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Ionic Liquids: Nondestructive, Nonvolatile Imaging Fluids for Submicrometer-Scale Monolayer Patterns

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Increasing attention is being paid to nano−micropatterning of organic molecular films, in particular, self-assembled monolayers (SAMs), which can spontaneously form on certain materials with ordered conformations; this suggests the future development of biomimetic chemical systems and molecular electronic devices.[1,2] To realize such advanced microdevices, preparation of structured SAMs with regulated placement of molecules in specific positions on substrate surfaces will be required. There have been multiple attempts to produce patterned SAMs by lithographic techniques using, for example, UV/vacuum UV (VUV) light,[3−5] scanning probe microscopy (SPM),[6,7] electron beams,[8,9] and focused ion beams.[10,11] The common strategy of these techniques is that a uniformly prepared SAM film on a substrate is partially removed. To demonstrate the usefulness of these patterning techniques, observation and evaluation of fabricated patterns in nano−micro regions have been important for assessing the performance of the microfabrication process.

Lateral force and Kelvin probe force microscopies (LFM/KFM) have been employed to evaluate patterned SAMs through differences in surface friction and surface potential between domains.[5,12] Disadvantages of these techniques include relatively low throughput and narrow observation area compared with optical or electron microscopy. Field-emission scanning electron microscopy (FE-SEM) has been applied to Langmuir−Blodgett films on silicon substrates without a conductive coating on the films.[13] It has been demonstrated that FE-SEM can map a distribution of monolayer packing states. Coplanar microstructures composed of two different types of organosilane SAMs have also been observed by FE-SEM.[14] Although FE-SEM is a powerful characterization tool,[13−17] damage to the monolayers during observation is a serious disadvantage in practical application.[17] Thus, an alternative imaging technique for nano−micropatterned monolayers over large areas that causes no damage and uses readily available equipment would be useful.

Ionic liquids (ILs) have been studied recently because of their advantages as solvents: low vapor pressure, wide use temperature ranges, thermal stability, nonflammability, ionic conductivity.[18−23] ILs are derived from organic cations and noncoordinating anions that together form salts with weak interactions; melting points are near or below room temperature. ILs have demonstrated utility in polymer synthesis, processing, and various applications.[20,23] We reported that ILs are useful probe fluids for contact angle analysis;[22] however, the interaction between ILs and solid surfaces, in particular, monolayer-covered surfaces terminated with various functional groups, has not been studied in detail. The imaging technique that we describe here is based on wetting differences of monolayer-covered (low surface energy) and uncovered (high surface energy) regions of photolithographically patterned silicon samples. The IL preferentially wets the high surface energy regions, and the low surface energy areas are dewetted of liquid. By taking advantage of differences in refractive indices and height between the IL-covered and uncovered regions, patterns of monolayers at submicrometer (500 nm) to micrometer scale can be imaged by optical/laser microscopy. The use of an IL as an imaging fluid is simple, effective, and practical for observation of patterned monolayers over large areas. It is an inexpensive alternative to FE-SEM and LFM/KFM; neither high vacuum nor expensive equipment is necessary.

Monolayers were prepared on UV/ozone-cleaned Si (10 × 10 × 0.5 mm^3) substrates by chemical vapor deposition methods. 1,3,5,7-Tetramethylcyclotetrasiloxane (Gelest, $C_4H_{16}O_4Si_4$, $D_4{}^H$) and bis((tridecafluoro-1,1,2,2,-tetrahydrooctyl)-dimethylsiloxy)methylsilane (Gelest, $CF_3(CF_2)_5CH_2CH_2Si(CH_3)_2O)_2SiCH_3H$, $F_{26}H$) were used without purification. Plasma-cleaned samples were placed, together with a small glass cup containing $D_4{}^H$ or $F_{26}H$, into a 60 cm^3 Teflon container in a dry N_2 atmosphere. The container was sealed with a Teflon cap and then heated for 72 h in an oven maintained at 80 °C ($D_4{}^H$) or 150 °C ($F_{26}H$). Isolated samples were rinsed with hexane and water and then blown dry with a N_2 stream. The hydrophilic Si^{SiO_2} surface (advancing (θ_A) and receding (θ_R) water contact angles of 0°/0°, respectively) became hydrophobic after either vapor phase treatment. In the case of $D_4{}^H$, θ_A/θ_R values for water, *n*-hexadecane, and IL[24] (Evonik, bis(hydroxyethyl)dimethylammonium methanesulfonate ($C_6H_{16}O_2N^+CH_3SO_3^-$) (BHDAMS), surface tension =66.4 dyn/cm) were 100°/98°, 30°/28°, and 96°/92°, respectively. For the $F_{26}H$ vapor phase chemical modification, contact angles were 110°/109°, 64°/62°, and 105°/102°, respectively. The resulting surfaces exhibit negligible contact angle hysteresis using each probe fluid. The thicknesses of the $D_4{}^H$- and $F_{26}H$-derived layers on the Si^{SiO_2} substrates were estimated by ellipsometry (Philips, PZ2000) to be 0.6 and 1.0 nm, respectively. We conclude that the adsorbed layers are monomeric. The derived monolayers are assumed to be covalently bound.[25]

The Si^{SiO_2} surfaces covered with $D_4{}^H$- and $F_{26}H$-derived monolayers were exposed to 172 nm VUV light generated from an excimer lamp (Ushio Inc., UER20-172 V; $\lambda = 172$ nm and 10 mW/cm^2) at 10^3 Pa for 1 min (no mask). Ellipsometry and X-ray photoelectron spectroscopy (XPS)[26] indicated that the film thickness decreased to ∼0.3 nm, which corresponds to a SiO_2 monolayer,[27] after 1 min of irradiation. In the case of the $F_{26}H$-monolayer-covered surface, fluorine and carbon concentrations (33.2 and 22.1 at.%, respectively, before irradiation) were absent, indicating that the monolayer was decomposed and eliminated from the surface. A time interval of 5 min (3 J/cm^2) was sufficient to decompose the $F_{26}H$-derived monolayers.

Samples were patterned using a photomask[28] contact method with irradiation conditions of 10^3 Pa, 5 min exposure (2.8 J/cm^2). BHDAMS was then spin-cast onto this patterned sample (1000 rpm

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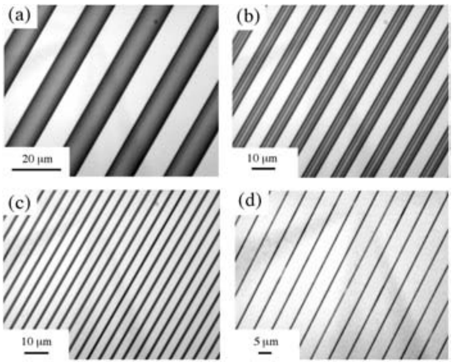

Figure 1. Optical microscopy images of the BHDAMS lines formed on patterned D_4^H-monolayer samples: (a) 10-µm width and separation, (b) 5-µm width and separation, (c) 1-µm-width line and 3-µm-width separation and (d) 500-nm-width line with 4-µm-width separation.

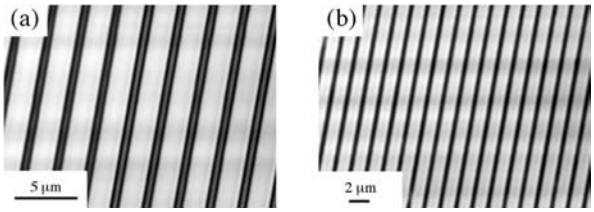

Figure 2. Laser microscopy images of BHDAMS lines formed on the patterned monolayer-covered samples: (a) 500-nm-width BHDAMS lines with 2-µm-width separation (D_4^H-derived monolayer-covered surface) and (b) 500-nm-width lines with 1-µm separation ($F_{26}H$-derived monolayer-covered surface).

for 2 s and 4000 rmp for 4 min). The wetting behavior of BHDAMS on both patterned D_4^H- and $F_{26}H$-monolayer-covered samples was observed by optical (Nikon, ECLIPSE ME600) and laser (Olympus, OLS3100) microscopy. Figure 1 shows typical optical micrographic images of photopatterned D_4^H-monolayer-covered samples after being spin-coated with BHDAMS. The dark and bright regions in these images correspond to photoirradiated (hydrophilic) and unirradiated (hydrophobic monolayer-covered) regions, respectively. IL was retained only on the high surface energy regions of the samples. The images shown in Figure 2 demonstrate evidence of submicrometer-scale (500 nm) imaging of patterned D_4^H- and $F_{26}H$-monolayer-covered samples by laser microscopy.

The nonvolatile liquid used in this study is water-soluble; it can be removed from the surface by simple rinsing with acetone, ethanol, and water. This allows multiple use of the patterned substrates without degradation of the monolayers. We have imaged IL patterns on samples after spin-coating/washing multiple times.

In summary, ILs are applicable for optical visualization of submicrometer-scale photopatterned monolayers. Because this imaging technique is based on nondestructive differential wetting by a nonvolatile ionic liquid, the patterns can be imaged and reused multiple times. This is an obvious advantage over destructive analyses for certain applications.

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