

# Room Temperature Photochemical Fabrication of Silica Glass Coatings using Vacuum Ultraviolet Excimer Lamps

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## 1. Introduction

Recently it becomes possible to fabricate silica glass coatings onto various kinds of materials by heating coated polysilazane films ;  $(-\text{SiH}_2-\text{NH}-)_n$  [1-3]. This technique attracts much interests in wide area of industry for making protective hard coatings, electrical insulating layers, thermal or chemical resistive films, highly transparent or anti-reflection coatings, and gas barrier coatings. To produce high quality silica glass coatings from the polysilazane precursor, heating processes above 600 C° are necessary to remove residual nitrogen atoms or Si-OH impurities. Lowering of the process temperature is necessary for fabricating high quality silica glass coatings onto thermally unstable substrates such as plastics or semiconductive devices.

In this paper, we demonstrate a room temperature photochemical fabrication of silica glass coatings by utilizing a vacuum ultraviolet (VUV) light irradiation obtainable by recently developed high power xenon excimer lamps. The quality of the photochemically fabricated coatings are elucidated here by spectroscopically investigating their chemical structures, and compared with the thermally fabricated coatings.

## 2. Experimental

Polysilazane solutions, used as received from Clariant Japan without further purification, were diluted with toluene, and spin-coated onto Si (100) substrates (10 x 10 x 0.5 mm, both sides polished). The Si substrates are carefully wiped with ethanol, and then photolytically cleaned by the VUV

irradiation just before using. Spin-coating was performed at 1500 rpm for 120 s, yielding film thicknesses ~ 500 nm after drying onto a hot plate at 50 C° for 10 minutes.

A xenon excimer lamp (Quark Systems, QEX-230SX, 172 nm, ~8 mW/cm<sup>2</sup>) was employed to irradiate VUV light on the sample. Irradiation time was about 1 hour. The lamp was placed within a small stainless chamber together with the polysilazane-coated Si substrate, and then filled with atmospheric pressured dry air at ~5 l/min flow rate. The distance between the lamp and the Si substrate was kept about 2 ~ 3 mm.

A quartz tube muffle oven (Asahi Rika ARF-50K) was used to thermally fabricating the coatings. In this case, samples were kept heated in air for about 1 hour.

An X-ray photoelectron spectrometer (Ulvac-Phi PHI-5500) was used to measure the X-ray photoelectron spectra (XPS) with aluminum K $\alpha$  X-ray source. An FT-IR spectrometer (Shimadzu FTIR-8200PC) was used to obtain infrared (IR) absorption spectra with wavenumber resolution of 4 cm<sup>-1</sup>.

## 3. Results and discussion

### 3.1 XPS spectra

Figure 1 shows Si2p, N1s and O1s XPS spectra of thermally (a-f) or photochemically (g) fabricated coatings from polysilazane, respectively. XPS spectra give information about atomic concentrations and chemical bonds at the surface (1 ~ 4 nm depth). As shown in the fig. 1(a-f), chemical shifts toward higher binding energy were

observed for the Si2p spectra as increasing process temperatures from "as depo" to 600 C°, indicating that Si-N bonds in the heated polysilazane surface were dissociated and recombined with oxygen atoms to form Si-O bonds. In consistent with the Si2p shifts, intensities of the N1s or O1s spectra were decreased or increased with process temperatures, respectively. The surface of the thermally fabricated coatings at 600 C° were completely converted to SiO<sub>2</sub> without any residual nitrogen atoms.

As shown in the fig. 1(g), the surfaces of photochemically fabricated coatings are found to be equivalent to that of the thermally fabricated coatings at 600 C°, because no residual nitrogen atom was detected for these coatings.

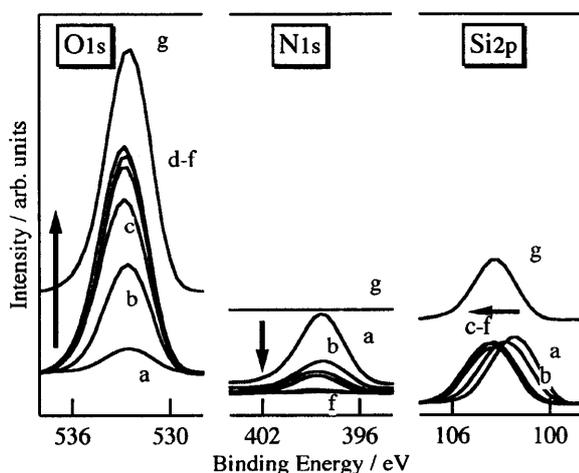


Fig. 1. X-ray photoelectron spectra of thermally (a-f) or photochemically (g) fabricated coatings : (a) as depo, (b) 200 C°, (c) 300 C°, (d) 400 C°, (e) 500 C°, (f) 600 C°, (g) VUV irradiated.

### 3.2 IR absorption spectra

Figure 2 shows IR absorption spectra of thermally (a-f) or photochemically (g) fabricated coatings from polysilazane, respectively. IR absorption spectroscopy gives average chemical information across the film depth. So complementary information can be extractable from the XPS and IR spectra of the coatings. As shown in the fig. 2(a-f), N-H stretching bands at 3370 cm<sup>-1</sup>, Si-H stretching bands at 2160 cm<sup>-1</sup>, and Si-N bands at 830 cm<sup>-1</sup> were decreased as increasing processing temperatures. Whereas Si-O bands at 1060 and 450 cm<sup>-1</sup> were increased. These spectral changes are reasonably explainable with the structural change from (-SiH<sub>2</sub>-NH)<sub>n</sub> (polysilazane) to SiO<sub>2</sub> (silica glass) occurring all over the film.

As shown in the fig. 2(g), it was found that the average chemical structure of photochemically

fabricated coatings across the depth is nearly equal to the thermally fabricated coatings between 200 ~ 300 C°.

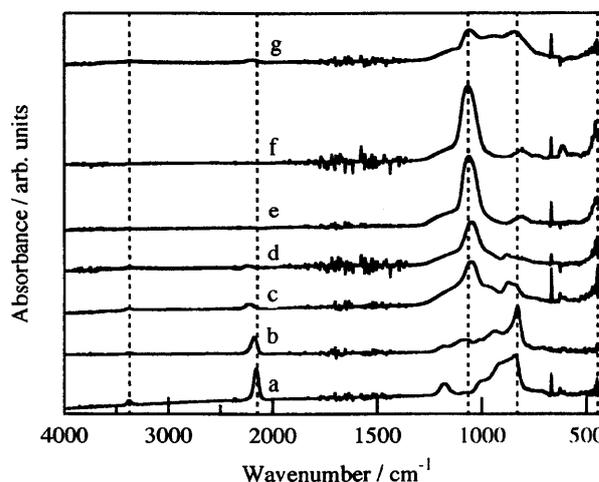


Fig. 2. IR absorption spectra of thermally (a-f) or photochemically (g) fabricated coatings : (a) as depo, (b) 200 C°, (c) 300 C°, (d) 400 C°, (e) 500 C°, (f) 600 C°, (g) VUV irradiated.

### 3.3 Discussion

From the XPS and IR spectroscopic investigations of photochemically fabricated silica glass coatings at room temperatures, there found a difference in quality between the surface and the bulk state of the coatings. For the photochemical conversion process from polysilazane to SiO<sub>2</sub>, it needs any kind of oxygen supply from gas phase such as O<sub>2</sub> molecule in dry air, O<sub>3</sub> or O radicals produced by VUV photolysis of O<sub>2</sub>, because polysilazane itself does not include oxygen atoms in its molecular structure. Thus that difference is explainable to the oxygen gas barrier characteristics of the photogenerated silica glass layer at the top of the silica glass coating.

### 4. Conclusion

In this study, the 172 nm VUV photoirradiation from recently developed high power xenon excimer lamps is found to be useful to achieve room temperature photochemical fabrication of quartz glass coatings from polysilazane.

### References

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