Journal of Sol-Gel Science and Technology (2022) 104:485–489
https://doi.org/10.1007/s10971-022-05897-8

INVITED PAPER: FUNDAMENTALS OF SOL-GEL AND HYBRID MATERIALS PROCESSING

Alcohol-induced deboronation of organoborosilicate thin films

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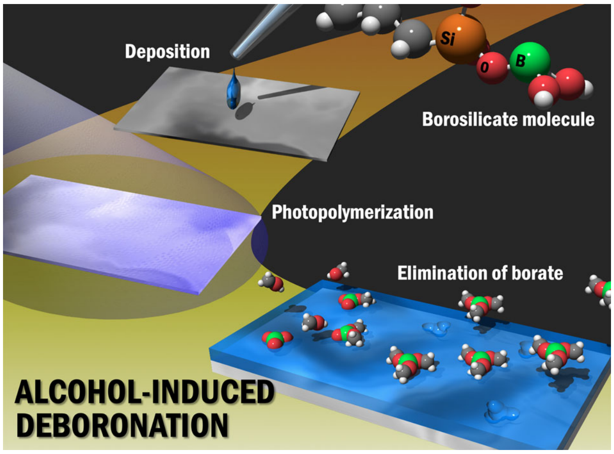
Received: 9 April 2022 / Accepted: 25 June 2022 / Published online: 14 July 2022

Abstract

The chemical and structural modification of organoborosilicate thin films was attempted by using alcohol-induced deboronation. A photocurable organoborosilicate was synthesized from 3-methacryloxypropyltrimethoxysilane and boric acid via a catalyst- and solvent-free and non-aqueous alcohol condensation process. The formation of Si-O-B linkage was suggested by ^{29}Si NMR spectroscopy. A colorless and transparent thin film of the organoborosilicate was prepared by UV irradiation. According to Fourier transform infrared spectroscopy, a peak attributed to the stretching vibration of borate disappeared after the alcohol treatment. Moreover, atomic force microscopy revealed the surface structural change of the thin film via the deboronation process. These results indicate that the borate was eliminated by the treatment, suggesting that this method enables to apply to the direct nanofabrication.

Graphical abstract



Keywords Borosilicate · Deboronation · Alcoholysis · Organic-inorganic hybrid · Microstructure · Thin film

Highlights

- A photocurable organoborosilicate was synthesized via catalyst- and solvent-free alcohol condensation.
- Borate was eliminated from the organoborosilicate thin film in the presence of methanol vapor.
- The thin film changed in chemical composition and structure due to methanol vapor treatment.

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- The deboronation from organoborosilicate is expected to apply to a new type of nanofabrication.

1 Introduction

Nanofabrication is a crucial technique in the semiconductor industry to manufacture highly integrated circuits at nanoscale resolution. The 3-nm fabrication processing, where the gaps between semiconductors are in the range of single nanometer scales (not a size of the object), is the most advanced fabrication in the industry and is very close to commercialization [1]. Generally, however, nanofabrication techniques require multi-step processes to fabricate patterned structures on the surface of substrates because pattern transfer processes from template layers to processing layers are mandatory. The resolution limit of the photolithography also hinders the integration of semiconductors.

In contrast, nanofabrication via self-assembly of molecules is expected as the next-generation fabrication approach. For instance, research on nanofabrication using molecular templating as the sacrificial nanopattern was reported [2]. Block copolymer self-assembly is also widely studied and has achieved single to tens nanometer fabrication [3]. These approaches are mainly based on the regulated molecular interactions such as van der Waals force, hydrophobic/hydrophilic interaction, amphiphilic interaction, and others [4]. Even in these processes, the resultant nanostructures of polymers must be transferred onto functional materials. A direct patterning via inorganic species is of great interest for the nanofabrication because the resultant patterns could be achieved without the transfer process, making the total fabrication more reliable and simpler.

To achieve such direct nanofabrication using inorganics as main components, we focused on the borosilicate glass as an attractive material. It is a type of glass which is composed of silicate and borate derivatives and forms porous structure by dissolving the borate phase in acids after the phase separation [5]. The conformation of the porous structure is random but bicontinuous structure as a result of spinodal decomposition between silicates and borates. On the other hand, we recently developed a novel synthetic method of organosilicates molecules which polymerize into an alternating copolymer network such as $-(\mathrm{Si-O-B-O-})_n$ [6–9]. Based on this achievement, it is possible to obtain organically modified borosilicate molecules (Fig. 1) as a precursor for organoborosilicates with a rational structure for nanofabrication. Deboronation after the formation of the thin film is possible for the chemical modification accompanied with physical (structural) change. Organic components will be used as the structure-directing agent (usually organic molecules which define the mesostructure of the resultant materials through the intermolecular interaction) for the nanofabrication. Therefore, this method will allow the borosilicate glass to form patterned organosilica structures in a molecular scale by the controlled micro phase separation.

In this work, the chemical and morphological change of the thin film after the deposition was attempted by the alcohol-induced deboronation of organoborosilicate thin films as the first step toward the establishment of the inorganic-based direct nanofabrication process. A photo-curable organoborosilicate was synthesized from 3-methacryloxypropyltrimethoxysilane and boric acid, and its thin films were prepared on substrates. An alcohol treatment was also carried out to eliminate the borate from the organoborosilicate thin film. Atomic force microscopy (AFM) revealed the surface structural change of the thin film via the deboronation process.

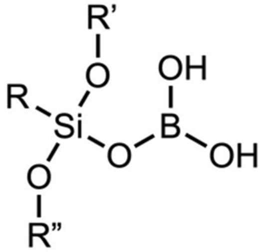
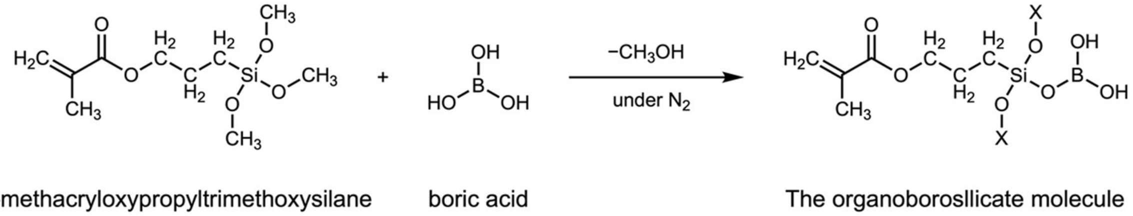


Fig. 1 Structure of the organoborosilicate molecule (R, R', and R'': organic functional groups, silicon, or boron)



Scheme 1 Proposed reaction scheme for the reaction of 3-methacryloxypropyltrimethoxysilane and boric acid (X: Si, CH_3, or H)

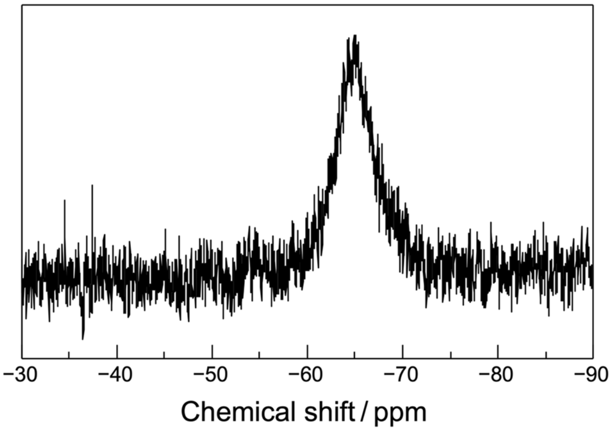


Fig. 2 ^{29}Si NMR spectrum of the organoborosilicate molecule in chloroform-*d*

2 Experimental

2.1 Materials

3-methacryloxypropyltrimethoxysilane (stabilized with dibutylhydroxytoluene), 1-hydroxycyclohexyl phenyl ketone (Omnirad 184), and 2-methyl-4′-(methylthio)-2-morpholinopropiophenone (Omnirad 907) were purchased from Tokyo Chemical Industry Co., Ltd. Boric acid ($B(OH)_3$), dichloromethane, chloroform-*d*, butyronitrile, and chromium(III) acetylacetonate were purchased from FUJIFILM Wako Pure Chemical Corporation. Tetramethylsilane was purchased from Sigma-Aldrich Co. LLC. All the reagents and solvents were of the highest quality available and were used as received. Glass and silicon substrates were ultrasonically cleaned with ethanol and acetone for 10 min each.

2.2 Synthesis of the organoborosilicate molecule

The organoborosilicate molecule was synthesized as previously reported with a slight modification [6]. 3-methacryloxypropyltrimethoxysilane (7.66 mL, 32.2 mmol) and boric acid (1.99 g, 32.2 mmol) were added to a separable flask and stirred under a nitrogen atmosphere. Under a nitrogen flow (~200 mL/min), the mixture was gradually heated from room temperature to 100 °C in 1 h. The reaction mixture was kept at 100 °C for 2.5 h, and then cooled to room temperature. The product was dissolved in dichloromethane and filtered to remove the unreacted boric acid. The filtrate was evaporated, and a colorless viscous liquid was obtained.

2.3 Preparation and deboronation of the organoborosilicate thin film

To the organoborosilicate molecule, photo-initiators (Omnirad 184 (3 wt%), 907 (2 wt%)) and butyronitrile (12.5 mL) were added, and the mixture was filtered under yellow light. The filtrate was deposited on a glass or silicon substrate by using a spin coater (1H-D7, MIKASA) for 5 s at 500 rpm followed by 15 s at 1500 rpm under an ambient atmosphere. Immediately after that, ultraviolet (UV, wavelength; 365 nm) was irradiated by a high-pressure mercury lamp (500 W, UVE-502S, SAN-EI ELECTRIC) for 1 h. For the deboronate treatment, the film was kept in methanol vapor (the film and methanol coexisted in a container) at room temperature for 30 min.

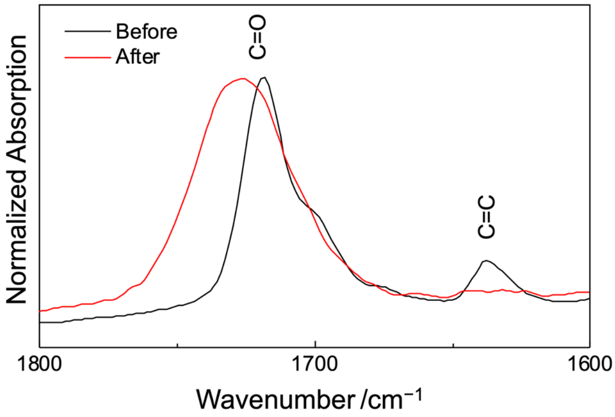


Fig. 3 FT-IR spectra of the organoborosilicate thin film before (black line) and after (red line) the UV irradiation

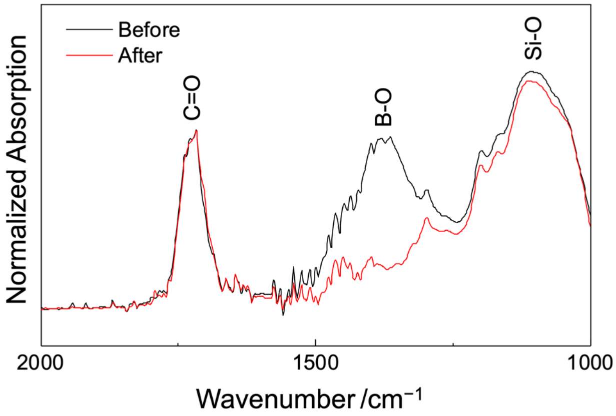


Fig. 4 FT-IR spectra of the organoborosilicate thin film before (black line) and after (red line) the methanol vapor treatment

2.4 Characterization

The organoborosilicate molecule was analyzed by a 400 MHz nuclear magnetic resonance spectrometer (NMR, ECX400, JEOL). The measurement was performed in chloroform-*d*. Chromium(III) acetylacetonate was used as a relaxation reagent and tetramethylsilane was used as an external standard at 0 ppm. The thin film of the organoborosilicate was analyzed by a Fourier transform infrared spectrometer (FT-IR, ALPHA, Bruker) and an atomic force microscope (AFM, MultiMode 8-HR, Bruker).

3 Results and discussion

3.1 Synthesis of the organoborosilicate molecule

The organoborosilicate molecule was synthesized from 3-methacryloxypropyltrimethoxysilane and boric acid via a catalyst- and solvent-free and non-aqueous alcohol condensation process. After the reaction under a nitrogen atmosphere at 100 °C for 2.5 h, colorless and transparent viscous liquid was obtained. The proposed reaction scheme is shown in Scheme 1. This reaction was performed under a nitrogen flow, and thus the generated methanol should be immediately removed from the reactor. Figure 2 shows ^{29}Si NMR spectrum of the product. A strong single signal was observed at −65 ppm which is 2 ppm larger than the chemical shift of T^3 unit composed of three siloxane bonds ($-Si(OSi\equiv)_3$) [10]. When a Si atom forms a borosiloxane bond instead of a siloxane bond, the NMR signal is known to shift by 2 ppm because of the lower magnetic shielding [11]. From these previous reports, it is considered that the signal at −65 ppm can be assigned to T^3 unit composed of two siloxane and one borosiloxane bonds ($-Si(OSi\equiv)_2(OB=)$). Considering from the starting composition (Si:B = 1:1), this result suggests the formation of the organoborosilicate molecule shown in Scheme 1.

3.2 Preparation and deboronation of the organoborosilicate thin film

The thin film of the organoborosilicate with a photo-initiator was deposited by spin coating followed by UV irradiation. After the UV irradiation, a colorless and transparent thin film was obtained. Figure 3 shows FT-IR spectra before and after the UV irradiation. The peak at 1637 cm^{-1} due to the stretching vibration of C=C significantly decreased after the UV irradiation [6]. This result indicates that photopolymerization of methacrylate occurred by the UV irradiation.

The deboronation process was performed under a methanol vapor atmosphere. It is well known that boric acid reacts easily with alcohols [12]. Figure 4 shows FT-IR spectra before and after the methanol vapor treatment. The coating solution was diluted four times with butyronitrile to adjust the thickness for the treatment. The peaks at 1110 cm^{-1}, 1385 cm^{-1}, 1637 cm^{-1}, and 1725 cm^{-1} were assigned to the stretching vibration of Si−O, B−O, C=C, and C=O, respectively. The peak at 1385 cm^{-1} due to the stretching vibration of B−O disappeared after the treatment. It should be noted that the borate was eliminated only in the presence of alcohol, but not by drying in vacuum. Therefore, the organoborosilicate and methanol vapor should react during this treatment. The proposed reaction scheme is shown in Scheme 2. The generated trimethyl borate (boiling point: 68 °C [13]) should be eliminated from the thin film.

Figure 5 shows AFM images of the thin film before and after the methanol vapor treatment. The coating solution was diluted ten times with butyronitrile to adjust the thickness for AFM measurements. The surface roughness (R_a (R_q)) before and after the methanol vapor treatment was 0.2 nm (0.2 nm) and 0.4 nm (0.6 nm), respectively. The increase in the surface roughness due to the methanol vapor treatment indicates that the surface roughness of the thin film has changed because of the borate evaporation. The

$$\equiv Si{-}O{-}B(OH)_2 + 3ROH \rightarrow \equiv Si{-}OH + B(OR)_3\uparrow + 2H_2O$$

Scheme 2 Proposed reaction scheme for the deboronation from the organoborosilicate

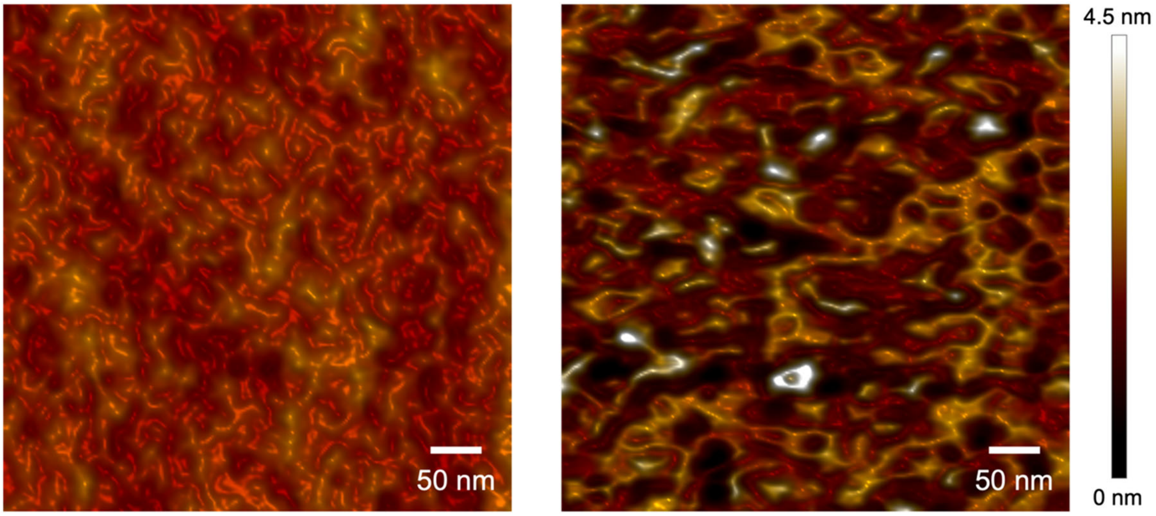


Fig. 5 AFM images of the organoborosilicate thin film before (left) and after (right) the methanol vapor treatment

condensation of silicate network would be a key to obtaining more rigid frameworks for nanofabrication. It is also possible by the present approach to justify the chemical composition of the resultant pattern, which will be organosilica or just silica after calcination. The deboronation approach is expected to apply to a new type of nanofabrication.

4 Conclusion

A photocurable organoborosilicate was synthesized from 3-methacryloxypropyltrimethoxysilane and boric acid by using a catalyst- and solvent-free and non-aqueous alcohol condensation process. The formation of Si-O-B linkage was suggested by ^{29}Si NMR spectroscopy. A colorless and transparent thin film of the organoborosilicate was prepared by UV irradiation. Deboronation from the thin film was performed under a methanol vapor atmosphere. FT-IR spectroscopy revealed that a peak at 1360 cm^{-1} due to the stretching vibration of borate disappeared after the methanol vapor treatment. Furthermore, changes in the surface roughness due to the methanol vapor treatment were observed by AFM. These results suggest that borates of organoborosilicates are selectively eliminated in the presence of alcohol vapor, altering the surface roughness. This phenomenon is expected to apply to a new type of nanofabrication.

Acknowledgements The present work is partially supported by grand-in-aids from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), administrated by Japan Society for the Promotion of Science (JSPS), and also by PRESTO, JST, Grant Number JPMJPR19I3, Japan.

Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

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