Application of Self-Assembled Monolayers to Micropatterning

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Ultrathin organic films of a few nm in thickness were applied as resist films for photolithography. These resist films were prepared on oxide-covered Si substrates from organosilane molecules. The films belong to a class of materials referred to as self-assembled monolayer (SAM). An organosilane SAM was micropatterned by irradiating through a photomask with a vacuum ultra-violet (VUV) light of 172 nm in wavelength, under the presence of atmospheric oxygen molecules. The VUV photodegradation mechanism was ascribed to dissociative excitation of C-C and other chemical bondings in the organosilane molecules and to subsequently proceeded oxidation with active oxygen species such as ozone and atomic oxygen generated simultaneously by the VUV-irradiation of atmospheric oxygen molecules. Consequently, the photomask image was transferred to the SAM. Micropatterns of 1 μm in width or finer were successfully transferred on the SAM.

Key words: organosilane self-assembled monolayer, micropatterning, vacuum ultra-violet light, excimer lamp, photolithography

1. Introduction

The Langmuir-Blodgett and molecular self-assembly techniques provide us crucial ways to prepare a variety of organic thin films of molecular-level thicknesses with well-ordered molecular arrangements [1]. Among various organized molecular thin films, monolayers constructed through chemisorption of organosilane molecules onto hydroxyl (OH)-terminated oxide surfaces [2] are of particular interest for practical applications, since such monolayers are markedly stable mechanically and chemically due to the strong immobilization through siloxane bondings and can be formed on oxide-covered silicon substrates which is an important material in microelectronics. Due to hydrophobic and van der Waals interactions between the alkyl chains of the organosilane molecules, the molecules are spontaneously organized into a thin layer of monomolecular thickness in which the molecules are closely packed each other [3,4]. Such a film belongs to a class of organic film known as self-assembled monolayer (SAM).

The self-assembling technique and the organosilane SAMs are expected to play key roles in future microdevices. Much attention is, thus, being denoted to the micropatterning of such SAMs [5-27] for construction of microstructures particularly in biological applications. The microcontact printing method [28], by which a micropatterned SAM is directly formed on a substrate using an elastomeric stamp, has been applied to organosilane SAMs as well [12,15]. However, conventional photolithography using photomasks [5,8,21,23-27] and other lithographic tools employing electron beams [9,11], ion beams [10], neutral atomic beams [16], or scanning probe microscopes [14,17-22] have been more frequently used in order to micropattern homogeneously prepared organosilane SAMs.

Among various patterning methods, photolithography is most practical, since it can transfer an entire pattern on a photomask to a SAM by a single exposure. Photopatterning of organosilane SAMs has been conducted so far using deep ultra-violet light near 200 nm or longer in wavelength based on the particular photochemistry of aromatic, mercapto and chloride organosilane SAMs [5,8,24]. In these cases, photopatterning of SAMs was based on photochemistries of particular chemical parts in the SAMs, that is, the aromatic rings, S-H and C-Cl groups. Although these approaches are successful, the photochemistries are not applicable to photopatterning of alkylsilane and, in particular, fluoroalkylsilane SAMs, in spite of the fact that theses SAMs are widely used for surface modification since more hydrophobic surfaces than those with the aromatic, mercapto and chloride SAMs are prepared. There have been a few reports on UV photopatterning of alkylsilane SAMs [26,27]. However, photochemical reaction rates for these processes were too slow, so that we have developed a promising alternative way by the use of vacuum ultra-violet (VUV) light whose wavelength is much shorter than 200 nm [21,23,25] in order to photopattern alkyl and fluoroalkyl SAMs. Here we report on the recent progress of our research on this VUV photopatterning of the SAMs.

2. Vapor phase growth of organosilane SAMs

Organosilane SAMs have been usually prepared at the liquid/solid interface by simply immersing a substrate in a solution of precursor molecules. Besides the

liquid phase process, the vapor phase process is also promising particularly because it has no need for the use of a large amount of solvents. Furthermore, the deposition of aggregated organosilane molecules, which frequently deteriorates the quality of the SAMs, is expected to be smaller in the vapor phase method than in the liquid phase method, since such aggregated molecules have lower vapor pressures and are rarely vaporized. Thus, the vapor phase method is considered to be practically convenient. Nevertheless, there have been only a small number of studies on the preparation of organosilane SAMs from the vapor phase [29-37].

In this study, SAMs were formed through a simple method described as follows [24,26,37]. Two types of precursors were employed, that is, n-octadecyl-trimethoxysilane [ODS: $H_3C(CH_2)_{17}Si(OCH_3)_3$] and fluoroalkylsilane (FAS), heptadecafluoro-1,1,2,2-tetrahydro-decyl-1-trimethoxysilane [$F_3C(CF_2)_7(CH_2)_2Si(OCH_3)_3$]. The chemical structures of these precursors and corresponding SAMs are shown in Fig. 1. A cleaned SiO_2/Si plate was placed together with a glass cup filled with organosilane liquid into a Teflon™ container. The container was sealed with a cap and placed in an oven maintained at 150 °C.

Vaporized organosilane molecules react with OH groups on a SiO_2/Si substrate, resulting in the formation of a SAM as illustrated in Fig. 1. Figures 2 and 3 follow the formation of ODS-SAM and FAS-SAM. When a SiO_2/Si substrate is treated, it becomes hydrophobic as shown in Fig. 2. The water contact angles of the ODS- and FAS-treated substrates increase with an increase in reaction time at the initial stage of CVD. However, they hardly increased even when the CVD process had been prolonged longer than 1 hour. The water contact angles of the ODS- and FAS-treated substrates reached 105 ~ 108° and 112 ~ 119°, respectively.

As clearly demonstrated in Fig. 3, the thicknesses of the films grown on the ODS and FAS-treated substrates increase and stop to increase similarly. A film of 2 nm in thickness was grown on the ODS-treated substrate at a reaction time longer than 3 hours, while a
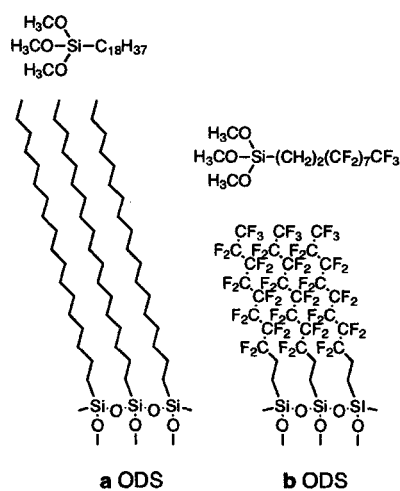
film of 1.1 nm thick was formed on the substrate treated with FAS at a reaction time longer than 1 hour. These thicknesses of the deposited films are shorter than the lengths of the corresponding precursor molecules; Those were estimated to be 2.35 and 1.34 nm for ODS and FAS, respectively, using molecular orbital calculations. The both deposited films are thus considered to be monomolecular layers composed of packed molecules inclined more than 30° to normal. ODS has a vapor pressure of 2 Torr at 150 °C, while FAS's vapor pressure is 1 Torr at 86 °C. Thus, FAS is expected to show a higher vapor pressure than ODS at our preparation temperature of 150 °C. This is the reason why ODS took a longer time to form a monolayer than FAS did.

3. VUV photodegradation of SAMs

Photodegradation of the SAMs was studied by using an apparatus as depicted in Fig. 4. A sample covered with a SAM was placed in a vacuum chamber which was evacuated by a rotary pump. Pressure in the chamber was controlled by introducing air through a variable leak valve. The sample was then irradiated with VUV light (a Xe_2 excimer lamp, Ushio Electric,
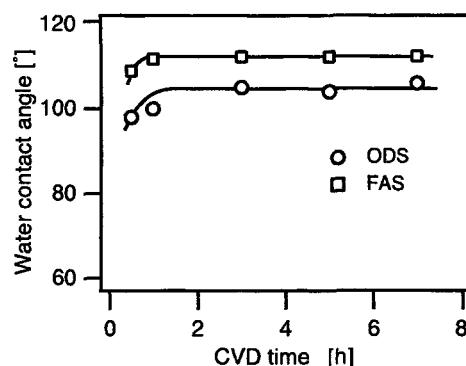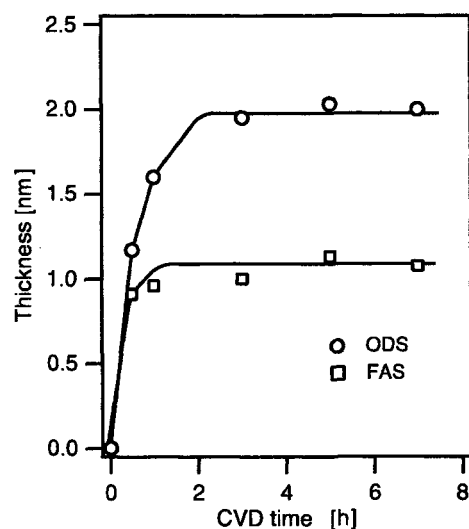

Fig. 2 Water contact angles of ODS- and FAS-SAMs.

Fig. 1. Chemical formula of ODS (a) and FAS (b) molecules and the corresponding SAMs.

Fig. 3 Thicknesses of ODS- and FAS-SAMs.

UER20-172V, λ = 172 nm and 10 mW/cm^2 outside of the window) through a quartz glass disk of 10 mm thick. Transparency of this quartz glass was ca. 70% at λ = 172 nm. The quartz disk was placed directly on the sample surface in order to simulate a situation when VUV patterning of SAMs is conducted since a sample is covered with a similar quartz plate, i.e., a photomask at that time. After the VUV irradiation for an appropriate period, the sample was taken out to measure its water contact angle using a contact angle meter based on the sessile drop method. Some of the photoirradiated samples were studied by infrared and x-ray photoelectron spectroscopies (IR and XPS).

Chemical changes in the VUV-irradiated ODS-SAM were studied based on water contact angle and XPS. Figure 5a shows water contact angles of ODS-SAM irradiated at a pressure of 10, 10^3 or 10^5 Pa. As VUV irradiation was prolonged, the water contact angles of the sample surfaces decrease and finally become almost 0°. The photodegradation rate of ODS-SAM is markedly accelerated when a pressure increases from 10 to 10^3 Pa. Oxygen may play some roles in the photodegradation. These results are the evidence that oxygen diffused through a very thin gap between the quartz disk and the sample surface. However, the rate decreases

Fig. 4 Schematic illustration of the VUV-irradiation experiments.

when the pressure further increases to 10^5 Pa. At this pressure, the intensity of VUV light reached to the SAM surface becomes considerably weaker, since VUV light is greatly absorbed by ambient oxygen (Transparency of 10-mm air layer at 10^5 Pa is ca. 10 %).

Absolute degradation rates of the SAMs were dependent not only on pressure but also on other system parameters including the evacuating rate, the chamber volume, the total lighting time of the excimer lamp and the distance between the lamp and a sample. However, the rates were primarily governed by the concentration of atmospheric oxygen.

Here we discuss the mechanism of the VUV photodegradation of ODS-SAM. VUV light dissociatively excites chemical bonds, e.g., C-C and C-H, to form radicals. Such radicals further react with oxygen in the atmosphere and may form oxidized products such as - COOH and -CHO groups. However, such oxidized products were not apparently confirmable in XPS of the irradiated ODS-SAM surface. It can be concluded that those are minor products. The photodegradation chemistry for irradiation at 172 nm in wavelength is thus not a chemical conversion from hydrophobic alkyl headgroups to hydrophilic headgroups. When organic molecules are irradiated with VUV light in the presence of atmospheric oxygen, the VUV light are simultaneously absorbed by organic and oxygen molecules. Active oxygen species such as ozone and atomic oxygen are generated due to the VUV excitation of the oxygen molecules. Since these activated oxygen species have strong oxidative reactivity to organic molecules, the decomposed ODS-SAM due to the direct VUV excitation further reacts with there, eventually converted to volatile species such as H$_2$O, CO and CO$_2$. Accordingly, ODS-SAM is finally removed from the substrate.

Changes in water contact angle of FAS-SAM due to VUV irradiation are shown in Fig. 5b as well. FAS-SAM degrades and becomes hydrophilic due to the VUV irradiation in a similar manner with ODS-SAM. The degradation rate also increases with an increase in concentration of atmospheric oxygen. The degradation rate at each of the pressures are approximately twice
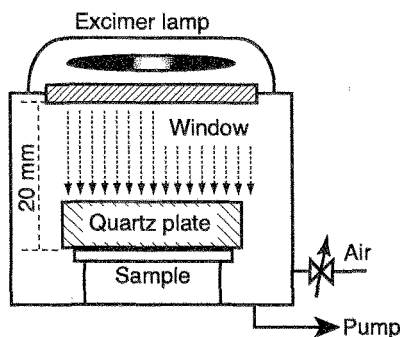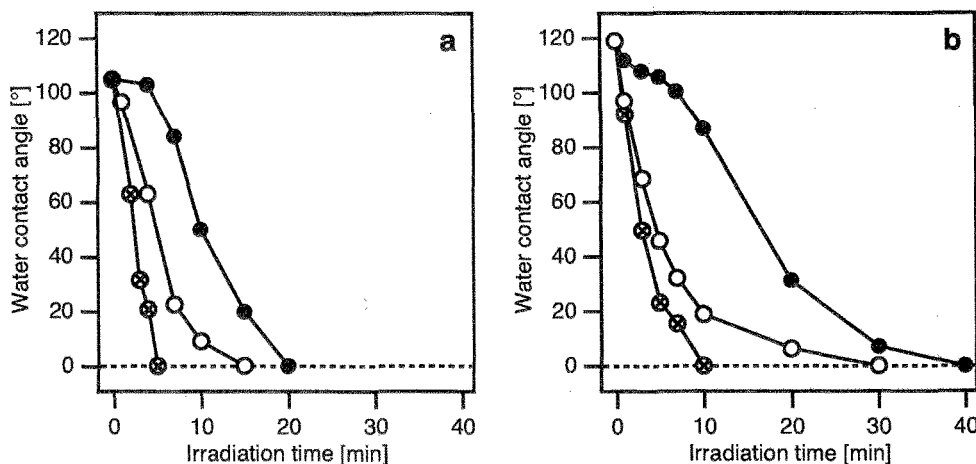

Fig. 5 Changes in water contact angle of ODS- (a) and FAS- (b) SAMs due to VUV irradiation at a pressure of 10 (O), 10^3 (⊗) and 10^5 (●) Pa.

lower than that of ODS-SAM at the same pressure. These results most likely due to a higher bonding energy of C-F, that is, 484 kJ/mol than those of other chemical bondings, i.e., C-C and C-H with energies of 348 and 412 kJ/mol.

The water contact angle of the FAS-SAM samples finally becomes almost 0° as shown in Fig. 5b, probably indicating that FAS-SAM has been removed. However, XPS of the VUV-irradiated FAS-SAM surfaces indicated that F atoms remained on the sample surfaces to some extent. Since these remained F atoms were removed by a rinse in pure water, those are considered to exist as water soluble compounds which might be products of VUV-generated F radicals and ions with SiO_2. In addition, about 30% of the remained F atoms could not be removed by the rinse. Those F atoms are likely to be presented as Si-OF formed through replacing H of Si-OH with F.

4. Micropatterning of the SAMs

As schematically illustrated in Fig. 6, a SAM prepared on a SiO_2/Si substrate was micropatterned by a mask-contact photolithography. A sample on which a photomask was placed was located in the vacuum chamber (Fig. 4) in which the pressure was controlled by introducing air through the variable leak valve. The photomask consisted of a 2-mm thick quartz glass plate with a 0.1 μm-thick chromium pattern. A weight, the quartz glass plate of 10 mm thick, was put on the photomask in order to attain a satisfactory contact between the mask and the SAM surface. The same Xe_2 excimer lamp used in section 3 served as a light source. The total light intensity at the SAM surface decreased down to 6.5 mW/ cm^2 due to absorption by the quartz plate and photomask's substrate when patterning was conducted in vacuum (Namely, attenuation due to oxygen absorption is negligible). Typically, the SAM was irradiated through the photomask for 10 min at a pressure of 10^3

Pa or for 20 min at a pressure of 10 Pa in order to complete VUV patterning.

Figure 7a show a lateral force microscope (LFM) image of ODS-SAM irradiated for 10 min with VUV light through the photomask. This VUV irradiation was performed at a pressure of 10 Pa. The image consists of two distinct regions which are bright 5 μm × 25 μm rectangular features and a dark surrounding area. These bright features correspond to the VUV-irradiated regions. Consequently, the irradiated ODS-SAM is concluded to possess a higher friction coefficient than that of the unirradiated ODS-SAM. Such an image contrast becomes more distinct with an increase in irradiation time. As shown in Fig. 7b, at an irradiation for 1 min, an LFM contrast is faint while, at irradiation periods of 4 and 10 min, the contrasts become ca. 6 and 40 times greater, respectively. The LFM contrast became to increase unrapidly when VUV irradiation was further prolonged and finally became to be almost unchanged at irradiation times more than 15 min, at which ODS-SAM was considered to be almost removed as expected from the results as shown in Fig. 5a.

The smallest feature succeeded in fabricating at present is shown in Fig. 8. Three lines, a, b and c, of which widths are 1.4, 0.9 and 0.9 μm, respectively are seen in this LFM image. These lines were printed by VUV irradiation through apertures of 1.2, 0.7 and 0.7 μm wide, respectively. The transferred linewidths were
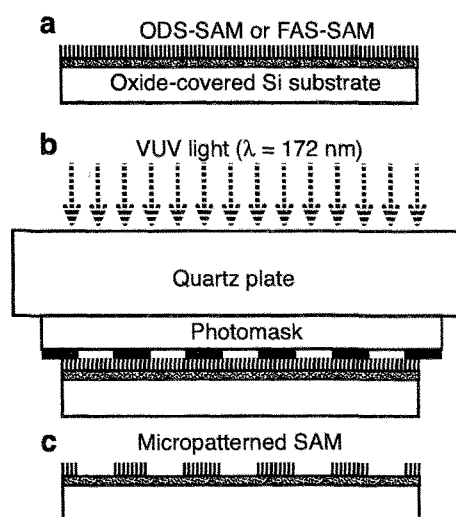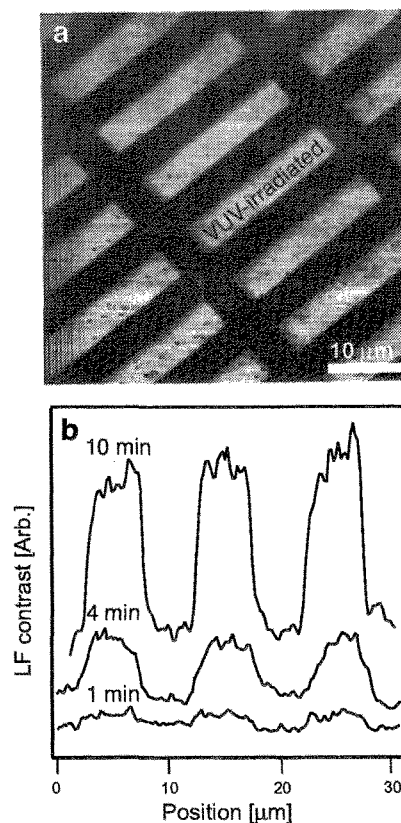

Fig. 6 Schematic illustration of VUV patterning of a SAM. a) preparation of a SAM on an oxide-covered Si substrate. b) VUV-irradiation through a photomask contacting to the SAM. c) the micropatternd SAM.

Fig. 7 a) LFM image of ODS-SAM irradiated for 10 min through the photomask. b) Cross sections of LF images for the samples irradiated for 1, 4 and 10 min.
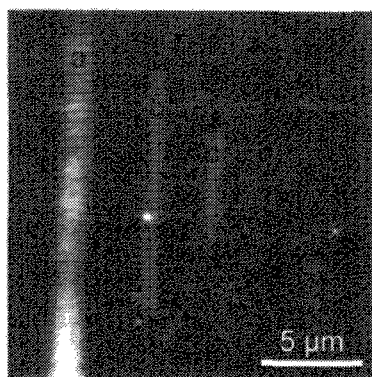
Fig. 8 LFM image of the VUV-patterned ODS-SAM. Patterning was conducted at a pressure of 10 Pa with an irradiation time for 20 min.

broadened ca. 0.2 μm from the aperture widths. Considering this edge sharpness, reproducible sub-μm patterning would be expectable by further optimizing the VUV patterning conditions.

FAS-SAM is also patternable by VUV light as can be expected from the results as shown in Fig. 5b. Details of VUV micropatterning of FAS-SAM have been published elsewhere [25]. Moreover, applications of VUV-patterned SAMs to various types of microfabrication processes have been also published [21,23,36-42].

5. VUV photolithography with proximal gap control

The degradation rates of the SAMs have been demonstrated to be governed mainly by the two factors. The first is the intensity of VUV light at the SAM surface. The second is the amount of oxygen supplied to the surface. In the present case as demonstrated in Fig. 5, it is difficult to satisfy these two factors simultaneously since the VUV light intensity decreases when the chamber pressure is increased in order to supply more oxygen molecules. Hence, we have constructed a new VUV lithography system as schematically illustrated in Fig. 9. In this system, a sample is placed in air in order to supply a large amount of oxygen, while the space between the photomask and the lamp window is purged with nitrogen to avoid the absorption of VUV light with oxygen molecules. Namely, the photomask works as a separation wall. Furthermore, a proximity gap between the photomask and the sample is controlled precisely at an accuracy of 0.1 μm using a mechanical stage.

We confirmed that ODS-SAM was decomposed and removed with only an exposure time for 2 min at a proximity gap of 1 μm. Even contacting the photomask to the sample surface, the SAM could be patterned with a 5-min exposure. These exposure times are much faster than those for the system used in section 4. As shown in Fig. 10, fine line patterns of 5 ~ 20 μm wide were successfully printed on ODS-SAM samples. The patterns on ODS-SAM were observed by a field-emission scanning electron microscope (FE-SEM). Due to the difference in secondary electron emission efficiencies between ODS-SAM and SiO₂, VUV-exposed regions are ob-
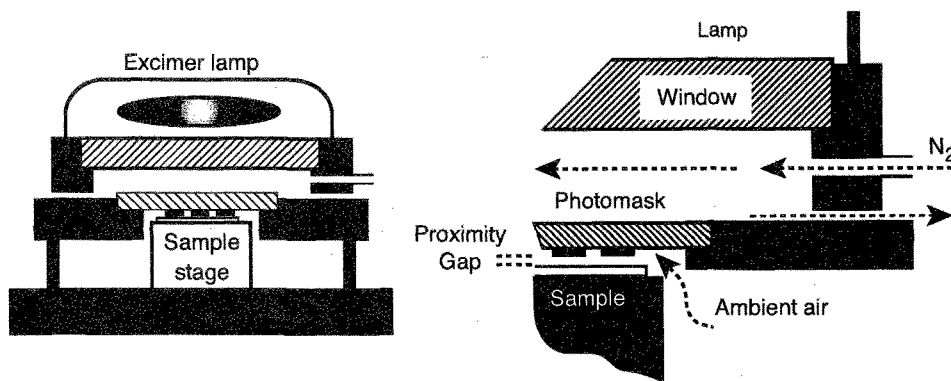

Fig. 9 Schematic illustration of the VUV lithography system.

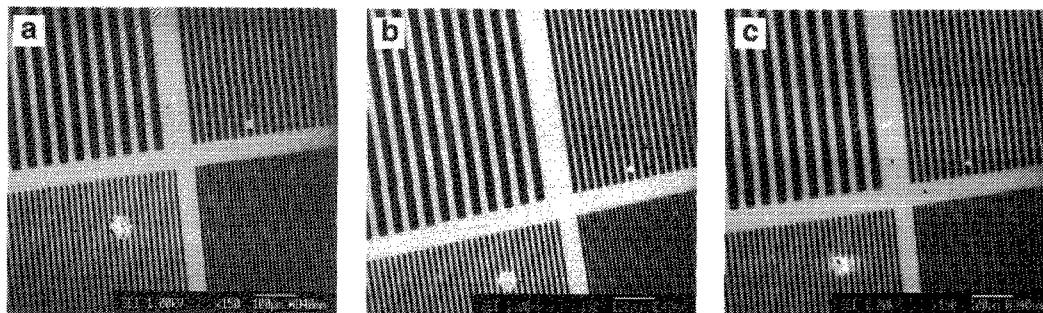

Fig. 10 FE-SEM images of patterned ODS-SAMs. a) Exposure time (t) = 5 min and proximity gap (PG) = 0μm. b) t = 3.3 min and PG = 0.1 μm. c) t = 2 min and PG = 1 μm.

served as the dark regions compared with the surrounding ODS-SAM [43].

6. Conclusion

The VUV light of 172 nm in wavelength has been an effective tool for micropatterning of alkylsilane and fluoroalkylsilane SAMs. The image of a photomask was printed on the SAMs through its photodecomposition. This VUV-lithography is generally applicable to micropatterning of any organic thin films, since its patterning mechanism involves cleavage of C-C and other bonds in organic molecules and subsequent oxidation with atomic oxygen species simultaneously generated from atmospheric oxygen molecules.

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