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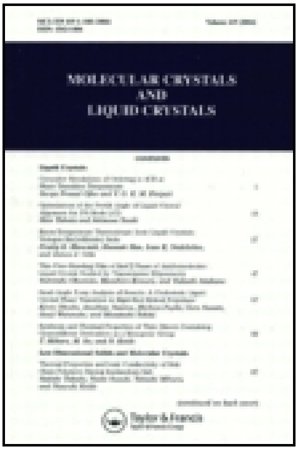

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Component Exchange in Phase-Separated LB Films of a Long-Chain Silane-Coupling Agent Mixed with Conventional Amphiphiles

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COMPONENT EXCHANGE IN PHASE-SEPARATED LB FILMS OF A LONG-CHAIN SILANE-COUPLING AGENT MIXED WITH CONVENTIONAL AMPHIPHILES

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Abstract The domains of amphiphiles such as arachidic acid or an azobenzene derivative in single-layer LB films mixed with a long-chain silane-coupling agent (F-Si) were selectively removed from Si wafers. The domain structures of the mixed LB films were restored by transferring the monolayers of the amphiphiles using the LB technique. The results indicate that the monolayers were transferred selectively on the hydrophilic Si-wafer surface and not on the F-Si film surface.

INTRODUCTION

Recently research has been carried out on the fabrication of mixed self-assembled monolayers using the LB technique or the adsorption method from solutions.[1-4] Amphiphilic thiols and silane-coupling agents have been spread at the air-water interface, and transferred onto appropriate solid substrates. The interesting point is that conventional amphiphiles are mixed to form domains in the monolayers and that the domains can be selectively removed, leaving specific structures on the substrates.[1,3] It has also been demonstrated that other thiols or silane-coupling agents adsorb from solutions onto the void parts of the transferred monolayers where the domains of the conventional amphiphiles used to reside.[1,3] In this paper, we report that the domains in phase-separated LB films can be exchanged using the LB technique.

EXPERIMENTAL

Materials

C20, C20-d39 (deuterated arachidic acid) and AZ were commercially available. The long-chain silane-coupling agent, F-Si, was synthesized as reported in a previous paper.[5]

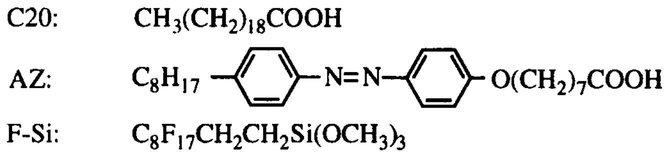

FIGURE 1 Chemical structures of the molecules used in this study.

Characterization

Monolayer measurements were done on a Lauda film balance at 290 K. Thermally oxidized Si wafers were used as substrates for the LB transfer at 25 mN m^{-1}. The Si wafers were ultrasonicated in methanol, kept in aqueous NH_4OH and H_2O_2 at 353 K for 10 min, and rinsed with water before use.

RESULTS AND DISCUSSION

Figure 2A shows the AFM image of a single-layer mixed LB film of F-Si and C20. A number of circular domains with almost constant height are seen, indicating the phase-separated structure of the mixed LB film. The domains are higher than the rest by ca. 1.4 nm, suggesting that the circular domains consist of C20 since C20 is longer than F-Si. This is consistent with the fact that the line tension of the domains of hydrocarbon is larger than that of fluorocarbon. Similar results have been reported in literature.[3]

Ultrasonication of the mixed LB film in methanol completely removed the circular domains while the region covered with F-Si seems intact as is seen in Figure 2B. The region where the circular domains used to reside is lower than the rest by ca. 0.6 nm. This shows that silanol groups on Si wafers are exposed in this region. The selective removal suggests that F-Si molecules are covalently bonded to Si wafers without heat treatment, resisting ultrasonication in methanol, while C20 molecules adsorbed physically on Si wafers are easily dissolved in methanol. The C20 molecules may play a role in this respect since pure LB films of F-Si were completely removed from Si wafers by ultrasonication in methanol. The resultant surface shows a specific feature that hydrophilic and hydrophobic regions coexist microscopically: the region where silanol groups are exposed is hydrophilic while the other part covered with F-Si is hydrophobic.

The microscopically hydrophilic / hydrophobic mixed surface presents a characteristic feature when the LB film of C20 is transferred on the surface. Figure 2C shows the AFM image of the surface after the transfer of a monolayer of C20. It is clearly seen that the circular domain structures are restored by this transfer, indicating that the monolayer of C20 is selectively transferred on the hydrophilic surface. The circular

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domains are higher than the rest by ca. 1.4 nm, coincident with the value for the as-deposited LB film. In other words, the monolayer of C20 probes the microscopic nature of the surface and adsorbs on the hydrophilic, though microscopically, part of the surface, failing to adsorb on the hydrophobic part. Essentially the same results were obtained using AFM when AZ is used instead of C20. This shows that the selective exchange of domain structures is not limited to C20 monolayers.

The IR measurements are consistent with the results of AFM. Figure 3 shows the transmission IR spectra of a single-layer LB film of F-Si and C20-d39 in the region of stretching vibrations of CD_2 (2195 cm^{-1}: CD_2 antisymmetric stretching, 2092 cm^{-1}: CD_2 symmetric stretching) after each treatment. The usage of C20-d39 is prerequisite since the stretching bands of CH_2 and CH_3 of C20 overlap with those of F-Si, making the precise analyses of the IR spectra difficult. These characteristic bands due to C20-d39 component disappeared by ultrasonication in methanol, which in turn indicates that the circular domains observed in the AFM images consist of C20. Furthermore these vibration bands due to C20-d39 were restored by the transfer of C20-d39 monolayer, indicating that the amount of C20-d39 transferred on the surface is almost the same with that of C20-d39 transferred as a mixed monolayer with F-Si in the initial transfer on Si wafers. This agrees well with the AFM observations that the domain structures were restored by the transfer of a C20 monolayer.

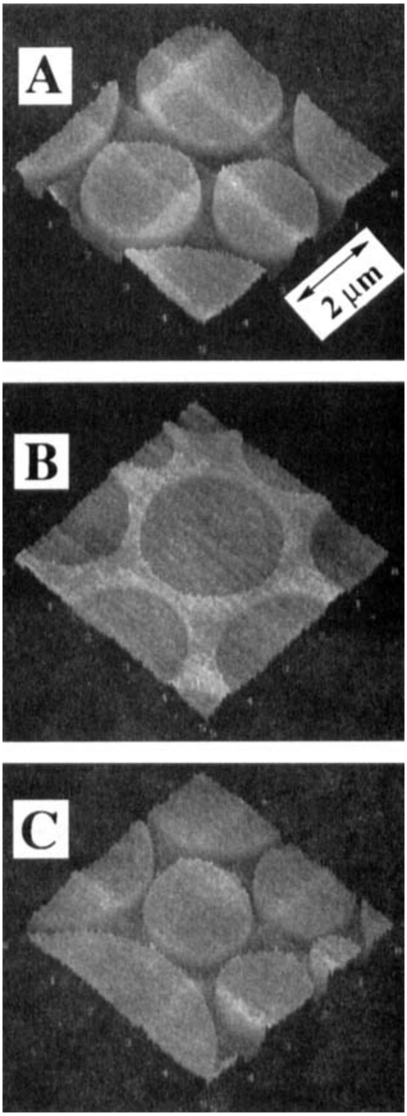

FIGURE 2 AFM images of a single-layer mixed LB film of F-Si and C20 (3 : 1) taken on a Seiko SPA 300 with an SPI probe station using dynamic force (noncontact) mode at 27 kHz. (A): as-deposited, (B): after ultrasonication in methanol, and (C): after the transfer of a monolayer of C20.

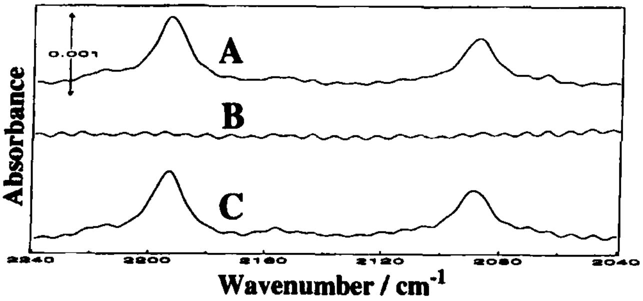

FIGURE 3 Transmission FT-IR spectra of a single-layer mixed LB film of F-Si and C20-d39 (3 : 1). (A): as-deposited, (B): after ultrasonication in methanol, and (C): after the transfer of a monolayer of C20.

CONCLUSIONS

This study indicates that the monolayer probes the surface of the substrate and is transferred selectively on the hydrophilic part of the surface. The technique presents a versatile method of exchanging selectively one of the components of the mixed LB films. Template LB films fabricated by appropriate combination of the components to control the domain size and shape can in principle be used, after the removal of the domains, to accommodate different molecules in the form of domains delineated by the F-Si monolayer even when the molecules introduced later, if fabricated from mixed spreading solutions, form domains with different size and shape or in an extreme case do not form domains.

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