Patterning of SnO₂ Thin Films by Combination of Lithographic Photoirradiation and Pyrolysis of an Organotin Polymer

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Photolithographic techniques used in the patterning of organic and inorganic materials such as biomolecules, electron conductive polymers, and catalysts as well as silicon and metals have recently received much attention as a preparation method for interfaces of various microdevices.[1–3] Particularly, SnO₂ will be of importance for preparation of photoactive electrodes because of its optical transparency as well as its electronic conductivity. However, patterning of SnO₂ thin films by wet etching is unsuccessful due to its high chemical stability. We have previously reported on the photochemical cross-linking/oxygenation reactions of thin films of poly(4-((trimethylsilyl)methyl)styrene) (PTMSMS).[4] We now report on the patterning of SnO₂ thin films by a lithographic photoirradiation and followed by pyrolysis of films of a tin analogue of PTMSMS, poly-(4-((trimethylstannyl)methyl)styrene) (**1**).[5] Interestingly, the photochemical formation of a cross-linking network is necessary for the pyrolytic conversion of the organotin polymer into SnO₂.[6]

Thin films of **1** (0.6–1 μm thickness) were prepared by spin-coating on quartz plates (29-mm diameter,

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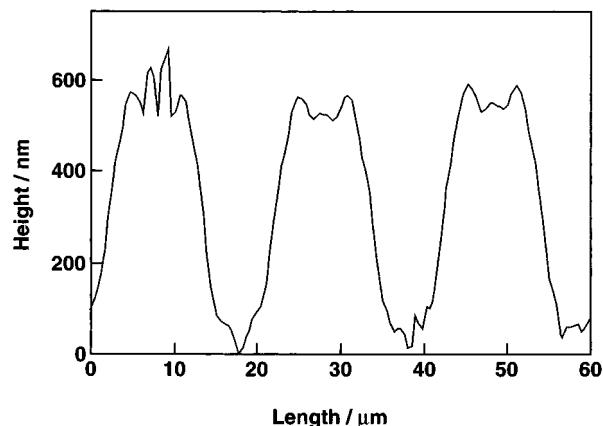

Figure 1. Cross-sectional atomic force microscopy (AFM) image of the line and space pattern of **1**. A thin film of **1** was irradiated with a KrF laser through a photomask and developed with xylene.

1-mm thickness) from its toluene solutions (80 g/L). A thin polymer film of **1** (0.68 μm thickness) was irradiated with 200 pulses using an excimer laser (Lumonics PM-884) operated with a KrF gas mixture (248 nm, 15 mJ pulse⁻¹ cm⁻²) at 10 Hz through a beam homogenizer (Leonix EWO-FI-60-248, beam size 12 × 12 mm²) in air. The irradiated film was developed with xylene, which is a good solvent for **1**, for 5 min to remove the unirradiated area and was dried in air. The irradiated area was insoluble in xylene, though a dissolution of the surface thin layer (<0.1 μm) of the irradiated area was observed by atomic force microscopy (AFM). After the development, the film was pyrolyzed in an electric oven at 500 °C for 2 h in air, and then a transparent thin film was obtained. The thin film was in good contact with the quartz substrate without any cracks or peeling in the whole area. Elemental analysis of the surface of the thin film by X-ray photoelectron spectroscopy (XPS) indicated the formation of SnO₂. The UV absorption spectrum of the SnO₂ film was identical with that reported[7] showing an onset at 321 nm, from which the bandgap energy was estimated to be 3.9 eV. This value agreed with that reported previously.[7]

Similar irradiation of films of **1** through a photomask followed by the development gave a negative pattern of the polymer. The pyrolysis also afforded a pattern of SnO₂ without considerable deformation of the pattern before and after the pyrolysis, though a reduction of the film thickness from 0.6 to 0.15 μm was measured by AFM as shown in Figures 1 and 2.

((Trialkylstannyl)methyl)benzene undergoes photochemical cleavage of benzylic C–Sn bond to give benzyl-type radical via its excited state in a high quantum yield.[8] The photoirradiation of **1** will cause the C–Sn bond cleavage to give a benzyl-type radical and trimethylstannyl radical. The benzyl-type radical on the surface of the polymer film in part would react with molecular oxygen in air. In contrast, the radical species inside the film, where the concentration of oxygen is low, will undergo radical recombination or the coupling of benzyl-type radicals to give a cross-linking network.

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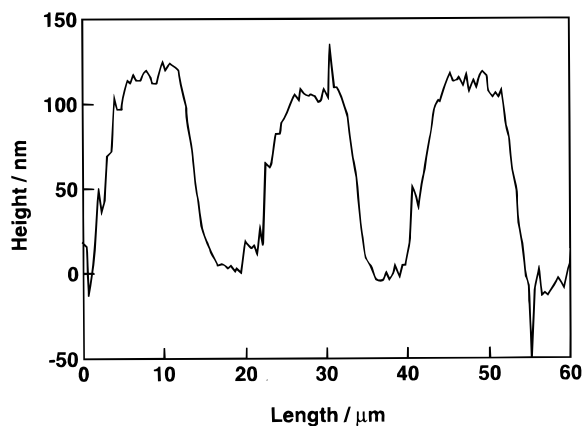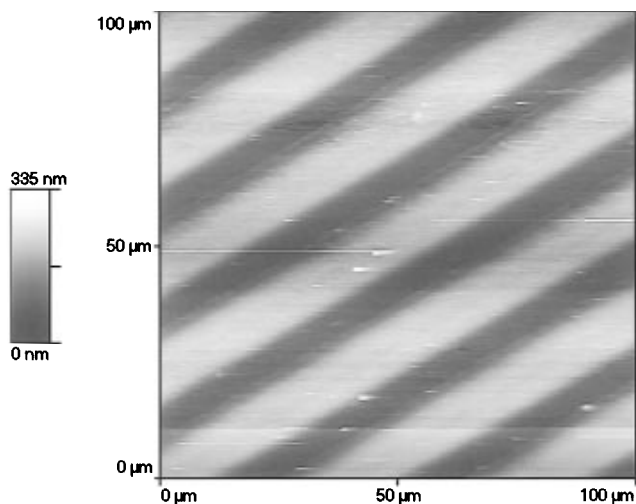(8) Soundararajan, N.; Platz, M. S. *Tetrahedron Lett.* **1987**, *28*, 2813.

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Figure 2. (a, top) AFM image of the line and space pattern of SnO_2 which was obtained by the pyrolysis of a developed film of **1** (see text). (b, bottom) Its cross-sectional AFM image.

Figure 3. Cross-sectional AFM image of the line and space pattern of SnO_2 which was obtained by the pyrolysis of an irradiated film of **1** without the development (see text).

Since complete conversion of the ((trimethylstannyl)-methyl)phenyl groups of **1** would not be necessary to form an insoluble cross-linking network polymer, most of the stannyl groups must remain in the network polymer in our irradiation condition except for elimination of the stannyl groups in part from the polymer. In fact no change in the Sn/C atomic ratio ($\approx$1/11) was observed by XPS analysis of the irradiated polymer before and after the development. The remaining stannyl group must be oxidized to SnO_2 during the thermal decomposition of the network polymer, although details are not clear at the present stage.

In thermal decomposition of polymers, formation of cross-linking network in the polymers will in general affect the degradation products or the rate of degradation. The pyrolysis of an unirradiated film of **1** at 500 °C for 2 h did not give SnO_2 film. The elemental analysis by XPS indicated that a trace amount of SnO_2 and graphite were left on the quartz plate. It is known

that pyrolysis of polystyrene derivatives gives their monomers under some conditions.[9] This could explain the present case: pyrolytic depolymerization occurs to give the corresponding styrene monomer and the monomer would be vaporized. The network may prevent a low molecular weight intermediate in the SnO_2 formation from escaping out of the polymer film and be, therefore, necessary for the conversion of **1** into SnO_2 in the solid state. We examined the pyrolysis of an irradiated film of **1** without applying the wet development. A negative pattern of SnO_2 similar to that obtained with the development was also formed at the irradiated part (Figure 3). The formation of SnO_2 did not occur in the unirradiated part of **1**, possibly owing to the pyrolytic depolymerization of **1** (see above), and this demonstrated a possibility for the reduction in the patterning process by omitting the wet development process, although the spatial resolution of the pattern at present, however, is not as high as that using the wet development. An optimization of the pyrolysis conditions will improve the spatial resolution.

The present work has demonstrated that an organotin polystyrene derivative **1** is a photoreactive precursor of SnO_2 thin films. Our method of preparing SnO_2 thin films has advantages over the conventional method[10] using low molecular weight tin compounds such as $SnCl_4$ or dibutyltin diacetate: (1) patterning of SnO_2 is available; (2) the use of poisonous low molecular weight tin compounds can be avoided. The lithographic photoirradiation of thin films of **1** causes the cross-linking of the polymer, which has been found to be necessary both for patterning and for molding during the pyrolytic conversion of **1** into SnO_2 without evaporation or diffusion of the pattern.

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(10) (a) Yagi, I.; Ikeda, E.; Kuniya, Y. *J. Mater. Res.* **1994**, *9*, 663 and references therein. (b) Also see the review: Dawar, A. L.; Joshi, J. C. *J. 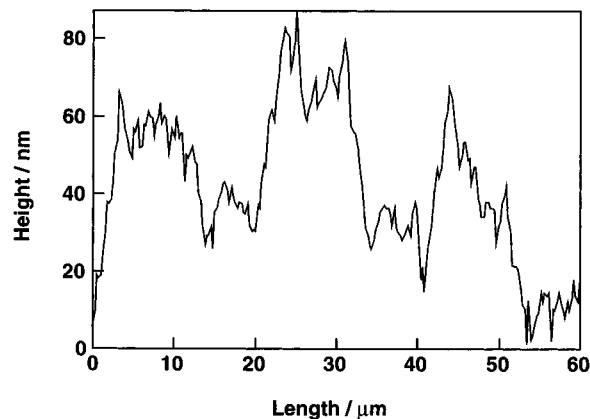Mater. Sci.* **1984**, *19*, 1.