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### **Micropatterning of Organosilane Thin Layers on Glass Surface by Laser Irradiation for Patterned Immobilization of Polyaminopolymers**

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## MICROPATTERNING OF ORGANOSILANE THIN LAYERS ON GLASS SURFACE BY LASER IRRADIATION FOR PATTERNED IMMOBILIZATION OF POLYAMINOPOLYMERS

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### ABSTRACT

Irradiation of thin layers of 3-(acylalkylthio)propylsilanes on quartz with KrF laser (248 nm) through a photomask formed their micropattern via selective photo-fragmentation of C-S bond, on which polyaminopolymers such as polyethyleneimine and protein were immobilized.

### INTRODUCTION

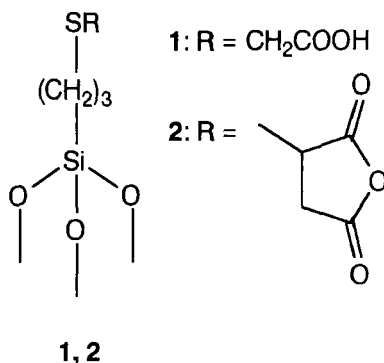
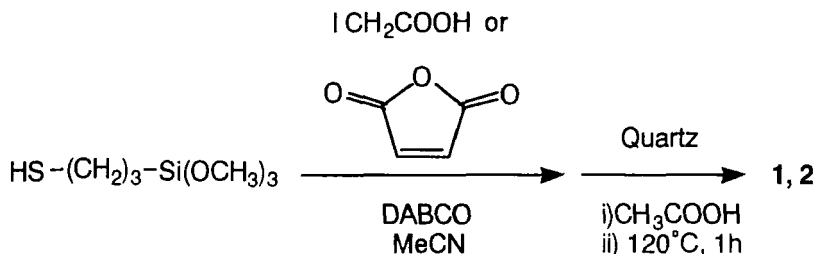
Interfacial thin layer of molecules or self-assembled monolayer covering the material provides surface functionality, leading to characteristic physical/chemical properties of material surfaces.<sup>1</sup> Photochemical process for spatial control of the functionality will be a key strategy for construction of micrometer-order chemical assemblies. We have demonstrated the introduction of functional molecules to several materials by spatially controlled surface modification through direct chemical bondings.<sup>2-4</sup> We report here photochemical micropatterning of organosilane thin layers of 3-alkylthiopropylsilanes on glass surface bearing carboxylic and carboxylic anhydride groups with KrF laser pulses, which is based on a selective fragmentation of C-S bond. The pattern of the acyl groups allows

further modification with polyaminopolymer such as polyethyleneimine, polyallylamine, or proteins, whose introduction is hardly achieved by graft polymerization.

## RESULTS AND DISCUSSION

Thin layers with carboxymethyl and succinic anhydride groups were prepared in the following procedure. Iodoacetic acid or maleic anhydride was added in a nitrogen-purged acetonitrile solution of 3-mercaptopropyltrimethoxysilane (MPS, 0.2% v/v) in the presence of tertiary amine such as 1,4-diazabicyclo[2.2.2]octane (DABCO), and the mixture was hydrolyzed after the reaction (30 min) by addition of water and acetic acid to deposit layers (layers **1** and **2**) on quartz substrates (9.5 x 15 mm<sup>2</sup>, 1 mm thickness), which were dried at 120°C for 1 h.<sup>5,6</sup>

The thin layer **1** was irradiated in air at 248 nm with a KrF excimer laser (Lambda Physik LPX 200) through a mesh (40 μm width) as a photomask. Fluence, repetition rate, and shot number of the laser pulses were 30 mJ cm<sup>-2</sup> pulse<sup>-1</sup>, 10 Hz, and 600 shots, respectively. After the irradiation, the sample was treated with a 10 mL of an aqueous solution containing ethyl(3-dimethylaminopropyl)-carbodiimide hydrochloride (EDC) (100 mg) and polyethyleneimine (average molecular weight: 70000) (3 wt%) for 12 h at room temperature. After rinsing with water, the sample was labeled with fluorescein isothiocyanate or rhodamine isothiocyanate in a 10-mL portion of a phosphate buffer solution of pH 7.4 by adding a 5 μL of a dimethylformamide solution of the fluorochrome (1.8 x 10<sup>-3</sup> M) to observe the micropattern of the polymer by fluorescence microscopy. Fluorescence micrograph of the substrate indicated formation of an image of the photomask, which means that carboxylic group is removed at the irradiated area (discussed below). The irradiation of **2** also gave fluorescent patterns, which however required a larger fluence of 60 mJ cm<sup>-2</sup> pulse<sup>-1</sup> than that for **1**. The advantage of the use of **2** will be high reactivity of succinic anhydride group to primary amines which allows one to omit the use of condensation reagent such as EDC. In addition, maleic anhydride is more reactive to MPS than iodoacetic acid in the preparation of **1** and **2**. In a similar manner, we have succeeded in the pattern formation of polyallylamine and several proteins with a spatial resolution of a few tens micrometer.



Primary photoexcitation of the layers will take place via intramolecular charge-transfer band of ( $\alpha$ -acylalkyl)alkylsulfide.<sup>7</sup> The present patterning was not achieved by the irradiation with a 254-nm line from a low-pressure Hg lamp, suggesting the incorporation of a multiphotonic process. However, laser ablation of the layers from the substrate was not plausible. Since ablation of the substrate requires a fluence larger than  $1.2 \text{ J cm}^{-2} \text{ pulse}^{-1}$ , this can be ruled out as a mechanism for the photopatterning.<sup>3,8</sup> XPS analysis of the irradiated area revealed that carbonyl carbon at 288 eV in C<sub>1s</sub> region was removed but sulfur atom still remained in a form of an oxide observed at 169 eV in S<sub>2p</sub> region. Water droplet wetted the irradiated area of the substrate for both **1** and **2** to mean that another hydrophilic group was formed there. These results suggest that laser irradiation leads to oxygenation of sulfur atom into sulfonic acid through fragmentation of the alkyl group. We recently have demonstrated photochemical

micropatterning of organosilane thin films of MPS and its phenyldisulfide derivative, which is based on cleavage of their S-H and S-S bonds and not C-S bond.<sup>3</sup> In the present case, selective cleavage of C-S bond in  $\alpha$ -acylalkylsulfides **1** and **2** into thyl and  $\alpha$ -acylalkyl radicals will be a plausible primary process of the photoreaction. This selectivity must be attributed to the weakness of C-S bond (65 kcal mol<sup>-1</sup>) as compared to C-C and C-Si bond (85 kcal mol<sup>-1</sup>), which is further favored by stabilization of radical center by the  $\alpha$ -acyl group. Mechanistic detail will be discussed in the coming paper.

As a conclusion, we demonstrated **1** and **2** as photoreactive thin layers for patterned immobilization of synthetic polyaminopolymers and proteins, which can be further functionalized through the amino groups.

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