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Micropatterning of Inorganic–Organic Hybrid Thick Films from Vinyltriethoxysilane

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ビニルトリエトキシシランから作製した無機–有機ハイブリッド厚膜の微細パターンニング

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Inorganic–organic hybrid films with a maximum thickness of about 40 μm were prepared from vinyltriethoxysilane (VTES) through a sol–gel process. UV light from a high-pressure mercury lamp was irradiated through a photomask on the hybrid films from VTES. IR and ^{29}Si NMR spectra of the coating films showed that C=C bonds in VTES were polymerized by UV irradiation. Micropatterns with a maximum height of about 40 μm were formed by the etching of unirradiated area of the films.

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1. Introduction

Fine patterning techniques of sol–gel derived films have attracted much attention for the practical applications of these films to devices like integrated optical circuits and micro-electronic memories. One approach to generate finely patterned oxide thin films is embossing of sol–gel derived thin films.^{1)–4)} For example, we reported on the preparation of pregrooves for optical memory disks on glass substrates by embossing of organically modified silica gel films from $\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$ ²⁾ or silica gel films containing poly (ethylene glycol).^{3),4)}

Another approach is utilization of the effects of UV lights on photosensitive precursor gel films. In the sol–gel method, interaction with UV light can be easily achieved by incorporation of photosensitive organic group in the starting materials. A fine patterning process for oxide thin films, in which the irradiation of UV light on the gel films from chemically modified metal alkoxides led to the change of solubility of these gel films in acidic solution or alcohol, has been reported.^{5)–10)} For the preparation of planar waveguides, photosensitive inorganic–organic hybrid films prepared by the sol–gel method have been studied extensively.^{11)–19)} In these studies on inorganic–organic hybrid films, trimethoxysilylpropylmethacrylate (TMSPM) has been favored as a precursor since the methacrylate group easily polymerizes under UV irradiation or thermal treatment,²⁰⁾ and the polymerization leads to an increase of refractive index to control waveguiding. We have reported on the preparation of inorganic–organic hybrid films from vinyltriethoxysilane (VTES), allyltriethoxysilane or TMSPM, and zirconium *n*-tetrapropoxide modified with methacrylic acid,²¹⁾ and found that patterns with a width of about 10 μm and thickness of about 15 μm were formed by the etching of unirradiated region of the films. For the application of those hybrid films to waveguides, thicker films without cracks and smaller organic content should be prepared.

In the present study, inorganic–organic hybrid films, the maximum thickness of which were about 40 μm , were pre-

pared only from vinyltriethoxysilane (VTES) by the sol–gel process. UV light from a high-pressure mercury lamp was irradiated through a photomask on the hybrid films for micropatterning of these films, and changes in structure and hardness of the coating films with UV irradiation were evaluated.

2. Experimental

VTES was hydrolyzed by 0.01 M aqueous HCl with an H_2O /alkoxide molar ratio of 1.5/1. After the solution was stirred for 4 h, benzoinisobutylether (BIE) was then added to the coating solution as a photoinitiator (BIE/VTES=0.05), and the solution was further stirred for 2 h. The obtained precursor sol was used for coating.

The coating was carried out on soda-lime-silica glass plates or Si substrates in a dipping-withdrawing manner at a withdrawal speed of 1 mm s^{-1} . Dip-coated films were dried for 1 h at R.T. and then at 70°C in an oven for 30 min. For the preparation of thick films, the precursor sol was cast on soda-lime-silica glass plates or Si substrates with a square ridge frame of white petrolatum (about 2 $\text{cm} \times 2 \text{cm}$). The substrates with cast sol were dried at room temperature, and then at 70°C in an oven for 30 min.

UV light from a high-pressure mercury lamp (about 150 mW cm^{-2}) was irradiated on the films through a photomask for 10 min under N_2 flow. After the UV irradiation, the films were immersed in aqueous NaOH solution (about 10 $\text{mass}\%$) for 10 min, and rinsed with distilled water.

FT–IR spectra of the coating films were measured for the dip-coated films on Si substrates with a Perkin–Elmer FT–IR 1650 spectrometer. ^{29}Si CP–MAS NMR spectra were recorded for the peeled off samples from the substrates, with a Varian Unity Inova 300 spectrometer at 59.59 MHz and with a pulse length of 4.7 μs , a recycle pulse delay of 10 s, and a sample spinning rate of about 2500 Hz.

For the evaluation of hardness of the films, the dynamic

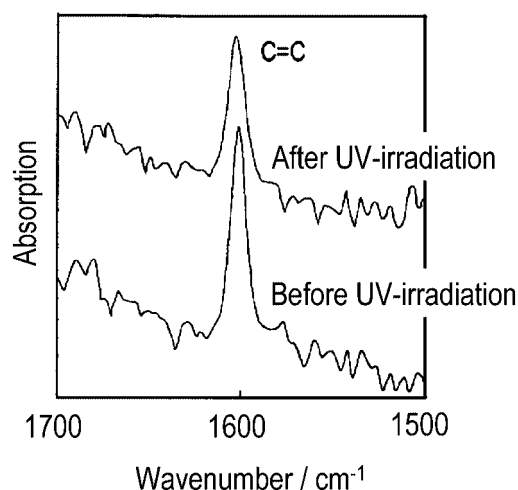


Fig. 1. FT-IR spectra of VTES-derived films before and after UV irradiation for 10 min.

hardness of the films on silicon substrate was measured with a dynamic ultra-microhardness tester (Shimadzu DUH-210). Penetration depth of an indenter during loading the indenter for 3 s was measured so that the dynamic hardness (DH) can be obtained from the following equation:

$$DH = \alpha(P/D^2)$$

where P (mN) is the load of the indenter, D (μm) is the penetration depth, and α is the constant value for an indenter (in this study, $\alpha = 3.8584$).

3. Results and discussion

Thick films without cracks were prepared by casting the precursor sol on the substrates, and the maximum thickness of the film was about $40 \mu\text{m}$. By dip-coating, the thickness of the coating films was about $1 \mu\text{m}$. By controlling the coating processes, coating films with a wide variety of the thickness can be obtained from hydrolyzed VTES.

Figure 1 shows FT-IR spectra of VTES coating films before and after UV irradiation for 10 min. The band at around 1600 cm^{-1} is assigned to $\text{C}=\text{C}$ stretching.²⁰⁾ With UV irradiation for 10 min, the intensity of the band due to $\text{C}=\text{C}$ at around 1600 cm^{-1} decreases by about 30%. This shows that UV irradiation leads to depletion of only part of $\text{C}=\text{C}$ bonds and most of the bonds remain unreacted. It was confirmed that further UV irradiation did not cause the decrease in the intensity of the band. These results suggest that the radical reaction was not propagated in the whole of VTES films.

Figure 2 shows ^{29}Si CP-MAS NMR spectra of VTES films before and after UV irradiation. Before UV irradiation, peaks due to T^2 and T^3 structural units are observed at -72 and -81 ppm, respectively. After UV irradiation, a new broad peak at around -60 ppm is appeared. In the previous study, a single peak was observed at -58 ppm in the spectra of VTES monomer, and the polymerized monomer showed a broad peak at -44 ppm; the peak position was shifted about 14 ppm with the radical polymerization of vinyl group.^{22),23)} Thus, the very broad peak at around -60 ppm observed in UV-irradiated VTES films in this study should be due to the structural units with polymerized organic chain. From the peak position, the Si units with polymerized organic chain in the films are assumed to mainly consist of T^2 species.

Table 1 shows the dynamic hardness of the VTES coating

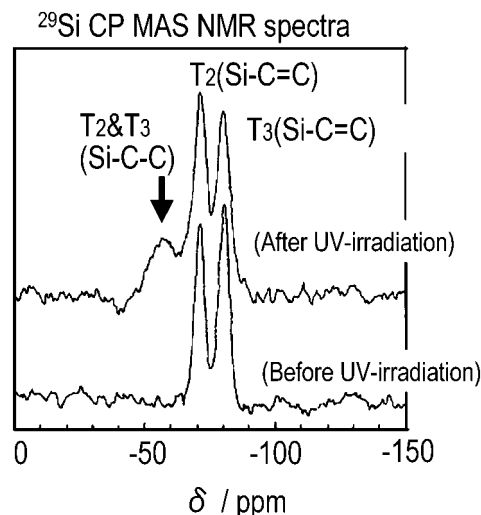


Fig. 2. ^{29}Si CP-MAS NMR spectra of VTES-derived films before and after UV irradiation.

Table 1. Dynamic Hardness of Coating Films on Si Substrates before and after UV Irradiation

	Dynamic hardness
VTES (before UV irradiation)	4
VTES (after UV irradiation)	35
PMMA	20
Glass	150~250

films on Si substrates before and after UV irradiation. The hardness for a poly (methyl methacrylate) (PMMA) plate with a thickness of about 3 mm and a soda-lime glass substrate with a thickness of about 1 mm is also shown for comparison. The dynamic hardness of unirradiated coating films from VTES is smaller than that of PMMA. However, after UV irradiation, the hardness increases. This indicates that the increase of hardness in the VTES films is due to the polymerization of $\text{C}=\text{C}$ bonds by UV irradiation.

With UV irradiation from a high-pressure mercury lamp through a photomask on the hybrid films, refractive index of the irradiated region was slightly increased and solubility of the films in alcohol or alkaline solution was decreased. **Figure 3** shows optical SEM images of micropatterns prepared using VTES on silica substrates. The thickness of the coating film before UV irradiation was about $40 \mu\text{m}$. By the etching of unirradiated region of the films with an alkaline solution, rectangular columns with edges of about $20 \mu\text{m}$ and height of about $40 \mu\text{m}$ were formed. The achievement of such large height in the micropatterns suggests the possible practical application of VTES-derived films to the microoptical components such as waveguides and photonic crystals.

In the formation of the VTES films, Si–O–Si network was formed during the hydrolysis, condensation and drying processes, and the siloxane network could be the steric hindrance for the polymerization of vinyl group. However, IR, ^{29}Si -NMR, dynamic hardness, and solubility results showed that depletion and polymerization of $\text{C}=\text{C}$ bonds did occur by the UV irradiation. It is reported that the hydrolysis and polycondensation of long-chain trialkoxy (alkyl) silanes give

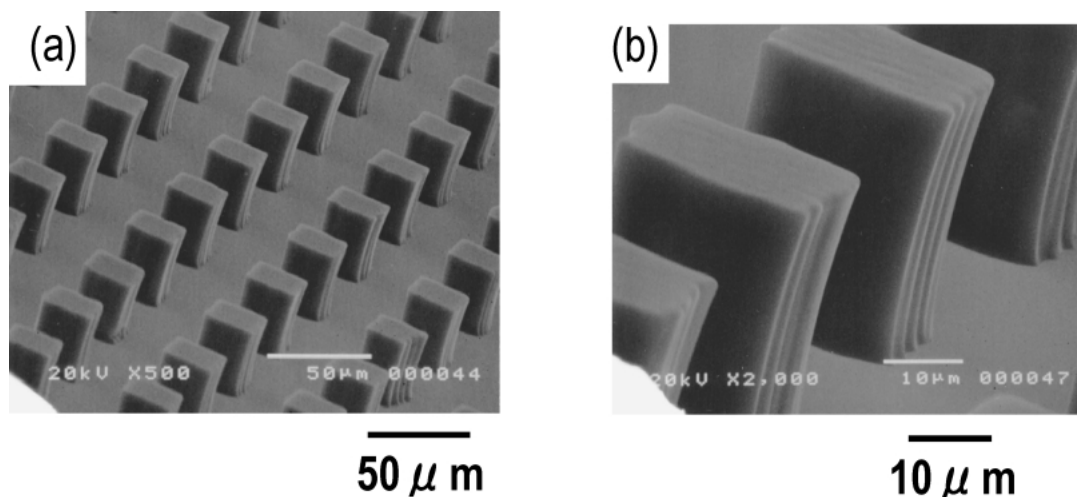


Fig. 3. SEM images of micropatterns prepared using VTES on silica substrates.

ordered structures based on molecular assembly.²⁴⁾ This gives an idea that the vinyl groups in the VTES films may partly self-organize in the hybrids, although vinyl group is very short organic group, and the vinyl groups were partly polymerized by the UV irradiation. The formation of organic network must lead to the increase in the hardness and the decrease in solubility for the alkaline solution. Since VTES has a shorter organic chain than TMSPM does, which has been favored as a precursor of hybrid optical materials, the hybrid films prepared from VTES are expected to show small optical loss in the near-infrared region due to C-H bonds in their use as waveguides.

4. Conclusions

Inorganic-organic hybrid films with a thickness of more than 10 μm were prepared from VTES. IR and ²⁹Si NMR spectra of the coating films have shown that part of C=C bonds in VTES were polymerized with the UV irradiation from a high-pressure mercury lamp, and the formation of organic network resulted in the increase in the hardness and the decrease in solubility for the alkaline solution. Micropatterns with a maximum height of about 40 μm were formed by the etching of unirradiated area of the films.

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