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Influence of Substrate Treatment on Self-Organized Pattern Formation by Langmuir–Blodgett Transfer

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Mesoscopic stripe patterns can be obtained by Langmuir–Blodgett (LB) transfer of L-α-dipalmitoylphosphatidylcholine (DPPC) onto solid substrates. In order to investigate the influence of substrates on the pattern formation, silicon slides treated by different cleaning processes were taken as model systems. A shift in the transfer pressure range for patterning was observed between plasma- and RCA-treated silicon. This can be explained with a model of equivalent states and taking into account the influence of microscale water films on the substrates.

Introduction

Micro- and nanoscale patterning of surfaces is of importance in a wide area of research fields and applications including biology, materials science, and medical science. There are two main strategies in surface patterning: the top-down approach such as electron-beam lithography and the bottom-up approach that utilizes self-assembly and self-organization of molecules or simple basic building blocks in order to achieve regular structures. The main advantage of most top-down strategies is the precise control over the structuring process. Very delicate structures such as those found in modern microprocessors are implemented by means of typical top-down strategies such as photolithography or UV lithography and electron-beam lithography. The disadvantage of most top-down strategies is that they are very elaborate and are usually time-consuming. Most bottom-up strategies that use self-assembly are much simpler and can often pattern over arbitrary sized areas during the process. Stripe patterning during Langmuir–Blodgett (LB) transfer was observed in the early 1990s,[1] and later our group proposed an easy way of patterning large mica surfaces with regular stripe patterns with submicrometer resolution.[2] Recently, also mixed component transfers yielding luminescent stripe patterns[3] or initiator patterns for polymer brushes[4] could be shown. Many other applications were demonstrated for this self-organized patterning process; for a full review, see ref 5. Many more fields of application such as chemical modification, etching, and imprinting were opened by switching to silicon substrates. It was observed that the periodicity of the stripe pattern was generally much smaller when silicon substrates were used. Also, due to the natural hydrophobicity of silicon, additional cleaning and pretreatment steps were necessary in order to prepare the silicon and render it hydrophilic. This motivated us to systematically investigate the influence of different surface chemistries on the pattern formation by preparations of the substrate with different cleaning treatments.

Experimental Methods

Materials. DPPC (L-α-dipalmitoylphosphatidylcholine, >99.9%) was purchased from Fluka and used without further

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purification. The chloroform used for the DPPC solution was HPLC grade. All chemicals used in the precleaning (chloroform, 2-propanol) of the substrate and in the RCA process (ammonium hydroxide, hydrogen peroxide) were of per analysi grade purity. Silicon (100) wafers with native oxide layer were sliced in 2×5 cm^2 pieces and used as substrate for the LB transfer. Additionally, mica substrates cut to 1.5×4 cm^2 were used in the heating experiments. MembraPure water with a resistance of 18.3 MΩ·cm was used in the cleaning process and as the subphase in the LB trough.

Substrate Preparation. Silicon substrates (2×5 cm^2) were sonicated consecutively in a bath of chloroform, 2-propanol, and pure water (15 min each). Two different treatments were applied after this precleaning procedure: either 2 min of O_2-plasma etching at 1 mbar and 300 W or 25 min in a mixture of ammonium hydroxide, hydrogen peroxide, and pure water (ratio 5:1:1) known as RCA-1. The RCA-treated samples were sonicated in pure water for an additional 10 min after treatment. Both types of substrate were stored under pure water after treatment and used within 1 h. The mica substrates used for the heating experiments were cleaved freshly and rinsed with purified water directly before transfer.

LB Transfer. The general procedure for the preparation of self-organized DPPC patterns is already described extensively elsewhere.[5] Briefly, the method used here included a commercial film balance (NIMA 312D) for the LB transfer and all experiments were conducted under clean-room conditions (class 10.000). The subphase thermostat was kept at 29 °C, yielding a temperature of about 26 °C at the air–water interface. The room temperature was kept at 22 °C, and the humidity was constant at about 37%. After the DPPC solution was spread onto the surface, the solvent was allowed to evaporate for 10 min. The resulting monolayer was then compressed up to a lateral pressure of 6.0 mN/m and allowed to rest for another 20 min. The trough barriers were kept fixed during the actual withdrawal of the substrate. Therefore, the lateral pressure dropped during the transfer, resulting in a pressure gradient from top to bottom on the substrate. The lateral pressure was recorded with respect to the dipper position to allow a reference of the position on the samples to a specific lateral pressure.

Self-Organized Pattern Formation by LB Transfer

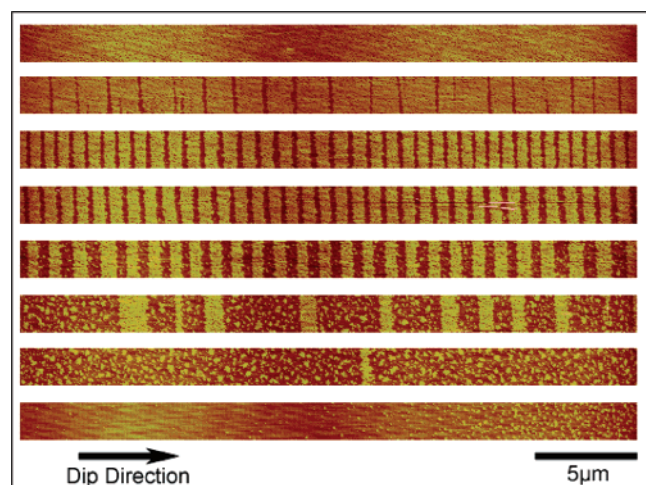*J. Phys. Chem. B, Vol. 112, No. 3, 2008* **825**

Figure 1. AFM micrographs of different areas on a silicon surface (plasma treated) after LB transfer with a transfer speed of 32 mm/min. The corresponding lateral pressures from top to bottom are 3.5, 3.0, 2.5, 2.3, 2.0, 1.5, 1.0, and 0.5 mN/m.
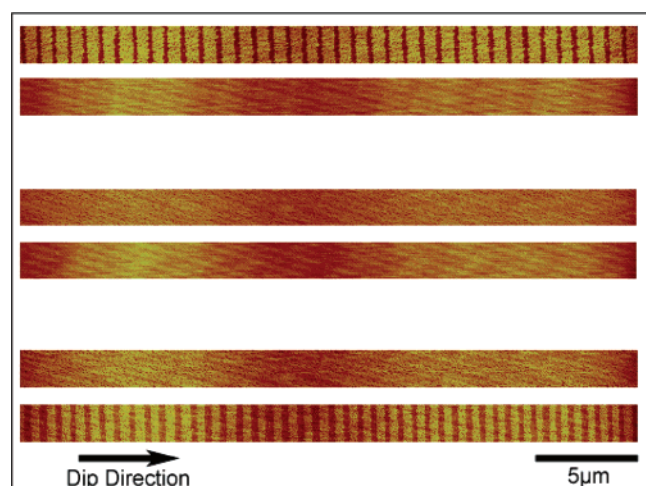

Figure 2. Direct comparison of transferred monolayers on plasma-treated (in each case upper image) and RCA-treated (in each case lower image) at the same transfer pressures. The transfer pressure was 2.5 mN/m for the upper images, 3.5 mN/m for the middle images, and 5.0 mN/m for the lower ones. Transfer speed was 32 mm/min for all images.

Measurements. Atomic force microscopic (AFM) images were obtained with a commercial instrument (Digital Instruments, Nanoscope IIIa, Dimension 3000, Santa Barbara, CA) operated in tapping mode. Si cantilevers (Nanosensors) with spring constants of 250−350 kHz were used.

The surface energies of the naked different treated substrates were determined by a modified sessile drop method as proposed by Schultz et al.[6,7] The static contact angles of droplets of pure water under a bulk phase of different alkenes (hexane, octane, decane, hexadecane) were measured with a commercial instrument (Contact Angle Measuring System G2, Krüss). The surface energy for cleaved mica was also determined in the same fashion for comparison and to confirm the validity of the current method.

Results

A typical result of our LB transfers can be seen in Figure 1. When the lateral pressure during transfer is higher (here 3.5 mN/m), a homogeneous monolayer of DPPC will be transferred onto the substrate (top). As the pressure drops, the monolayer will break up and channel-like structures will emerge, first parallel (not shown here) and then perpendicular to the withdraw direction (second micrograph from top). The channels parallel to the withdraw direction vanish with further decrease in lateral pressure, and the perpendicular channels become very regular (middle) before finally the pattern becomes irregular again and the condensation stops (lower two micrographs). This general behavior for different pressure ranges is observed on all samples and is in good agreement with previous work.[5]

In a direct comparison to the plasma-treated substrates, the whole pattern formation is shifted toward higher lateral pressures on the RCA-treated substrates. The upper pictures in Figure 2 show the samples at a lateral pressure of 2.5 mN/m. There is a regular stripe pattern formed on the plasma-treated substrate but no visible condensation at all on the RCA-treated substrate. In the middle images, the lateral pressure is 3.5 mN/m. Here the monolayer on the plasma-treated sample is almost compact already (except for some lines parallel to the withdraw direction), whereas the RCA-treated sample still shows no visible condensation. Finally, in the lower pictures ($p = 5.0$ mN/m), the stripe patterning on the RCA-treated substrate is very regular whereas the monolayer on the plasma-treated sample is absolutely compact. Table 1 summarizes the pressure ranges for stripe patterning on the different treated substrates and for different withdraw speeds. The transfer pressure at which the stripe patterning starts is for all withdraw speeds about 2.5 mN/m higher on the RCA-treated sample than on the plasma-treated substrate. Also, the transfer pressure at which the transition to a compact monolayer occurs is about 2.0−2.4 mN/m higher on the RCA-treated samples compared to the plasma-treated samples.

The amount of transferred material (indicated by the slope of the surface pressure vs dipper position graph, see Supporting Information) remains almost constant over the whole transfer, although it decreases somewhat at lower surface pressures. The average slope is a little bit higher on plasma-treated samples for all transfer speeds (Table 2), indicating a slightly higher DPPC transfer compared to RCA-treated samples. Note that there is still transfer of DPPC onto the substrate in areas where there is no DPPC film visible on the sample by AFM. This is explained by two different phases on the substrate (see Discussion).

When we consider the periodicity and the widths of stripes and channels with respect to the transfer pressure, there is also a common trend visible at all transfer speeds regardless of the substrate treatment. Figure 3 shows this behavior for a plasma-treated substrate and a transfer speed of 32 mm/min (a) and for the same transfer speed on a RCA-treated sample (b). The width of the stripes increases whereas the width of the channels decreases with increasing transfer pressure. This yields a minimum in the periodicity (about 800 nm for plasma-treated

TABLE 1: Transfer Pressure Ranges for Patterning on Different Treated Substrates and for Different Withdraw Speeds

transfer speed (mm/min)	16		32		64	
treatment	plasma	RCA	plasma	RCA	plasma	RCA
pressure (mN/m) at						
start of patterning	1.3	3.7	1.5	4.1	1.7	4.3
most regular pattern	2.0	4.2	2.3	5.0	2.5	5.2
transition to compact monolayer	2.7	4.7	3.3	5.7	3.7	5.9

TABLE 2: Average Slopes of Transfer Pressure vs Dipper Position Graphs at Different Transfer Speeds

transfer speed (mm/min)	plasma slope (N/m²)	RCA slope (N/m²)
16	0.144	0.128
32	0.111	0.107
64	0.133	0.119

TABLE 3: Surface Energies of the Different Substrates

	γ_S^D (mN/m)	γ_S^P (mN/m)	γ_S (mN/m)
mica	33.3 ± 3.0	89.7 ± 0.8	123.0 ± 3.8
mica (Schultz et al.)[7]	30 ± 2.5	90	120 ± 2.5
silicon (plasma)	3.2 ± 1.5	85.1 ± 0.4	88.3 ± 1.9
silicon (RCA)	17.4 ± 2.5	88.1 ± 0.6	105.5 ± 3.1

samples and 750 nm for RCA-treated samples at this transfer speed). The most regular stripe pattern occurs for all transfer speeds and for both treatments always at the respective minimum in periodicity.

We determined the surface energies of the related substrates by contact angle measurement. The results are presented in Table 3. The surface energy of mica was determined to check the validity of our measurements and is in good agreement with the literature. Regardless of treatment, the silicon samples were shown to have lower surface energies than mica (especially the nonpolar part γ_S^D, which is 1/2 for RCA-treated samples and 1/10 for plasma-treated samples).

We proposed that microscale water films on the substrate surface may play a crucial role in influencing the pattern

formation. To test this notion, subsequent heating of mica substrates covered with DPPC patterns was conducted for 1 h at 80 °C in a dry (~0% relative humidity (RH)) or wet (~100% RH) environment. Typical results are shown in Figure 4.

The pattern survives heating in a dry environment, whereas the topographic pattern is destroyed by heating in a wet environment. Note that the effects seen here are not due to diffusion of the DPPC molecules under the wet conditions. In the case of mixed transfer dye patterns (where the DPPC molecules in the channels are labeled by fluorescent dye), the fluorescent pattern remains unaltered although the topographic pattern is destroyed (see Supporting Information). This indicates that the individual DPPC molecules remain in place during heating. The DPPC film appears to undergo a phase transition (from a liquid condensed phase to a liquid expanded phase) rather than diffuse.

Discussion

In order to understand the experimental findings, we utilize a model of equivalent states proposed by Peterson.[8] He and his co-workers separate the surface pressure into an interfacial term that describes the interaction between the monolayer and the substrate and an internal pressure term. Thus, the total surface pressure experienced by a monolayer will change during transfer onto substrates depending on the difference in monolayer−substrate interfacial energy. In our experiments all transfers are conducted at transfer pressures lower than the critical pressure for the DPPC monolayer to undergo the phase transition from a liquid expanded (LE) to liquid condensed (LC) phase.
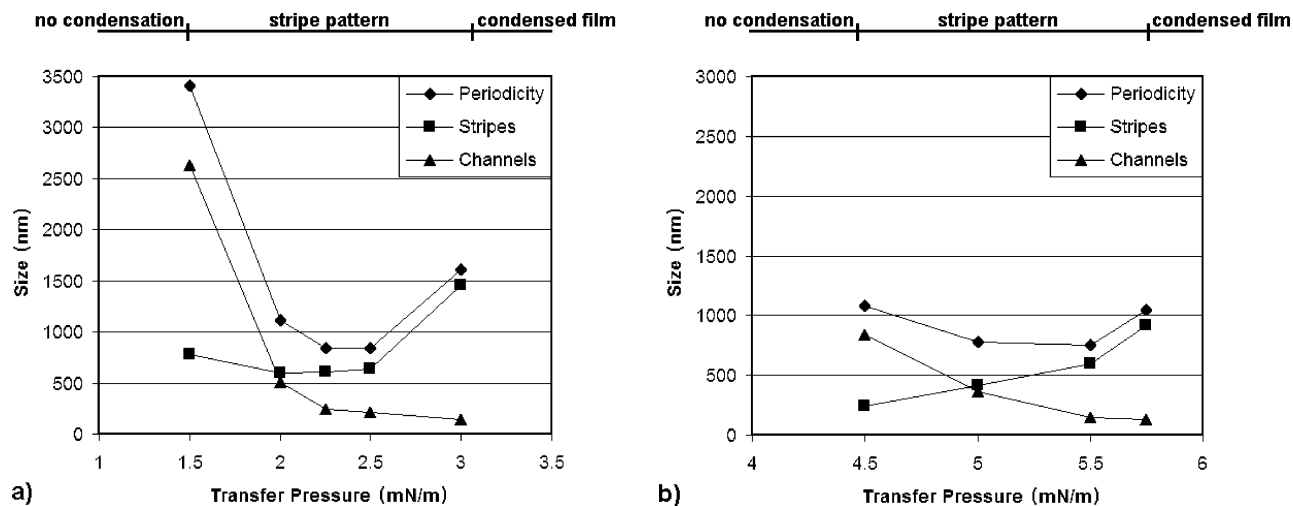

Figure 3. Periodicity, stripe width, and channel width at a transfer speed of 32 mm/min with respect to transfer pressure for (a) plasma-treated and (b) RCA-treated samples.
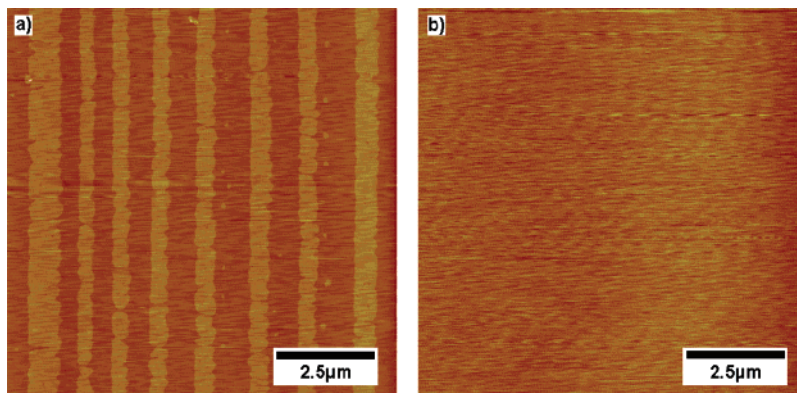

Figure 4. Patterned mica substrate after heating for 1 h at 80 °C in (a) dry environment and (b) wet environment.

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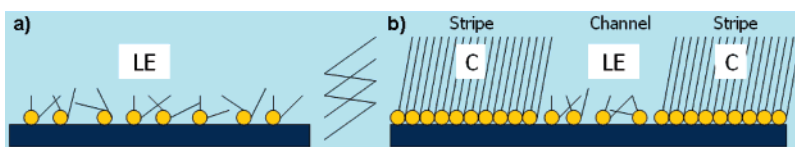*J. Phys. Chem. B, Vol. 112, No. 3, 2008* **827**

Figure 5. Scheme of DPPC Langmuir−Blodgett film on a substrate transferred (a) at very low pressure and (b) at a higher pressure suitable for stripe pattern formation.

Assuming a sufficiently higher interfacial mediated pressure between the monolayer and silicon compared to that between the monolayer and water, it follows that there is a condensed phase monolayer on the substrates at sufficiently high transfer pressures although the monolayer is in the LE phase on the water before transfer. At low transfer pressures the difference in the interfacial pressure is not sufficient to evoke the phase transition, so the LE phase is present on the silicon substrate after transfer. We assume that the LE phase is normally not visible with AFM under ambient conditions due to a lack of contrast. The recorded drop in surface pressure during transfer indicates ongoing transfer of DPPC even in areas of the sample where there is no AFM-observable DPPC layer and supports this notion. X-ray photoelectron spectroscopic (XPS) measurements showed an almost uniform average concentration on the whole sample. The pressure shift of ∼2.5 mN/m between the RCA- and plasma-treated silicon substrates indicates a higher interfacial mediated pressure on the plasma-treated silicon. The trend of increasing pressure p_c for phase transfer $p_{c,water} > p_{c,RCA} > p_{c,plasma}$ fits well to what one would expect from the chemistry. Since RCA-treated silicon exhibits more hydroxyl groups on the surface than plasma-treated silicon,[9] it should adsorb more ambient water vapor and interact more "water-like" with the DPPC film. This behavior could not be explained by examining only the respective surface energies alone. The explorative heating experiments shed light on the influence of thin water films in the micro- to nanometer range on the pattern formation process. They indicated that a water film is crucial for the potential of phase transition of the DPPC film. Another possible explanation for the differences between plasma- and RCA-treated substrates may relate to the amount of water adsorbed on the surface during LB transfer, although in all cases there is no water visible to the naked eye.

The results also have some interesting implications on the supposed mechanism for the stripe patterning. The stripes parallel to the transfer direction, which occur at high transfer pressures, can be explained by the Maragoni effect fingering instabilities and were successfully modeled.[10] For the stripe patterns perpendicular to the transfer direction it is unclear as to the cause, and the proposed stick−slip models need some ad hoc assumptions introduced to account for these patterns. The results presented here strongly suggest that the channels separating the stripes are not bare substrate but rather are filled with DPPC in the LE phase while the stripes are DPPC in the condensed phase (Figure 5b), while the areas transferred at lower transfer pressure than necessary for pattern formation are covered completely with the LE phase (Figure 5a). This conclusion has been supported recently by direct AFM observa-

tion of different height steps in stripe pattern defects.[11] This implies that models that employ pressure oscillations at the meniscus[12] may account for this behavior.

Conclusion

A systematic study of the influence of substrate treatment on DPPC stripe pattern formation was performed. The results obtained can be explained in terms of equivalent states. The data give some interesting insights into stripe pattern formation and strongly suggest an alternating LE/LC phase sequence as the pattern morphology. This should lead to more detailed consideration of meniscus pressure oscillation models for stripe pattern formation. Furthermore, this work motivates future experiments to investigate the experimental parameters surrounding stripe pattern formation on other substrates (e.g., gold or other metal films or polymers), because in this study experimental parameters were shown to play a major role in pattern formation on different surfaces. Also, the role of the microscale or nanoscale water films was shown to influence pattern formation and should be taken into account by performing experiments with humidity-controlled transfers.

Supporting Information Available: Transfer pressure graphs; fluorescence microscopy images of heated mica samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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