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Vacuum Ultraviolet Laser-Induced Surface Alteration of SiO_2

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Intense vacuum ultraviolet laser radiation is generated from rare gas excimer lasers. 9.8 eV photons from an argon excimer laser change surfaces of SiO_2 to silicon. The reaction proceeds without the aid of reactive gas or solution and is thus called the "superdry process". 9.8 eV photons create excitons via an efficient one-photon absorption process, and then these high-density excitons induce bond-breaking between Si and O.

KEYWORDS: laser material processing, vacuum ultraviolet wavelength, rare gas excimer laser, silicon dioxide, microelectronics, superdry process

§1. Introduction

Laser material processing has become one of the most important techniques for the fabrication of electronic and optic devices. In almost all cases so far, ultraviolet (UV) excimer lasers such as ArF and KrF excimer lasers have been used for chemical vapor deposition, etching, doping, lithography and other processes, exploiting the advantages of their high photon energies. Lasers which provide high power output in the vacuum ultraviolet (VUV) spectral region are considered to be more attractive for material processing. It should be noted, however, that VUV laser development has not been successful so far, so VUV laser material processing has yet to be attempted.

The generation of high-power VUV laser radiation at wavelengths shorter than the ArF excimer laser line at 193 nm still remains a challenge. Frequency mixing,[1,2] harmonic generation[3] and anti-Stokes Raman scattering[4] are used for spectroscopic purposes, but the available flux is rather limited. The other candidate is synchrotron radiation (SR), which has been used worldwide, but the flux is still too low. Thus, rare gas excimer lasers, which have been made possible by high-power electron beam pumping, are at present the most feasible method of generating intense VUV radiation.[5] Among them are an argon excimer laser oscillating at 126 nm, whose photon energy is 9.8 eV, and a krypton excimer laser oscillating at 146 nm (8.5 eV). The argon excimer laser developed by us has the ability to generate a pulse having 80 mJ total energy within 5 ns and 16 MW peak power.[6,7]

Such VUV photons are ideally expected to react directly with the solid surfaces and modify the sample surfaces. Recently, Akazawa *et al.* demonstrated photostimulated etching of SiO_2 films by using synchrotron radiation without an etchant gas, with the use of the SR beam peaked at 100 eV.[8] In this paper, we show that VUV excimer lasers induce desorption and silicon precipitation in the surface layers of SiO_2 without any reactive gas or solution, namely via the "superdry process".

§2. Experimental

Prior to the description of the laser-induced surface alteration, we shall describe the high-power rare-gas excimer lasers as illustrated in Fig. 1. High-purity argon or krypton gas was flowed into a stainless steel anode pipe 5 mm in diameter, 80 cm long and 80 μm thick. The laser gas was excited by an electron beam accelerated at 700 kV. The laser cavity, located at both ends of the anode pipe, was composed of a SiO_2 plate and a MgF_2 single crystal plate. The output mirror had 63% transmittance and 8% reflectance at 126 nm. The output energy of the 5 mm-diameter laser beam, which came out through the output mirror and MgF_2 window, was measured in vacuum. The output characteristics largely depend upon the kind of reflector materials used. The highest values of output energy per pulse and peak power so far obtained for the argon excimer laser were 80 mJ in 5 ns and 16 MW, respectively, with a SiC-MgF_2 cavity[6,7]

Crystalline (or glassy) SiO_2 mirrors were used as a reflector. For the argon and krypton excimer lasers, the surfaces were found to be imprinted by beam patterns even when the laser output energies were relatively low at

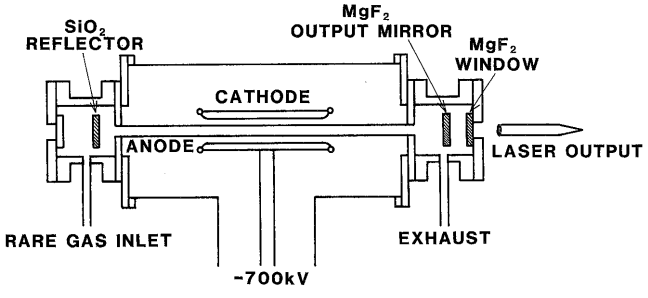


Fig. 1. Schematic illustration of the electron beam pumped rare gas excimer laser.

around 5 mJ. Clear beam patterns 5 mm in diameter were observed after only one shot, and the patterns became clearer after multiple shots. In this paper, we observed the beam patterns on the SiO_2 mirrors made by 1 to 5 shots of the argon and krypton excimer lasers, which provide output energies per pulse of about 10 and 25 mJ, respectively. The energy fluences were estimated to be 125 and 250 mJ/cm^2 on the mirror surface, respectively, based on the output energies and transmittance of the MgF_2 mirror and window. It should be added here that the beam patterns were formed only by the laser irradiation, because no patterns could be observed without the lasing even though the gas was excited by the electron beam.

The beam patterns were first observed with an optical microscope for observing topographic features. Then X-ray photoemission spectroscopy (XPS) analyses were performed on a Shimadzu ESCA 1000 spectrometer using a MgK_α X-ray source (E=1253.8 eV). From XPS analyses, silicon, oxygen, and carbon atoms were detected on the sample surfaces. For calculation of the binding energy of each peak, the peak position of the 1 s core level spectrum of oxygen was assumed to be 532.8 eV. Photoelectrons coming from a selected area of which the minimum size is 0.2 mm diameter, are analyzable with the XPS spectrometer.

§3. Results and Discussion

The beam patterns could be observed clearly with the naked eye as well as with an optical microscope. The scattered light due to the enhanced surface roughness probably makes the beam patterns visible. The surface temperature estimated on the basis of the deposition energy and one-dimensional thermal-diffusion is far above the melting temperature of 1720°C due to the 125 mJ/cm^2 laser radiation. The beam patterns for both types of laser irradiation were visible. It can be concluded here that as far as such thermal effects are concerned, no differences are found between the argon and krypton excimer laser-induced beam patterns.

To obtain information about the bonding nature, we examined the X-ray photoemission spectra. Figure 2(a) shows Si-2*p* core level emission spectra taken from a crystalline SiO_2 surface. Curve 1 shows a spectrum from an unirradiated part, namely the virgin SiO_2 surface; curve 2, one from a krypton excimer laser-induced beam pattern, and curve 3, one from an argon excimer laser-induced beam pattern. For comparison, spectrum 4 from a silicon wafer with a naturally oxidized layer is also shown. In all curves, the main peaks are seen at 103.4 eV, which corresponds to the binding energy of Si-2*p* in SiO_2. In curves 3 and 4, subpeaks appear around 99.3 eV. These peaks are identified as the peaks from Si-2*p* core level emission in bulk silicon. The peak heights and widths are found to be changed by the laser irradiation as detailed below.

Figure 2(b) shows spectra of O-1*s* core level emission. The curve notations have the same meanings as the Si-2*p* spectra in Fig. 2(a). The peak positions remain unchanged for the O-1*s* spectra, but the heights and widths are found to be changed by the laser irradiation. The peak heights are halved by the laser irradiation, and the widths become broad. As described in detail later, the areas of the respective peaks remain unchanged by the krypton excimer laser irradiation, but are reduced to about 70% of the original value in curve 1 by the argon excimer laser irradiation. We can conclude here that the argon excimer laser irradiation induces silicon precipitation and oxygen desorption in the surface layer of SiO_2.

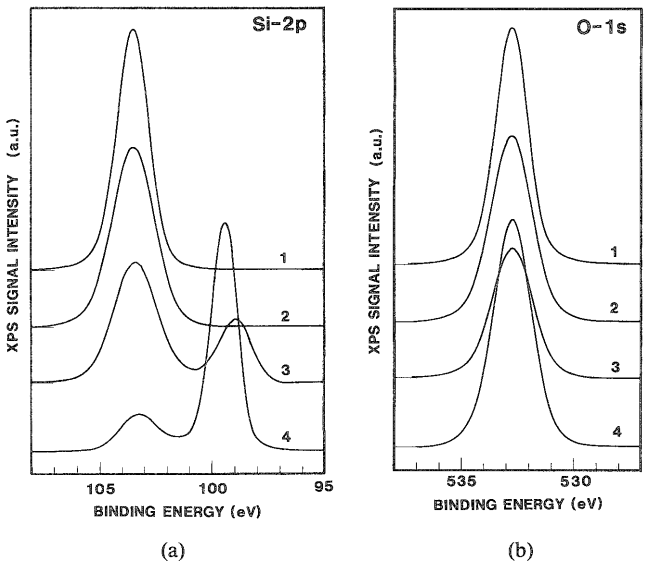
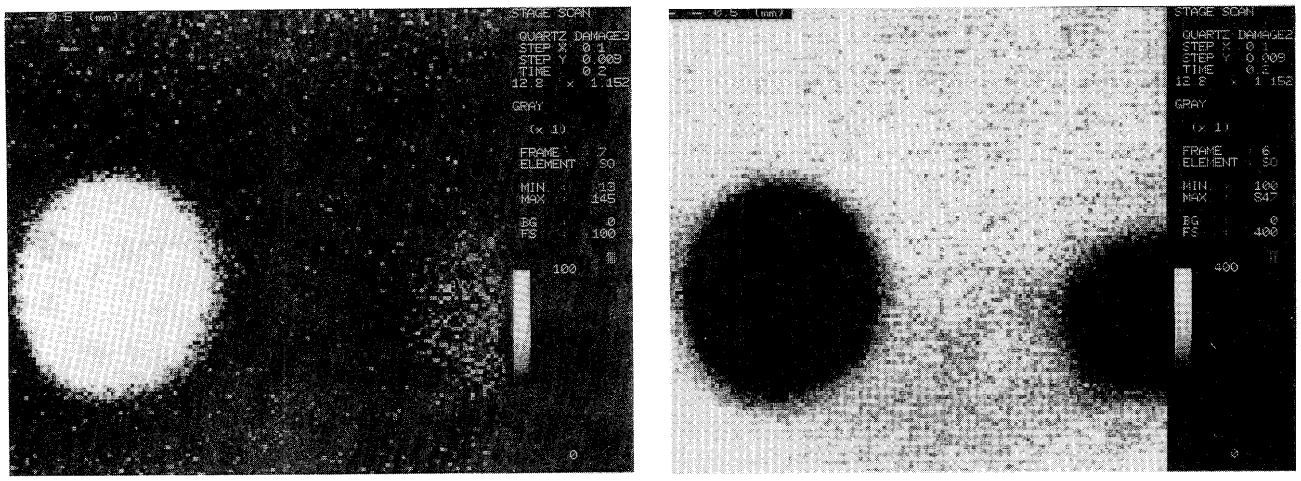


Fig. 2. (a) Si-2*p* and (b) O-1*s* core level spectra for crystalline SiO_2. Curves labeled 1 were spectra taken from an unirradiated part, curves 2 from an irradiated part by a krypton excimer laser, and curves 3 from an irradiated part by an argon excimer laser. These figures also show the spectra taken from a silicon wafer with a naturally oxidized thin layer as the curves labeled 4.

Figures 3 (a) and 3 (b) show images indicating the two-dimensional distribution of 99.3 and 103.4 eV photoelectrons, respectively, for a sample surface. In these figures, two beam patterns are visible: the one on the left-hand side of the figure was induced by 5 shots of the argon excimer laser, the one on the right-hand side by one shot. The densities of the photoelectrons are indicated with the use of the brightness of image elements of 0.2×0.2 mm^2 square. The brighter spots in the image indicate the higher density of the electrons with a given energy. The darker spots correspond to an area of low density. The bulk silicon is included only in the circular areas in Fig. 3(a), which corresponds nicely to the beam patterns caused by exposure to the argon excimer laser irradiation. We can clearly see that bulk silicon appears uniformly in the beam pattern, and that the 5-shot pattern is much clearer than the 1-shot pattern. Figure 3(b) shows that SiO_2 is depleted in the beam patterns and that the multiple shots induce greater depletion of SiO_2.

Table I lists the binding energies, peak heights, widths, and peak areas calculated based on the heights and widths. In the case of the krypton excimer laser irradiation, the heights of both Si-2*p* and O-1*s* peaks decrease, but the widths broaden. As a result, the areas of the peaks remain unchanged. In the case of the argon excimer laser irradiation, on the other hand, the Si-2*p* peaks split into two, (1) corresponding to SiO_2 and (2) to bulk silicon,



(a) (b)

Fig. 3. Two-dimensional images for the crystalline SiO_2 surface taken with (a) 99.3 eV Si-2*p* emission of bulk silicon and (b) 103.4 eV Si-2*p* emission of SiO_2: the right-hand side pattern is induced by one shot of the argon excimer laser and the left-hand side pattern is induced by five shots.

Table I. Some chracteristics of observed XPS spectra.

Photon energy [eV]	Sample	Peak assignment	Binding energy [eV]	Height [cps]	Half-width [eV]	Area [cps:eV]	Area ratio O-1*s*/Si-2*p*
No	SiO_2	Si-2*p*	103.45	6366	1.70	10.8	4.9
		O-1*s*	532.80	31184	1.69	52.7	
8.5	SiO_2	Si-2*p*	103.40	4816	2.20	10.6	4.9
		O-1*s*	532.80	24651	2.12	52.3	
9.8	SiO_2	Si-2*p*(1)	103.40	3165	2.30	7.3	5.0
		Si-2*p*(2)	98.90	1620	1.73	2.8	
		O-1*s*	532.80	17158	2.11	36.2	
No	Si wafer	Si-2*p*(1)	103.25	1060	2.20	2.3	
		Si-2*p*(2)	99.35	6968	1.30	7.0	
		O-1*s*	532.80	9752	1.98	19.3	

and the area of O-1*s* peak decreases. It could be concluded that oxygen desorbs from the surface layer due to the argon exclmer laser irradiation. The interesting point is, however, that the area ratios of O-1*s* and the bulk silicon component of Si-2*p* peaks are 5.0, which is almost the same value as those in the cases of the unirradiated and krypton excimer laser-irradiated parts. These findings imply that composition of SiO_2 remains unchanged by the laser irradiation. It should be noted here that the argon excimer laser irradiation induces silicon enrichment without any intermediate states such as SiO_x. The broader peaks of Si-2*p* and O-1*s* spectra indicate that the bonding angles and lengths are changed by both types of laser irradiation. This might be caused by the thermal effect; namely the temperature of the surfaces rises above the melting point of SiO_2, and the crystalline SiO_2 enters the amorphous state. The oxidized layer on the silicon wafer is considered to be amorphous. On the other hand, silicon precipitated in the surface layer of the sample has a sharp peak and is thus considered to be crystalline rather than amorphous.

Next we consider the mechanism of the silicon precipitation. On the silicon precipitation, the photon energies are critical: 9.8 eV photons can break the bonds, but 8.5 eV photons do not. The fundamental band gap energy of SiO_2 is 9 eV, which falls just between 9.8 and 8.5 eV. 9.8 eV photons over the band gap break the bonds, but 8.5 eV photons below the gap do not. 9.8 eV photons from the argon excimer laser induce the band-to-band transition of electrons, generating excitons efficiently by one-photon absorption. Itoh *et al.* have found that ionization radiation bombardment on glassy SiO_2 creates self-trapped excitons, subsequently inducing permanent defects in the samples.[9,10] We can apply the same kind of mechanism to our case, i.e., that silicon precipitation is induced via exciton creation. 9.8 eV photons from an argon excimer laser induce band-to-band electronic transition via efficient one-photon absorption, create excitons, relax to the self-trapped states, induce bond breakage, and finally precipitate silicon.

It should be added here that clear beam patterns were observed on the MgF_2 output mirror surfaces too. Fur-

thermore, they were considered to be mainly due to rising surface temperature. The details will be described elsewhere.

§4. Conclusions

9.8 eV photons from an argon excimer laser were found to induce silicon precipitation in the surface of SiO_2. The thickness of the silicon precipitation layer might be at most 50 nm, which corresponds to the penetration depth of the laser light into SiO_2. The reaction proceeds without any reactive gas or solution, namely via the "superdry process". With the coherent properties of a laser beam, this reaction might become an important technique for microelectronics fabrication.

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