Various structural changes in SiO$_2$ introduced by one-photon excitation with undulator and two-photon excitation with excimer laser

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Abstract

Excitation at higher energies beyond the ultraviolet (UV) edge (~9 eV) in amorphous SiO$_2$ (a-SiO$_2$) can be achieved by two-photon process with ArF excimer laser as well as by one-photon process with undulator radiation. Photo-induced phenomena with two kinds of light sources are reported. Frequency decrease of the Si–O stretching vibration in infrared absorption spectrum was observed in the a-SiO$_2$ by one-photon process with 14.1 eV rays and higher. Frequency decrease can be explained with transition from regular six membered ring (6 Si and 6 O in a loop) to three and four membered rings (3 (4) Si and 3 (4) O in a loop) in a-SiO$_2$ network. In case of two-photon process with ArF excimer laser, ablation was observed. Threshold fluence ~1 J cm$^{-2}$ is apparently necessary to commence ablation by a single pulse. Ablation introduced with a single pulse above the threshold fluence did not influence stoichiometry of SiO$_2$. In contrast, for lower fluence below the threshold, the ablation commenced after several pulses accompanied with oxygen loss and ablated thickness increased via a cumulative process. Photo-ablation below the threshold fluence 1 J cm$^{-2}$ obeyed two-photon excitation process, in contrast, ablation obeyed multi-photon process above the threshold fluence. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

It is important to study the photo-induced phenomena in amorphous SiO$_2$ (a-SiO$_2$) because it is one of the most important optical materials for ultraviolet (UV) and vacuum ultraviolet (VUV) regions. Here, photo-induced phenomena in a-SiO$_2$, reported previously, were reviewed briefly. Braren and Srinivasen described the use of UV laser etching of various glasses which offers a conventional dry method for drilling of via holes in the glass layers in semiconductor packages [1]. Ablation of fused silica has also been carried out using standard nanosecond excimer laser pulses at 193, 248 and 308 nm by Ihlemann and coworkers [2,3]. Takigawa found the generation of silicon in the surface layer of SiO$_2$ by irradiation with an ArF excimer laser ($\lambda = 126$ nm, $E = 9.87$ eV) [4]. Fiori and Devine have demonstrated that oxygen loss was observed by Auger-electron spectroscopy (AES) in a thin (~15 Å) SiO$_2$ film exposed to 248 nm laser irradiation for 1 h at an energy density of 100 mJ cm$^{-2}$ (pulse duration 10 ns, repetition frequency 20 Hz) [5]. They also observed the photo ablation of SiO$_x$ ($x < 2$) films by providing an energy per pulse ranging from 20 to 10$^3$ mJ cm$^{-2}$ at the sample surface. Laser might introduce two-photon process as well as one-photon process [6].
Two-photon excitation with ArF excimer laser (λ = 193 nm, E = 6.4 eV) can reach up to 12.8 eV. Yet, we know little about the difference between one-photon excitation with 12.8 eV ray and two-photon excitation with ArF excimer laser. Fig. 1 is redrawn from the optical absorption data [7] on the VUV-ray-absorption for a-SiO$_2$ versus photon energy. A sharp peak located at 10.2 eV has been assigned to a Wannier exciton band formed by the breaking of a single Si–O bond. The next broad band in the region of 12–13 eV was attributed to the band to band transition, which corresponds to a transition from the non-bonding oxygen p levels to the anti-bonding levels. The next band at 14.4 eV has been attributed to the excited states of the self-trapped exciton. In the present work, excitation at higher energies beyond the UV edge (9 eV) in a-SiO$_2$ was performed by either one-photon process introduced with undulator radiation or two-photon excitation with ArF excimer laser to examine the photo-induced phenomena.

2. Experimental

Amorphous SiO$_2$ films 200 nm and 1.03 μm thick were thermally grown on the silicon wafers having (1 0 0) face in O$_2$ or a mixture of O$_2$/H$_2$ atmosphere at 1000°C, respectively. The 200 nm thick SiO$_2$ film for undulator radiation was etched with HF solution (HF:H$_2$O = 1:100) at 25°C down to ~35 nm thickness because the 200 nm thickness is too thick for VUV rays above 9 eV to penetrate the film. The undulator installed in an electron storage ring for synchrotron radiation was used as a light source for photo-excitation. Full-width at half-maximum (FWHM) of the undulator radiation is ~8% of the photon energy. Photon energy generated from the undulator was controlled by the electron energy. CaF$_2$ or LiF crystal plate was used as the filter to remove higher harmonic contributions generated from undulator radiation as by-products. Transmittance change of the filters was monitored with a photomultiplier. Irradiation was performed in vacuum. Infrared (IR) absorption was measured with Fourier transform IR spectro-photometer using light at normal incidence.

To examine the spatial distribution of photo-induced defects in thermal SiO$_2$, chemical etching rate with HF solution (HF:H$_2$O = 1:100) was performed at 25°C. Etching rate distribution as a function of depth was determined by a Talystep mechanical measurement. X-ray photoelectron spectroscopy (XPS) was carried out with monochrome Al Kα source (hv = 1486.6 eV). X-ray beam size on the sample was estimated about 300 μm × 700 μm. Irradiation was performed in air at room temperature with an ArF excimer laser operating at λ = 193 nm. Energy per pulse was ranged down to 300 mJ cm$^{-2}$ up to 2.14 J cm$^{-2}$ by variable focusing. Pulse duration was ~20 ns. Repetition frequency was ~0.5 Hz to avoid sample heating. The ablated thickness was measured directly using a Talystep mechanical measurement.

3. Results

Differential IR absorption spectra of a-SiO$_2$ irradiated with 14.1 and 17.8 eV rays are shown in Fig. 2(A) and (B). Spatial distributions of IR spectrum were obtained as follows. Firstly, IR spectra were measured. Then about 2–10 nm of the film was etched off the front face and IR spectra were measured again. The difference gave the IR spectrum in the etched volume of the original sample.

We next removed an additional amount of the film, and repeated the above procedure. Spectrum in the top surface region has a peak at 1072 cm$^{-1}$. Spectra in the region of 5–25 nm from the top surface show the peak...
shift to the lower frequency side down to \(~1042\) cm\(^{-1}\) with peak broadening.

Fig. 3 presents the ablated thickness normalised to the original thickness obtained by single shot as a function of fluence. Circles and squares represent the result of 200 nm thick SiO\(_2\) and 1.03 \(\mu\)m thick SiO\(_2\), respectively. In both SiO\(_2\) films irradiated with a laser pulse fluence below 1 J cm\(^{-2}\), no thickness change was detected. Above threshold fluence \(~1\) J cm\(^{-2}\), ablated thickness increased with fluence until the whole film thickness disappeared. Both plots of 200 nm thick SiO\(_2\) films and 1.03 \(\mu\)m thick SiO\(_2\) films are almost on the same line.

XPS Si 2p measurement was also carried out on a virgin a-SiO\(_2\) film, a-SiO\(_2\) films irradiated with ArF excimer laser at fluence 800 mJ cm\(^{-2}\) with 6, 25 and 30 shots. A new peak at 99.3 eV assigned to Si\(^0\) was generated with irradiation. In contrast, Si\(^0\) peak was not detected in laser a-SiO\(_2\) films irradiated with ArF excimer with fluence above 1 J cm\(^{-2}\) which introduced ablation by one shot.

4. Discussion

Si–O–Si bridging bond angle can be calculated from the Si–O bond stretching mode in IR absorption spectrum using

\[
\omega^2 = \omega_m^{-1}(1 - \cos \theta) + \frac{4}{3} \omega_{\text{Si}}^{-1}
\]  

(1)

based on the central force model [8], where \(\omega\) is peak frequency, \(\omega_m\) angular frequency, \(\theta\) the Si–O–Si brid-
ging bond angle, \( m_0 \) and \( m_\text{Si} \) the mass of the oxygen and silicon, respectively. Spectra in Fig. 2 have two peaks at 1072 and 1042 cm\(^{-1}\). Frequency shift from 1072 to 1042 cm\(^{-1}\) corresponded to the decrease of Si–O–Si bridging bond angle from 144° to 129° from Eq. (1). It is explained that transition from regular six membered rings to planar three and four membered rings occurs (3 (4) Si and 3 (4) O in a loop) because planar three membered rings have Si–O–Si bridging bond angle \( \theta \sim 129^\circ \). We assume that the transition from regular six membered ring to three membered ring needs at least photo-excitation into excited states of the STE. In other words, band to band excitation is not sufficient to induce the transition. It is an interesting result that planar three membered ring was not generated at the top surface where VUV light was launched. We speculate that planar three membered rings, which are located at the top surface, act as traps for OH or H contained in the air so that they may be eliminated.

5. Summary

In the present work, numbers of three and four membered rings in a-SiO\(_2\) network increases with the one-photo excitation using 14.1 or 17.8 eV ray. These excitation energies correspond to excitations into excited states of the self-trapped exciton in a-SiO\(_2\). In contrast, no change was observed with 12.6 eV ray which corresponds to excitations into the exciton band. In the present work, we have examined a-SiO\(_2\) films exposed to 193 nm laser radiation at very high energy densities up to 2.14 J cm\(^{-2}\). We found that the threshold fluence for ablation by single pulse was located at \( \sim 1 \) J cm\(^{-2}\). Ablation was also observed below the threshold fluence (\( \sim 1 \) J cm\(^{-2}\)) with increase of the number of shots. Structure in the SiO\(_2\) film after ablation was examined by XPS. Oxygen loss was observed with radiation below the threshold fluence, in contrast radiation above the threshold fluence introduced ablation without oxygen loss.

References