Designed surface construction by photo-induced vapor-phase assisted surface polymerization of vinyl monomers using immobilized free radical initiators

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To build up finely designed patterns on solid surfaces, consecutive vapor-phase assisted surface photo-polymerization (VASP) of methyl methacrylate and styrene was carried out under UV-irradiation through a stripe-patterned photo-mask on Si-wafer and Au-plate surfaces, resulting in the reproduction of designed and multi-layered patterns made of block copolymer chains grafted from the surfaces.

The fine surface design of solid materials as a subject of study has been attracting the interest of a growing number of researchers in consequence of its increasing importance in various fields. These fields are especially those where the nature of the surface plays a crucial function such as in printing, coating, fiber, membrane, and biomedical materials.[1] In these areas, the ability to produce fine surface architecture, found for example in continuous microarrays and complex patterns, has been extensively demonstrated by using various advanced techniques, *e.g.*, (1) surface initiated polymerization (SIP) with free radical, atom-transfer radical (ATRP), anion, iniferter polymerization methods;[2] (2) micro-contact printing with free radical polymerization, ATRP, ring-opening metathesis polymerization (ROMP) methods, and “grafting on” the surface;[3] and (3) photolithography with free radical, iniferter, ATRP methods,[4] and “grafting on” the surface.[5] These technologies have made the design of fine patterns easy to reproduce on solid surfaces.

Recently, study of the construction of these fine surface architectures has been developing from 2D-patterning to 3D-construction. In order to construct these 3D designed architectures with fine structures, well-controlled liquid processes such as micro stereo lithography have been developed.[6] However, there are still some problems associated with the liquid process, such as the high viscosity of the monomer solution, the swelling of products in solution, volume shrinkage in the subsequent drying process, and the difficulty of achieving monomer change. A more simple and precise constructing process may be achievable by a vapor-phase assisted polymerization (VASP) technique, which is able to construct the fine structures on the surface without the above problems. Fu *et al.*[7] and Wang and Chang[8] have reported on the 3D-constructing by ROMP of norbornenes and ring opening condensation of *N*-carboxyanhydrides on Au-plate and silicon oxide surfaces.

To give a durable surface modification, covalent bonding of the coating materials to surfaces is required. Two reliable grafting procedures are “grafting from” and “grafting on” surfaces, with especially the former, because of its high grafting density which utilizes living polymerization methods, being used for permanent modifications of surfaces. Some reports have dealt with the SIP using controlled polymerization methods, such as anionic, iniferter, nitroxide-mediated, ROMP, and ring-opening condensation methods,[2c,d,4c,8,9] to make polymer chains propagate from substrate surfaces. On the other hand, the free-radical polymerization method is the most convenient and robust technique, because the reaction is independent of moisture levels and tolerates a large variety of organic functional groups. Huang *et al.* successfully synthesized the covalently bonded graft-chains on Au surface using an azo-type free radical initiator immobilized on the surface in a solution.[2a] They showed that the polymer layer accumulated on the surface with a thickness that increased linearly with reaction time. However, no detail of the characterization of the obtained polymers was given.

There are some reports that deal with VASP of vinyl monomers by free radical initiators; for example, Chan *et al.*[10] investigated the chemical vapor deposition of 2-hydroxyethyl methacrylate and glycidyl methacrylate by azo- and peroxide-type free radical initiators on Si substrate, in which the molecular weight of deposited polymer chains was controllable based on the monomer to initiator ratio. We have been focusing on the combination of physically controlled VASP[11] with a photo-induced polymerization technique,[12] producing block copolymers on surfaces by using the free radical initiators. The earlier reported results encouraged us to develop the designed fine structures by covalently bonding on substrate surfaces. In this article, we tried to produce some two- and three-dimensional architectures by combining the VASP technique and a surface patterning technique with a photo-induced polymerization method. The result was a formation of finely patterned architectures created by covalently bonding block copolymers on Si-wafer and Au-plate surfaces.

First, the Si-wafer (20 × 20 mm^2) surface was modified with a solution of (3-aminopropyl)trimethoxysilane (5 wt% in toluene)[13] and the Au-plate (10 × 25 mm^2) was modified by a solution of 2-aminoethanethiol hydrochloride (1.0 mM in tetrahydrofuran (THF)).[14] Both the modified substrates were then functionalized by the introduction of an azo-group as a free-radical initiator according to the method reported by Schmidt *et al.*[14] as shown in Scheme 1.

To fabricate the designed lattice-pattern on a surface, the photo-induced VASP of methyl methacrylate (MMA) was carried out at

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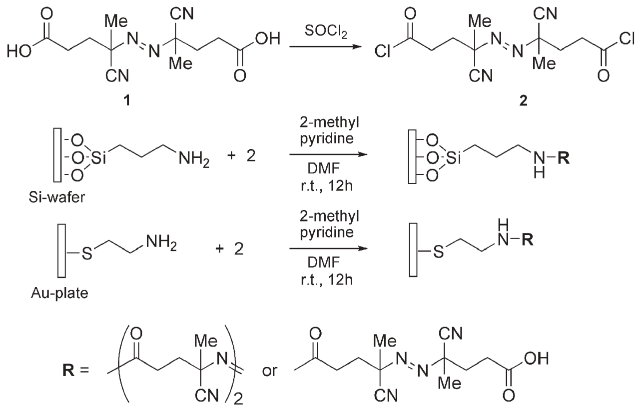


Scheme 1 Immobilization of azo-type free-radical initiator on Si-wafer and Au-plate surfaces.

40 °C for 24 h in a saturated vapor-phase of MMA (23.7 kPa) under UV-irradiation through the lattice patterned photo-mask with a slit width of 100 μm. The patterns were irradiated with UV light with a point light source from a 320 W high-pressure mercury lamp (MORITEX Co., MUV-202-U) at an intensity of 49 mW cm^{-2} (λ = 280–320 nm) at a distance of 10 cm from the substrate surface. The polymerization of MMA was initiated by free radicals generated *via* the photochemical decomposition of the azo-initiators, resulting in the accumulation of polymer chains in the patterned area irradiated. After the VASP, physisorbed monomers and polymer chains on the surface were completely removed by immersing in THF four times at room temperature for 5 min while irradiating under the supersonic wave and rinsing with THF. The grafting polymer chains on the surface were measured with a microscopic FTIR equipped with an image-mapping system: DIGILAB FastImage IR/Stingray system in a reflection absorption mode and an atomic force microscope (AFM) SII Nanopics 2100 in a tapping mode.

The reflection absorption FTIR spectrum of the polymer chains grafted in the lattice pattern area exhibited a typical characteristic absorption band of PMMA at 1725 cm^{-1}. Fig. 1 depicts AFM images of the accumulated lattice patterns on the Si-wafer surfaces. These patterns must be made up of the polymer chains grafted on the surface. The thickness of the resulting accumulation was in a range of approximately 20–25 nm as shown in Fig. 1. The thickness profiles were broad peaked in shape, rather than having a flat table-like profile, because of the UV-light radiating from the point source of light underwent diffusion as it passed through the slit of the photo-mask.

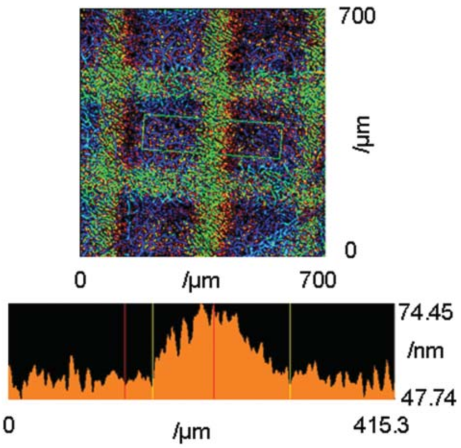
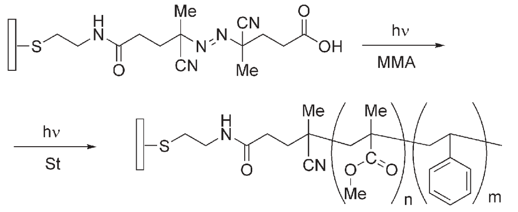
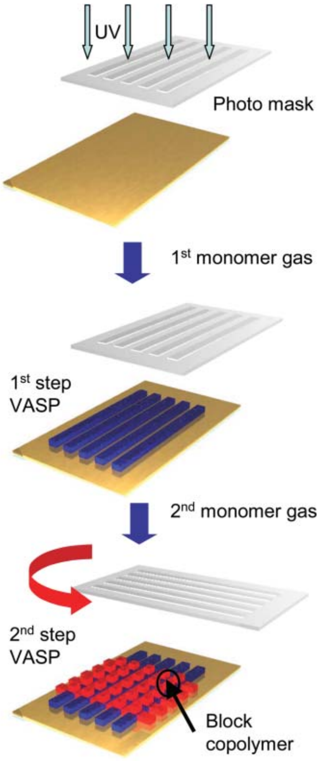


Fig. 1 Tapping mode AFM images of PMMA chains accumulated by photo-induced VASP.



Scheme 2 Block copolymerization by consecutive VASP on the initiator immobilized surfaces.

To make the best use of the living nature of the VASP method,[11a] construction of multi-layered patterns by block copolymerization was tried by consecutive application of VASP (Scheme 2), in which the monomer vapors of MMA and styrene (St) were fed consecutively on the azo-functionalized Au-plate surface. Scheme 3 outlines the procedure for building up a patterned accumulation through consecutive copolymerization. In the first step, VASP of MMA was carried out in a saturated vapor-phase of MMA under UV-irradiation through a stripe-patterned photo-mask at 40 °C for 24 h. After the first reaction, remaining MMA vapor was thoroughly removed *in vacuo*, followed by the introduction of St vapor (2.2 kPa at 40 °C), rotation of the photo-mask through 90°, and irradiation with UV light to start the second-step reaction. VASP of St was carried out at 40 °C for 24 h. After the second reaction, any remaining St vapor was removed



Scheme 3 Outline of the building up process of the multi-layered patterns by photo-induced consecutive VASP of MMA and St-monomers.

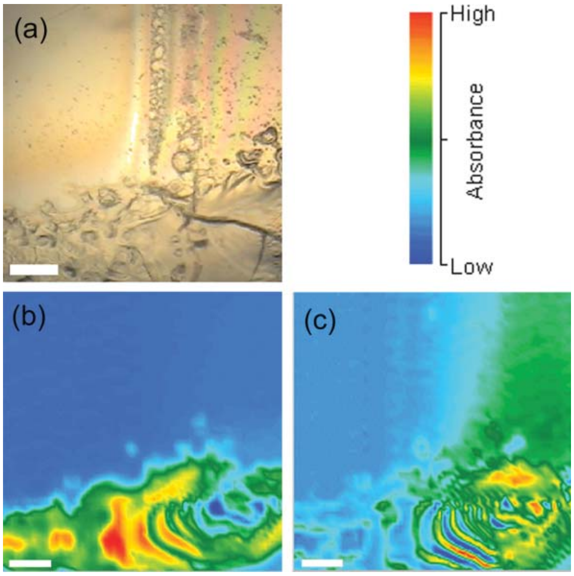


Fig. 2 Microscopic reflection absorption FTIR images of accumulated polymer pattern by VASP of MMA and St on Au-plate surface. (a) Microscope image of a crossing stripe pattern; (b) microscopic reflection absorption FTIR image visualized by the IR absorption at 1150 cm^{-1} for PMMA; and (c) visualized by the IR absorption at 1607 cm^{-1} for PSt. Bar: 100 μm.

in vacuo. Physisorbed monomers and polymer chains were completely removed with THF in the same way as the above mentioned homo-grafting of MMA. Previously, in a similar manner it was determined that the block copolymer: poly(MMA-*block*-St) was formed on the surface with a high block-structure ratio of 81.4%.[12] Thus, the block copolymer chains must be grafted from the Au-plate surface in a similar way.

After the consecutive VASP and the after-treatment, the accumulated polymer pattern on the Au-plate surface was observed by microscopic FTIR. Fig. 2(a) shows the microscopic image of a crossing point of the vertical and horizon stripe patterns accumulated on the surface. Fig. 2(b) and (c) show microscopic FTIR absorption mapping images. These images were visualized at two particular wavenumbers: 1150 and 1607 cm^{-1}, by which the characteristic absorptions of $\nu_{C\text{–}O\text{–}C}$ for PMMA and $\nu_{C=C}$ for PSt, respectively, are preferentially detectable. As shown in Fig. 2(b), the horizontal stripe pattern indicates that the PMMA chains grafted on the Au-plate surface are the first accumulated polymer chains. The vertical stripe pattern in Fig. 2(c) exhibits the PSt chains as being the secondly accumulated polymer chains. The same images were also obtained with other particular wavenumbers: 1730 and 1607 cm^{-1} as the characteristic absorptions of $\nu_{C=O}$ for PMMA and $\nu_{C=C}$ for PSt, respectively. In the areas that were not exposed to UV-light, no accumulation of polymer chain was detected. This means that the graft-polymerization from the surface occurred *via* photo-induced reactions, not *via* a thermal reaction.

Interestingly, both the PMMA and PSt chains were detected in the crossing area of the stripes, indicating a phase separation at the top layer of the accumulation. This indicates that the phase separation behavior must occur during the solvent extraction and following drying processes. The co-existence of both sequences in this area strongly suggests the formation of block copolymer: poly(MMA-*block*-St) as previously reported.[11*a*,12] This accumulation of the block copolymer demonstrates the building up of the designed pattern structures as shown in Scheme 3.

In conclusion, by building up polymer chains grafted from the substrate surface using the photo-induced VASP technique it was possible to construct finely designed 3D-structures on Si-wafer and Au-plate surfaces that had been functionalized beforehand by a photo-chemically active azo-initiator. The VASP of MMA successfully proceeded to form covalently bonded polymer chains on the surfaces according to the designed fine patterns. Moreover, by consecutive VASP of MMA and St it was possible to build up a multi-layered structure consisting of different chemical structural layers with designed fine patterns on solid surfaces. In this way, we have achieved the synthesis of block copolymer chains grafted from substrate surfaces by using the free-radical initiator. The relatively long reaction time has the potential to be shortened by accelerating the reaction rate through controlling the monomer concentration and the UV irradiation conditions. It is anticipated that this photo-induced polymer-grafting strategy by VASP will be widely used for many applications needed in the construction of designed fine structures on solid surfaces.

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