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J. Am. Chem. Soc., **2008**, 130 (36), 11848-11849 • DOI: 10.1021/ja803852w • Publication Date (Web): 14 August 2008

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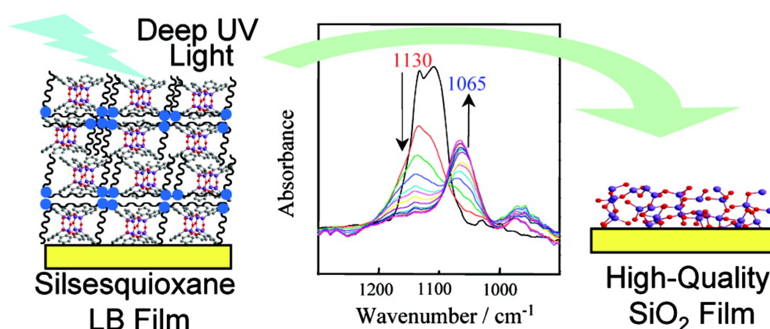

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Published on Web 08/14/2008

Photoinduced High-Quality Ultrathin SiO_2 Film from Hybrid Nanosheet at Room Temperature

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For developing industrial applications in the field of optoelectronics, development of a high-quality thin silicon dioxide (SiO_2) film has been increasingly important[1] despite the increasing popularity of alternative materials.[2] Diverse silicon oxidation methods and mechanisms have been investigated extensively in recent decades.[3] Thermally oxidized SiO_2 films are now commercially available and are generally grown or annealed at high temperatures (about 1000 °C) to yield high quality. However, these thermal methods can severely damage the substrate and engender defect formation. Consequently, a few organic polymers have become attractive as alternatives to permit the use of a plastic substrate.[4] Nevertheless, the thin organic dielectric films must not only have excellent electrical properties, but also processability, low roughness, and low concentrations of impurities. Moreover, it is difficult to satisfy the demands of commercial applications such as high performance, high breakdown voltage, and long-term stability. Therefore, for developing flexible devices with plastic substrates, low-temperature preparation of SiO_2 is urgently required.[5]

Results of prior studies have shown that organic−inorganic hybrid materials satisfy requirements such as ease of processability and compatibility. An ultrathin hybrid nanosheet containing polyoctahedral silsesquioxane (POSS) has been designed to prepare densely packed ultrathin POSS films using the Langmuir−Blodgett (LB)[6] technique. The LB technique enables POSS to have a multilayered structure with nanoscale precision. This nanoarchitecture is a good candidate for fulfilling further requirements for increasing device miniaturization. Herein, we demonstrate a flexible approach to building up high-quality ultrathin SiO_2 films using a deep UV lamp. An organic−inorganic hybrid nanosheet prepared using the LB technique[7] was used as a precursor for SiO_2 film preparation. Extremely smooth and robust SiO_2 film was produced at room temperature through photoirradiation.

The precursor hybrid material, poly(*N*-dodecylacrylamide-*co*-3-methacryloxypropyl-T8-heptaphenyl POSS), p(DDA/SQ) was synthesized using free radical polymerization (Figure 1a). Details related to the synthesis of p(DDA/SQ) are available in a previous report.[8] The p(DDA/SQ) nanosheet was deposited onto a substrate by vertical dipping with surface pressure at 30 mN/m using the LB technique. The absorbance of the nanosheet at 194 nm increases linearly with the increased number of deposited nanosheets (Supporting Information, Figure S1), underscoring the remarkable capability of a hybrid nanosheet to produce a multilayered structure with nanoscale precision. The surface morphology of the hybrid nanosheet showed quite a smooth surface and uniform distribution of POSS moieties in the p(DDA/SQ) nanosheets. The precursor p(DDA/SQ) nanosheets were irradiated to prepare a SiO_2 film. As illustrated by the AFM image depicted in Figure 1b, the photoirradiated film was flat (rms 0.45 nm in $2 \times 2\ \mu m^2$). The resulting film thickness, as measured using photoirradiation, was one-fifth

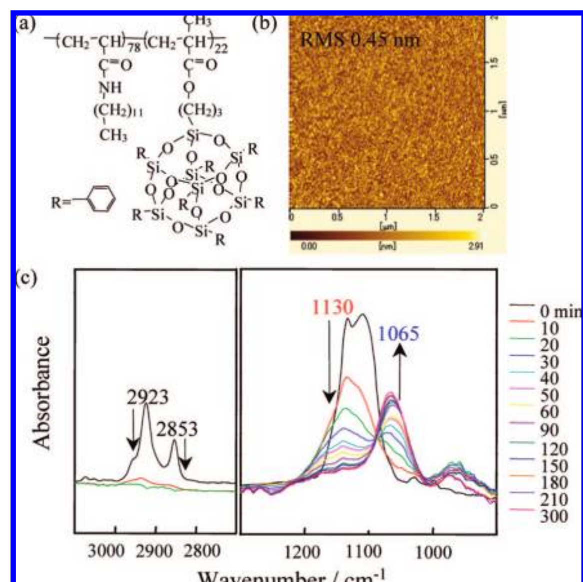

Figure 1. (a) Chemical structure of p(DDA/SQ); (b) tapping-mode AFM image of photooxidized SiO_2 film; (c) FTIR spectra of a p(DDA/SQ) hybrid nanosheet upon photoirradiation.

less than that of the pristine film, irrespective of the number of hybrid nanosheets. This predictable decrease in thickness is explainable by selective removal of organic moieties from the photoirradiated nanosheet. The photooxidized SiO_2 film density was also determined using a quartz crystal microbalance (QCM): 2.24 g/cm^3, which is comparable to that of a thermally oxidized SiO_2 film. Furthermore, the mechanical properties of hybrid nanosheets before and after photoirradiation were investigated using nanoindentation.[9] The hardness and shear modulus of the films changed considerably, from 0.19 and 2.62 GPa to 1.74 and 32.22 GPa, respectively. These dramatic changes in the density and mechanical properties are probably attributable to the change in chemical structure by photochemical reaction as well as the dissociation of organic moieties in hybrid nanosheets. The salient implication is that a Si−O−Si network structure based on SiO_2 can be created using photooxidation.

Figure 1c depicts FTIR spectra of p(DDA/SQ) nanosheets during photoirradiation at room temperature. The bands at 2853 and 2923 cm^{-1}, which are ascribed to symmetric and asymmetric vibrations of the C−H groups, decreased and subsequently disappeared with photoirradiation. Complete removal of DDA from the nanosheet by photoirradiation was also confirmed from the UV−vis spectra (Figure S3). The sharp absorption peak at 1130 cm^{-1} based on Si−O−Si cage structure decreased with photoirradiation. Corresponding to the decrease of 1130 cm^{-1} absorption peak, increased absorbance at 1065 cm^{-1} was observed. The peak position is

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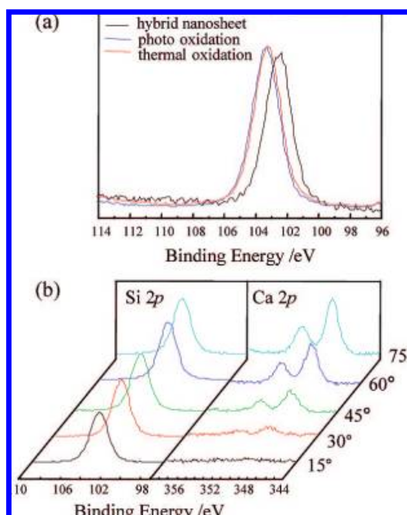

Figure 2. (a) XPS spectra of Si 2p core level for the hybrid nanosheet before photoirradiation (black), photooxidized SiO_2 (blue), and thermally oxidized SiO_2 film (red). (b) AR-XPS spectra on the takeoff angle from 15° to 75° of a photooxidized SiO_2 film.

identical to that of a Si−O−Si network structure of conventional SiO_2 film.[10] The experimental results provide an effective mechanism for photochemical reaction induced by deep UV irradiation. The energy of the deep UV lamp is sufficient for any bond energy in p(DDA/SQ); it results in photocleavage in the hybrid nanosheet. After cleavage of the bond, extremely reactive Si, O_2, and O species will immediately and mutually react to form silicon dioxide and a small amount of silanol.[11] It is noteworthy that no change in peak position (1065 cm^{-1}) was observed with varying the number of deposited layers.

X-ray photoelectron spectroscopy (XPS)[12] confirmed that the p(DDA/SQ) nanosheet is a good precursor for high-quality SiO_2 film formation at room temperature (Figure 2). The XPS spectra of the p(DDA/SQ) nanosheet, photooxidized SiO_2 film, and thermally oxidized SiO_2 film (Furuuchi Chemical Corp.) displayed strong Si 2p peaks at 102.48 eV, 103.25 eV, and 103.23 eV, respectively. The Si 2p peak (102.48 eV) of the hybrid nanosheet before photooxidation is based on Si groups of POSS. That peak was shifted to the Si 2p core levels of the typical SiO_2 film by photoirradiation. The Si 2p fwhm of photooxidized SiO_2 film showed 1.96 eV, in excellent agreement with that of the thermally oxidized SiO_2 film, which was purchased as a reference. Furthermore, to investigate the depth profile of the oxidation states, the angle-resolved XPS spectra were measured by changing the takeoff angle from 15° to 75°. No change in either of the Si 2p peak positions or fwhm of the photooxidized SiO_2 film was observed through the whole range, although the increase of the Ca 2p peak based on CaF_2 substrate as the takeoff angle increased. These results from the surface, bulk, and interface of the films suggest that the Si^{4+} concentration is uniform at all depths within the film, and that the photooxidized SiO_2 film is of high quality with no suboxide species. For typical SiO_2 film formation from Si by photo, ozone, or thermal oxidation, the transition layer formation is an unavoidable result at the SiO_2/Si interface.[1,13] This work provides a straightforward procedure for creating a high-quality ultrathin SiO_2 film. The p(DDA/SQ) nanosheets act as a versatile template for the SiO_2 film. Using them, it is possible to coat any substrate completely with p(DDA/SQ) nanosheets. The photooxidized SiO_2 film has another outstanding feature: photopatterning. Figure 3 portrays AFM images of photopatterned SiO_2 films. The SiO_2 film emerges in negative tone mode. The line width is identical to that of the photomask. The direct writing of SiO_2 patterns with high resolution offers a wide range of possibilities for practical applications.

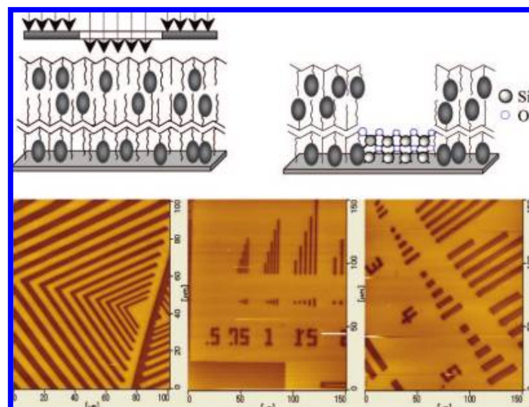

Figure 3. AFM images of the photopatterened SiO_2 films.

In summary, we have demonstrated a photoinduced high-quality SiO_2 film produced from a p(DDA/SQ) hybrid nanosheet. The method is simple and available at room temperature; photooxidation process requires no initiator or annealing process involving post-baking. We obtained an ultrathin, 1.6-nm-thick high-quality SiO_2 film, as demonstrated above. The film thickness is predictable and easily reproduced. Because it depends strongly on the amount of SQ in the hybrid nanosheet, the SiO_2 thickness can be determined easily by controlling the precursor hybrid nanosheet. This approach is a practical means to develop flexible optical and electrical devices.

Acknowledgment. This work was supported by Grants-in-Aid for Scientific Research (S) (no. 17105006) from the Japan Society for the Promotion of Science. This work was also supported by the Special Education and Research Expenses from the Ministry of Education, Culture, Sports, Science and Technology.

Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA803852W