Femtosecond laser induced defects in various silica glasses

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Received January 8, 2004

The mechanism of near infrared (IR) focused femtosecond (fs) laser induced defects in silica glasses produced by different methods is systematically investigated through measurements of absorption, fluorescence, and electronic spin resonance (ESR) spectra. The influence of impurities and hydroxyl groups on defects is discussed. The results show that ES silica glasses containing high OH and few defects are much stable under fs laser irradiation. It is also verified that Si E'_δ center formation has no direct relation with chloride ions.

OCIS codes: 320.7130, 160.2750, 300.6250.

High purity silica glass is widely used in laser systems as lenses or other optical components. Due to the development and application trend of shorter pulse width, shorter wavelength and higher energy laser technology, silica glass stability is becoming more and more important.

Recently, defects induced in silica glasses by infrared (IR) femtosecond (fs) laser are verified by optical absorption, photoluminescence and electronic spin resonance (ESR) spectra measurements[1,2], but the creation mechanism for the defects is still unclear. Understanding the processes of fs laser induced defects in fused silica glass is helpful to improving its quality.

In this paper, we report the results of near IR fs laser induced defects in various silica glasses produced by different methods. Influences from impurities, precursors, and OH groups are analyzed.

The setup of fs laser irradiation is shown in Fig. 1. The regenerative amplified Ti:sapphire laser outputs 120-fs pulses of 800-nm wavelength with repetition rate of 1 kHz and average power of 700 mW. The diameter of the beam is about 5 mm. Laser pulses are focused through a microscope into the silica samples setting on the surface of a three-dimensional (3D) stage controlled by a computer. Laser energy is attenuated by a Glam prism. The precision of the stage is 1.25 μm. Irradiation process could be monitored by a charge coupled device (CCD) *in situ*. The diameter of the beam at the focus is about 10 μm estimated from the diffraction limit (objective lens numerical aperture (NA) = 0.1). In the experiment, the stage moving speed is 10 mm/s, the interval of the spots and lines are all 10 μm.

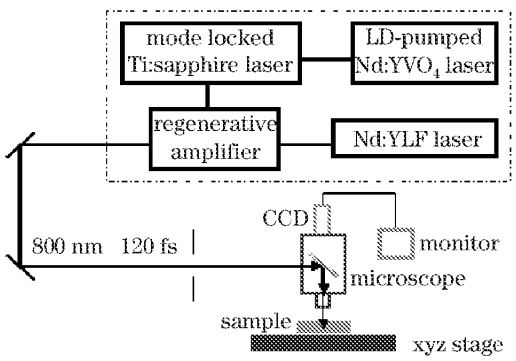

Fig. 1. Experimental setup.

Commercial silica glass samples come from Nippon Silica Glass Co. in Japan. The characteristics of the samples could be found out in http://www.tqgj.co.jp. The surfaces of the sample are optically polished and its size is $5 \times 5 \times 2$ mm^3.

Absorption and fluorescence spectra are measured with Jasco V-570 UV/Vis/NIR Spectrophotometer and Jasco FP-6500 Spectrofluorometer respectively. ESR spectra are performed using Bruker ER200D-SRC operating at X-band ($\nu = 9.80$ GHz) with field modulation of 100 kHz at room temperature. The amplitude of modulation is 0.8, microwave power is 12.6 mW, scan width is 5.0 mT and the center of magnetic field is 349.0 mT. Londe factors (g) are assigned by comparing with standard sample DPPH.

The absorption spectra of the silica glasses before and after fs laser irradiation are shown in Fig. 2. It is shown that after fs laser irradiation, the absorbances of all the

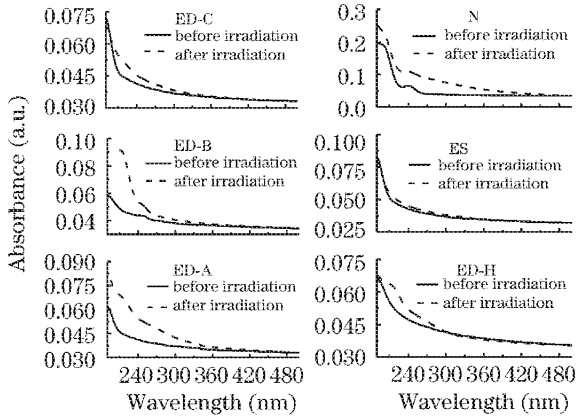

Fig. 2. Absorbance spectra of various silica glasses before and after fs laser irradiation.

absorption spectra increase in the region of 190 to 450 nm. In ED-B, band of 215 nm appears, which is generally related to E′ center[3]. There is no obvious band formed in other glasses, which might be due to the low content of defects averaged in the samples.

Excited by the light of 248 nm, all the emission bands of the silica glasses before and after laser irradiation are shown in Fig. 3. Signal intensity in ED-B and N is stronger than the others. After irradiation, bands of 282 and 286 nm in N and band of 450 nm in ES are decreased. Band of 400 nm in ED-C increased.

There is no ESR signal detected in the samples before laser irradiation, as shown in Fig. 4. After irradiation, E′ centers are detected in all the samples. The ESR spectra show different profiles in the samples which might be connected with the lattice network. In ED-B and ED-C, two variants of E′ center, E'_δ and E'_γ, are detected. The signal intensity of ES is quite weak compared to the others, which means a few E′ center formed. From the results, we could not find out the corresponding relationship between intensity of ESR signal and content of OH groups. E′ centers induced in the silica glasses are quite

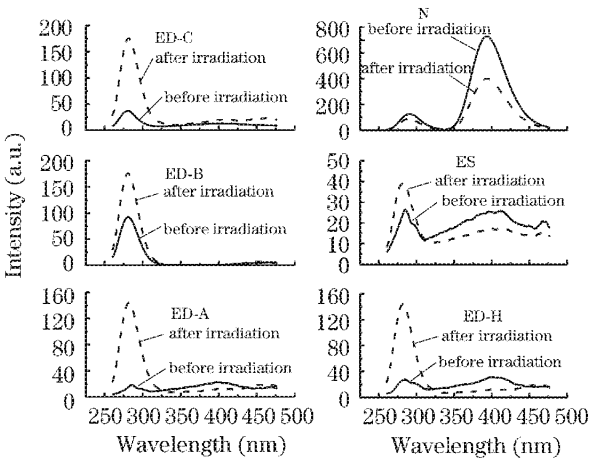

Fig. 3. Fluorescence spectra of various silica glasses before and after fs laser focused irradiation.

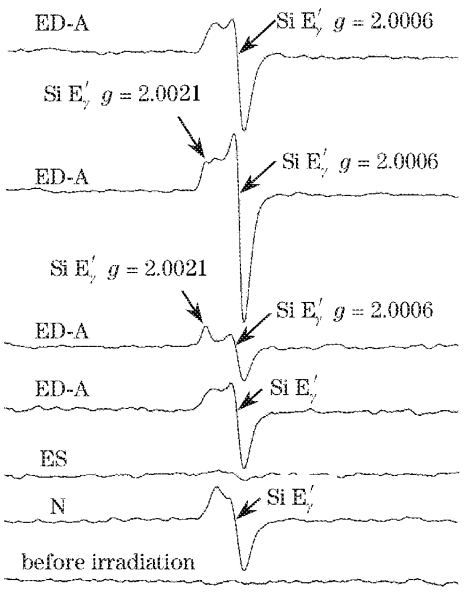

Fig. 4. ESR signal before and after laser irradiation.

stable at room temperature, which can maintain after one year.

Considering no linear absorption appears in pure silica glasses before IR fs laser focused, the multiphoton absorption is the main reason for the defects creation under the ultrafast high power laser irradiation[1,2]. Under the single shot pulse irradiation, the process of defect generation could be divided into two stages. One is before the end of the pulse. Valence band electron is excited to the conduction band due to multiphoton absorption. The kinetic energy of the free electrons increases in the laser field and creates new electrons by collisions. Such repetition processes would result in avalanche ionization[4]. Under the ultrashort high power laser irradiation, free electrons absorb energy from the laser field faster than they transfer to the lattice. Second is after the end of a pulse. The energy of free electrons couples to the lattice through phonons and gives rise to the increment of lattice temperature. Violent lattice distortion would take place around the focusing area. Thermal effect is the main reason for lattice distortion under fs laser irradiation[5].

In the experiment, there are no paramagnetic defects detected before laser exposure. The diamagnetic defects are oxygen vacancies, which have two variants, relaxed oxygen deficient center (ODC(I)) and non-relaxed oxygen deficient center (ODC(II))[6,7]. The atomic structures are ≡Si−Si≡ and ≡Si··Si≡, (symbols ' · ' and ' ≡ ' denote unpaired electron and three Si—O bonds, respectively.) The absorption bands of the defects are at 163 and 248 nm and the emission bands are at 295 and 400 nm[6,7], respectively.

Band $B_2\beta$ with absorption spectrum at 241 nm emits light at 295 and 400 nm[6,7]. There are several explanations for its origin, such as correlation to impurity Ge[8], or interstitial O_2^-[9], or generated from the bond O—O between Si—O—O—H groups[10] or divalent silicon (Si_2^0)[11]. We detect emission band of 400 nm in all silica glasses, and find out that it exists with the emission bands of neutral oxygen vacancy simultaneously. So emission band of 400 nm might arise from divalent silicon (Si_2^0), which is another kind of neutral oxygen vacancy. Thus, three oxygen vacancies exist in the silica glasses, relaxed oxygen deficient ODC(I), non-relaxed oxygen deficient ODC(II), and divalent silicon (Si_2^0). Before and after fs laser irradiation, the main defects in ED-B are ODC(II) and those in N are divalent silicon (Si_2^0) with band $B_2\beta$. After fs laser irradiation, in most silica glasses the content of divalent silicon (Si_2^0) decreases and ODC(I) or ODC(II) increases.

The content of oxygen vacancy in silica glasses change could be understand as lattice distortion because the laser energy deposition and thermal effect around the focusing area enhance the defect creation. Under the structure relaxation, Oxygen atoms displaced from the original sites during structure relaxation and resulted in the intermediate oxygen atoms and oxygen vacancy. The processes could be simplified as

$$\equiv \mathrm{Si} - \mathrm{O} - \mathrm{Si} \equiv \rightarrow \equiv \mathrm{Si} \cdot \cdot \mathrm{Si} \equiv + \mathrm{O}. \quad (1)$$

It is generally deemed that oxygen deficient center is precursor of E′ center. When holes trapped at oxygen vacancies, E′ center formed[12]. The chemistry processes

could be written as

$$\equiv \mathrm{Si} - \mathrm{Si} \equiv \rightarrow \equiv \mathrm{Si} \cdot {}^{+}\mathrm{Si} \equiv + e^{-}. \quad (2)$$

E′ center is a paramagnetic center, firstly assigned by Weeks in 1965[13]. There are several variants of E′ center. The small difference could be discriminated by ESR spectra[14]. The general atomic structure of E′ centers is a neutral silicon atom bonded to three oxygen atoms and one unpaired electron in a dangling sp^3 orbit.

The content of divalent silicon (Si_2^0) decreases after fs laser irradiation, especially in N, which can be understand as divalent silicon (Si_2^0) transformed into E′ center by photoionization[3] or trapping holes[3], or firstly transformed into oxygen vacancy and then into E′ center[3] as shown in expression (2).

Bonds Si—Cl and Si—H for loss one electron could also form E′ center[15,16]. Bond Si—Cl broken might be the main reason for E′ center formation in ED-C due to the high content of Cl. There are two candidates for the source of hydrogen atoms, Si—H and Si—OH. Dissociation of Si—H bonds could easily occur in wet oxygen deficient ED-A and ED-H silica glasses.

In ED-B and ED-C, E'_δ centers are also discovered. E'_δ center is firstly assigned by D. L. Griscom[16] and gave the atomic structure comprising a cavity containing one unpaired electron and three chloride ions bonded with four silicon atoms. Unpaired electron delocalized equally over four silicon atoms. Later, R. Tohmon[17] found that oxygen vacancies were the pivotal factor for E'_δ center formation and proposed that E'_δ center would be an unpaired spin delocalized over the two neighboring silicons. In our experiment, E'_δ centers are discovered in ED-B and ED-C, not in ED-A, although all of them containing chloride ions. This might be another proof for E'_δ center's formation that has no direct relation with chloride ions.

In conclusion, fs laser induced defects are systematically studied in silica glasses produced by different methods. Laser energy deposition and thermal effect are the main reasons for the defect creation. Precursors, impurities and lattice network affect the defect generation. ES silica glasses containing high OH and few defects are much more stable than the other silica glasses under IR fs laser irradiation.

This work was supported by the National Natural Science Foundation of China (No. 10074011) and the Ministry of Science and Technology of China (No. 2001CCA04600). Q. Zhou's e-mail address is kerryqling@sohu.com.

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