

STRESS-INDUCED PHOTOLUMINESCENCE IN PURE SILICA OPTICAL FIBERS

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Changes in photoluminescence (PL) originating from non-bridging oxygen hole centers (NBOHCs) are investigated by applying tensile stress up to 4 GPa to silica optical fibers. The formation of NBOHCs, that is, Si–O bond breakage, is related to the formation of valence alternative (VA) defects in silica glass. The PL intensity increases with increasing applied stress and almost reverts to the initial state on release of the stress. The concentration of NBOHCs induced by a stress of 4 GPa is, however, very low (about 10^{14} spin/g). Thus, it is found for the first time that applied stress causes the Si–O bond breakage, which is the first step for the formation of VA defects. Moreover, the reversible change in PL intensity indicates that dangling bonds cannot be converted easily to VA defects in silica glass.

1. Introduction

Two defect models, that is, a point defect center and a valence alternation (VA) model, are proposed for a defect structure in silica glass. In the former model, three defect centers: E' center [1], non-bridging oxygen hole center (NBOHC) [2] and peroxy radical (PR) [3] are identified as intrinsic defect centers in silica glass irradiated with γ -ray, X-ray and energetic electrons. Using electron spin resonance (ESR) techniques, E' centers and PRs are found to be associated with oxygen vacancies and interstitials, respectively [4,5]; they are considered to be a type of Frenkel defect pair. NBOHCs, as their name implies, are found to be due to dangling oxygen ions [6]. These suggest that oxygen vacancies, interstitials and dangling bonds exist in the silica glass network as precursors.

On the other hand, a typical VA defect is considered to be three-coordinated oxygen centers [7,8]. It has however been difficult to ascertain the formation mechanism of VA defects experimentally because they are non-paramagnetic. In VA defect formation, the first step is considered to be breaking of a Si–O bond in the network and the second step is the reaction of the dangling neutral

silicon site with a bonded oxygen atom [9,10]. Thus, the bond breaking is essential for the VA defect formation.

In this paper, we discuss Si–O bond breakage due to applied stress using high-strength optical fibers. Changes in structure of the silica glass network with stress have been investigated by neutron scattering [11] and Raman scattering spectroscopies [12,13]. In those studies, no changes with regard to defects have been observed because both neutron scattering and Raman scattering spectroscopies are insensitive to low content defects. Then, we have investigated changes in photoluminescence (PL) caused by application of high tensile stress to pure silica optical fibers because PL originates purely from defects in silica glass. As a result, we clarified the bond breakage due to applied stress in silica glass for the first time.

2. Theoretical considerations

Silica optical fibers have a mechanical strength of about 5 GPa at room temperature [14]. This value is a few tenths as large as the theoretical strength (22 GPa) of silica glass, which is evaluated from the binding energy and surface energy of

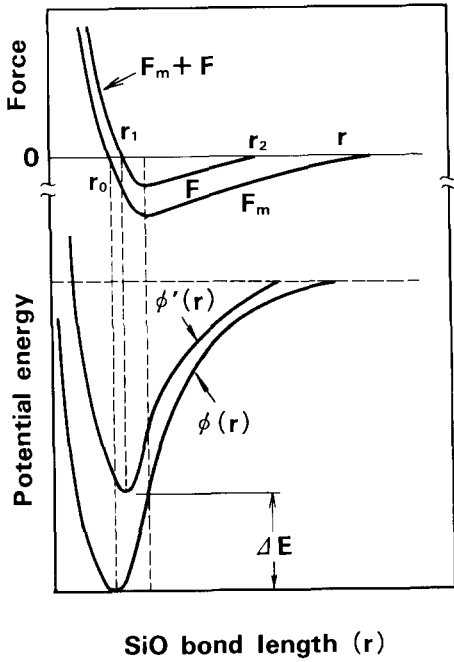
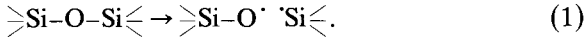


Fig. 1. Schematic configurations of potential energy and force in Si-O bond.

silica glass. If a stress of about 5 GPa is applied to silica glass, the stress concentration due to defects in the silica glass network can break Si-O bonds as follows:



This bond breaking results in a gain in energy greater than the binding energy, so that two dangling bonds are a highly unlikely defect pair under normal conditions. However, this defect pair may be stable in a network subjected to high tensile stress.

To discuss the influence of stress on the bond breakage in more detail, we consider a change in the potential energy $\phi(r)$ and force $F(r)$ of a Si-O bond (r = the distance between Si and O), as shown in fig. 1. Under the applied stress, the following simple equation on the force balance is applicable:

$$F(r) + \alpha A \sigma = 0, \quad (2)$$

where A is the fiber cross sectional area and α is a constant representing the stress concentration effect. The two roots of eq. (3) are designated r_1 and

r_2 as shown in fig. 1. The potential energy changes with applied stress, and is given by

$$\phi'(r_1) = - \int_{r_1}^{r_2} [F(r) + \alpha A \sigma] dr. \quad (3)$$

The stress-induced decrease in the binding energy is given by

$$\Delta E = \phi'(r_1) - \phi(r_0) \sim \alpha A \sigma r_2, \quad (4)$$

where $\phi(r_2) \sim 0$, $\phi(r_1) - \phi(r_0) \sim 0$ ($r_0 \sim r_1$), $r_1 \ll r_2$. Assuming that $\phi(r)$ is the Born-Mayer type potential, r_2 rarely depends on σ in the low stress region. Therefore, ΔE is approximately proportional to σ .

The stress-induced change in defect concentration is given by

$$n(\sigma) = n_0 \exp[-(E - \Delta E)/kT_f], \quad (5)$$

where $E = \phi(r_0)$ and T_f is a fictive temperature of silica glass. If $E \gg \Delta E$, the relationship between defect concentration and applied stress is given by the following equation:

$$n(\sigma) = n(0)(1 + B\sigma), \quad (6)$$

where B is a constant.

3. Experimental procedure

Samples used were pure synthetic silica fibers 125 μm in diameter. They were drawn from a preform fabricated by a vapor phase axial deposition method and coated with silicone resin about 150 μm thick. The OH concentration in optical fibers was estimated to be less than 1 ppm from the OH absorption peak at 945 nm. The fictive temperature of optical fibers was determined to be about 2100 K [13].

Photoluminescence of optical fibers was excited by a He-Cd laser at a wavelength of 325 nm with output power of 8 mW. A PL spectrum emerging from the fiber end section was detected from 200 to 900 nm by a Si photodiode array with an image-intensifier. A method of applying a load to optical fibers was described elsewhere [13]. The length of the stressed portion of optical fibers was changed from 2.3 to 19 m, while that of the unstressed portion was about 6 m.

4. Results and discussion

In the measurement of PL spectra from the fiber end section, fiber elongation due to applied stress affected the transmitted light intensity. Figure 2 shows the relationship between intensity ratios of transmitted light and applied stress at various wavelengths in optical fiber 19 m long. The optical losses of optical fiber at wavelengths of 325, 430 and 650 nm were 1500, 120 and 100 dB/km, respectively. The ratio of decrease in transmitted light intensity is larger with a higher absorption coefficient. This is because the decrease in transmitted light is due to fiber elongation. It is therefore found that the transmitted light intensity in optical fibers tends to decrease with increasing applied tensile stress.

A PL spectrum of optical fibers excited by the He-Cd laser are shown in fig. 3. Two peaks are observed near 430 nm and 650 nm. These peaks originate from a fiber drawing process because they were not observed in a silica glass preform. The PL near 650 nm is ascribed to NBOHCs [15,16], and the PL near 430 nm is considered to be due to E' centers [17].

When we investigated changes in PL spectra with applied stress. *The PL peak wavelength re-*

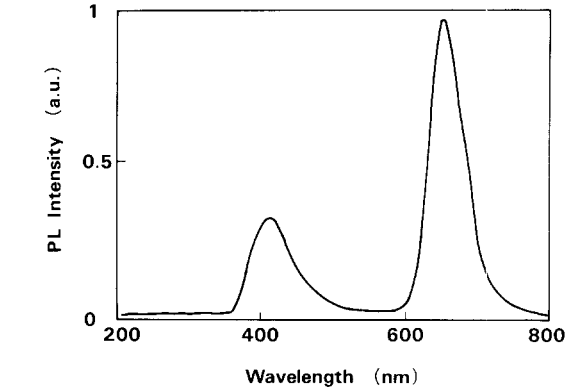


Fig. 3. PL spectrum of as-drawn pure silica optical fibers.

mained unchanged with applied stress. This indicates that stress-induced PL should result from the same defects as drawing-induced defects. On the other hand, the PL intensity, which is defined by a peak area of the spectrum, changed with applied stress. The results for stressed optical fibers 2.3 m long are shown in fig. 4. It is clear that the 650 nm PL increases in intensity with increasing applied stress and that the change is reversible. Taking into account the results shown in fig. 2, it is reasonable that the increase in PL intensity, transmitted in optical fibers, is due to the increase in NBOHC concentration. Moreover, it is found that the relationship between the PL intensity and applied stress follows eq. (6) reversibly. These results suggest that high tensile stress applied to silica glass breaks a Si-O bond, as represented by eq. (1).

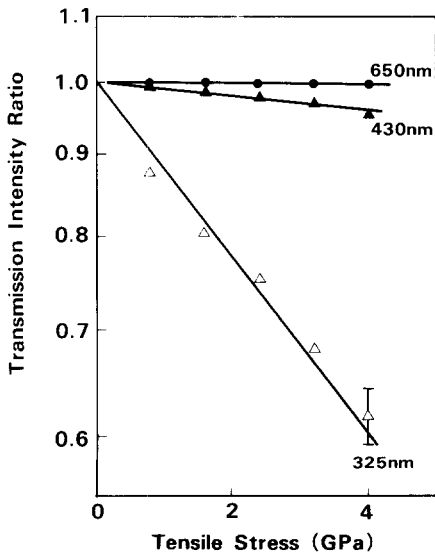


Fig. 2. Relationship between transmitted light intensity and applied stress in optical fibers 19 m long.

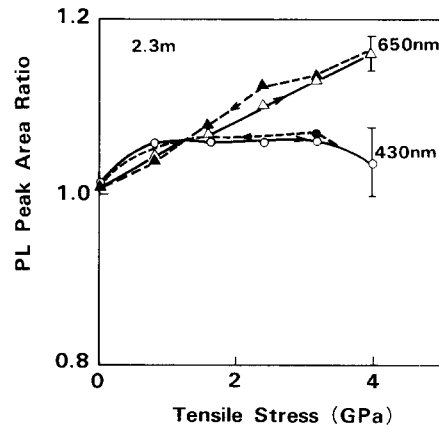


Fig. 4. Relationship between PL intensity and applied stress.

The PL near 430 nm also increases in intensity with increasing applied stress. Since E' centers are generated at the same time as shown in eq. (1), the increase in 430 nm PL intensity is reasonable. Moreover, the increase in PL intensities was almost independent of the stressed length. This is because the laser intensity at the wavelength of large absorption coefficient decreases within a short length [18].

We estimated the quantity of the stress-induced PL from the concentration of drawing-induced NBOHCs in unloaded optical fiber, which is nearly 10^{15} spin/g [16]. *As described in eq. (5), the stress-induced defect concentration in silica glass should depend on T_r , which is very high in silica optical fibers [13].* Since the increased intensity of PL near 650 nm is about one tenth of the initial value in fig. 4, the concentration of stress-induced NBOHCs is estimated to be of the order of 10^{14} spin/g or less. This very low concentration is consistent with the fact that the elastic energy of elongation almost results in the bond stretching of the silica glass network [11]. It is inferred that microscopic stress concentration, which leads to bond breakage, is mainly ascribed to drawing-induced structural changes.

These results elucidate the fact that high tensile stress can break the Si–O bond, though the concentration of the broken bonds is very low. Bond breakage is considered to be a prerequisite for VA defect formation in silica glass. The broken bond however almost reverts to the initial state. This implies that the presence of dangling bonds is not favored in a silica glass network, as mentioned by Greaves [7] and Lucovsky [8]. In other words, it indicates that more energy is necessary for the conversion of dangling bonds to VA defects.

5. Conclusions

We investigated stress-induced changes in photoluminescence by application of high tensile stress to optical fibers. As a result, it was found that very high tensile stress applied to silica glass broke Si–O bonds of which the concentration was of the

order of 10^{14} g⁻¹. This very low concentration suggested that Si–O bonds were broken by local stress concentration due to defect centers in optical fibers. Moreover, the bond breakage appeared to be reversible in silica glass. The analysis of the change in the Si–O potential energy with applied stress indicates that more energy was necessary for the conversion of dangling bonds to VA defects.

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