In situ spectroscopic measurement of transmitted light related to defect formation in SiO_2 during femtosecond laser irradiation

N. Fukata,[a] Y. Yamamoto, and K. Murakami
Institute of Applied Physics, University of Tsukuba, 1-1-1 Tennoudai, Tsukuba 305-8573, Japan

M. Hase and M. Kitajima
National Institute for Materials Science, 1-2-1 Sengen, Tsukuba 305-8578, Japan

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We measured real-time spectra of light transmitted through SiO_2 specimens during irradiation of amplified ultrashort laser with a fluence of 540 mJ/cm^2. The real-time spectra exhibit a peak at around 400 nm, which significantly depends on the irradiation time. The observation and identification of defects were performed by measurements of electron spin resonance (ESR). Both dependences of the peak at around 400 nm on irradiation time and laser power are in good agreement with those of the ESR signal intensity of positively charged oxygen vacancies (E' center). This strong correlation shows that self-trapped excitons are created followed by the formation of the E' center and finally that of ESR inactive centers, namely, oxygen-deficiency centers. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1623939]

Femtosecond laser pulses can be used to make microscopic modifications in optically transparent materials. This is due to the impressive ability of femtosecond laser pulses to induce multiphoton absorption even for wide-gap materials. It is possible to accurately fabricate optical components without a large effect of heating since the duration of the pulse is significantly shorter than the time scale for electron energy transfer to the lattice.[1] Stuart *et al.* measured laser-induced damage thresholds for fused silica for pulses ranging from 270 fs to 1 ns.[1] In the case of pulses longer than a few tens of picoseconds, damage occurred via conventional heat deposition resulting in the melting and boiling of the dielectric materials, while in the case of damage caused by subpicosecond pulses, it was characterized by a nonthermal process. To date, many studies have been performed to fabricate optical components such as optical waveguides, gratings, and photonic crystals.[2–8]

From a basic point of view, measurements of electron spin resonance (ESR), photoluminescence, and optical absorption have been performed to identify defects induced by femtosecond laser irradiation.[9] Very recently, the propagation of femtosecond laser pulses in fused silica was investigated both experimentally and numerically and the results showed filamentary propagation.[10] To understand the local structural change caused by femtosecond laser irradiation, it is necessary to perform *in situ* measurements of the damage process with femtosecond laser irradiation. Recently, dynamics of plasma formation and bulk refractive index modification in silica glass excited by a tightly focused femtosecond laser were investigated with a time-resolved pump-probe transmission technique by Cho *et al.*[11] The spectra of transmitted light, however, have not been observed.

In this letter, we show that our *in situ* measurement can be a useful method to detect the local structural change in SiO_2 and to understand the phenomena during femtosecond laser irradiation. To investigate the dynamics of local structural change in SiO_2 specimens induced by femtosecond laser irradiation, we focus attention on the change in the spectrum of light transmitted through these specimens in real time. ESR measurements are also performed to identify defects introduced by femtosecond laser irradiation.

SiO_2 glass (Toshiba ceramics, T1030) was used as the laser target. The size of specimens for the measurements was about $2\times10\times1$ mm^3. Femtosecond seed pulses from a Ti:sapphire laser oscillator, operating at a wavelength of 800 nm with a pulse duration of about 100 fs, were amplified to a pulse energy of 500 mW in a 100 kHz regenerative-amplifier system. After compensation of the amplifier dispersion, pulses 400 fs in duration were obtained. Laser pulses with a power of 450 mW were focused on samples to a diameter of about 30 μm with a 10 cm focal-length lens. The fluence is estimated to be about 540 mJ/cm^2. A low-pass filter with a cutoff wave number of 750 nm was placed between the specimen and a spectrometer with a photodiode array. The measurement range of the spectrometer was 350–1000 nm. The wavelength calibration was performed by using a halogen lamp. The SiO_2 samples for ESR measurements were set on an electronically controlled $X-Y$ stage to control the focused position and irradiated from ten different positions for each duration of irradiation to gain ESR signal intensities. The ESR measurements were carried out at room temperature and 20 K by using a JEOL X band ESR spectrometer. The derivative of resonant microwave absorption with respect to magnetic field was measured using a lock-in amplifier and magnetic field modulation with an amplitude of 0.05 mT and a frequency of 100 kHz. Microwave power supplied to the cavity was set at 4×10^{-3} W. An external ESR standard signal of Mn^{2+} in MgO was used to take into account possible changes in the quality factor of the resonator among separate measurements.

A spectrum of light transmitted through SiO_2 during femtosecond laser irradiation is shown in Fig. 1(a). The typi-

[a]Electronic mail: fukata@bk.tsukuba.ac.jp

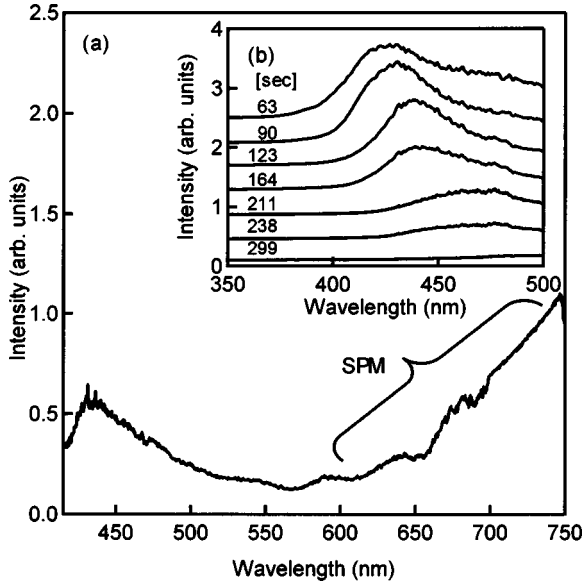

FIG. 1. (a) The spectrum of transmitted light through SiO_2 during femtosecond laser irradiation and (b) its irradiation time dependence.

cal white-light continuum caused by self-phase modulation (SPM)[12] of the femtosecond laser light is observed in the region from 750 to around 600 nm. In addition to the SPM band, a peak was observed at around 400 nm. In order to study the origin of the peak, the irradiation time dependence was obtained and shown in Fig. 1(b). The intensity of the peak initially increased and then decreased with irradiation time. Moreover, the position of the peak changed with irradiation time, suggesting the peak is related to some structural change, e.g., defect formation, during irradiation.

To investigate the formation of defects due to irradiation with a femtosecond laser, we performed ESR measurements after irradiation. The ESR signal with g factors of 2.0007 and 2.0015 was observed as shown in Fig. 2(a). These g factors are in good agreement with an oxygen vacancy defect having an unpaired electron spin in a dangling sp^3 hybrid orbital of a Si atom bonded to three oxygen atoms in SiO_2.[13–16] This defect is well-known as E' center ($\equiv Si\cdot$) and the charge state is positive.[17] The ESR signal intensity of E' center reached a maximum at an irradiation of 60 s as shown in Fig. 2(b). The decrease in the signal intensity after 60 s means that the E' centers became ESR inactive centers with increasing irradiation time. Such centers are formed by the formation of a so-called oxygen-deficiency center (ODC)[16] by capturing electrons or the recovery of Si–O–Si bonds by retrapping oxygen atoms. Based on the following result, the latter case is ruled out. If Si–O–Si bonds are reformed by retrapping oxygen atoms, the band due to SPM would also have to be recovered. The intensity of the SPM band, however, decreased with irradiation time. Hence, the decrease in the ESR signal intensity of the E' center probably corresponds to the former case resulting from a change from a positive to a neutral state.

Considering the formation of the E' center and the subsequent formation of the ODC, the decrease in the intensities of the transmitted light can probably be explained as follows. The local structural change from SiO_2 to a Si-rich structure due to the formation of oxygen-vacancy defects such as the E' center and the ODC increases the refractive index in the

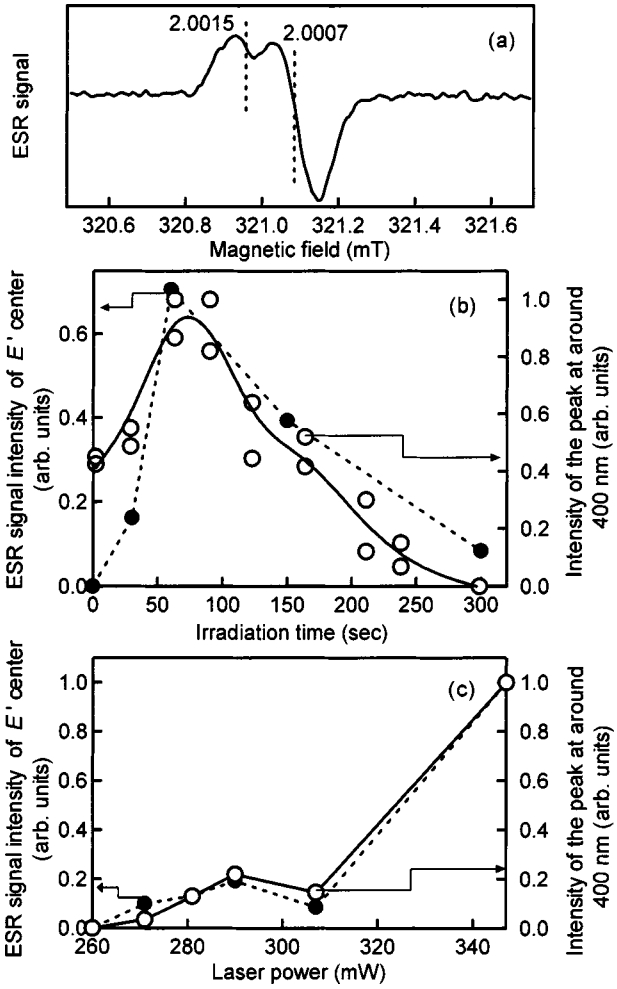

FIG. 2. (a) The ESR signal of E' center observed at 20 K, (b) the dependences of the ESR signal intensity and the peak at around 400 nm on laser irradiation time, and (c) those on laser power. The ESR measurements in (b) and (c) were performed at RT.

irradiated area of the specimen.[2] This effect gives rise to an increase in absorption and reflection in the irradiated parts of the specimen, and therefore the intensities of the transmitted light decrease.

Both dependences of ESR signal intensity on laser irradiation time and laser power are in good agreement with those of the intensity of the peak observed at around 400 nm as shown in Figs. 2(b) and 2(c), respectively. Two possibilities are considered as the origin of the peak at around 400 nm. One possibility is that this peak is due to the recombination of self-trapped excitons (STEs) formed by femtosecond laser irradiation. The other possibility is that it is due to second harmonic generation (SHG). SHG should be exactly observed at 400 nm, namely, at the position of half of the wavelength of the femtosecond laser (800 nm). The peak observed in this study, however, showed the red shift from 400 to 450 nm with irradiation time. Thus, the possibility of the latter case can be ruled out. The luminescence due to STEs in SiO_2 is observed at about 2.8 eV ($\sim$440 nm).[18] The configuration coordinate diagram for STE and E' center in SiO_2 is shown in Fig. 3. The STEs are produced by formation of an exciton composed of a hole at the upper valence band and an electron in the conduction band via multiphoton absorption in SiO_2, followed by lattice distortion due to

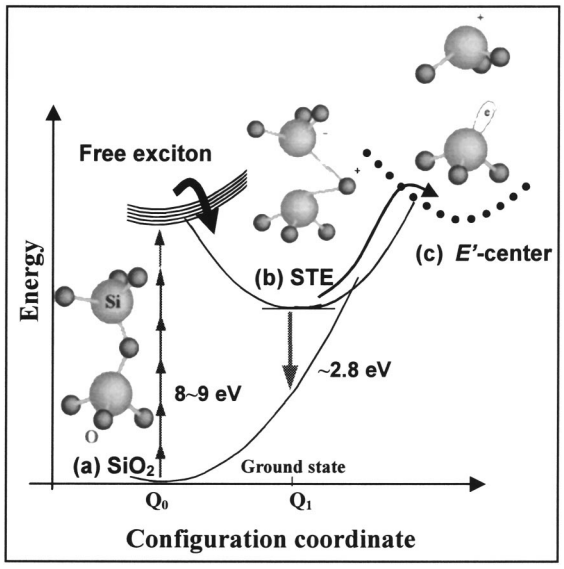

FIG. 3. Configuration coordinate diagram for STE and E' center in SiO_2. Free excitons are formed by multiphoton absorption (a). Then free excitons are localized by self-induced lattice distortion due to strong electron-phonon interactions and form STEs (b). A part of STEs leads to the breaking of one of the Si–O bonds, namely the creation of E' centers (c).

strong electron-phonon interactions [Fig. 3(b)]. A part of such STEs leads to the breaking of one of the Si–O bonds in SiO_2 and the consequent creation of E' centers [Fig. 3(c)].[19] Indeed, the ESR signal of the E' center was observed as shown in Fig. 2(a). No peak at around 400 nm was observed in a SiO_2 specimen with high concentrations of impurities. This result shows that the existence of impurity levels suppresses the recombination of STEs, supporting the former possibility. The redshift of the peak at around 400 nm shows a reduction in the separation between the ground state and the excited state of the STEs level, suggesting a local structural change in the specimen. Thus, the observation of light transmitted through SiO_2 during femtosecond laser irradiation enables us to clarify the dynamics involved in the generation of defects and the subsequent local structural change in real time.

In conclusion, we investigated the effect of femtosecond laser irradiation on SiO_2 specimens in real time by measuring the change in the spectra of light transmitted through these specimens. We also performed ESR measurements to identify defects introduced by irradiation with the femtosecond laser. The peak due to STEs was observed at around 400 nm just after irradiation and its position changed with irradiation time. Both dependences of the peak at around 400 nm on irradiation time and laser power are in good agreement with those of the ESR signal intensity of positively charged oxygen vacancies, namely, E' center. The strong correlation shows that STEs are created followed by the formation of E' centers and finally that of the ODCs. Hence, the local structural change from SiO_2 to a Si-rich structure is caused by femtosecond laser irradiation. We have here in presented an approach to understanding the effect of femtosecond laser irradiation on SiO_2 in real time and the method holds promise of yielding various information of value for the fabrication of microscopic optical components.

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