Ultraviolet Irradiation Hardening of Hafnia Films Prepared by Sol–Gel Processes

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ソル-ゲル法により作製したハフニア薄膜の紫外線照射による硬化

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Sol–gel-derived hafnia films containing formic acid as an organic ligand were hardened by ultraviolet (UV) irradiation. Transparent hafnia sols were prepared by treating hafnium hydroxide with a formic acid aqueous solution. The gel films were hardened to scratch hardness of over 9H by UV irradiation using a high-pressure mercury lamp for 2.5–10 min. A formato ligand was found to be bridged to Hf ions in a bond involving two metal ions by analyzing the FTIR spectra of the hafnia powders before and after UV irradiation. The hardening process of the hafnia gel films was investigated using the thermal programmed desorption (TPD) technique. The amount of CO and CO₂ generated from the formato ligands decreased after UV irradiation, as did the amount of H₂O generated from HOH in the gel, indicating that the formato ligands and OH in the gel were eliminated by UV irradiation, resulting in pencil hardness of over 9H.

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1. Introduction

Sol–gel processes are widely applied to prepare ceramic powders and thin films. Many studies of sol–gel-derived powders and films have been reported over the last two decades.1–3) To fabricate these films, organic ligands, such as formic acid, acetic acid, 2,4-pentanedione and 2-aminoethanol, are used in the processes to control sol formation and gelation time or to stabilize sol structures through coordinate bonding to metal ions.4–6) Many metal oxide and inorganic–organic hybrid films and powders have often been prepared by using formic acid for acid catalysis4–6) and as metal–formate precursors,7–9) solvents9–10) and reagents of acidolysis.11)

Ultraviolet (UV) irradiation processes have been proposed for fabricating metal oxide films by the sol–gel method instead of using a firing process as has conventionally been done.12–17) Several types of UV light sources have been used for fabricating metal oxide films. There is a report concerning photo-assisted processes using a high-pressure mercury lamp for fabricating films,17) which is a common and inexpensive UV source.

We have reported the preparation of HfO₂ and HfO₂–Y₂O₃ films by sol–gel processes and demonstrated for the first time that such films are hydrophobic.18,19) We have also described the UV hardening of sol–gel-derived hafnia films containing oxalic acid.17)

Temperature programmed desorption (TPD) is an excellent technique for analyzing adsorbed gases on the surface of bulks and films and for analyzing the species that evolve from the components of film samples and from the surface and subsurface of bulk samples.20) Thus, TPD is a useful method for investigating ceramic powder surfaces and thin films. A TPD study of the surfaces of silicon nitrides washed with H₂O and without washing indicated that the surface properties were changed as a result of the washing process.21) The structural properties of silica films prepared by chemical vapor deposition (CVD) and sol–gel techniques have been investigated by TPD.22–30) These studies revealed that the silica films contained different organic components depending on the fabrication processes and starting materials used such as tetraethoxysilane. The results also suggest that TPD can be applied to analyze the formation processes of sol–gel-derived metal oxide films. We have investigated the firing processes of sol–gel-derived titania films obtained from different Ti sources by TPD and found that the firing processes differed according to the Ti sources used and that the film crystallization temperature depended on the Ti:O ratio in the gel films.30) We have also analyzed the UV hardening process of hafnia films containing oxalic acid by the TPD technique and reported that the amount of acid decreased after the UV irradiation process.17)

This paper reports that sol–gel-derived hafnia gel films containing formic acid as an organic ligand were hardened by UV irradiation using a high-pressure mercury lamp to pencil hardness of over 9H as evaluated by the pencil test of scratch hardness. With respect to protecting the surfaces of devices or materials, it is of considerable interest and importance industrially that metal oxide films can be hardened to such a high level through a simple preparation process. This paper also describes the hardening process of the hafnia films analyzed by TPD.

2. Experimental

2.1 Type A hafnia film preparation

Hafnium chloride (5.44 g) was dissolved in H₂O (32 g) in a N₂ atmosphere. To the solution, 29% aqueous ammonia (10 ml) was added to precipitate hafnium hydroxide, and the precipitate was washed with water to a level of pH 7 of the filtrate. To the precipitate, a mixture of H₂O (32 g) and 98% formic acid (15.57 g) was added, followed by heating at 80–90°C for 3 h to obtain a clear transparent hafnia sol. The sol was coated on alkali-free glass substrates (1.1 mm thick) and silicon wafers (400 µm thick), followed by application of UV irradiation to the gel films (type A) for 2.5–10 min using a high-pressure mercury lamp (H1000L, Toshiba Lighting & Technology Corp.) to obtain the hafnia films (type A).
2.2 Type B hafnia film preparation
Hafnium chloride (8.0 g) was dissolved in 99.5% ethanol (60 g) in a N₂ atmosphere. A mixture of 60% HNO₃ (13.35 g) and H₂O (2.04 g) was added to the solution, followed by heating at 50°C for 3 h to obtain the hafnia sol (type B). The hafnia films (type B) were prepared by coating the sol on alkali-free glass substrates (1.1 mm thick) and silicon wafers (400 µm thick), followed by application of UV irradiation as mentioned above.

2.3 Measurement
The hardness of the films was evaluated by a pencil scratch hardness method using a Toyoseiki P-TYPE scratch meter according to the procedure specified in Japanese Industrial Standard (JIS) K5600-5-4 described in reference 17. The X-ray diffraction (XRD) patterns of the products were measured with a Rigaku RAD-2 X-ray diffractometer using graphite-filtered Cu Kα radiation. The refractive index and thickness of the films were measured using a Miozatoi DHA-OLX ellipsometer employing a He-Ne laser (632.8 nm). Fourier-transform infrared (FT-IR) spectra were recorded with a Perkin-Elmer Spectrum One. TPD curves of the hafnia gel films before UV irradiation and of the hafnia films after UV irradiation were measured in the temperature range of 50–800°C with a constant heating rate of 20°C/min under a pressure of 10⁻² Pa with TPD equipment (EMD-WA 1000 S/W, ESCO). A thermocouple was used to measure the surface temperature of the specimens, which were 318–361 nm in thickness and 1 cm × 1 cm in size. The amount of Hf ions in the films was analyzed qualitatively by inductively coupled plasma atomic emission spectrometry (SPS-1700HVR, Seiko Instruments).

3. Results and discussion
3.1 Hardness of hafnia films
All the transparent hafnia sols were successfully spin-coated on alkali-free glass and silicon wafer substrates to obtain crack-free, transparent films after UV irradiation.

The pencil hardness of the type A hafnia films was measured after both UV irradiation and heating at 100°C for 2.5–10 min. UV irradiation in this study contained both photo and heat processes because the film surfaces showed temperatures of about 100°C during UV irradiation. Thus, the hardness of the films was evaluated after the processes of UV irradiation and heating at 100°C.

The hardness of the type A hafnia films is shown in Fig. 1. The type A hafnia gel films (not irradiated with UV light) show a hardness level of H, but after UV irradiation for over 5 min the films were hardened to over 9H. On the other hand, the hardness of the gel films after heating alone reached a level of 7H. These results show that film hardness of over 9H was obtained by UV irradiation, which contained both photo and heat processes, whereas that level of hardness was not obtained by the heat process alone.

The pencil hardness results for the type B hafnia films after UV irradiation and heating at 100°C for 10–60 min are shown in Fig. 2. The hardness of the type B hafnia gel films (not UV-irradiated) was below 6B, but it rose to over 9H after UV irradiation for more than 30 min. However, after the heating process alone, the film hardness was below 6B and never rose higher. These results indicate that the type A hafnia gel films obtained from hafnium hydroxide and containing formic acid reached the highest level of pencil hardness after the films were irradiated by UV light.

Transmittance spectra of both types of hafnia gel films before UV irradiation were measured and those in the ultraviolet region are shown in Fig. 3. Both films showed high transmittance of about 95% in the visible light region. The transmittance of the type A gel film was high at wavelengths above 280 nm in the ultraviolet region as well as in the visible light region, but decreased at wavelengths below 280 nm. In contrast, that of the type B gel film was high (about 95%) in the ultraviolet region and decreased only at wavelengths below
240 nm. These results suggest that the type A gel film had a smaller optical gap than the type B gel film, enabling it to absorb some of the emission lines of the high-pressure mercury lamp.

The optical gap of both types of hafnia gel film was determined using the transmittance and absorption spectra obtained by the method mentioned in references 32–35. The type A and type B hafnia gel films before UV irradiation showed a band gap of 4.2 and 5.2 eV, respectively. The high-pressure mercury lamp used here exhibited strong emission lines in the UV and visible regions, such as the g-line (435.9 nm), h-line (404.7 nm) and i-line (365.0 nm), as well as emission lines of 238 nm (5.2 eV) and 244 nm (5.1 eV) in the higher energy region. The lamp presumably activated the type A hafnia gel films since their band gap was lower than the energy of the emission lines of the lamp in the higher energy region. However, the type B hafnia gel films took a longer time to harden than the type A films and were not hardened only by heating at 100°C, indicating that the films were hardened by photo process. The type B gel films showed band gap energy similar to that of the UV lamp in the higher energy region, resulting in hardening of the films to pencil hardness of over 9H by UV irradiation for a long time.

Water droplet contact angles on the type A hafnia films prepared with UV irradiation for 2.5–10 min were measured. The angles were about 53° immediately after the films were irradiated with UV light. The angles, however, increased with elapsed time and reached maximum values of between 84° and 91° after seven days, which were similar to those (about 90°) of sol–gel-derived HfO2 films prepared by firing.15 The type B hafnia films with UV irradiation for 30–60 min also showed contact angles of about 90° after seven days, indicating a hydrophobic film surface.

The refractive index and thickness of the type A hafnia films after UV irradiation for 10 min were 1.68 and 189 nm, respectively, and the corresponding values of the type B films were 1.66 and 205 nm, respectively. The refractive indices of both types of film were lower than that (1.84) of a hafnia film prepared by UV irradiation and containing oxalic acid37 and that (1.890) of a hafnia film prepared by firing at 550°C.15 The thickness of both types of film was less than that (361 nm) of the UV-irradiated film containing oxalic acid37 but thicker than that (118 nm) of the fired film.15

The XRD patterns of the type A and type B hafnia films after UV irradiation were measured. The structures of the type B films were amorphous because the XRD patterns showed no reflection except for a halo-like pattern in the measured region (2θ=5°–90°).

3.2 FT-IR spectra of hafnia powders

FT-IR absorption spectra of the type A hafnia gel powders before UV irradiation and type A hafnia powders after UV irradiation for 2.5–10 min were measured. The spectra from 500–4000 cm⁻¹ are shown in Fig. 4. All the hafnia gel powders show similar absorption spectra. Large absorption was observed at about 3500 cm⁻¹ and is ascribed to vibration of H2O adsorbed on the powders. Two absorption bands (arrows in the figure) with large intensities in the range of 1000–1750 cm⁻¹ are observed. The bands of the samples are similar and those after UV irradiation for 10 min are 1595 and 1374 cm⁻¹, respectively. Formic acid shows absorption bands at 1567 and 1366 cm⁻¹ that are ascribed to its antisymmetric (νs(COO)) and symmetric (νs(COO)) vibrations.36 The two absorption bands of the samples in the region are ascribed to vibrations of νs(COO) and νs(COO) of the formato ligands coordinated to Hf ions.

Fig. 4. FT-IR absorption spectra of type A hafnia gel powder (not irradiated by UV light) and type A hafnia powder after UV irradiation. Numbers denote UV irradiation time (min).

Fig. 5. Possible coordination structures of formato ligands to metal ions.

Formato ligands can coordinate to metal ions in three types of bonding in metal complexes, which are illustrated in Fig. 5. Type I is a unidentate coordination of one O atom of the formato ligand with one metal ion, and type II is a chelating of two O atoms to one metal ion. Type III is an example of a bridging of two O atoms to two metal ions. These types of bonding are ascribed on the basis of vibrations of νs(COO) and νs(COO) in the range of 1000–1750 cm⁻¹ in the IR absorption spectra.36 The Δ values [νs(COO) – νs(COO)] of chelating complexes are less than that of formic acid.36 In the bridging type, the Δ values are greater than that of the chelating type and close to that of formic acid.36 The Δ value (221 cm⁻¹) of the gel after UV irradiation for 10 min is close to and not less than that (201 cm⁻¹) of the formic acid. This result indicates that the coordination structure of the formato ligands in this study is that of type III (bridging).

3.3 TPD curves of the films

To investigate the hardening process by UV irradiation, TPD curves of the type A hafnia gel films before UV irradiation and those of the type A hafnia films after UV irradiation for 10 min were measured. Several TPD curves were observed in the temperature regions of 50–180°C and 180–350°C, which corresponded to evolved gases from the films. TPD curves of m/z 18, 28 and 44 that evolved from the type A hafnia gel films are shown in Fig. 6. The TPD curve of m/z 18 is due to H2O and shows peaks at 79, 112 and 247°C. The peaks observed at
79 and 112°C are ascribed to the evolution of physisorbed H$_2$O because of the low desorption temperature.\textsuperscript{17,31}

However, the assignment of the curve at the higher temperature is rather complicated. Gun'ko et al.\textsuperscript{30} have reported that TPD curves ascribed to H$_2$O at temperatures below 200°C were caused by unimolecular desorption having a first-order reaction equation and that a curve above 277°C could be explained by unimolecular desorption from micro pores. Redhead\textsuperscript{37} has calculated that TPD curves show asymmetric and symmetric shapes corresponding to first- and second-order gas desorption, respectively. Nishide et al. reported that the TPD curve of H$_2$O observed at 225°C from a sol-gel-derived titania gel film is ascribed to the associated desorption of chemisorbed water (Ti–OH) from the gel film.\textsuperscript{31}

Owing to its symmetric shape, it is thought that the curve at the temperature of 247°C was not caused by H$_2$O from the micro pores in the gel film. The curve is ascribed to the associated desorption of chemisorbed water (Hf–OH) from the gel film, similar to that in sol-gel-derived titania gel films.\textsuperscript{31}

The TPD curves of m/z 28 and 44 were due, respectively, to CO and CO$_2$ evolved from the gel film by decomposition of the formato ligand, and show peaks at approximately 240°C. However, the TPD curve of m/z 28 contained both real CO and a fragment of CO$_2$. Thus, the real TPD curves of CO were calculated by eliminating the fragment from the observed curves.

The TPD curves of H$_2$O and the real ones of CO before and after UV irradiation are shown in Figs. 7 and 8, respectively. The peak intensities of H$_2$O at 247°C and of CO decreased after UV irradiation, indicating that the amount of chemisorbed water and formato ligand in the film was reduced by UV irradiation.

3.4 Quantitative analysis of the evolved species

The quantitative values of H$_2$O evolved from Hf–OH and CO and CO$_2$ evolved from the formato ligand before and after UV irradiation were calculated from their peak areas by applying the parameters obtained from the standard values of the H$_2$ that evolved in the silicon wafer.\textsuperscript{30} The amount of Hf ions in the films was analyzed quantitatively by inductively coupled plasma atomic emission spectroscopy to obtain the molar ratios of the species that evolved from the gel films in relation to Hf ions. The molar contents of H$_2$O, CO and CO$_2$ to Hf ions are listed in Table 1. The relative values of the molar ratio of the species after UV irradiation to those before UV irradiation are also listed in parentheses.

For the hafnia gel film before UV irradiation, the molar ratios of H$_2$O, CO and CO$_2$ to Hf ion were 0.89, 1.5 and 0.096, respectively. However, after UV irradiation, the ratios decreased to 0.78, 1.0 and 0.063, respectively. The amounts of H$_2$O, CO and CO$_2$ in the films after UV irradiation decreased to 88%, 67% and 66%, respectively. These results indicate that the coordinated OH and formato ligands present before UV irradiation decreased in amount to 88% and 66–67% after irradiation, respectively. This suggests that OH and formato ligands were eliminated by UV irradiation to form Hf–O–Hf bonds.

Based on these results, the following observations can be made about the structure and hardness of the type A hafnia gel film before UV irradiation and its UV hardening process. The type A gel film contained formato ligands bridged to Hf ions and Hf–OH. This structure showed pencil hardness of H
before UV irradiation. The value was higher than that (below 6B) of the type B film, which did not contain the bridged bond, indicating that the H-level hardness can be ascribed to the bridged structure. UV irradiation decreased the amount of bridged formato ligands and coordinated OH to 66–67% and 88%, respectively, resulting in the formation of Hf–O–Hf bonds. This change in the film structure by UV irradiation resulted in hardening of the film to pencil hardness of over 9H.

4. Conclusion

The fabrication and properties of sol–gel-derived hafnia films hardened by UV irradiation were investigated. Transparent hafnia sols (type A) were prepared by treating hafnium hydroxide with H2O and formic acid. The gel films were hardened by UV irradiation, using a high-pressure mercury lamp for 2.5–10 min, to over 9H as evaluated by the pencil test of scratch hardness. The water droplet contact angles of the films reached a maximum value of 84°–91° after seven days, indicating that the hardened films showed hydrophobicity like that of fired hafnia films obtained at 550°C. The bonding structure of the formato ligands and the hardening process were analyzed on the basis of their FT-IR spectra and TPD curves. Formato ligands bridge to two Hf ions with type III bridging. In the TPD experiment, H2O evolved from Hf–OH and CO and CO2 evolved from the formato ligands in the type A hafnia gel films at temperatures between 180 and 350°C, and the amount of H2O, CO, and CO2 decreased to 88%, 66%, and 67% after UV irradiation, respectively. It can be concluded that the formato ligands in the films were eliminated by UV irradiation, resulting in pencil hardness of over 9H and hydrophobicity.

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