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Fabrication of patterned high-density polymer graft surfaces. II. Amplification of EB-patterned initiator monolayer by surface-initiated atom transfer radical polymerization

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Abstract

Patterned films of a low-polydispersity polymer densely end-grafted on a silicon substrate were fabricated for the first time by the combined use of electron beam (EB) lithography and living radical polymerization; a focused EB was scanned on an initiator-immobilized substrate to selectively bombard and decompose the initiator, and then the EB-induced pattern was amplified by the atom transfer radical polymerization (ATRP) technique using Cu/ligand complexes. Ellipsometric and atomic force microscopic studies indicated that doses sufficiently larger than 2000 μC/cm^2 would completely decompose the monolayer of the initiator, 2-(4-chlorosulfonylphenyl)ethyltrichlorosilane, and that the surface-initiated ATRP could amplify the EB-produced fine pattern of the initiator monolayer. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Atom transfer radical polymerization; Electron beam lithography; Polymer brush

1. Introduction

Artificially designed fine patterning of polymer films is often demanded in various fields of science and technology such as those related with microelectronics and functional sensor devices. For this purpose, a polymer resist layer is usually spin-coated on a substrate and patterned by lithographic techniques. However, such a polymer film has a limited applicability as a functional surface because of its insufficient stability against temperature, solvents, and mechanical forces. Thus, a number of different approaches have been made to fabricate a patterned polymer layer that is stable, e.g. even in a wet system. For example, Rühe et al. [1] prepared a patterned graft layer by selectively photoinitiating polymerization from an azo-compound chemically immobilized on a surface. In this case, the grafting proceeded in a conventional free radical polymerization process, so that the chain length and chain length distribution of graft polymers were poorly controlled, resulting in a poor resolution of the graft pattern. Recently, living radical polymerization (LRP) techniques have been successfully applied to surface-initiated graft polymerization to densely end-graft low-polydispersity polymers on a surface [2–19]. In our previous paper [17], we demonstrated that a surface-initiated LRP technique could amplify the two-phase morphology of the initiator monolayer fixed on a substrate with a spatial resolution as high as ca. 100 nm. Hawker and co-workers [20] also applied the surface-initiated LRP to a self-assembled initiator monolayer patterned with a μm-resolution by the microcontact printing method.

This paper describes the first attempt to fabricate a finely patterned graft layer with a nano-scale resolution by the combined use of surface-initiated LRP and electron beam (EB) lithography. The fabrication process, which consists of two steps, is schematically shown in Fig. 1. The first step is the EB-lithographic patterning of the initiator monolayer fixed on a substrate; a focused EB is scanned on the substrate to selectively bombard and decompose the initiator. EB lithography is a promising technique to achieve a spatial resolution as high as 10 nm [21,22]. However, insufficient permeability of EB can provide undesirable results especially for thick resist layers. This drawback is absent in the present system where the monolayer of the initiator is patterned. In fact, an ultrafine pattern was created by EB-patterning a self-assembled monolayer (SAM) [23,24]. The second step is the amplification of the EB-induced pattern by surface-initiated LRP. The controlled

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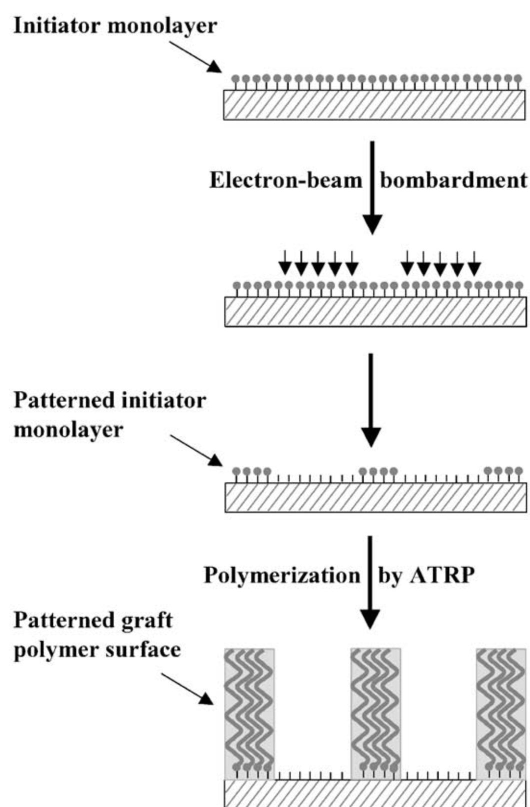

Fig. 1. Schematic illustration of fabrication of a patterned graft polymer layer by electron beam patterning followed by controlled graft polymerization.

growth of a high-density graft layer achievable by this method would retain the resolution of the EB-produced fine pattern and reduce the formation of defects in the polymer layer. In this work, 2-(4-chlorosulfonylphenyl)ethyltrichlorosilane (CTCS) or 2-(4-(2-bromo)propionyloxymethyl phenyl) ethyldimethylchlorosilane (BCS) fixed on a silicon wafer will be used as an initiator surface for the atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA). The EB-dose dependence of the initiator bombardment and the spatial resolution of the patterned polymer-grafted surface will be examined.

2. Experimental

2.1. Materials

MMA obtained from Nacalai Tesque, Inc., Kyoto, Japan, was distilled under reduced pressure over CaH_2 before use. 4,4′-Di-*n*-heptyl-2,2′-bipyridine (dHbipy) was prepared by the dithilation of 4,4′-dimethyl-2,2′-bipyridine followed by coupling with *n*-hexyl bromide according to the method of Matyjaszewski et al. [25]. Toluene (Nacalai Tesque, Inc.) was distilled over CaH_2. *p*-Toluenesulfonyl chloride (TsCl) and copper bromide (CuBr, 99.0%), purchased from Nacalai Tesque, Inc., were used without purification.

Two ATRP initiators, which can be fixed on a silicon wafer, were used: one was CTCS, which was obtained from Gelest, Inc., Tullytown, PA, USA as a 50 wt% dichloromethylene solution. The other was BCS, which was synthesized by reaction of 4-vinylbenzyl alcohol (Seimi Chemical Co., Ltd, Kanagawa, Japan) with 2-bromopropionyl bromide followed by hydrosilylation with dimethylchlorosilane. The detailed procedures have been described elsewhere [18]. The BCS was stored as a 20 wt% dichloromethane solution to prevent side reactions.

Unless otherwise specified, all other reagents were purchased from commercially available sources and used without purification.

2.2. EB patterning and graft polymerization

The initiator CTCS was immobilized on an oxidized silicon wafer by the SAM deposition technique; the wafer was dipped in dry toluene containing CTCS (ca. 2 wt%) for 18 h and then washed several times with toluene and finally with tetrahydrofuran. BCS was immobilized in the same way except that 2 wt% triethylamine was added in a BCS solution for immobilization and the treated substrate was washed with toluene, ethanol, and water. The initiator monolayer fixed on the wafer was EB-patterned by an EB lithography system (JEOL JBX-5000SF). The EB was exposed on the wafer in a line-and-space pattern as shown in Fig. 2. Ten sets of pattern with various doses ranging from 200 to 2000 $\mu C/cm^2$ were drawn on the same wafer. The accelerating voltage and the beam current were set to be 50 kV and 20 pA, respectively. The dose was controlled by changing the scanning speed (the exposure time). The full width at half maximum (FWHM) of the beam was about 10 nm.

The graft polymerization of MMA was carried out at 90 °C for 12 h by dipping the patterned wafer in a degassed diphenyl ether solution of CuBr (10.5 mM), dHbipy (21.0 mM), MMA (5.0 M) and TsCl (5.0 mM). TsCl was added as a free initiator to control the polymerization as

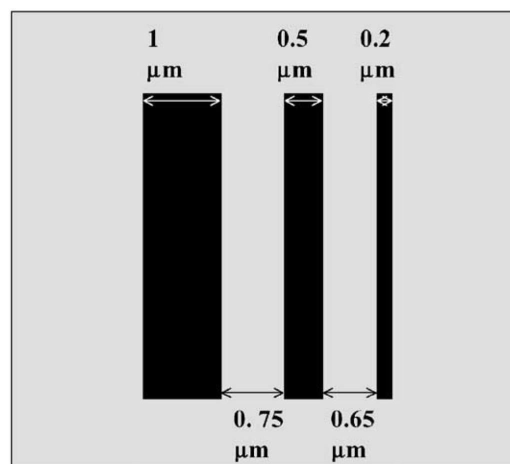

Fig. 2. A set of line-and-space patterns prepared by EB exposure.

well as to produce free reference polymer. The number- and weight-average molecular weights (M_n and M_w) and polydispersity index (M_w/M_n) of the reference polymer are known to well approximate those of the graft polymer [2,3].[1] After the polymerization, the grafted wafer was washed with toluene in a Soxhlet apparatus for 12 h to remove ungrafted (free) polymers and impurities.

2.3. Measurements

Monomer conversion and the M_n and M_w of the free polymers produced in the solution were determined by poly(methyl methacrylate) (PMMA)-calibrated gel permeation chromatography (GPC: 8010 high-speed liquid chromatograph, Tosoh Corp., Tokyo, Japan). Atomic force microscopic (AFM) observations were performed at room temperature with a contact-mode atomic force microscope (Seiko Instruments Inc., Chiba, Japan, SFA300 controlled by SPI3600) using a V-shaped Si_3N_4 cantilever (Park Scientific Instruments, Sunnyvale, CA, USA, spring constant 0.064 N/m). Topographic images were taken in air in constant-force mode with an applied force of 0.2 nN at a scanning speed of 25 μm/s unless otherwise noted. The ellipsometric measurements were performed by an analyser-rotating ellipsometer (DVA ellipsometer, Mizojiri Optical Co., Ltd, Tokyo, Japan) equipped with a He–Ne laser (632.8 nm). The polarizer angle and the incident angle were fixed at 30 and 70°, respectively. The thickness was calculated from the ellipsometric angles, Δ and Ψ, by assuming that the refractive index of the PMMA graft layer was 1.49, the value for PMMA bulk film.

3. Results and discussion

In order to prepare a patterned graft layer, MMA was graft-polymerized on the CTCS-fixed substrate, which had been patterned by the EB lithographic technique as shown in Fig. 2. The chlorosulfonylphenyl moiety of the CTCS is one of the best initiating groups for ATRP of MMA [26–29]. After the polymerization, the free polymer produced in solution was characterized by GPC as a measure of the graft polymer, and the M_n and M_w/M_n values of the free polymer were estimated to be 69,000 and 1.22, respectively. The ellipsometric analysis revealed that the thickness of the graft layer in a dry state was 55 nm on the substrate area without any EB treatment. These data give an estimate of graft density of 0.48 chains/nm^2, which is nearly the same as the previously reported value [2].

The grafted surface on the EB-patterned region was observed by AFM. Fig. 3 shows an AFM image and a cross-sectional profile of the region patterned with the highest EB dose. Comparison of Figs. 2 and 3 clearly shows that the valleys and hills in Fig. 3 correspond to the EB-exposed and -unexposed regions, respectively. As shown in the cross-sectional profile, the height difference Δh between the exposed and unexposed regions was estimated to be about 44 nm on the average. This value is somewhat smaller than the above-noted graft-layer thickness of 55 nm (without the EB treatment).

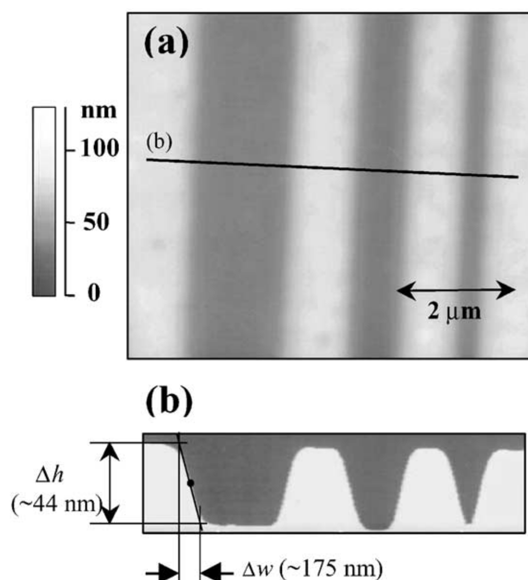

Fig. 3. (a) The AFM image and (b) the cross-sectional profile of the patterned graft layer on the CTCS-fixed substrate obtained after 12 h of graft polymerization of MMA. The dose of electron beam was 2000 μC/cm^2 in the irradiated regions.

First, we will discuss the EB-dose dependence of Δh. As Fig. 4 shows, the Δh value increases with increasing EB-dose. An increase of Δh means a decrease of the thickness of

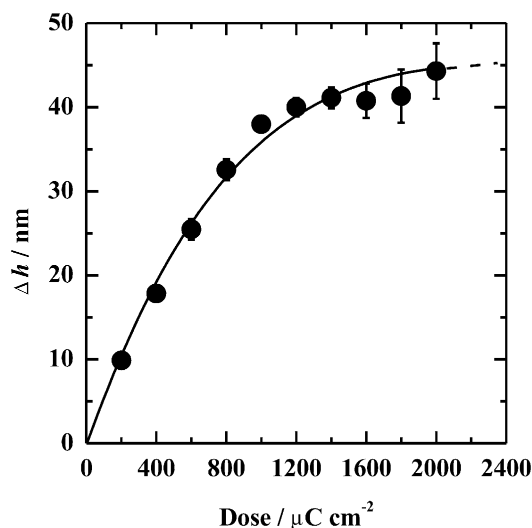

Fig. 4. Relationship between EB dose and height difference (Δh) after the graft polymerization of MMA for 12 h on a CTCS fixed substrate.

[1] To directly confirm this, the graft polymerization was carried out on initiator-fixed silica particles with a larger specific surface area instead of a flat substrate, and the graft chains were cleaved by treatment with HF solution. GPC analysis confirmed that they have nearly the same molecular weight as the free polymer (unpublished data).

the graft layer of the EB-exposed region, since in the studied dose level, the initiator is only incompletely decomposed. The graft polymerization was carried out on the wafer, on which 10 sets of pattern with various doses ranging from 200 to 2000 μC/cm^2 were drawn. This suggests that all the graft polymers produced on any region should have nearly the same M_n as the free polymer [2,3].[1] Therefore, a decrease in the layer thickness should be ascribed to a decrease in the graft density caused by decomposition of the initiator by EB-exposure. The Δh value (44 nm) at the highest dose studied here is about 80% of the thickness (55 nm) of the (EB-unexposed) graft layer. Fig. 4, therefore, suggests that doses sufficiently larger than 2000 μC/cm^2 will be required to completely decompose the initiator.

The spatial resolution of the graft layer will be discussed on the basis of the cross-sectional profile shown in Fig. 3(b). In this case with a dose of 2000 μC/cm^2, most of the initiator molecules on the EB-exposed region should be decomposed as mentioned earlier. The spatial resolution Δw, defined as the boundary width, i.e. the distance between the two points at which the tangential line at the midpoint of Δh intersects the valley and hill levels, was estimated to be about 175 nm on the average. This value seems to be consistent with the fact that the finest line of a 200-nm width (Fig. 2) was clearly observed in the AFM image and its depth was nearly the same as that of the other lines (Fig. 3(b)). As discussed in our previous paper [17], the controlled graft polymerization can produce a patterned graft layer with a spatial resolution higher than about 100 nm. Thus, the lower resolution obtained here is presumably ascribed to the patterning process. The EB lithographic system used in this study is reported to have a minimum line width of 30 nm in the specification. However, this resolution is guaranteed for a dose of 300 μC/cm^2 exposed on a spin-coated PMMA film with a thickness of 50 nm. In the present case, much larger EB-doses were required to cope with the low sensitivity of CTCS for the decomposition, and this has possibly lowered the resolution.

In order to evaluate the EB sensitivity of the other type of initiator, BCS, the pattern of the initiator monolayer produced by the EB lithography was amplified by the same procedures as described earlier. In this case, the 2-bromopropionyloxy moiety is the initiating group for the ATRP [18]. The M_n and M_w/M_n values of the free polymer were estimated to be 60,000 and 1.31, respectively, and the thickness of the graft layer measured by ellipsometry was about 30 nm. From these data, a graft density of 0.30 chains/nm^2 can be calculated. This value is smaller than that for the CTCS system (0.48 chains/nm^2), indicating that while BCS is a good initiator for styrene, it is a poorer one for MMA (the graft density for styrene/BCS system was about 0.4 chains/nm^2). The AFM observation of the graft layer revealed that at a dose of 2000 μC/cm^2, the height difference Δh was about 20 nm. This value is about 70% of the layer thickness, which is smaller than the corresponding value (80%) for the CTCS system, showing that the EB sensitivity of BCS is lower than that of CTCS.

4. Conclusions

We have succeeded in preparing a patterned graft layer with a spatial resolution of about 175 nm by applying EB lithography followed by surface-initiated ATRP. It was confirmed that the surface-initiated ATRP amplifies the fine pattern of the initiator monolayer produced by EB decomposition. In the studied systems, however, the spatial resolution of the graft layer was primarily determined in the EB patterning process, where very large EB doses were required to cope with the relatively low EB sensitivity of the initiators. The initiator CTCS had a higher EB sensitivity than the initiator BCS. Improvement in the EB sensitivity of the initiators should bring about an enhanced pattern resolution.

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