## Micropatterning of Organic–Inorganic Hybrid Film Using Photosensitive Sol–Gel System Consisting of Double-decker-shaped Multifunctional Silsesquioxane

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The micropatterning of an organic–inorganic hybrid film consisting of a double-decker-shaped multifunctional silsesquioxane was achieved using a photosensitive sol–gel system containing a titanium alkoxide modified with  $\beta$ -diketone. Negative patterns with a high-resolution of ca. 1 µm were obtained by UV-irradiation.

The organic-inorganic hybrid materials have received considerable interest in the past decade because of the prospect of developing materials with unique microstructures at the nanometer scale and properties which cannot be obtained from either a single material or conventional composites mixed on a micrometer scale. The most extensively explored approach to preparing the organic-inorganic nanohybrids is the incorporation of metal nanoparticles into a polymer matrix. For example, the hybridization of silica nanoparticles and a polymer matrix yields unique thermal, mechanical, and chemical properties,<sup>1</sup> where inorganic moieties are prepared by sol-gel technique. Recently, new approach to nanohybrid materials using polyhedral oligomeric silsesquioxane (POSS) as an inorganic moiety has attracted a lot of attention.<sup>2</sup> The POSS has a nanometer-sized silica-like cage structure functionalized with various kinds of organic groups.<sup>3</sup> The POSS as a building block provides elegant designs and the controllable reaction for organic-inorganic hybrid materials. The interface between organic and inorganic moieties can be controlled by the chemical reaction of the functional group of POSS. By changing the POSS structure, for example, the organic side chains and the ring structure, we can control the nanostructure of a hybrid film. In this paper, we report the micropatterning using a novel photosensitive organic-inorganic hybrid system consisting of a multifunctional silsesquioxane.

The double-decker-shaped silsesquioxane (DDSQ) is a multifunctional silsesquioxane with a wide variety of functional groups.<sup>4</sup> The chemical structure of the DDSQ silanol (DDOH) which has an open-cage structure with four silanol and eight phenyl (Ph) groups is depicted in Scheme 1. The DDOH was purchased from Chisso Petrochemical Corporation. The silanol group has a high reactivity with metal alkoxides and forms a Si-O-metal bond. The mixing of multifunctional DDOH and titanium methacrylate triisopropoxide (TMTP) in 2-methoxyethanol gave white precipitates immediately. This result suggests the reaction of the silanol group of DDOH with isopropoxide group of TMTP. The reaction rate can be controlled by the chelate formation of the metal alkoxide with a  $\beta$ -diketone because the chelate ring is in general durable against hydrolysis.<sup>5</sup> In the case of the TMTP combined with benzoyl acetone (BA) as a chelate agent, the chemical structure (I) as depicted in Scheme 1 is expected for the modified metal-alkoxide. A clear yellow solution was prepared by mixing a 0.025 M DDOH and a 0.1 M TMTP/BA chelate in 2-methoxyethanol. The mixed solution showed no precipitation for several days at room temperature in contrast to that of DDOH and TMTP without BA. An excess molar ratio of the isopropoxide group to the silanol group was employed to reduce the residual silanol group in the hybrid film. The DDOH/TMTP/BA hybrid film was prepared by spin-coating of the solution onto a glass substrate (2000 rpm, 30 s) and post-baked for 1 min at 130 °C on a hotplate. The methacrylate group of the TMTP is a soft-segment to prevent cracking of the sol–gel film.

Figure 1 shows the absorption spectra of DDOH, TMTP, BA, and the hybrid film spin-coated on a quartz substrate. The



Scheme 1. Chemical structures of double-decker-shaped silsesquioxane silanol (DDOH), titanium methacrylate triisopropoxide (TMTP), benzoyl acetone (BA), and  $\beta$ -diketonato complex of TMTP (I).



Figure 1. Absorption spectra of (a) DDOH, (b) TMTP, (c) BA in 2-methoxyethanol, and (d) DDOH/TMTP/BA hybrid film.



**Figure 2.** Changes in optical absorption spectra under UV-irradiation for DDOH/TMTP/BA hybrid film.

absorption band of the DDOH at 263 nm is assigned to the phenyl group substituted to the silsesquioxane cage. The broad absorption band of the TMTP in the UV region is attributable to the methacrylate group. The BA showed strong absorption band at 309 nm, which completely disappeared in the absorption spectrum of the DDOH/TMTP/BA hybrid film and new bands were observed at 365 and 269 nm as shown in Figure 1d. These absorption bands can be attributed to the chelate ring as depicted in Scheme 1.<sup>5</sup> Figure 2 shows the changes in optical absorption spectra of the DDOH/TMTP/BA hybrid film under UV-irradiation. The UV-irradiation using a high-pressure mercury lamp  $(360 \,\mathrm{mW/cm^2})$  brought about the decrease of the intensity of both absorption bands. The absorption bands at 365 and 269 nm almost disappeared and the film became transparent after the UV-irradiation for 10 min. The monochromatic UV irradiation at the wavelength of 365 nm using a mercury-xenon lamp with an interference filter also caused the uniform photobleaching of both the bands at 365 and 269 nm. After the UV irradiation using the high-pressure mercury lamp, the decrease of the film thickness from 211 to 177 nm was observed.

The photosensitive sol-gel system was applied to fabricate the micropatterns of the organic-inorganic hybrid film consisting of DDOH. By photodecomposition of the chelate ring, the reaction between DDOH and TMTP can be initiated, which induces the characteristics of a negative resist. Figure 3a shows an optical micrograph of the micropatterns of the hybrid film obtained by UV-irradiation using a high-pressure mercury lamp for 10 min through a photomask, where unirradiated area was removed by development using toluene as an eluent. A highresolution line and space pattern with 1 µm period is seen in the micrograph. Such micropatterns showed a high thermal stability up to 300 °C. Figure 3b is the micropattern prepared by laser-direct drawing technique using the 248.6-nm line of a Ne-Cu laser, where the laser beam was focused on the DDOH/TMTP/BA hybrid film using an objective lens and the focal point was scanned by a computer-controlled xyz stage. An optically transparent micropattern with various shapes can be prepared freely using such a laser direct drawing technique.

In conclusion, the micropatterning of an organic–inorganic film consisting of a multifunctional silsesquioxane was achieved using a photosensitive sol–gel system. New application possibilities of organic–inorganic nanohybrid materials in optoelectronic technology must be opened by the patternable characteristics in combination with the optically transparent and thermally



**Figure 3.** Optical micrographs of micropatterns of the DDOH/ TMTP/BA hybrid film prepared by (a) UV-irradiation through photomask and (b) laser-direct drawing using the 248.6-nm line of a Ne–Cu laser.

stable properties of silsesquioxanes. The hybridization method using  $\beta$ -diketonate complexes of metal alkoxides also makes it possible to incorporate various kinds of metals into silsesquioxane hybrid film and to modify the optoelectronic properties.

## References

- Y. Chujo, T. Saegusa, Adv. Polym. Sci. 1992, 100, 11; C. V. Avadhani, Y. Chujo, Appl. Organomet. Chem. 1997, 11, 153;
   R. O. R. Costa, W. L. Vasconcelos, J. Non-Cryst. Solids 2002, 304, 84; X. L. Ji, S. C. Jiang, X. P. Qiu, D. W. Dong, D. H. Yu, B. Z. Jiang, J Appl. Polym. Sci. 2003, 88, 3168;
   P. Hajji, L. David, J. F. Gerard, J. P. Pascault, G. Vigier, J. Polym. Sci. Polym. Phys. 1999, 37, 3172; T. Ogoshi, Y. Chujo, Macromolecules 2005, 38, 9110.
- P. G. Harrison, R. Kannengiesser, Chem. Commun. 1996, 415; J. V. Crivello, R. Malik, J. Polym. Sci., Part A: Polym. Chem. 1997, 35, 407; C. Zhang, F. Babonneau, C. Bonhomme, R. M. Laine, C. L. Soles, H. A. Hristov, A. F. Yee, J. Am. Chem. Soc. 1998, 120, 8380; C. Zhang, R. M. Laine, J. Am. Chem. Soc. 2000, 122, 6979; J. Choi, J. Harcup, A. F. Yee, Q. Zhu, R. M. Laine, J. Am. Chem. Soc. 2001, 123, 11420; K.-M. Kim, K. Adachi, Y. Chujo, Polymer 2002, 43, 1171; K.-M. Kim, Y. Chujo, J. Mat. Chem. 2003, 13, 1384.
- 3 Silicon-Containing Polymers, ed. by R. G. Jones, W. Ando, J. Chojnowski, Springer-Verlag, New York, 2000.
- 4 M. Seino, T. Hayakawa, Y. Ishida, M. Kakimoto, K. Watanabe, H. Oikawa, *Macromolecules* 2006, *39*, 3473; K. Yoshida, K. Ito, H. Oikawa, M. Yamahiro, Y. Morimoto, K. Ohguma, K. Watanabe, N. Ootake, U. S. Patent 20040249103A1. 1111.
- N. Tohge, G. Zhao, F. Chiba, *Thin Solid Films* 1999, 351, 85;
  H. Segawa, S. Adachi, Y. Arai, K. Yoshida, *J. Am. Ceram. Soc.* 2003, 86, 761.