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Fluorine-doping concentration and fictive temperature dependence of self-trapped holes in SiO₂ glasses

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Fictive temperature (T_f) and fluorine (F)-doping concentration dependences of self-trapped holes (STHs) in silica glasses created by UV irradiation at low temperatures have been studied by the electron-paramagnetic-resonance method. It was found that the yield of STH decreases with decreasing T_f and increasing F-doping concentration. In combination with infrared spectra measurements, the correlation among T_f , F-doping concentration, Si–O bond length, and Si–O–Si bond angle was elucidated. We conclude that the change in both T_f and F doping can modify the network of SiO₂ glass, leading to the suppression of the formation of STHs. © 2005 American Institute of Physics. [DOI: 10.1063/1.1980536]

INTRODUCTION

As a photomask material in projection photolithography of semiconductors with a F₂ excimer laser (wavelength of 157 nm) for the next generation ultralarge scale integrated circuit fabrication technique, a high transparency in the vacuum ultraviolet range is desired. SiO₂-based glass is one of the candidates because of its good transparency and radiation resistance and lower thermal-expansion coefficient. Recently, appropriate manufacturing processes or doping has been used to increase the transparency of SiO₂. For instance, many investigations were devoted to the effect of F doping on the physical properties of SiO₂ glass, and the transmission loss in F-doped SiO₂ glass at 157 nm was found to be one order of magnitude lower than that in the F-free sample.^{1–4} It is well known that F can widen the optical band gap without inducing any optical absorption in the transparent region of silica glass; the substitution of F into the SiO₂ network can make the glass network more stable and can decrease the structure disorder by encouraging the structural relaxation.^{4,5} Such investigation may yield an improved method to prepare silica-glass optical elements having superior transparency and durability for excimer laser applications.

Understanding the formation of various color centers in SiO₂ glasses is an important issue to improve the properties of the material. Previous investigations on F-doped SiO₂ glass focused mainly on the radiation-induced defects at room temperature such as the E' center and the nonbridging oxygen hole center (NBOHC). It was found that F doping can effectively suppress the generation of the E' center. The precursors, which are strongly dependent on the preparation history and are often dominant sources of radiation-induced defects, can also be removed by F doping.^{2,6–8}

This study pays close attention to a kind of self-trapping

phenomenon that has been widely observed at alkali halides.⁹ Griscom observed a self-trapped hole (STH) in α -SiO₂ by the electron-paramagnetic-resonance (EPR) method and ascribed the spectrum to two kinds of STHs, STH₁ and STH₂.¹⁰ Microscopically, the STH₁ center consists of a hole trapped at a 2p nonbonding orbital of an O atom bridging two Si atoms, and the STH₂ center, a metastable defect where the hole is rapidly tunneling between two bridging O atoms. Such assignment has been confirmed by our recent experimental results; the main features of the EPR spectrum of STH in SiO₂ glasses exhibit two kinds of different saturation and decay behaviors.¹¹ On the other hand, Pacchioni and Basile and Kaneta investigated the generation mechanism of STH in SiO₂ using the *ab initio* quantum-chemical simulations.^{12,13} They found that STH₁ is characterized by a strong elongation of the Si–O distances, and STH₂ is related not only to a small elongation of the Si–O bond compared to the regular lattice but also to a significant reduction of the O–Si–O angle from the classical tetrahedral value of 109° to about 85° when the structure of STH₂ is geometrically optimized.

We previously reported that fictive temperature T_f , being a high temperature at which amorphous silica is allowed to reach an equilibrium state before a rapid quench to room temperature,¹⁴ can significantly affect the yield of STH in pure SiO₂ glass.¹⁵ Here we extended our study to the T_f dependence of the yield of STH in silica glasses with various F-doping concentration. Since the formation of STH is associated with the local distortion which can be probed by vibrational spectra,^{16,17} we discuss the significant effect of F doping and T_f on structural modification in combination with infrared (IR) spectra measurements, and explain why the STH yield can be suppressed in the samples with high F-doping concentration and low T_f .

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FIG. 1. The spin density of STH as a function of T_f at several different F-doping concentrations.

EXPERIMENTS

Silica glasses with different F concentrations from 0 to 5 mol % were used. Both of them were prepared by the vapor phase axial deposition method. The concentrations of OH and Cl were too low to be detected. The samples with different T_f were prepared by thermal annealing at different temperatures in air. An ArF excimer laser (MPB Technologies, PSX-100 with a wavelength of 193 nm) was used to irradiate the sample at 77 K for 30 min in order to create STHs. The power density, repetition rate, and pulse duration are 80 mJ/cm², 60 Hz, and 5 ns, respectively. Following that the sample was rapidly transferred to another liquid-nitrogen Dewar that was inserted in the EPR cavity. A JEOL system model FA100, operated at around 9.48 GHz, was employed to record the first derivative of the absorption curve with respect to the magnetic field. The modulation frequency and the width were kept at 100 kHz and 0.05 mT, respectively. The microwave power was kept at 0.1 mW in order to get the unsaturated maximum amplitude of the EPR spectrum based on our previous results.¹¹ The absolute spin concentration due to the STH was evaluated referring to CuSO₄·5H₂O crystal of a known weight. A Perkin Elmer 2000 spectrophotometer was used to record the IR spectra for all samples.

RESULTS AND DISCUSSION

In order to check the possible preexisting point defects that could act as the precursors, the samples without UV irradiation were first measured by the EPR method at both room and low temperatures. No signal can be detected. The samples with UV irradiation at room temperature were also checked; only the E' center can be seen. The NBOHC, which is stable at room temperature and usually observed using high microwave power,¹⁸ cannot be observed in our samples. Therefore we conclude that EPR signals from our low-temperature irradiated samples consist mainly of STHs and E' centers.

Since E' center does not seriously overlap with the STH component in EPR spectra, we double integrated the first derivative of the absorptive curve and got the sum of the yields of STH₁ and STH₂ following the previous work.¹⁵ Figure 1 shows the yield of STH defects as a function of T_f at several different F-doping concentrations. It can be seen that, for the samples with the same doping concentration, the yield increases almost linearly with increasing T_f . On the

FIG. 2. The absorption spectra for 2 mol % F-doped silica glasses at several different T_f .

other hand, the gradient of the line has a rapid change if F-doping concentration increases and then almost keeps constant for high F-doping samples. Totally, we cannot find which factor is dominant and both F-doping concentration and T_f seem to have comparable contribution to the yields of STH.

To understand how F doping and T_f can modify the glass network as well as the yield of STHs, we measured the IR spectra of all the samples. An absorption band around 2260 cm⁻¹ was investigated. This band is an overtone of the stretching vibration band of the Si–O–Si bond bridges and is correlated to the distribution of the Si–O–Si angle in the silica-glass network.⁵ The T_f dependence of IR-absorption spectra for the samples with 2 mol % F doping is shown in Fig. 2, where it is evident that this band shifts to high wave number with decreasing T_f . We chose the wave number where the band has a maximum absorbance as peak position. We found that the peak position exhibits almost linear to T_f , as shown in Fig. 3. The slight bias from the linear behavior for the samples with high T_f is due to the very short relaxation time, less than 0.1 s in these samples, leading to difficulty in preparing the samples. On the other hand, peak position as a function of F-doping concentration for the samples with T_f of 1100 °C is shown in Fig. 4. The change of peak position clearly exhibits two different behaviors: the shift of the peak position to high wave number is slow at low doping concentrations, then becomes rapid at the doping of more than 2 mol %. However, both decreasing T_f in Fig. 3 and increasing F-doping concentration in Fig. 4 can upshift the IR-absorption band, implying that they play similar roles in averaging bond angle.⁵

FIG. 3. The linear behavior of the absorption peak around 2260 cm⁻¹ vs T_f for 2 mol % F-doped silica glasses.

FIG. 4. The IR peak position vs F-doping concentration for the samples with T_f of 1100 °C.

The change of this IR-absorption band is closely related to the change of silica network structure, which consists of a series of SiO_4 tetrahedra, as shown in the top panel of Fig. 5. The change in T_f and F-doping concentration will modify the Si–O bond length and Si–O–Si bond angle θ , leading to the change of IR spectra.^{2,5,6,18} Generally the smaller wave number corresponds to the smaller bond angle that correlates with increasing structural disorder.^{5,18} In this model, the O–Si–O bond angle α is always fixed at 109°. However, the study of the topology of the networks indicated that the formation of the disorder will accompany the broadening of the θ intertetrahedral bond angle and tetrahedral distortion in order to maintain connectivity.¹⁸ Therefore the bond angle α in a real system should be slightly deviated from the ideal structure. The first-principle cluster model calculations have confirmed that increasing bond length is accompanied by the decrease in both α and θ angles.^{12,13}

A diagram in the low panel of Fig. 5 was used to explain all the experimental results we observed. The upshift peak with decreasing T_f in Fig. 3 and with increasing F doping in Fig. 4 indicates increasing θ bond angle and shortened Si–O bond length. Consequently, decreasing T_f can modify the θ angle as increasing F-doping concentration does. Since STH is characterized by the elongation of Si–O bond length and the reduced α ,^{12,13} which must simultaneously accompany

FIG. 5. The diagram illustrating the correlation between the T_f , F-doping concentration, structure disorder, and the yield of STH. The top is a silica tetrahedral showing a simple network structure.

the reduced θ angle as stated above, we concluded from Fig. 5 that both high F-doping concentration and low T_f can suppress the formation of STH.

The increasing F-doping concentration in Fig. 4 causes almost the same IR peak shift as the decreasing temperature in Fig. 3, hinting that F-doping samples can easily be prepared at low temperatures. This is consistent with the previous results, where F doping can encourage structural relaxation and can make the annealing of the sample easier at low temperatures.⁵ On the other hand, it is not clear why the yield of STH changes rapidly when the F-doping concentration is less than 1 mol %. Arai *et al.* also reported that F doping can greatly suppress the yield of E' when F-doping concentration is less than 1 mol %, but it almost has no effect on NBOHC.⁷ The response of F doping to the various defects seems to be selective; its physical origin is interesting and needs further study.

CONCLUSION

In summary, we have measured T_f and F-doping dependences of the EPR spectra of silica glasses irradiated by UV laser at low temperatures. It was found that the yield of STH decreases with decreasing T_f and increasing F-doping concentration. In combination with IR measurements, we conclude that the change in both T_f and F doping can modify the Si–O–Si bond angle and Si–O bond length, leading to the suppression of the formation of STHs.

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