

Probing the Diffusion of Vacuum Ultraviolet ($\lambda = 172$ nm) Induced Oxidants by Nanoparticles Immobilization

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PACS codes: 81.16.c; 81.16.Dn; 81.16.Rf; 61.46.-w

Keywords: VUV patterning, monolayer, photo-oxidation, gold nanoparticles

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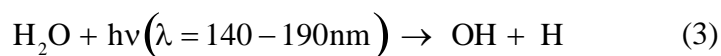
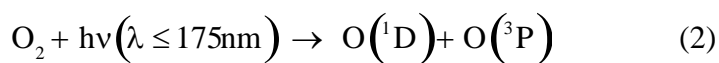
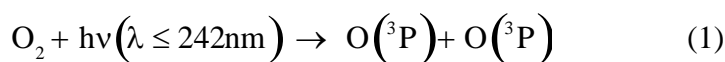
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Abstract

Vacuum ultraviolet (VUV, $\lambda = 172$ nm) patterning of alkyl monolayer on silicon surface has been demonstrated with emphasis on the diffusion of VUV induced oxygen-derived active species, which are accountable for the pattern broadening. The VUV photons photo-dissociates the atmospheric oxygen and water molecules into the oxygen-derived active species (oxidants). These oxidants photo-oxidize the hexadecyl (HD) monolayer in VUV irradiated regions (OP Khatri et al. Langmuir, 2008, 24, 12077), as well as the little concentration of oxidants diffuses toward the masked areas. In this study, we performed VUV patterning at a vacuum pressure of 10 Pa to track the diffusion pathways for the oxidants with help of gold nanoparticles (AuNPs; $\phi = 10$ nm) immobilization. At VUV irradiated sites AuNPs are found as uniformly distributed, but adjacent to the pattern boundary we observed quasi-linear arrays of AuNPs, which are determined by diffusion pathways of the oxidants. The diffusion of oxidants play vital role in pattern broadening. The site selective anchoring of AuNPs demonstrates the utility of VUV photons for the construction of functional materials with microstructural architecture.

1. Introduction

Photopatterning of organic monolayer has been recognized as versatile approach to construct the chemical template for site selective deposition of nanoparticles, nanowires, metals, biopolymers, dendrimers, carbon nanotubes, etc [1-6]. The fabrication of such micro-dimensional features with spatial distribution of nano-objects has received considerable attention in recent years due to their potential applications in semiconductor industries, bio-medical devices, sensors, photonic chips, etc [7-9]. The photopatterning of organic monolayer (as a photoresist thin film) promises the uniform micropatterning on a large scale with high throughput. The wavelength of the light and the nature of organic thin film are important parameters to determine the photo-etching mechanism and the quality of photopattern. A great number of investigations have been carried out on photochemistry and patterning of organic monolayer using different types of UV sources, including the mercury lamp [10,11], Xe excimer lamp [12,13], and excimer lasers [14-16]. The site-selective and precise surface functionalization and/or anchoring of various nano-objects for the different applications require patterned monolayer with the monitored photochemistry of organic monolayer. The low and continuous dose of UV photons from the excimer lamp etches the ultrathin (~ 2 nm thickness) monolayer at the mass level compared to that of excimer lasers, where the VUV photons exposure area is low. The photodegradation of alkyl monolayer is primarily determined by the wavelength of UV light. The direct photolysis of alkyl monolayer requires a $\sigma - \sigma^*$ transition (C-C, C-H) induced by the absorption of photons with wavelength shorter than 160 nm [17]. The atmospheric oxygen and water molecules absorb the UV photons of selective wavelength and form the oxygen derived active species (oxidants) as follows [11,18,19]:



These strong oxidants, particularly electronically excited atomic oxygen [$O(^1D)$] show strong oxidative reactivity towards the alkyl monolayer and gradually photo-oxidize the alkyl monolayer through the intermediate product containing polar functional groups like $-CHO$, $-COOH$ etc [2, 20]. Here, we report the vacuum ultraviolet (VUV, $\lambda = 172$ nm) patterning of structurally ordered hexadecyl (HD) monolayer on a silicon surface through a quartz photomask, with emphasis on the diffusion of VUV induced oxygen-derived active species at a vacuum pressure of 10 Pa. The Xe excimer lamp was used as a VUV photon source.

The dimension of photopattern determines by the size of apertures printed on a photomask, however the pattern broaden to more than the apertures size, due to many factors such as vacuum pressure inside the VUV chamber, roughness of photomask and the sample surface, and proximate gap between the photomask and sample [2,21]. Recently, we have reported that the pattern becomes wider with increasing the vacuum pressure, associated with an increase of oxidants concentration and their ease in diffusion [2]. In this paper, very tiny gold nanoparticles (AuNPs, $\phi = 10 \pm 1.5$ nm) were immobilized on the VUV patterned template to map the photo-oxidation of HD monolayer and probe the diffusion pathways for oxidants at the vacuum pressure of 10 Pa. The quasi-linear arrays of AuNPs adjacent to the pattern sites were observed due to the partial degradation of HD monolayer under the masked area by the diffusion of oxidants. These events are accountable for the pattern broadening.

2. Experimental Detail

Phosphorus-doped, n-type silicon (111) substrate was treated with 5% HF and then with 40% NH_4F to form a hydrogen-terminated surface (H-Si). Hexadecene (HD) and *n*-aminopropyltriethoxysilane (APS) were used as monolayer precursor. The HD monolayer on a H-Si was prepared by visible light ($\lambda > 422 \text{ nm}$) activation without forming an interfacial oxide film [22]. The elimination of hydrogen atom from H-Si surface by photon irradiation initiate the chain reaction with alkenyl groups ($-\text{C}=\text{C}$) of hexadecene molecules, resultant HD monolayer formation through a Si-C covalent linkage. The water contact angle on the HD monolayer (roughness: $0.4 \pm 0.1 \text{ nm}$ over $2 \times 2 \mu\text{m}^2$) was estimated as 110° , reveals the formation of a conformationally ordered methyl-terminated monolayer. The VUV patterning of the HD monolayer was performed using a Xe excimer lamp (light intensity: $10 \text{ mW}\cdot\text{cm}^{-2}$) as the VUV ($\lambda = 172 \text{ nm}$) source. The photodegradation of HD monolayer was examined as a function of VUV irradiation time at vacuum pressure of 10 Pa using a 2 mm thick quartz plate (93% transparency at 172 nm) instead of a 2 mm thick photomask to optimize the irradiation time. The HD monolayer was photopatterned by irradiated with VUV light through a quartz photomask consisting of 500 nm wide apertures separated by 1 and 4 μm wide chromium thin film (roughness: $1.4 \pm 0.3 \text{ nm}$ over $2 \times 2 \mu\text{m}^2$). The 5 mm distance was maintained between the VUV source and photomask during the photopatterning and the sample was placed in center of VUV chamber just below the VUV light source (tube) in such a direction that VUV light falls straightly on photomask, which avoid the grazing incidence effect on pattern broadening. This effect becomes prominent, when the finite distance is maintained between the photomask and sample surface [21], however in this study photomask and sample surface are in contact with modest pressure.

To probe the broadening of photopattern, an APS monolayer was deposited on the VUV patterned template by a chemical vapor deposition method [23]. The strong affinity of APS toward the hydroxyl/oxide moieties on pattern sites facilitated the formation of an amino terminated

monolayer, while the HD covered hydrophobic surface remained untreated with the APS molecules. This is followed by the immobilization of citrate-functionalized gold nanoparticles (AuNPs, $\phi = 10 \pm 1.5$ nm). The immobilization of AuNPs on VUV patterned sites originated from the electrostatic interaction between the citrate coating of AuNPs and the amino groups of the APS monolayer [23]. A JEOL JSM-7400F field emission scanning electron microscope (FESEM) was used to examine the distribution of AuNPs arrays. X-ray photoelectron spectroscopy (XPS, Kratos Analytical Ltd., ESCA 3400) measurements were performed to monitor the chemical changes in the HD monolayer caused by VUV irradiation and AuNPs immobilization.

3. Results and Discussion

Figure 1 shows the change in water contact angle of HD monolayer as a function of VUV photons irradiation time at a vacuum pressure of 10 Pa, using a 2 mm thick quartz plate instead of the photo-mask. The oxygen derived active species induced by VUV light, first oxidize the methyl terminal part of HD monolayer and then form the polar functional groups (-CHO, -COOH) containing intermediate product, resulting in the decrease in water contact angle. The increase in VUV irradiation time leads to the gradual photo-oxidation of methylene units of HD monolayer and finally surface becomes fully hydrophilic due to the formation of silicon oxide/hydroxide surface at an irradiation time of 900 s. Hence for the VUV patterning 900 s was considered as an optimized time to degrade the monolayer at a vacuum pressure of 10 Pa. A large number of the studies on UV patterning of organic monolayer illustrated the fabrication of micro-dimensional features without monitoring the (a) vacuum pressure and (b) surface roughness of sample and photomask during the photopatterning process, which play vital role in pattern broadening [2, 24]. Such factors limit the sub-micron patterning.

Here, we executed VUV patterning of HD monolayer in submicron dimension at vacuum pressure of 10 Pa with an aim to restrict the diffusion of oxygen-derived active species and probe the diffusion pathways for oxidants. Figure 2 shows the schematic illustration of VUV patterning of HD monolayer and an APS monolayer preparation on the VUV patterned sites. The APS molecules deposited on the photo-oxidized sites, attract the AuNPs due to the electrostatic interaction between the citrate stabilized AuNPs and amino groups of APS monolayer [23], while HD monolayer remained untreated, resultant AuNPs immobilized only on photopatterned sites. The XPS characterization has been performed to examine the chemical changes during VUV patterning and AuNPs deposition. Figure 3 shows the XPS spectra of C 1s spectral regions for (a) pristine HD monolayer and (b) VUV patterned HD monolayer with site selective deposition of AuNPs. The presences of strong signal at 285.1 eV assigned to C-C/C-H in Figure 3a represents the HD monolayer. The appearance of new signal at 288.6 eV with increased intensity at 286.6 eV are assigned to COO and CO respectively, and the reduction in intensity of C-C/C-H signal in Figure 3b for a chemical template with site-selective deposition of AuNPs reveal the (a) photo-degradation of HD monolayer on pattern sites, (b) partial oxidation of few of the HD molecules into the COOH moieties, and (c) presence of citrate coating on the AuNPs. The Au 4f (Figure 3c) signals that appeared at 84.0 and 87.7 eV are attributed to the $4f_{7/2}$ and $4f_{5/2}$ respectively and reveal the presence of AuNPs on the VUV patterned HD functionalized silicon surface.

At a vacuum pressure of 10 Pa, the VUV irradiated regions under the photomask apertures were completely degraded by VUV induced oxygen derived active species. A little concentration of these oxidants diffuse towards the masked regions through the nano-scopic channels available between the photomask and HD-functionalized silicon surface as illustrated in Figure 2g and partially photo-oxidize the HD monolayer into the polar functional groups containing products [20].

Figure 4 shows the FESEM images of AuNPs arrays tethered on the two different types of chemical templates patterned at a vacuum pressure of 10 Pa. The chemical templates as shown in Figures 4a-c and 4d-f were fabricated using 500 nm apertures (on photomask) separated by 1 and 4 μm wide chromium film, respectively. In all these images the width of the pattern was estimated to be larger (~ 600 nm) than the photomask apertures size (500 nm). At VUV irradiated regions, the HD monolayer was completely photo-oxidized and formed the silicon oxide and hydroxide moieties. The diffusion of VUV induced oxygen derived active species through the nanoscopic channels executes the partial oxidation of HD molecules under the masked area, which contained $-\text{COOH}$ groups as terminal parts. The AuNPs were tethered on both, completely photo-oxidized and partially oxidized regions with help of APS monolayer.

The small size (10 nm) AuNPs were used to map the partial photo-oxidation of HD monolayer under the masked region and probe the diffusion pathways for oxidants. The amplitude of diffusion of oxygen-derived active species decreases with increase in the distance from the pattern boundaries as revealed by AuNPs distributions in Figure 4. Near the pattern boundaries, ~ 50 nm wide area from the both sides of pattern shows the uniform distribution of AuNPs in addition to the VUV irradiated regions, resulting in total pattern width of ~ 600 nm. Probably in these extended regions all HD molecules experience the partial oxidation and formed the $-\text{COOH}$ terminal groups, resulting in uniform AuNPs deposition. The presence of quasi-linear AuNPs arrays (can be seen more explicitly in Figure 4b,c, e, and f, as indicated by arrows) adjacent to the pattern boundaries represents the track, where the monolayer has been partially oxidized by the diffusion of VUV induced oxygen-derived active species. These quasi linear arrays are distributed in 200 ± 50 nm wide areas from the both side of the pattern. These tracks were probably formed due to the roughness of the photomask

and the HD-functionalized silicon surface. Hence, the broadening of photo-pattern can be monitored by the change in the diffusion of oxidants and available channels for the diffusion.

Conclusions

In this study, we report the photopatterning of HD monolayer by VUV induced oxygen derived active species at vacuum pressure of 10 Pa. The amplitude of diffusion of oxidants decreases with increase in distance from the pattern boundaries. The quasi-linear arrays of AuNPs adjacent to pattern boundaries reveal the diffusion pathways unambiguously, provided by the roughness of photomask. Here, we had successfully fabricated the ~600 nm wide pattern, which is quite small compare to microscopic pattern reported by many researchers through the photopatterning of the organic monolayer.

Acknowledgment

The authors gratefully acknowledge the financial support from a Grant-in-Aid for Scientific Research (No. 19049010) on priority area "Strong Photon-Molecule Coupling Fields (470)" from the Ministry of Education, Culture, Sports, Science and Technology of Japan. Author OP Khatri acknowledges the Japan Society for the Promotion of Science for a JSPS postdoctoral fellowship.

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Figure Captions

Figure 1: Change in water contact angle for HD monolayer as a function of VUV irradiation time at vacuum pressure of 10 Pa.

Figure 2: Schematic illustration of VUV patterning of a HD monolayer and immobilization of AuNPs. (a,b) The HD monolayer was prepared by visible light activation of hydrogen-terminated silicon surface in the presence of hexadecene. This is followed by (c) VUV exposure of HD monolayer through the photomask at vacuum pressure of 10 Pa. (d-e) The VUV irradiated regions on silicon surface was backfilled by an APS monolayer. (f) The AuNPs are tethered on the APS monolayer, while HD modified surface remained untreated. (g) An enlarge view of VUV patterning reveals the diffusion of VUV induced oxygen-derived active species through the nanoscopic channels between the photomask and HD monolayer surface.

Figure 3: XPS spectra of C 1s signal for (a) the pristine HD monolayer and (b) after the immobilization of AuNPs on the VUV patterned (predefined) sites. (c) Au 4f signal due to AuNPs, immobilized on the VUV patterned surface.

Figure 4: FESEM images of AuNPs arrays tethered on the VUV patterned silicon surface. The images (a-c), and (d-f) correspond to the different chemical templates, fabricated by VUV patterning of HD monolayer using 500 nm wide apertures printed on photomask, which are separated by 1 and 4 μm chromium thin film, respectively. An APS monolayer was deposited on these VUV patterned templates before the AuNPs immobilization. The bright and dark features correspond to the AuNPs and HD monolayer, respectively. VUV exposure time: 900 s, Vacuum pressure: 10 Pa.

Figure 1

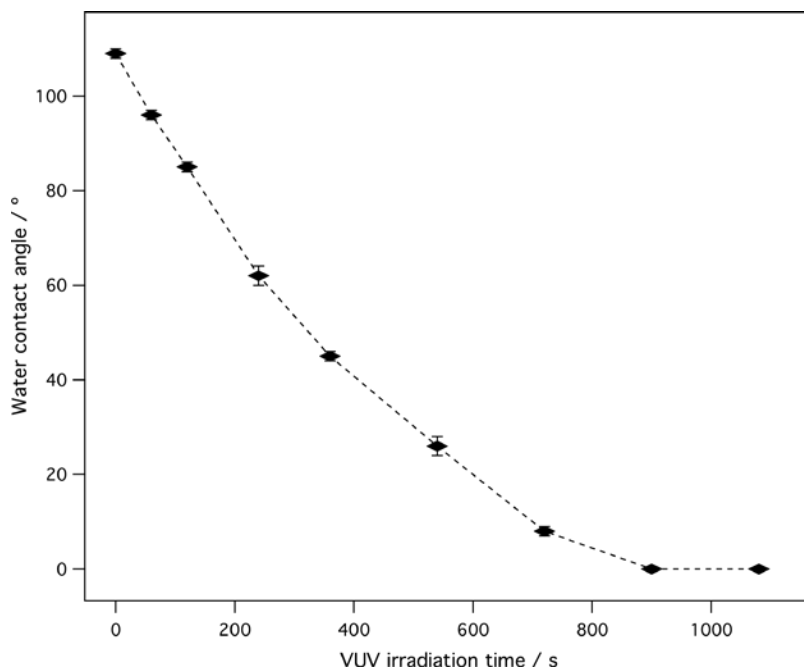


Figure 2

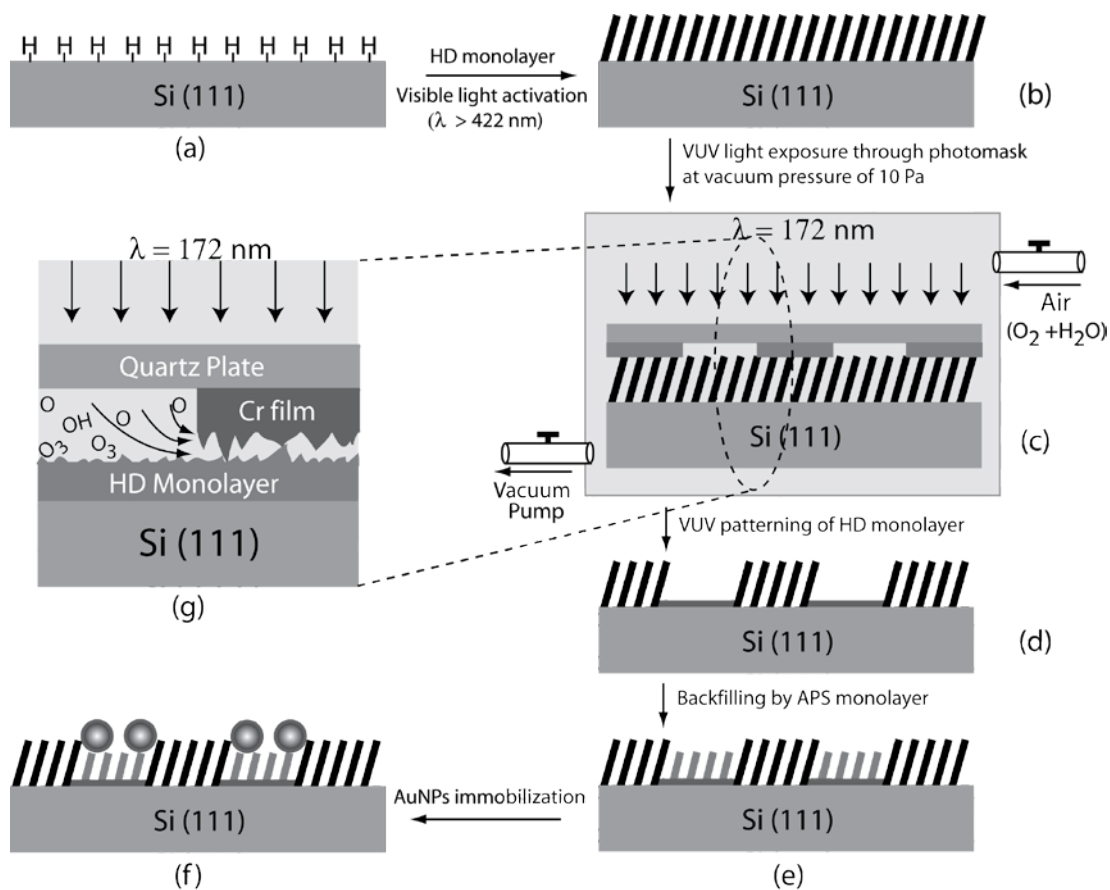


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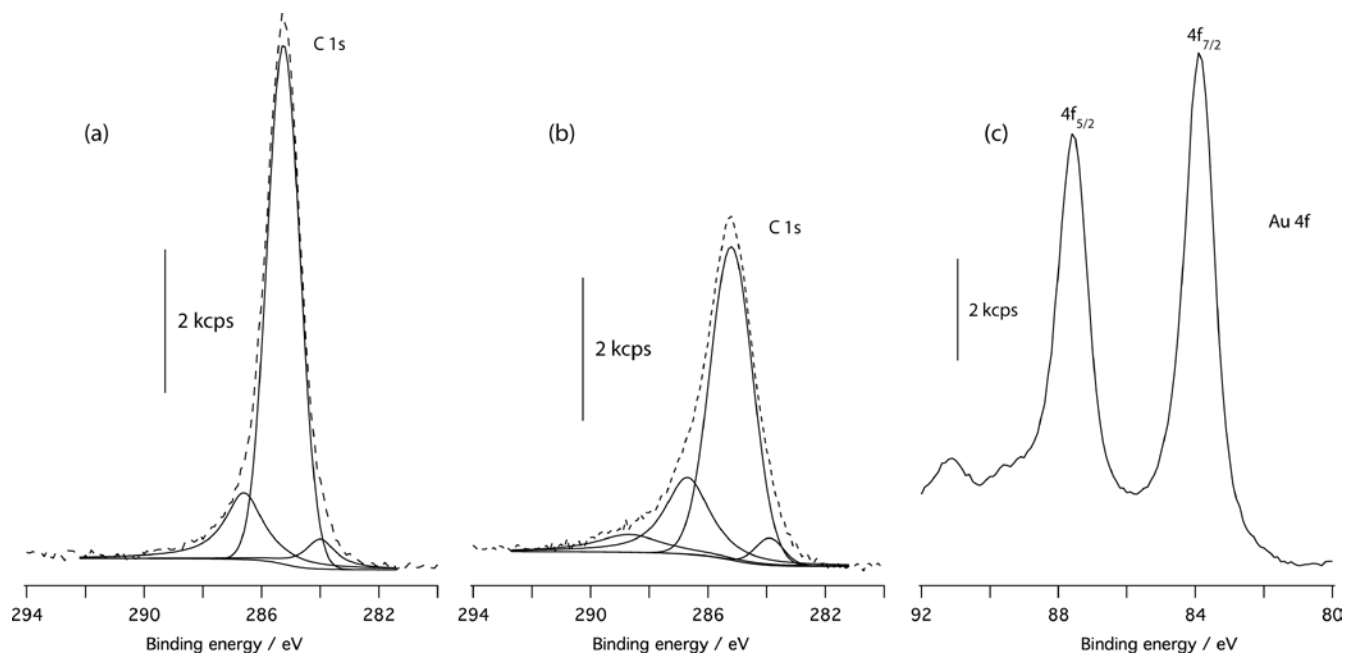


Figure 4

