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Laser-Induced Chemical Dry Etching of SiO_2

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Thermally grown SiO_2 on Si has been photochemically etched in an NF_3+H_2 gas mixture by ArF excimer laser (193 nm in wavelength) irradiation. In-situ X-ray photoelectron spectroscopy of the etched surface and in-situ infrared absorption measurements of the reactive gas have revealed the elementary process of etching reactions on the surface and resulting products in the gas phase.

§1. Introduction

Photochemical processes have attained considerable attention as a new submicron device technology because selective deposition, etching, and doping can be accomplised without the use of photolithography and because the silent reactions with the least damage of active layers and low process temperatures are well fitted to miniaturization of VLSI devices. Among the photoprocesses, etching of Si and SiO_2 is increasing its importance. Ehrlich et al. [1] have studied on the photochemical etching of Si in a Cl_2 gas using a cw Ar ion laser as an excitation source. Further studies on the etching of Si by using a Xe-Hg lamp or XeCl excimer laser have been reported by Sekine et al. [2] and Arikado et al. [3] and they have succeeded in direct pattern transfer onto polycrystalline silicon surface. The photochemical etching of SiO_2 has not yet been reported. In this paper photochemical etching of SiO_2 in an NF_3+H_2 gas mixture by ArF excimer laser irradiation has been investigated and the kinetics of etching reactions on the SiO_2 surface has been revealed by in-situ X-ray photoelectron spectroscopy (XPS) together with in-situ infrared (ir) absorption measurements of the reactive gas.

§2. Experimental

An ArF excimer laser light (Lambda Physik EMG 103E, 193 nm in wavelength) was irradiated at a repetition rate of 80 Hz onto a Si wafer covered with thermally grown SiO_2 with thicknesses of 10-300 nm or quartz sheet (0.3 mm in thickness) in an NF_3+H_2 gas mixture with hydrogen content of 0-4 mol %. NF_3 has been used in plasma etching of Si and SiO_2 [4], and mixing of NF_3 gas with H_2 has also been attempted for improving the etching selectivity of SiO_2 with respect to Si [5]. The remaining oxide thickness on the silicon substrate was monitored by the infrared absorption of the Si-O stretching mode at 1060 cm^{-1} and was also monitored by the multi-beam interferometry. Etched pattern of SiO_2 was directly observed by the secondary electron micrograph (SEM). The X-ray photoelectron spectra (Shimadzu ESCA750 Spectrometer) were measured immediately after the photochemical treatment without exposing the

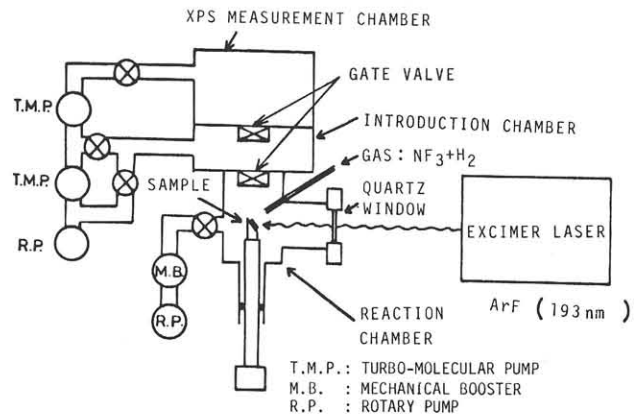


Fig. 1 Schematic diagram of experimental apparatus.

	LOW PRESSURE TREATMENT (1min)	ATMOSPHERIC PRESSURE TREATMENT (2min)	ETCH RATE (Å/sec)
A	LIGHT ⇒ SiO_2 Si		SMALL
B		⇒	SMALL
C	⇒	⇒	1.2
D	⇒	⇒	0.9
E	⇒	⇒	0.7

Table 1 Etch rate of SiO_2 for various configurations between laser and substrate.

sample surface to the atmospheric ambient (see Fig. 1), and the chemical bonding feature near the surface was analyzed. The optical molar extinction coefficient of NF_3 gas and the in-situ infrared spectra of the gas in the reaction chamber were also measured to investigate the etching mechanism.

§3. Results and Discussion

The photochemical etching of SiO_2 occurs by ArF laser irrdiation, when the SiO_2 surface is preirradiated in an NF_3+H_2 gas mixture at a low pressure (NF_3=480 Pa, H_2=20 Pa), followed by photoprocessing at an atmospheric pressure (NF_3=9.8x10^4 Pa, H_2=2.6x10^3 Pa). The low pressure pretreatment is inferred to chemically activate the SiO_2 surface by photo-created fluorine radicals. This is verified by in-situ XPS spectra as described later. Table 1 shows the etching rate of SiO_2 for various configurations between laser light and SiO_2 surface. The etching rate was evaluated by the etched depth divided by the atmospheric pressure treatment time, because the etching proceeds mainly during the atmospheric pressure treatment. The etching of SiO_2 occurs even by using the incident laser beam parallel to the sample surface in the low pressure treatment or in the atmospheric one. Therefore, etching precursors such as F, NF, NF_2, and HF must be created in the gas phase by laser irradiation. The results described here are obtained for the configuration of (c) in Table 1. When there is no pretreatment, the etching of SiO_2 starts to proceed after 2 min laser irradiation, presumably because frequent deexcitation of adsorbed fluorine radicals by impinging grand-state molecules

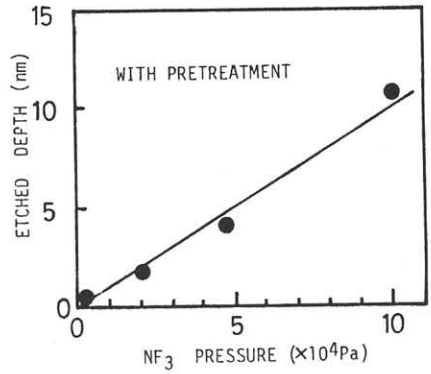


Fig. 2 NF_3 pressure dependence of etched depth of SiO_2 during atmospheric treatment for 5 min with low pressure pretreatment for 1 min.

needs the incubation time to initiate the reactions. Gas pressure dependence of the etching rate is measured to examine the etching mechanism during the atmospheric pressure treatment. The etched depth is plotted as a function of NF_3 pressure in Fig. 2. For avoiding the complexity of secondary reactions betwen H_2 and NF_3, hydrogen gas was not admixed in this experiment. The etched depth is proportional to the gas pressure, suggesting that the etching rate is primarily determined by the concentrations of the etching precursors created by laser irradiation. When hydrogen is added, the etching rate is significantly enhanced with increasing the partial pressure up to 2.6x10^3 Pa, above which the deposition of a thin film togeher with the etching of SiO_2 was observed.

In order to clarify the dissociation rate of the NF_3 gas and to esimate the light intensity on the sample surface, the optical molar extinction coefficient of the etching gas has been measured and determined to be 3.2 litter/mol.cm. The light intensity on the sample surface is estimated to be 30 and 99 % of that at the window for atmospheric and low pressure (500 Pa), respectively. The result indicates that efficient creation of etching precursors proceeds during the atmospheric pressure treatment, while the low pressure treatment can provide rather limited amount of precursors although deexcitation of fluorine radicals on SiO_2 is less frequent. For further understanding of the etching reactions, the in-situ X-ray photoelectron spectra of the SiO_2 surfaces on each step of the potochemical processes were measured. Figure 3 illustrates the XPS signal intensities of Si(2p), F(1s) and N(1s),

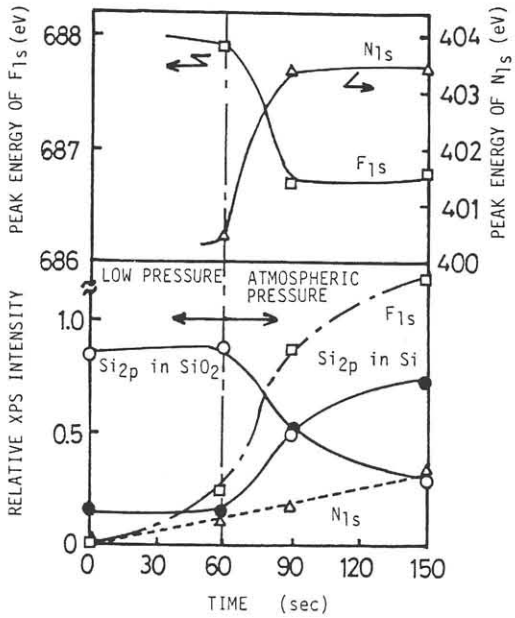
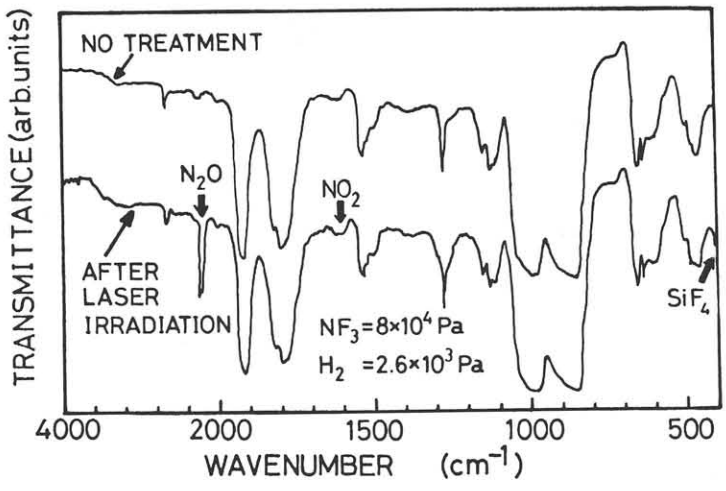


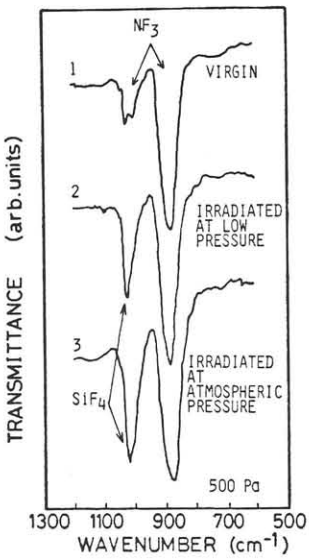
Fig. 3 The X-ray photoelectron intensities and their chemical shifts for the sample with low pressure treatment.

and their chemical shifts as a function of etching time. The nitrogen and fluorine XPS peaks increase during the low pressure phototreatment, and subsequent increase in N(1s) and F(1s) signals accompanied with their appreciable chemical shifts is observed during the atmospheric pressure treatment. Correspondingly, the SiO_2 layer is progressively etched out after the total treatment time of 150 sec including low and atmospheric pressure processes. The residual oxide thickness is estimated to be 1.5 nm from the X-ray photoelectron signal intensity ratio of Si(2p) in SiO_2 (103.5 eV) to Si(2p) in Si substrate (99.3 eV) [6]. Contrary to this, the atmospheric pressure phototreatment without low pressure pretreatment results in the absence of the nitrogen signal and extremely small F signal on the SiO_2 surface. The XPS signal intensity ratio of Si(2p) in SiO_2 to Si(2p) in Si substrate remains unchanged even after total treatment time of 150 sec. The small Si signal at 99.3 eV observed comes from the scribed edge of the sample. The chemical shifts of N(1s) and F(1s) signals in Fig. 3 are interpreted in terms of their electronegativities. Initial XPS signals from N(1s) and F(1s) arises from the adsorbed atoms on the SiO_2 surface produced by dissociation of NF_3 by laser irradiation. Then, they start to react with SiO_2 to create SiF and NO surface bonds during excimer laser irradiation. Because of the large electronegativity of F compared to Si, fluorine atom is a little negatively-charged, resulting in the chemical shift toward lower binding energy. In the case of nitrogen, the electron cloud of nitrogen tends to move to oxygen due to the smaller electronegativity of N than that of O, and hence the N(1s) signal shifts toward higher energy. The line shape of the F signal on the surface with and without low pressue treatment are also quite different, suggesting the difference in the chemical state of fluorine atoms on SiO_2. Such pronounced difference in chemical bond natures of fluorine and nitrogen atoms on SiO_2 caused with and without low pressure pretreatment could be related to the difference in the etching rate during the atmospheric pressure treatment with and without pretreatment. From the result of Fig. 3 it is likely that the SiO_2 surface is activated by low pressure treatment and then the etching reactions can efficiently proceed in the atmospheric pressure treatment.

In-situ infrared absorption measurements of the etching gas during excimer laser irradiation was carried out to reveal the reaction products in the gas phase. The gas cell consists of the Si ir windows and a stainless steel reaction chamber. The sample cell was filled with the etching gas and the excimer laser was irradiated onto the oxidized Si in the cell and the referene cell is evacuated by a turbo-molecular pump. Figure 4 (a) illustrates the infrared spectra of NF_3(8.0×10^4 Pa)+H_2(2.6×10^3 Pa) gas mixture before and after 6 min laser irradiation. The ir spectra during excimer laser irradiation exhibit almost the same absorption peaks as that after laser irradiation, that is, the short life time products are not mesured in this experiment. By the irradiation new absorption peaks indicated by arrows are observed. All other absorption peaks originate in NF_3 gas. The new absorptions are assigned as the vibrational mode of N_2O and NO_2 at 2220 cm^{-1}, NO_2 at 1620 cm^{-1}, and SiF at about 400 cm^{-1}. The origin of the oxygen atoms in N_2O and NO_2 could be attributed to SiO_2 and partly to the adsorbed H_2O on the surface of the stainless steel chamber. To clarify the absorption in the range



(a)



(b)

Fig. 4 The infrared spectra of NF_3+H_2 gas mixture before and after 6 min laser irradiation at atmospheric pressure (a) and low pressure (b).

800 to 1100 cm^{-1}, ir measurement at lower pressure was carried out by evacuating the photoprocessed gas down to 500 Pa as shown in Fig. 4 (b), curve 3. In the figure the spectra from virgin gas (NF_3=480 Pa, H_2=20 Pa) (curve 1) and from low pressure gas irradiated with excimer laser during ir measurement (curve 2) are also shown as references. A clear absorption by the SiF stretching mode at 1020 cm^{-1} becomes visible. Absence of infrared absorption due to HF molecules could be partly attributed to its small ir sensitivity. We assume that HF would also be created because of the high reactivity of NF_3 with H_2. From this result the following reaction could be suggested as a possible mechanism of the photochemical etching of SiO_2:

$$SiO_2+NF_3+H_2 \xrightarrow{h\nu} SiF_4+NO_2+N_2O+HF. \quad (1)$$

Figure 5 represents an example of etching pattern of SiO_2. The sample is processed in NF_3(480 Pa)+H_2(20 Pa) for 2 min followed by the atmospheric pressure treatment (NF_3=9.8x10^4 Pa, H_2=2.6x10^3 Pa) for 40 min by using a 50-nm-thick alminum multi-stripe pattern mask.

§4. Conclusion

It is demonstrated that silicon dioxide is etched by 193 nm excimer laser irradiation in an NF_3+H_2 mixed gas. It is suggested as an etching mechanism that the adsorbed F and N atoms on SiO_2 react with the surface Si-O bonds and produce volatile SiF , NO_2, and N_2O.

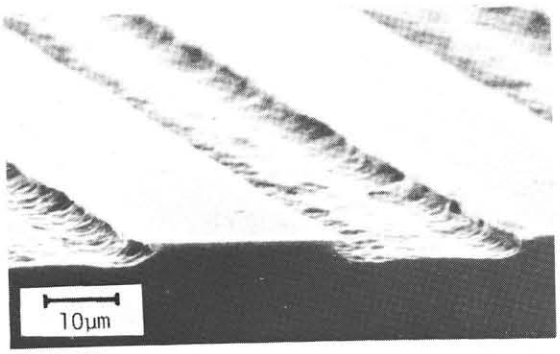


Fig. 5 SEM photograph of etched SiO_2 with Al multiple stripe pattern.

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