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# Photochemical Micropatterning of Silylated Glass Surface Bearing 3-Phenyldithiopropyl Group by KrF Laser Irradiation

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Thin film of 3-phenyldithiopropyltrimethoxysilane (**1**) was prepared as a photoreactive surface of masked thiol by in-situ reaction of 3-mercaptopropyltrimethoxysilane (**2**) with diphenyldisulfide before deposition of the film on quartz substrate. The film of **1** undergoes photochemical oxygenation of sulfur atom more efficiently than that of **2** upon KrF laser (248 nm) irradiation, where a thiyl radical is incorporated as a common intermediate.

Molecular-order thin films such as self-assembled monolayer have been studied from scientific and practical viewpoints for these two decades. Chemical modification of the films has attracted much interest concerning microfabrication for electronic or biochemical devices.[1,2] Physical and chemical properties of surface are highly influenced by the presence of the monolayer. For instance, introduction of a monolayer on silicon[1a] or gold[1b] surfaces prevents them from chemical etching. Photochemical micromodification of film surface as a use of ultrathin photoresists has been proposed.[1a] On the other hand, chemical functionality of the film surface also provides its versatility. Terminal functional groups such as amino or mercapto groups are useful for immobilization of biomolecules such as antibodies or enzymes.[2] Especially, mercapto group is a key functional group in protein chemistry and potentially convertible to other functional groups by the use of various alkylating reagents. Silane coupling reagents such as 3-mercaptopropyltrimethoxysilane (MPS) readily provide mono to eight layers with mercapto functionality onto glasses and metal oxides for this purpose.[3a]

Although photochemical patterning of mercapto group by irradiation of MPS film with a low-pressure Hg lamp has been reported recently,[2] the group can be excited only by the 185-nm line because of low absorption of alkyl thiols at 254 nm ($\varepsilon < 50$ mol$^{-1}$ dm$^3$ cm$^{-1}$). In addition, mercapto group tends to be oxidized to disulfide in air. These seem to leave some ambiguity in the mechanism The photochemical patterning with a deep UV light source will be limited by requirement of a specialized optical setup. We expect that the masking of mercapto group in a form of aryldithio substituent as a chromophore should enhance the reactivity of MPS monolayer for the surface micropatterning of mercapto group on quartz. The introduction of the phenylthio group will afford

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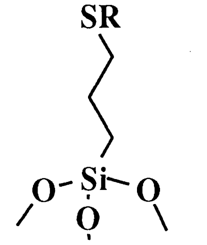

**1**: R = $SC_6H_5$;
**2**: R = H

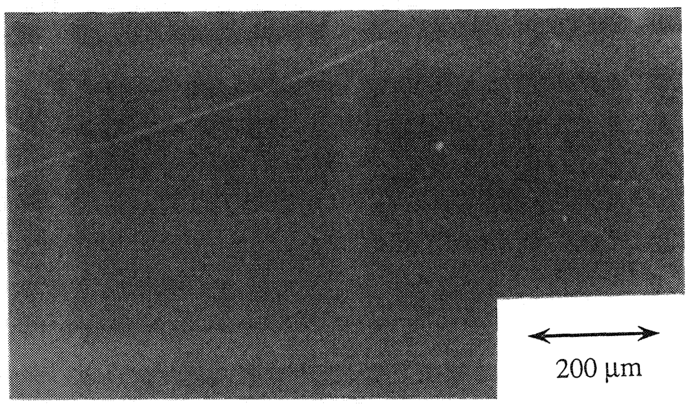

Fig. 1. Fluorescent micropattern of TRITC-labeled ovalbumin bound to unirradiated area of a thin film of **1** on quartz (see text).

benzene-like absorption ($\varepsilon \approx 10^4$ mol$^{-1}$ dm$^3$ cm$^{-1}$) around 248 nm to the film, which is much larger than those of alkyldisulfides ($\varepsilon = 10^2 - 10^3$ mol$^{-1}$ dm$^3$ cm$^{-1}$) and thiols ($\varepsilon < 100$ mol$^{-1}$ dm$^3$ cm$^{-1}$). Photoreactions of alkyldisulfides are known to proceed via excitation to n,$\sigma^*$ state of S-S bond[4,5] to give products mainly from homolytic cleavage of the weak S-S bond (bond energy ≈ 55 kcal mol$^{-1}$) and fewer C-S bond.[6] In the case of diaryldisulfide, the cleavage of S-S bond is more selective.[6] This group can be removed to give easily thiol group (demasking) by reduction with dithiothreitol (DTT). We here report for the first time the micropatterning of thiol functionality using a quartz surface silylated with 3-phenyldithiopropyltrimethoxysilane. This is based on the KrF laser irradiation at 248 nm and subsequent chemical modification of the surface.

Conversion of mercapto group of MPS into phenyldisulfide was carried out by reaction of MPS with diphenyldisulfide before reaction with quartz substrate. To a 20-cm$^3$ portion of methanolic solution of MPS (1% v/v), a small excess (1.1 eq) of diphenyldisulfide was added. Water (4% v/v) and acetic acid (4% v/v) was added to the mixture after the reaction with MPS (ca. 15 min). The quartz substrate (9.5 x 15 mm$^2$, 1 mm thickness) was placed in the mixture for 5 min to deposit a thin film of 3-phenyldithiopropylsilane (**1**), and was washed with chloroform and methanol. It was heated at 120 °C to complete condensation of the film with glass surface.[3] The presence of phenyl group in the film was confirmed by appearance of a satelite peak of $C_{1s}$ located at 290 - 293 eV in an X-ray photoelectron spectrum (XPS) of **1**, whereas the spectrum of the MPS film **2** did not show the satelite peak. Sulfur was obseved at 164 eV in $S_{2p}$ region to indicate its divalent state. The reduction of the disulfide in **1** to thiol was confirmed by treatment of the film with a methanolic solution of DTT and subsequent labeling with N-(1-pyrenyl)maleimide (MPI), which became fluorescent by the reaction with mercapto group,[7] whereas the film MPI was not labeled without DTT.

The film **1** was irradiated with a KrF excimer laser (Lambda Physik LPX 200) through a mesh as a photomask in air. Fluence, repetition rate, and shot number of the laser pulses were 30 mJ cm$^{-2}$ pulse$^{-1}$, 1 Hz, and 600 shots, respectively. After the irradiation, the sample was treated with a methanolic solution of DTT and modified with an acetonitrile solution of 3-maleimidobenzoic acid N-hydroxysuccinimide ester (MBS)[8] for 1 h at room temperature. The substrate was immersed in a phosphate buffer solution (pH 7.4) of ovalbumin (albumin from egg) for 1 h. The micropattern of ovalbumin was labeled with fluorescent dye such as fluorescein isothiocyanate (FITC) or tetramethylrhodamine isothiocyanate (TRITC) for observation. Fluorescence micrograph of the substrate as shown in Fig. 1 indicates formation of an image of the photomask, which means that disulfide in the film **1** is reacted at the irradiated area. The selectivity of the reaction of **1** with

DTT/MBS/albumin was confirmed by a control experiment: oxidation of the unirradiated surface of **1** to sulfonic acid with $H_2O_2$[9)] followed by the cross-linking procedure prevented the pattern formation.

As a control experiment, similar irradiation of the film **2** with 600 shots of the pulse of 30 mJ cm$^{-2}$ pulse$^{-1}$ followed by the treatment with DTT, MBS, albumin, and dye did not result in the formation of the fluorescent micropattern as shown in Fig. 1. The pattern formation for **2** required more than 3000 shots of the pulses of 30 mJ cm$^{-2}$ pulse$^{-1}$. These result indicates that the film **1** is more sensitive than **2** to KrF laser irradiation.

XPS analysis of the irradiated surface of **1** indicated growth of a new peak at 169 eV and decrease of the peak at 164 eV in $S_{2p}$ region corresponding to oxidation of divalent sulfur to sulfur oxide, and disappearance of the satelite peak of $C_{1s}$ corresponding to loss of the phenyl group. Intensity of sulfur at 169 eV was weakened but comparable to that at 164 eV before irradiation to rule out fragmentation reactions of S-$CH_2$, $CH_2$-$CH_2$, and $CH_2$-Si bonds leading to loss of two sulfur atoms.[10)] Any peaks around 286 and 288 eV corresponding to C-O and C=O bonds did not appear upon the irradiation, which means that carbon atoms in the film were not oxygenated. Ablation of the quartz substrate also can be ruled out, since a value of 1.2 J cm$^{-2}$ pulse$^{-1}$ was reported for the threshold of ablation of fused silica at 248 nm,[11)] which is much larger than the fluence applied here. The irradiated area for both **1** and **2** was wetted by contacting it with water. Furthermore, selective adsorption of cationic dyes such as rhodamine 6G perchlorate to the irradiated area was observed as shown in Fig. 2, indicating the presence of anionic species.[12)] On the basis of the hydrophilicity and the binding energy of sulfur atom in XPS of the irradiated surface,[9)] it was concluded that the sulfur atom was oxygenated into sulfonic acid by the photoreaction. Neither the film **1** nor **2** led to the pattern formation upon irradiation of a total intensity larger than 20 J cm$^{-2}$ with a high-pressure Hg lamp (> 280 nm) or low-pressure Hg lamp (254 nm), though excitation of phenyl group was expected. This nonlinear photochemical behavior with respect to laser fluence is in contrast to the photoreactions of disulfides in solution and probably a characteristic phenomenon to solid. One explanation for the present photochemical behavior of the films is a fast recombination process between a thiyl radical and a radical fragment (phenylthiyl radical or hydrogen radical), which are formed by selective fragmentation of S-S or S-H bond, in the case of low fluence because of an extremely low diffusion condition of solid. On the other hand, when the radicals are formed densely with a high fluence of laser light, coupling between the radical fragments will retard the recombination to leave the thiyl radical as an intermediate.[13)]

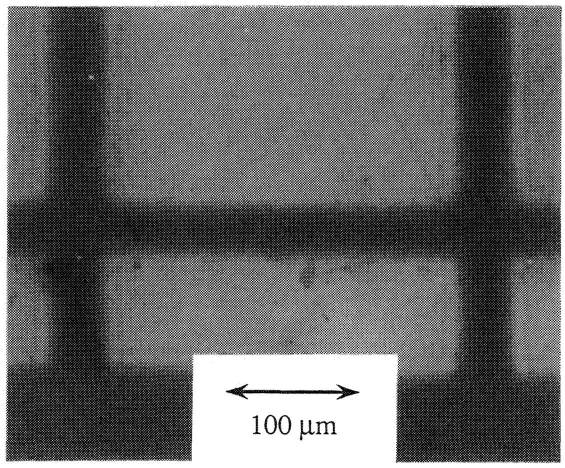

Fig. 2. Fluorescence micrograph of an irradiated surface of **2**, on which rhodamine 6G perchlorate was adsorbed from its aqueous solution.

Alternative explanation is due to a multiphotonic process, where some excess photon energy is used for elimination of the fragment radicals from the film in addition to the bond cleavage.[14)] As a result, oxygenation of sulfur atom occurs in the present patterning. The absorption efficiency of the laser light must play an important role in the relative reactivities of **1** and **2**. Relative stabilities of phenylthiyl and hydrogen radicals also may be another factor determining their reactivities.

The present work has demonstrated micropatterning of thiol at the surface with a resolution of a few tens micrometer at present by the use of a thin film with a photoreactive masked thiol moiety. It will be applicable to immobilization of other chemical functions in microdomains and will also provide a basis in designing photoreactive molecular-order thin films.

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