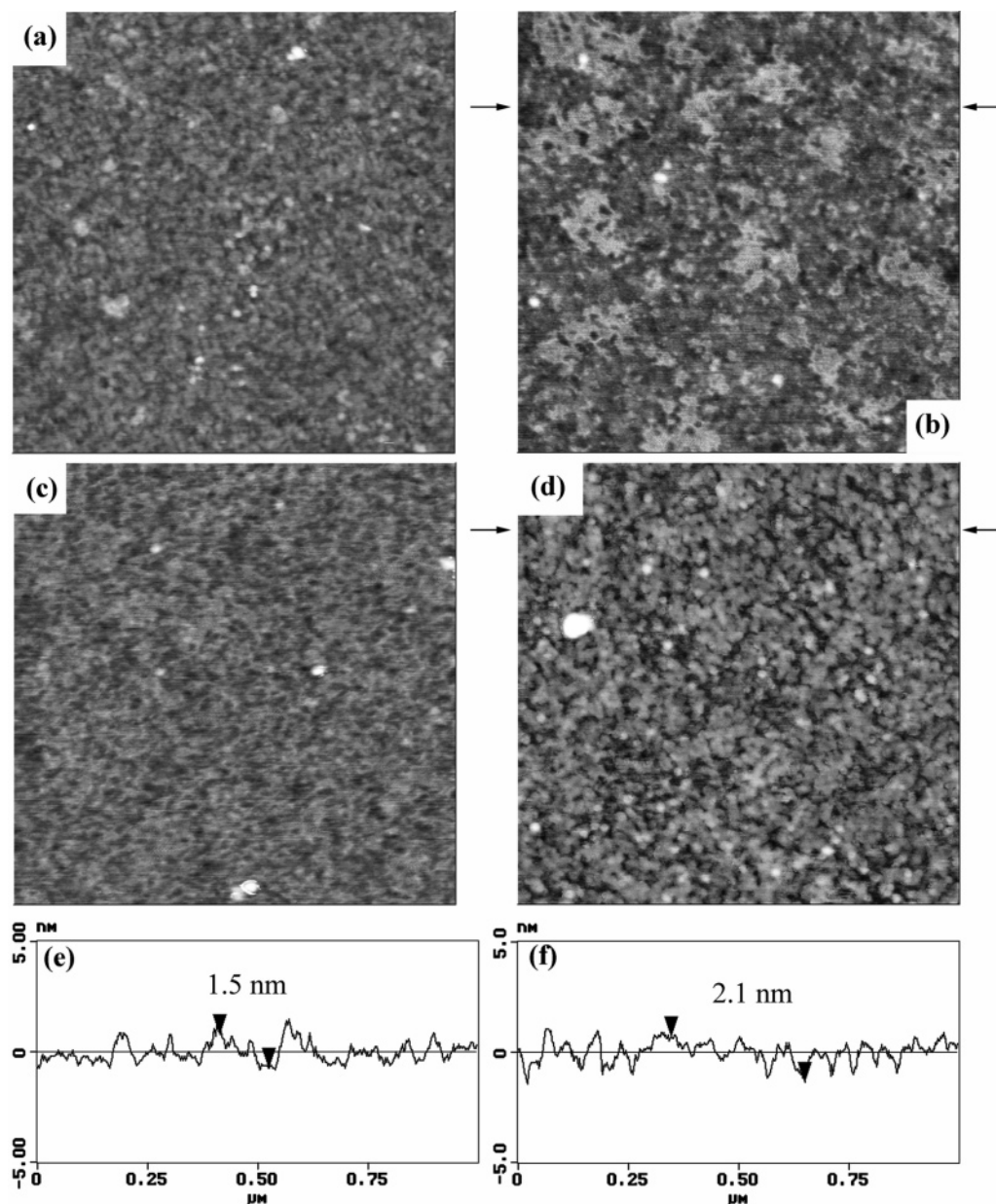


Figure 9. AFM images of films prepared by contact printing from 10 mM toluene solutions of OTS at 45 °C. For (a) the printing time was 30 s and the average film thickness was ~ 8 Å, for (b) 60 s and ~ 15 Å, for (c) 90 s and ~ 20 Å, for (d) 150 s and ~ 24 Å. All images are $1\ \mu\text{m} \times 1\ \mu\text{m}$ scans. Insets (e) and (f) shows height profile taken between the arrows in (b) and (d), respectively.

is not limited only to those molecules on the stamp surface but also involves to some degree those present below the surface of the stamp.

Thus, a high interfacial water content present in the reaction environment, and possibly a high effective flux of ink molecules, rapidly drives (via irreversible interfacial reactions) the adsorption isotherm toward a limiting high mass coverage (~ 12 Å), even at temperatures well above its apparent values of T_c .

Effects of Mass Transfer on the Mechanism of Film Formation by Contact Printing Alkyltrichlorosilanes. One of the more interesting observations made in the course of this study was that, for the case of the contact printing of OCT, the best films were obtained when the stamp was loaded with an intermediate 50 mM solution of OCT in toluene. Significantly lower concentrations (5 mM) and higher concentrations (100 mM) afforded films that exhibited large numbers of irreversibly adsorbed island defects. We believe the latter features are most likely aggregates of siloxane polymers formed by adventi-

tious hydrolysis of the ink while still on the stamp. Why, then, is the number of these polysiloxane islands minimized at an intermediate ink concentration?

We believe the diffusive transport of material from the stamp to the substrate must involve to a significant degree OCT molecules that are absorbed into a near surface boundary layer of the PDMS stamp. If so, then the film growth process involves two different mechanisms for the transfer of material from the stamp to the substrate: direct transfer of species present on the surface of the PDMS stamp, and diffusive transfer of species present within the near-surface boundary layer. The latter process, being dependent on the diffusion rate and solubility of the adsorbate in PDMS, should be exceptionally sensitive to molecular structure. The tendency of the system to form either a monolayer phase or a more complex structure involving adherent multilayer domains as well will then depend on the nature of the species present near the contact interface and their mass transfer rates.

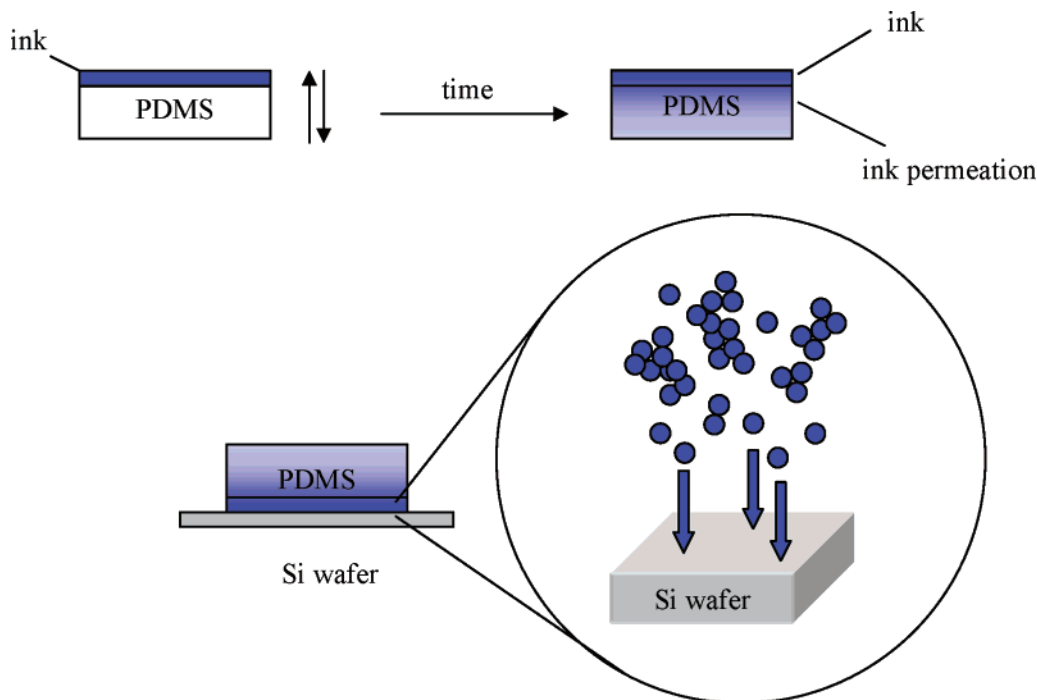


Figure 10. When a PDMS stamp is exposed to an ink solution, some of the ink molecules diffuse into the stamp, the depth of permeation depending on the time and the ink chain length. Thus, for equal times, a short-chain ink should penetrate some distance into the stamp whereas a long-chain ink should remain closer to the surface. Between the time the stamp is loaded with ink and subsequently used for printing, some of the ink molecules are hydrolyzed and some near the surface may evaporate (if the molecular weight is sufficiently low). When the stamp is brought into contact with the substrate, both high and low molecular weight species are transferred to the substrate surface. For OCT printing at sufficiently high ink concentrations, a diffusive phase transfer at the ink–substrate interface seems to dominate the ink transfer process. For OTS printing, there may be a competition between diffusive phase transfer of ink and direct transfer of polysiloxane species.

When a PDMS stamp is loaded with ink, the ink molecules permeate the stamp (as judged by its cloudy appearance when heavily inked and allowed to age in air). Between the time the stamp is loaded with ink and subsequently used for printing, some of the ink molecules near the surface may evaporate (if the molecular weight is sufficiently low) thus rendering the stamp surface relatively “ink-free”. More importantly, the action of water in the air will cause some of the ink molecules, both on the surface and in the interior, to hydrolyze and form polysiloxanes. When the stamp is brought into contact with the substrate, both intact ink molecules and mono/polysiloxanes can transfer to the surface, but at rates that will depend on how far they are from the stamp surface and how quickly they diffuse. The low molecular weight species (intact ink molecules) will certainly diffuse more quickly.

The data suggest that, when the OCT concentration in the ink is low, the stamp bears a high fraction of polymerized OCT with respect to low molecular weight OCT species, resulting in a higher probability of adherent polymeric deposits. When the stamp is loaded with OCT at sufficiently high ink concentrations to load the near-surface regions of the stamp, the ink transfer process will be dominated by the diffusion of molecules from the near-surface regions of the stamp to the substrate. Because the unhydrolyzed ink will diffuse more rapidly than the high-molecular-weight polysiloxanes, the resulting films will contain few polysiloxane islands.

We note that the upper concentration limit seen for optimal film quality is also easily rationalized by this qualitative model. A very high concentration of OCT should increase its near-surface concentration on the stamp and, as a result, the flux to the substrate–stamp interface. A large excess of OCT at this boundary should lead to further

deposition of OCT on top of the existing monolayer, resulting in the formation of polymeric multilayer structures. The monomer flux that passivates the surface at lower silane ink concentrations must ultimately be overcome by a competitive adsorption of cross-linked, high-molecular-weight materials as might aggregate at the stamp–contact interface.

The ink concentration has a very different effect on the contact printing of OTS. Increasing the concentration of OTS in the ink solution within ranges comparable to those explored for OCT did not improve the quality of the OTS films obtained. The mass transfer rate effects seen were always offset by concomitant increases in the quantity of polymeric structures being deposited at the higher OTS concentrations. At least two alternative explanations can be advanced to account for this observation: (1) the degree of unproductive OTS polymerization on the PDMS stamp increases with the OTS ink concentration; (2) the rate of mass transfer of monomeric OTS species is comparable to that of cross-linked OTS siloxanes formed on the stamp. The simplest interpretation we can offer is one that again considers the relative role played by the permeation of the adsorbate (here OTS) into the PDMS stamp. It is clear that the depth of permeation of an adsorbate ink will depend on the time allowed and, for these materials, on the ink chain length. The permeation of OTS into PDMS should be less pronounced than was the case for OCT. The back diffusion rate of absorbed monomers from the stamp should be lower as well. Both properties argue that a more important role in the assembly process has to be played by species lying very close to (or at) the contact interface. This model is shown schematically in Figure 10.

The most striking feature of the OTS data is revealed by the structural evolution seen in the AFM images

presented in Figures 8 and 9. The two temperatures used here (25 and 45 °C) should bracket the T_c value for OTS. This effect, if relevant to the mass transfer processes that contribute to contact printing, should lead to very different domain structures in the transferred films at all the imaged coverages lying along the growth profile. Surprisingly, however, the surface morphologies seen at both printing temperatures are very similar (the principal difference being the slightly faster growth rate at 45 °C). Both samples show features consistent with a growth process that involves the aggregation of molecules into high-coverage domains that ultimately coarsen and coalesce as the coverage increases. The fractal appearance of the aggregate structures seen (e.g., Figures 8c and 9b) suggest that, over at least some portion of the growth, the rate is transport limited.^{24,31,32,35,37} Although the overall morphology is one that closely resembles that seen for surfaces in which a liquid and a solid-phase coexist,^{24,31,32,35,37} the very similar sizes of the high-coverage domains and their positioning relative to one another is inconsistent with a T_c value between 25 and 45 °C.

One other additional peculiarity can also be gleaned from an examination of the quantitative fits to the film thickness vs time data shown in Figure 7. The striking feature to note here is that, at both 25 and 45 °C, the best fits yield a limiting thickness of 26.2 Å, one corresponding to a dense assembly of essentially all-trans conformer chains. This aspect of the data is very difficult to rationalize for a simple assembly process operating in one case above T_c and, in the other, below it. As noted above, such sensitivities have been documented in studies of solution-based depositions (although the exact value of T_c has not been established unambiguously, the temperatures used here should safely bracket it).^{22–24,31}

Several models can be envisioned that might explain the discrepancies noted above. The AFM images shown in Figures 8 and 9 could indicate that some form of organization of the OTS (either as aggregates or high coverage islands) occurs on the PDMS stamp—that is to say that the OTS segregates from the PDMS (and forms solidlike aggregates) upon the evaporation of the solvent used to cast the ink. The evolution of fractal-like domains, however, suggests that the latter process cannot be completely efficient and that some growth must involve diffusion to the surface and migration of OTS monomers.

The process conditions used in contact printing appear well suited to facilitate contributions from such phenomena to the growth mechanism, but further work will be required to resolve these questions.

Our data also show that contact printing OTS at higher temperatures accelerates the deposition process, a sensitivity expected for diffusive transport and reaction of small OTS-derived species. Unlike SAMs formed by immersion, which reach full coverage slowly and only if the immersion temperature is below T_c , contact printing results in the rapid formation of full coverage SAMs even when they are prepared at temperatures above T_c . Evidently, the high concentration of OTS at the stamp interface forces the adsorption process along these lines. The main effect of the higher temperatures, then, is to facilitate the coarsening of the OTS domains as the contact time increases.

We note that the significant humidity sensitivity seen for OCT is not as strongly manifested for OTS. Similar limiting mass coverages are reached (as past work has shown) even when printing is conducted under conditions of widely varying humidity. We are not completely sure how to interpret this latter distinction except to note that incompletely reacted OTS fragments might be less susceptible to loss via desorption (or rinsing) than would similar OCT species. Even if this were so, this difference remains a difficult one to rationalize mechanistically. Such uncertainty notwithstanding, the complex structural evolution and mass transfer properties seen here suggest a need for further research on printing processes involving less complicated ink chemistries. The SAMs formed by alkanethiols on Au and Ag substrates might be good candidates for such studies.⁴¹

Acknowledgment. This work was supported by the Department of Energy (DEFG02-91ER-45439) and the National Science Foundation (CHE 0097096). Surface analyses were carried out at the Center for Microanalysis of Materials, University of Illinois, which is supported by the Department of Energy under Contract DEFG02-91ER45439.

LA040038F

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