Formation of SnO_2 Thin Film by Pyrolysis of a Photo-Cross-Linked Organotin Polymer

Toshiyuki Tamai*,† and Nobuyuki Ichinose*,‡,§

Osaka Municipal Technical Research Institute, 1-6-50 Morinomiya, Joto-ku, Osaka 536-8553, Japan, and Kansai Research Establishment, Japan Atomic Energy Research Institute, 25-1 Mii-minamimachi, Neyagawa, Osaka 572-0019, Japan

Received August 26, 1999; Revised Manuscript Received January 31, 2000

ABSTRACT: Micropatterns of a SnO_2 thin film were obtained by lithographic photoirradiation followed by pyrolysis of thin films of an organotin polymer poly(4-((trimethylstannyl)methyl)styrene) (**1**). Irradiation of the polymer thin film by a KrF laser through a photomask followed by development gave a negative pattern of the insolubilized polymer. The following pyrolysis afforded a pattern of SnO_2 without significant deformation of the pattern except for a reduction of the film thickness. The pyrolysis of the irradiated film without the development also gave a negative pattern of SnO_2. The cross-linking of the organotin polymer caused by the irradiation was necessary both for lithographic processing and for SnO_2 formation. In the conversion of the polymer to SnO_2 during the pyrolysis, the cross-linked network seems to encapsulate low molecular weight intermediates, preventing their escape from the polymer film.

Introduction

Films of SnO_2 have optical transparency and electric conductivity and can be of importance for preparing light-transmitting electrodes for optoelectronic devices.[1−3] SnO_2 is also useful as a coating material owing to its high chemical stability. On the other hand, the chemical stability prevents patterning of SnO_2 thin films by wet etching. SnO_2 thin films are generally prepared by vacuum evaporation, sputtering, chemical vapor deposition, dip coating, and spray pyrolysis.[1−3] Spray pyrolysis is a simple method that is particularly advantageous for large-area coating.[2,3] $SnCl_4$ and low molecular weight organotin compounds are typical source compounds for spray pyrolysis, and their thermal decomposition mechanism has been studied intensively.[3] However, these low molecular weight precursors are known to be poisonous.

The use of a polymeric precursor will resolve the problems of patterning and toxicity. Patterning of polymeric materials can be performed by the photolithographic techniques. Photolithographic techniques used in the patterning of organic and inorganic materials have recently received much attention for preparing interfaces in various microdevices.[4,5] Introduction of organotin groups into a polymer structure would reduce their vaporization in air and solubility into biotissues. Polystyrene derivatives are typical polymers that can be easily synthesized. If a heteroatom functionality (X) is introduced at the benzylic position of poly(4-methylstyrene), the benzylic C−X bond is generally sensitive to ultraviolet light of <300 nm.[6] We have studied the UV-laser irradiation of polymer surfaces to introduce various chemical functionalities.[7,8] An example is the formation of carboxylic acid groups at the film surface and the insolubilization of thin films of poly(4-((trimethylsilyl)methyl)styrene) (PTMSMS) upon KrF laser irradiation.[7] Selective cleavage of the benzylic C−Si bond of PTMSMS by the irradiation gave a benzyl-type radical, which reacts with oxygen leading to the formation of carboxylic acid or to coupling yielding a cross-linked structure. The cross-linking reaction was an apparent two-photon reaction, which is characteristic of the laser-induced reaction. By contrast, irradiation of polystyrene caused oxidative degradation of the polymer main chain, which was initiated by the C−H bond cleavage of the polymer main chain followed by a radical-chain reaction.

We now report on the patterning of SnO_2 thin films by a combination of lithographic photoirradiation and pyrolysis of films of poly(4-((trimethylstannyl)methyl)-styrene) (**1**).[9] Photoirradiation causes cross-linking that is necessary both for the lithographic processing and for SnO_2 formation.[10,11] The effect of the cross-linked network formation on the thermal degradation rate of the polymers was studied by thermal gravimetric analysis (TGA). We discuss the mechanism of the pyrolytic conversion of the organotin polymer to SnO_2 in the cross-linked network which would encapsulate the precursor of SnO_2 during the pyrolysis.[5]

Experimental Section

Polymer **1** ($M_w = 2.1 \times 10^4$, $M_n = 3.4 \times 10^4$, $M_w/M_n = 1.7$, determined by GPC using polystyrene standard samples)[11b,12] and poly(4-((trimethylsilyl)methyl)styrene) (PTMSMS, $M_w = 7.7 \times 10^4$, $M_n = 3.4 \times 10^4$, $M_w/M_n = 2.3$)[13] were prepared by the radical polymerization of 4-((trimethystannyl)methyl)-styrene (**2**) and 4-((trimethylsilyl)methyl)styrene (TMSMS),[14] respectively. Thin films (0.6−1 μm thickness) of **1** and PTMSMS were prepared by spin-coating on quartz plates (29 mm diameter, 1 mm thickness) from their toluene solutions (80 g/L). The polymer films were irradiated in air in contact with a photomask or directly with a laser beam (248 nm, 15 mJ cm^{-2} $pulse^{-1}$) from a Lumonics PM-884 excimer laser operated with a KrF gas mixture at 10 Hz through a beam homogenizer (Leonix EWO-FI-60-248, beam size 12 × 12 mm^2). The irradiated polymer films were developed with xylene for 5 min, dried in air, and observed by contact mode atomic force microscopy (AFM, Topometrix TMX-2100). The surface composition of the films was analyzed by measuring Sn_{3d}, O_{1s}, and C_{1s} X-ray photoelectron spectra with a Shimadzu ESCA-850S spectrometer. X-ray photoelectrons were collected at a take-off angle

† Osaka Municipal Technical Research Institute.
‡ Japan Atomic Energy Research Institute.
§ Present address: The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki 567-0047, Japan.

10.1021/ma991461b CCC: $19.00
Published on Web 03/11/2000

of 90° with respect to the sample surface. The carbon 1s binding energy (284.6 eV) for a trace amount of hydrocarbon originally present in air was used to calibrate the binding energy. The UV spectra of the film were measured on a Shimadzu UV-2100 spectrophotometer. The films of **1** (200 μm thickness) cast on quartz plates from its toluene solutions (333 g/L) were irradiated by an electron beam (380 krad s^{-1}, a Van de Graaff accelerator, Nisshin-High Voltage, model AK-S) for 40 min in air. Thermal gravimetric analysis (TGA) was performed with Seiko TG/DTA 220. Samples were heated from 30 to 590 °C at a rate of 10 °C min^{-1} in air.

Results and Discussion

A thin polymer film of **1** (0.68 μm thickness) was irradiated with 200 pulses using a KrF excimer laser (15 mJ cm^{-2} $pulse^{-1}$) in air on the area of 12 × 12 mm^2. 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, despite the slight dissolution of the surface thin layer (<0.1 μm) of the irradiated area that was observed by atomic force microscopy (AFM). After development, pyrolysis of the film in air in an electric oven at ca. 500 °C for 2 h gave a transparent thin film. The thin film was in good contact with the quartz substrate without any cracks or peeling. Elemental analysis of the film surface by X-ray photoelectron spectroscopy (XPS) showed peaks of Sn($3d_{5/2}$) at 487.0 eV, Sn($3d_{3/2}$) at 495.5 eV, and O_{1s} at 531.1 eV, indicating the formation of SnO_2.[15] The UV absorption spectrum of the SnO_2 was identical to that reported[16] showing an onset at 321 nm, from which the band gap energy was estimated to be 3.9 eV. This value agreed with that reported previously.[16] Similar irradiation of films of **1** through a photomask followed by the development gave a negative pattern of the polymer. The pyrolysis yielded a pattern of SnO_2 without a significant deformation of the pattern, though a reduction of the film thickness from 0.60 to 0.15 μm was observed by AFM as shown in Figure 1.

((Trialkylstannyl)methyl)benzene (benzyltrialkylstannane) undergoes photochemical cleavage of the benzylic C−Sn bond to yield a benzyl-type radical via its excited state in a high quantum yield.[17] It is supposed that the photoirradiation of **1** induces a cross-linked network formation involving benzyl-type radicals as key intermediates and leads to the insolubilization of the film. Formation of the polymer network will in general affect the thermal degradation products or the rate of degradation.[5,18] The pyrolysis of an unirradiated film of **1** at ca. 500 °C for 2 h did not lead to a SnO_2 film. Elemental analysis by XPS indicated that only a trace amount of carbonaceous substance containing SnO_2 was left on the quartz plate. Poly(4-((trimethylsilyl)methyl)styrene) (PTMSMS), an analogue of **1**, is also photo-cross-linkable.[8] However, a similar pyrolysis of a photo-cross-linked PTMSMS film did not yield a SiO_2 film.

Thermal gravimetric analyses (TGA) of the cross-linked and un-cross-linked polymers were carried out to study their pyrolytic decomposition. The film of **1** (200 μm thickness) cast from its toluene solution was irradiated for 40 min by an electron beam (EB, 380 krad s^{-1}) from a Van de Graaf accelerator in air at room temperature, yielding bulk of cross-linked **1**.[19] The irradiated film was completely insoluble and did not swell in xylene. TGA profiles of the cross-linked (EB-irradiated) and un-cross-linked (unirradiated) **1** from 30 to 590 °C in air are shown in Figure 2. The weight of the un-cross-linked **1** decreased gradually as the temperature was raised from 280 to 590 °C. The decomposition point was 333 °C. The weight of the cross-linked **1** decreased gradually from 50 to 500 °C at a slower rate than that of un-cross-linked sample and then decreased rapidly at 507 °C; the weight loss based on the initial weight was 43% at 500 °C (61% for un-cross-linked **1**) and 57% at 510 °C. The total weight loss was 60% for the cross-linked **1** and 69% for the un-cross-linked **1**. The result of the un-cross-linked **1** is similar to that of polystyrene.[20] The polystyrene decomposes above ca. 280 °C mainly by depolymerization. In the cross-linked **1**, the slow weight loss under 280 °C may be due to the loss of low molecular weight components that are formed by the main chain scission induced by EB irradiation. The

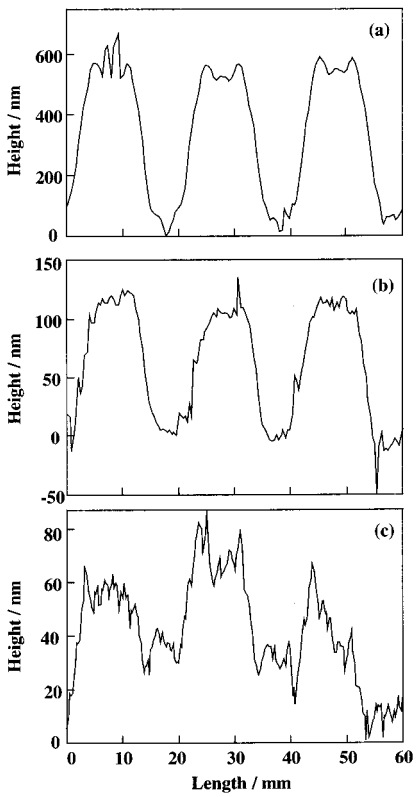


Figure 1. Cross-sectional images obtained by contact mode atomic force microscopy (AFM) of the line and space patterns made of **1** prepared by the lithographic irradiation and the development with xylene (a) and SnO_2 prepared by pyrolysis of irradiated films of **1** with development (b) and without development (c) (see text).

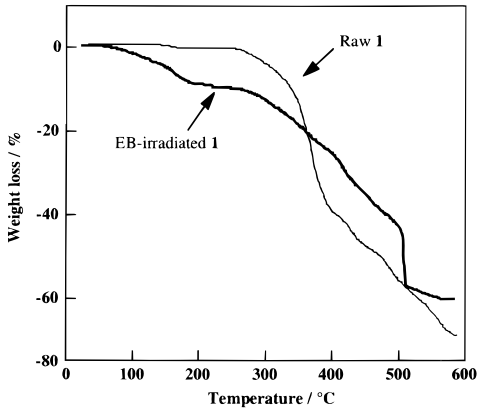


Figure 2. TGA profiles for electron beam (EB) irradiated and unirradiated **1**.

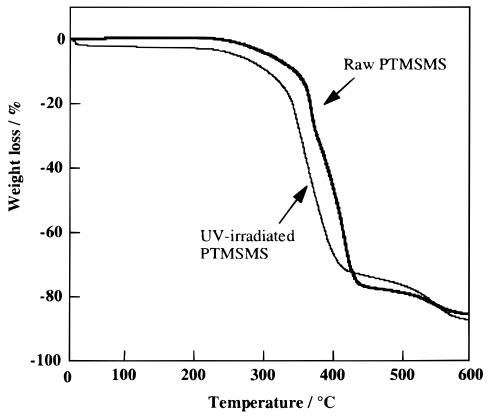


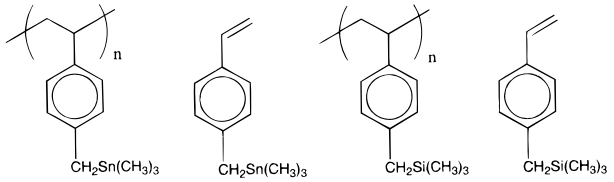
Figure 3. TGA profiles for KrF laser (UV) irradiated and unirradiated PTMSMS.

following slow weight loss from 280 to 500 °C could be due to a thermal decomposition of the polystyrene structure, which is less efficient than that of the un-cross-linked **1**. The rapid decrease at 507 °C is probably due to the pyrolytic conversion of the organotin groups to SnO_2. These contrasting results show that the cross-linking affects the conversion of **1** to SnO_2. TGA of the cross-linked (KrF laser-irradiated) and un-cross-linked (unirradiated) PTMSMS samples was also performed. Both PTMSMS samples showed similar TGA profile as shown in Figure 3. The weight decreased gradually from 280 to 430 °C, and the weight losses at 510 °C were ca. 80%. The cross-linking scarcely affected the pyrolytic decomposition of PTMSMS. Their decrease of weight was faster and ended at a lower temperature than that of un-cross-linked **1**.

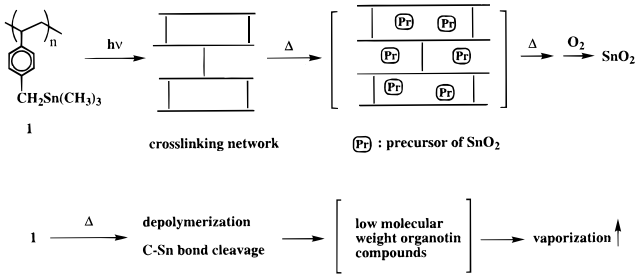
Photoirradiation of **1** causes the benzylic C−Sn bond to cleave, forming a benzyl-type radical and a trimethylstannyl radical. The stannyl radical could probably react with molecular oxygen or dimerize to give low molecular weight organotin compounds such as stannol, stannoxane, and distannane, although the details are not clear at present. The benzyl-type radical in the film surface layer would in part react with molecular oxygen from air. Inside the film, the concentration of oxygen is low and some of the benzyl-type radicals may undergo coupling to form a cross-linked network. However, most of the benzyl-type radicals would undergo recombination with the stannyl radical reproducing the benzylstanane structure. Because the glass transition temperature of **1** lies above room temperature[12] and the mobility of the benzyl-type radical is expected to be low under the present conditions, most of stannyl groups would remain unchanged after the photoirradiation. In fact, no change in the Sn/C atomic ratio (≈1/11) was observed by XPS analysis of the irradiated polymer before and after the development. The remaining trimethylstannyl groups and the low molecular weight organotin compounds in the network polymer must be oxidized to SnO_2 during the pyrolysis.[21] Photoirradiation and EB irradiation cross-link the polymer chains in a different manner. EB irradiation would give methine radicals in the main chain, which couple, yielding a cross-linked network.[22]

In the un-cross-linked polymer film precursors of SnO_2 such as the low molecular weight organotin compounds would evaporate during the pyrolysis. It is known that pyrolysis of polystyrene derivatives gives their monomers under certain conditions,[23] and in the un-cross-linked polymer film, pyrolytic depolymerization should occur to yield the monomer 4-((trimethystannyl)-

Scheme 1



Scheme 2



methyl)styrene (**2**), which decomposes to low molecular weight volatile organotin compounds.

We examined the pyrolysis of a photoirradiated film of **1** without applying the wet development. A negative pattern of SnO_2 similar to that obtained with the development was also formed (Figure 1c). The formation of SnO_2 did not occur in the unirradiated part of **1**, possibly owing to the pyrolytic depolymerization of **1** and the following evaporation of the low molecular weight compounds. This demonstrates a possibility of simplifying the patterning process by omitting the wet development, although the spatial resolution of the patterning is, at present, not as high as that with the wet development. The pyrolysis of a low molecular weight organotin compound bis(tributyltin)oxide in the cross-linked and un-cross-linked PTMSMS film was also studied. The PTMSMS film containing 1 mol equiv of bis(tributyltin)-oxide to the (trimethylsilyl)methyl group was prepared by spin-coating on a quartz plate. The photoirradiated and unirradiated films were pyrolyzed at ca. 500 °C for 2 h in air. Only the irradiated sample yielded a SnO_2 film. These results show that the polymer films containing organotin compounds need to be cross-linked for conversion of the organotin group to SnO_2 by pyrolysis.

The conversion of **1** to SnO_2 requires the cross-linking network, which retards the depolymerization of **1** and encapsulates the low molecular weight intermediates, preventing their escape from the polymer film (Scheme 2).[24,25] The pyrolysis of a cross-linked PTMSMS film did not yield a SiO_2 film. In the TGA of PTMSMS, the cross-linking did not affect the TGA profile drastically, in contrast to those of **1**, and the weight loss was faster and ended at a lower temperature than that of un-cross-linked **1**. It is expected that the thermal decomposition of the trimethylsilyl group during the pyrolysis is less efficient owing to the high CH_3−Si bond dissociation energy as compared to that of the CH_3−Sn bond (the mean bond dissociation energies at 298 K: CH_3−Si-$(CH_3)_3$, 317.7 kJ mol^{-1}; CH_3−Sn$(CH_3)_3$, 223.9 kJ mol^{-1}).[26] The boiling point of 4-trimethylsilylmethylstyrene (TMSMS) under atmospheric pressure is expected to be lower than that of **2** (boiling points under reduced pressure: TMSMS, 79−81 °C under 133.3 Pa; **2**, 70 °C under 9.3 Pa).[13,14a] TMSMS would be more volatile and stable thermally than **2**. Around 300 °C, both **1** and

PTMSMS would start to decompose to corresponding styrene monomers. It is assumed that **2** decomposes without evaporation to give low molecular weight fragments (the precursor of SnO_2), which will stay inside the cross-linked film until 500 °C and then will be converted to SnO_2. TMSMS would evaporate from 300 to 400 °C without pyrolytic decomposition to SiO_2. This different behavior of **2** and TMSMS could explain the contrasting result of the pyrolysis of the films.

The present work has demonstrated that an organotin polymer **1** is a SnO_2 precursor and is activated by photochemical cross-linking network formation. The photochemical cross-linking is necessary for the lithographic processing of the film as well as for the SnO_2 formation. The cross-linked network acts as a microscopic reactor for the conversion of the organotin groups to SnO_2 during the pyrolysis. The present method for preparing SnO_2 thin films has two advantages over the conventional method[1−3] using low molecular weight tin compounds such as $SnCl_4$ or dibutyltin diacetate: (1) patterning of SnO_2 is possible; (2) the use of poisonous low molecular weight tin compounds is avoided. In addition, we have demonstrated a possible simplification of the patterning process by omitting the wet development process. Optimization of the pyrolysis conditions will improve the spatial resolution of the patterning.

Acknowledgment. The authors are indebted to Professor K. Mizuno (Osaka Prefecture University) and Dr. M. Izaki (Osaka Municipal Technical Research Institute: OMTRI) for helpful discussions and Dr. Y. Agari (OMTRI) for thermal gravimetric analysis measurements.

References and Notes

(1) Park, S. H.; Son, Y. C.; Willis, W. S.; Suib, S. L.; Creasy, K. E. *Chem. Mater.* **1998**, *10*, 2389 and references therein. Also see review: Dawar, A. L.; Joshi, J. C. *J. Mater. Sci.* **1984**, *19*, 1.

(2) Shanthi, E.; Banerjee, A.; Dutta, V.; Chopra, K. L. *J. Appl. Phys.* **1982**, *53*, 1615. Haitjema, H.; Woerlee, G. F. *Thin Solid Films* **1989**, *169*, 1. Fujimoto, M.; Urano, T.; Murai, S. *Jpn. J. Appl. Phys.* **1989**, *28*, 2587.

(3) Yagi, I.; Kaneko, S. *Chem. Lett.* **1992**, 2345. Yagi, I.; Ikeda, E.; Kuniya, Y. *J. Mater. Res.* **1994**, *9*, 663.

(4) Sugawara, T.; Matsuda, T. *Macromolecules* **1994**, *27*, 7809. Bergstedt, T. S.; Hauser, B. T.; Schanze, K. S. *J. Am. Chem. Soc.* **1994**, *116*, 8380. Potochnik, S. J.; Pehrsson, P. E.; Hsu, D. S. Y.; Calvert, J. M. *Langmuir* **1995**, *11*, 1841. Rozsnyai, L. F.; Wrighton, M. S. *Langmuir* **1995**, *11*, 3913. Avey, A. A.; Hill, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 237. Pirrung, M. C. *Chem. Rev.* **1997**, *97*, 473. Bohme, P.; Vedantham, G.; Przybycien, T.; Belfort, G. *Langmuir* **1999**, *15*, 5323. Xia, Y.; Rogers, J. A.; Paul, K. E.; Whitesides, G. M. *Chem. Rev.* **1999**, *99*, 1823.

(5) Watanabe, A.; Komatsubara, T.; Ito, O.; Matsuda, M. *J. Appl. Phys.* **1995**, *77*, 2796.

(6) Imamura, S.; Sugawara, S. *Jpn. J. Appl. Phys.* **1982**, *21*, 776. Nakayama, Y.; Matsuda, T. *Macromolecules* **1996**, *29*, 8622.

(7) Ichinose, N.; Kawanishi, S. *Macromolecules* **1996**, *29*, 4155; *Langmuir* **1997**, *13*, 5805.

(8) Tamai, T.; Hashida, I.; Ichinose, N.; Kawanishi, S.; Inoue, H.; Mizuno, K. *Polymer* **1996**, *37*, 5525. Ichinose, N.; Tamai, T.; Kawanishi, S.; Hashida, I.; Mizuno, K. *Langmuir* **1997**, *13*, 2603.

(9) Preliminary communications: Tamai, T.; Ichinose, N.; Kawanishi, S.; Nishii, M.; Sasuga, T.; Hashida, I.; Mizuno, K. *Chem. Mater.* **1997**, *9*, 2674. Tamai, T.; Ichinose, N.; Agari, Y. *Macromol. Rapid Commun.* **1999**, *20*, 179.

(10) Pyrolysis of polystannane giving SnO_2 has been reported. Imori, T.; Lu, V.; Cai, H.; Tilley, T. D. *J. Am. Chem. Soc.* **1995**, *117*, 9931.

(11) Organotin polymers for electron beam and UV lithography were reported: (a) MacDonald, S. A.; Steinmann, F.; Ito, H.; Lee, W.-Y.; Willson, C. G. *Polym. Mater. Sci. Eng.* **1983**, *49*, 104. Labadie, J. W.; MacDonald, S. A.; Willson, C. G. *J. Imaging Sci.* **1986**, *30*, 169. Labadie, J. W.; MacDonald, S. A.; Willson, C. G. *Macromolecules* **1987**, *20*, 10. (b) Kato, N.; Yamazaki, N.; Nagasaki, Y.; Kato, M. *Polym. Bull.* **1994**, *32*, 55.

(12) Kawakami, Y.; Hisada, H.; Yamashita, Y. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 1307.

(13) Nakanishi, K. Ph.D. Thesis, University of Osaka Prefecture, 1993.

(14) (a) Reynolds, W. F.; Hamer, G. K.; Bassindale, A. R. *J. Chem. Soc., Perkin Trans. 2* **1977**, 971. (b) Kawakami, Y.; Karasawa, H.; Aoki, T.; Yamamura, Y.; Hisada, H.; Yamashita, Y. *Polym. J.* **1985**, *17*, 1159.

(15) Morgan, W. E.; Van Wazer, J. R. *J. Phys. Chem.* **1973**, *77*, 964. Lin, A. W. C.; Armstrong, N. R.; Kuwana, T. *Anal. Chem.* **1977**, *49*, 1228.

(16) Nagasawa, M.; Shinoyama, S.; Makishima, S. *Jpn. J. Appl. Phys.* **1965**, *4*, 195. Bedja, I.; Hotchandani, S.; Kamat, P. V. *J. Phys. Chem.* **1994**, *98*, 4133.

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

(18) Ohshita, J.; Yamashita, A.; Hiraoka, T.; Shinpo, A.; Kunai, A.; Ishikawa, M. *Macromolecules* **1997**, *30*, 1540.

(19) TGA of photo-cross-linked **1** is preferable to compare its result with that of the pyrolysis of the photoirradiated thin film of **1**. However, **1** has a large absorption cofficient (1.85×10^4 cm^{-1}), and only its thin film (<0.4 μm) is expected to be photo-cross-linkable. Photo-cross-linking was not suitable for preparation of an appropriate amount of cross-linked **1** for TGA. Therefore, EB-cross-linking was adopted for this purpose.

(20) Karasz, F. E.; Bair, H. E.; O'Reilly, J. M. *J. Phys. Chem.* **1965**, *69*, 2657. Inoue, H.; Helbig, M.; Vogl, O. *Macromolecules* **1977**, *10*, 1331.

(21) The film thickness was reduced from 0.6 to 0.15 μm upon the pyrolytic conversion of **1** to SnO_2. The expected thickness of the SnO_2 film is calculated to be around 0.06 μm from the density of **1** and SnO_2 for quantitative conversion of the tin group in **1** to SnO_2. The SnO_2 films prepared by the present method may have some defects or vacant space inside the film, although crack or defect was not observed on the film surface by AFM.

(22) Kato, N.; Takeda, K.; Nagasaki, Y.; Kato, M. *Ind. Eng. Chem. Res.* **1994**, *33*, 417.

(23) Itsuno, S.; Ito, K. *J. Org. Chem.* **1990**, *55*, 3950 and references therein.

(24) The pyrolysis of an unirradiated **1** at ca. 250 °C for 20 min gave a solid insoluble in xylene. In the course of pyrolysis of unirradiated **1** in an electric oven at ca. 500 °C, thermal cross-linking may occur under 250 °C; however, the extent of cross-linking would be insufficient for retarding the depolymerization and for the encapsulation.

(25) Hardening of resist patterns by UV irradiation for preventing the flow of lithographic microimage of the resist at temperatures above 210 °C was reported: Hiraoka, H.; Pacansky, J. *J. Vac. Sci. Technol.* **1981**, *19*, 1132; *J. Electrochem. Soc.* **1981**, *128*, 2645.

(26) Pilcher, G.; Skinner, H. A. In *The Chemistry of the Metal−Carbon Bond*; Hartley, F. R., Patai, S., Eds.; John Wiley: Chichester, 1982; Vol. 1, Chapter 2, p 69.

MA991461B