Patterning of Self-assembled Thin Films Using Vacuum Ultraviolet Irradiation Through Anodic Porous Alumina Mask

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The high-throughput patterning of self-assembled monolayer (SAM) on Au substrates could be achieved by vacuum ultraviolet (VUV: $\lambda = 172$ nm) irradiation through an anodic porous alumina mask. The fluorescence image of the patterned SAM indicated the formation of a hole array on the submicron scale identical to that in the alumina mask.

The process of patterning organic thin films has attracted considerable interest for the fabrication of various functional devices.[1] Among these, the formation of a fine pattern of self-assembled monolayer (SAM) is important because it can form functional uniform thin films with thickness on the molecular scale. For the patterning of SAM, the use of several types of process, such as photolithography or electron beam lithography, has been reported so far.[2–5] However, the process with a high-throughput for the patterning of SAM from the submicron to the nanometer scale has not been established. In the present report, we describe a new process that allows the high-throughput patterning of SAM on the submicron scale, which is important for the production of functional devices inexpensively, using an anodic porous alumina mask. Anodic porous alumina, which is formed by the anodization of Al, has a highly ordered hole arrangement.[6] Pretexturing by imprinting using a mold with an ordered array of convexes yields an anodic porous alumina with an ideally ordered hole arrangement.[7] One of the useful applications of a highly ordered anodic porous alumina is its use for mask processing in vacuum evaporation or dry etching.[8] In the present work, an anodic porous alumina mask was applied to the paterning of SAM by etching using vacuum ultraviolet (VUV: $\lambda = 172$ nm) irradiation for the first time. VUV irradiation through the alumina mask was found to effectively etch the SAM on a Au substrate and generated a fine pattern of SAM corresponding to the mask. The use of an anodic porous alumina mask is advantageous in the easy preparation of fine patterns from the submicron to nanometer scales. This process will be used for the preparation of several types of functional device based on SAM, because the process allows the patterning of SAM with a high-throughput in an atmospheric environment.

Figure 1 shows the schematic for the patterning of SAM using VUV irradiation through the alumina mask. The anodic porous alumina used for the masks was prepared by a process similar to that reported previously.[7,8] Briefly, an Al sheet (99.99% purity) was anodized for 5 min at a constant voltage of 200 V in 0.1 M phosphoric acid solution at 0 °C after the pretexturing treatment of Al by imprinting using a SiC mold with an ideally ordered array of convexes of 500 nm period. In this process, an ordered array of concaves prepared by imprinting generates an ideally ordered hole arrangement in the anodic porous alumina during the anodization.[7] After anodization, a pore-widening treatment was carried out to adjust the pore sizes using a 10 wt % phosphoric acid solution. The barrier layer at the bottom part of the porous alumina was removed by Ar ion etching to make through-holes, after the removal of the Al substrate in a saturated $HgCl_2$ solution.[8] The formation of SAM on the Au substrate, which was prepared by vacuum deposition of Au on a Si substrate, was carried out by immersing the Au substrate in ethanol solution containing 5 mM 11-mercapto-1-undecanol (Sigma) for 24 h at room temperature. After rinsing the Au substrate in ethanol and ultrapure water, the alumina mask was set up on the substrate. The preparation of fluorescence-dye-labeled

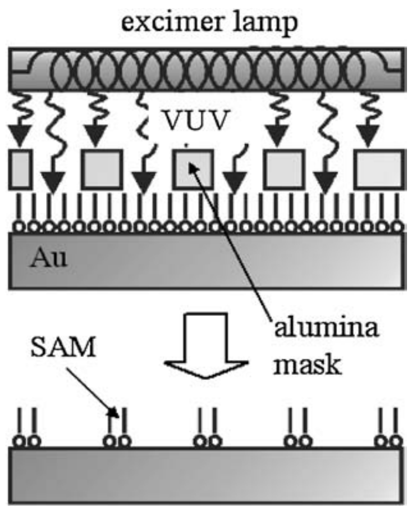

Figure 1. Schematic of patterning of SAM using VUV irradiation through the anodic porous alumina mask.

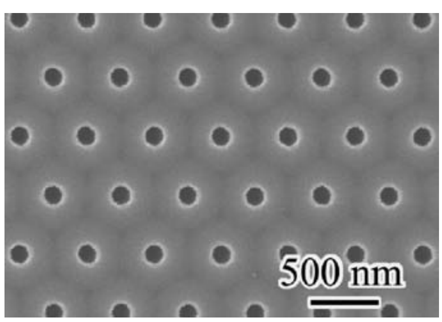

Figure 2. SEM image of the anodic porous alumina masks.

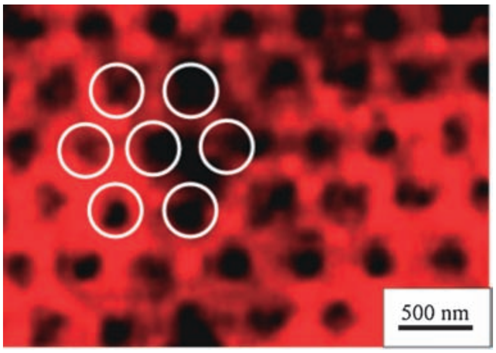

Figure 3. Typical fluorescence image of fluorescence-dye-labeled SAM patterned by VUV irradiation through the anodic porous alumina mask; irradiation time: 10 min.

SAM was carried out by adding a solution of 1 mM Alexa-Fluor 546 to 5 mM 8-amino-1-octanethiol in 0.1 M PBS with 1 M bicarbonate. In this reaction, Alexa-Fluor 546 was introduced into the end of 8-amino-1-octanethiol through the amino group. VUV Irradiation of the samples was carried out using an excimer lamp ($\lambda_{max} = 172$ nm) in an atmospheric environment. The distance of the lamp and the sample was usually 2 mm or less.

The electrochemical measurement of Au electrodes with a patterned SAM was conducted using a conventional three-electrode system, in which a Pt wire was used as a counter electrode and a Ag/AgCl (KCl sat.) electrode was used as a reference electrode.

Figure 2 shows a scanning electron microscopy (SEM) image of the anodic porous alumina masks used for the VUV etching. The diameter and interval of the holes were 135 and 500 nm, respectively. The depth of the holes was 300 nm, which corresponded to the aspect ratio (ratio of the hole depth divided by the hole diameter) of 2.

Figure 3 shows a fluorescence microscopic image of the fluorescence-dye-labeled SAM patterned by VUV irradiation through the alumina mask. From Figure 3, ordered dark spots can be observed in the image. The size and interval of these spots corresponded to those in the alumina mask used for the patterning. This means that the molecules of 8-amino-1-octanethiol could be removed selectively by the VUV irradiation through the alumina mask. Nonuniformity in the image presumably originated from the unevenness of the irradiation light. The detailed mechanism of the patterning is not clear at the present stage, but it is thought that the active species formed by photoexcitation contributed to the patterning of SAM.

The patterning of SAM on Au can also be demonstrated by the measurement of the electrochemical properties of Au with a patterned SAM. The Au substrate with SAM having an ordered hole array is expected to behave as a microelectrode array. Figure 4 shows the typical cyclic voltammograms of the Au electrode with a patterned SAM in 1 mM $[Ru(NH_3)_6]Cl_3$ solution. When compared with the background response, a sigmoidal response due to the reduction and oxidation of $Ru(NH_3)_6{}^{3+}$, which is characteristic of the microelectrode array, was confirmed in Figure 4. From this result, the patterning of SAM by VUV irradiation could be confirmed. The disagreement of the curve from that of an ideally fabricated microelectrode array is thought to originate from the insufficient interval in the electrode, which caused an overlap of the diffusion layer. To ensure a sufficient interval between the electrodes, the process for the preparation of porous alumina with selective through-holes will be applied. In this process, the anodization of Al with a pretextured pattern by a mold with deficiency sites and selective through-holing based on the difference of the bottom layer between the imprinted and umimprinted sites generate porous alumina with selective through-holes.[9] The use of such alumina for the mask in VUV etching will improve the properties of the microelectrode array prepared by the present process.

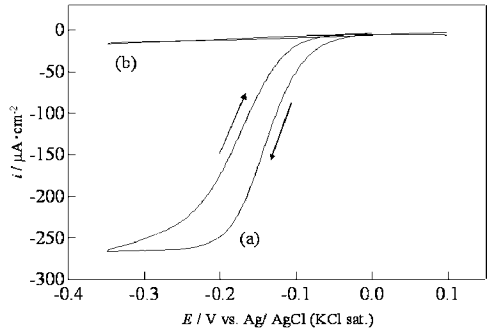

Figure 4. Typical cyclic voltammograms for redox reaction of $[Ru(NH_3)_6]Cl_3$ obtained for Au electrode with patterned SAM in 0.1 M aqueous KF solution (N_2 atmosphere) with (a) and without (b) 1 mM $[Ru(NH_3)_6]Cl_3$; Potential scan rate: 1 mV s^{-1}.

In conclusion, high-throughput patterning of SAM on a Au substrate could be achieved by VUV irradiation through an anodic porous alumina mask. From the fluorescence image of a patterned SAM, it could be confirmed that the patterned SAM has an ordered structure on the submicron scale identical to that of an anodic porous alumina mask. The patterned SAM obtained by the present process will be applied to the preparation of several types of functional device, such as electrochemical or biochemical devices.

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