Improvement of Vacuum-Ultraviolet Transparency of Silica Glass by Modification of Point Defects

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Silica glass is an important optical material in deep-ultraviolet (DUV, $\lambda \lesssim 300$ nm) and vacuum-ultraviolet (VUV, $\lambda \lesssim 200$ nm) spectral regions. However, DUV–VUV transparency of silica glass is significantly influenced by the presence of structural imperfections (point defects). This article describes point defects in silica glasses of low metallic impurity contents (“synthetic” silica glasses), and optical and chemical properties of these point defects. It is shown that controlled doping with specific point defects can improve the transparency and radiation hardness of silica glass in DUV–VUV spectral region. Such doped species include network modifiers that relax the glass structure and mobile interstitial hydrogen molecules. Utilization of these techniques in developing photomask substrates for F₂ laser photolithography and DUV optical fibers for ArF laser transmission is presented.

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1. Introduction

DEEP-ULTRAVIOLET (DUV) and vacuum-ultraviolet (VUV) spectral ranges refer to wave-lengths shorter than ~ 300 nm and ~ 200 nm, respectively. DUV–VUV light sources, in particular excimer lasers such as KrF ($h\nu = 5.0$ eV, $\lambda = 248$ nm), ArF ($h\nu = 6.4$ eV, $\lambda = 193$ nm), and F₂ ($h\nu = 7.9$ eV, $\lambda = 157$ nm) lasers, become increasingly important in photolithography, laser processing, and photochemical reactions. **Figure 1** shows optical absorption spectra of silica glass from infrared (IR) to VUV spectral region.¹⁾ Silica glass is one of the most important optical materials at DUV–VUV spectral region because the shape workability is good and the DUV–VUV transparency is the best among commercial optical glasses currently available.

In general, silica glasses for optical applications are prepared by vapor-phase methods. This type of silica glass is often referred to as “synthetic silica glass” and the concentration of metallic impurities is very low. As a consequence, IR transmittance of synthetic silica glasses becomes high enough to realize the optical fiber telecommunication. However, the DUV–VUV transmittance of synthetic silica glass is often far

from the theoretical limit determined by the Rayleigh scattering and the Urbach absorption edge.^{1),2)} The transmission loss originates from structural imperfections in silica glass (“point defects”), which are formed during the manufacturing processes or generated later by photoinduced reactions. However, scientific understanding of point defects has been insufficient in fabricating silica glasses with good transmittance and hardness to DUV–VUV laser light.

This article is intended to outline DUV–VUV optical properties and chemical reactivities of point defects found in synthetic silica glasses currently available, and to describe ways to improve the DUV–VUV transparency of silica glass by modification of point defects.

2. Optical and chemical properties of point defects in synthetic silica glass

A. Strained Si–O–Si bonds

Silica glass is an amorphous material and its atomic configuration is disordered. Studies by X-ray diffraction³⁾ and nuclear magnetic resonance⁴⁾ have indicated that the main origin of the disorder is the distribution of the bridging angle between two SiO₄ tetrahedra (Si–O–Si angle). In contrast, deformation of the SiO₄ tetrahedra is relatively small. These characteristics are well reproduced by a silica structure constructed by molecular dynamics calculations.^{5),6)} **Figure 2** shows distributions of Si–O–Si angles, O–Si–O angles, and Si–O bond lengths in this model structure. Compared to the Si–O–Si bonds at the central part of the distribution, those belonging to the tail parts are much more strained and termed “strained Si–O–Si bonds”.

α -quartz is a crystalline silica polymorph. Similarly to silica glass, it also consists of SiO₄ tetrahedra connected at their corners into a three-dimensional network. However, Si–O–Si bonds in α -quartz have nearly the same angle and are not strained. The VUV absorption edge of α -quartz is located at higher energy than that of silica glass (**Fig. 1**).⁷⁾ The VUV absorption edge of silica glass is shifted to lower energy by high-pressure densification,⁸⁾ which decreases the average Si–O–Si angle.⁹⁾ The distribution of Si–O–Si angle is more gently modified by thermal annealing.¹⁰⁾ The VUV absorption edge of silica glass is shifted to lower energy with an increase in fictive temperature from 900 to 1400°C. This change is

Fig. 1. Optical absorption spectra of silica glass and α -quartz (adapted from Ref. [1] with permission).

Fig. 2. Distributions of Si-O-Si angle (a), O-Si-O angle (b), and Si-O length in a silica structure consisting of 648 atoms. The structure is obtained by periodic classical molecular dynamics calculations.^{5),6)} The maxima of the distributions are located very close to the values of an α -quartz structure calculated using the same set of inter-atomic potentials (dashed lines). The experimentally determined values of α -quartz are also shown by dotted lines. Thick arrows indicate Si-O-Si angles of small ring structures [(Si-O)_n where $n=3$ and 4] in silica glass.¹²⁾ The $n=3$ ring is nearly planar with an Si-O-Si angle at $\sim 130^\circ$, whereas the $n=4$ ring can be puckered with decreasing the Si-O-Si angle from the planar value ($\sim 160^\circ$).

concurrent to the decrease in the average Si-O-Si angle and concentration increase in small ring structures (Si-O)_n where $n=3$ and 4.^{10),11)} These small rings are typical strained bonds that are directly detectable by Raman spectroscopy,¹²⁾ and are not present in α -quartz consisting of the $n=6$ and 8 rings. These observations indicate that the strained Si-O-Si bonds are responsible for the optical absorption near the VUV absorption edge of silica glass.

Cleavage of Si-O bond,

is a dominant origin of the radiation-induced point defects in silica glass.^{11),13)-16)} It is likely that the strained Si-O-Si bonds are primarily cleaved because the formation of X- and γ -ray-induced dangling bonds (E' center, $\equiv \text{Si}^*$, and non-bridging

Fig. 3. Dependence of the photoinduced concentrations of E' center and NBOHC on pulse energy of F_2 laser.^{18),19)} Concentrations of KrF- and ArF-laser-induced E' centers are also shown. Fictive temperature of the samples are set at 900 or 1400°C. All samples are exposed to 3×10^4 laser pulses.

oxygen hole center, NBOHC, $\equiv \text{SiO}^*$) are enhanced both by the high-pressure densification¹⁷⁾ and by increasing fictive temperature.¹⁶⁾ F_2 laser light interacts with the strained Si-O-Si bonds more directly: it excites the VUV absorption of the strained Si-O-Si bonds and causes reaction Eq. (1) via one-photon absorption processes, as shown in Fig. 3.^{11),18),19)} Furthermore, at large F_2 laser pulse energies this reaction turns into a two-photon process, which is most likely due to two-step absorption via real intermediate states.^{18),19)} As a consequence, this F_2 -laser-induced two-photon process is much more efficient than the same reaction caused by simultaneous two-photon absorption of KrF or ArF laser light, which does not directly excite the VUV absorption band of strained Si-O-Si bonds.

E' centers have an intense optical absorption band at 5.8 eV, and NBOHCs exhibit two optical absorption bands of comparable intensities at 4.8 and ~ 6.5 eV. These absorption bands significantly reduce the DUV-VUV transmittance of synthetic silica glasses. The 6.5 eV absorption band of NBOHC has been identified recently both by experimental^{20),21)} and theoretical²²⁾ studies.

B. Network modifiers

Although the concentrations of the metallic impurities are very small, synthetic silica glasses contain a small amount of non-metallic impurities originating from chemical compounds used for the manufacturing. The main impurities are hydrogen, fluorine, and chlorine atoms. These elements are monovalent and serve as network modifiers that break up the glass network.

Hydroxyl group (SiOH) is the most common network modifiers in synthetic silica glasses. It is incorporated in silica glasses while hydrolyzing silane-based precursor gas molecules in oxygen-hydrogen combustion flame. SiOH groups exhibit a characteristic IR absorption band at $\sim 3670 \text{ cm}^{-1}$, which is associated with the Si-O-H stretching mode. This IR absorption band undergoes a low energy shift when the bonding configuration of SiOH groups is altered from isolated free state to hydrogen-bonded state^{23),24)} by cooling,²⁵⁾ F_2 laser irradiation,²⁶⁾ heavy exposure to γ -rays,²⁷⁾ or by increasing the fictive temperature.²⁸⁾

SiOH groups exhibit a VUV optical absorption band above

~ 7.3 eV.^{25),29)–32)} This absorption band is shifted to higher energy along with the structural alternation of SiOH groups from the isolated to the hydrogen-bonded states.^{25),26)} Isotope exchange of H with D causes a high energy shift almost equal to the difference in the zeroth vibrational levels between the O–H and O–D oscillators (~ 0.06 eV), indicating that the potential surface of the excited state is dissociative against the stretching of O–H bond.³²⁾ Hence, direct VUV photoexcitation of SiOH groups results in an efficient photolysis of the SiO–H bond (quantum yield ~ 0.1 – 0.2) to form a pair of NBOHC and mobile hydrogen atom (H^0),^{33)–35)}

Hydride (SiH) group is another form of hydrogen bound to the silica network. Optical properties of SiH groups remain elusive. It is likely that the optical transition of SiH groups is located at higher energy than the absorption edge of silica glass^{36),37)} and its DUV–VUV absorption is very weak.³⁸⁾ On the other hand, there are suggestions that the Si–H bonds are photolyzed by DUV–VUV laser light,^{39)–41)}

Fluorine and chlorine atoms originate from the silane precursor compounds such as SiCl_4 and SiF_4 as well as dehydration agents such as Cl_2 , SOCl_2 , CCl_4 , and CF_4 used to remove SiOH groups. They attach to a network silicon atom with replacing one of the four bridging oxygen atoms, and thus form chloride (SiCl) and fluoride (SiF) groups. However, an NMR study has shown that in heavily fluorine-doped silica glasses (SiF 3 mass%), a part of silicon atoms can be five-coordinated with one fluorine and four bridging oxygen atoms.⁴²⁾ SiF groups are detectable via their characteristic Raman band at 945 cm^{-1} ,^{43)–46)} whereas selective detection of SiCl groups is difficult.

SiCl groups undergo various chemical reactions with reactive molecules incorporated in interstitial voids of silica glasses by thermal annealing. SiCl groups generate interstitial Cl_2 and HCl molecules,

through reactions with interstitial O_2 and H_2O molecules, respectively.⁴⁷⁾

It is considered that SiCl group is a main source of radiation-induced point defects because the concentrations of radiation-induced defects in chlorine-doped silica glasses are generally larger than those in chlorine-free glasses.^{48),49)} H^0 s created via Eq. (2) convert SiCl groups to E' centers and HCl molecules,⁴⁷⁾

By analogy, chlorine-related radicals (ClO_x where $x = 2, 3$) are formed in F_2 -laser-irradiated silica glasses containing both SiCl groups and interstitial oxygen molecules (O_2).⁵⁰⁾ This reaction would be due to cracking of SiCl groups with oxygen atoms (O^0) generated by the F_2 laser photolysis of O_2 . In addition, resultant interstitial Cl_2 , HCl, and ClO_x would be further decomposed by DUV–VUV light to participate in secondary reactions.

Controversy still remains concerning the photoinduced defect formation from SiCl groups. A Si–Cl bond is dissociated by X- and γ -rays to form a pair of E' center and a chlorine atom (Cl^0).^{15),51)} The formation of Cl^0 , however, is not observed in a chlorine-doped silica glass exposed to F_2 laser light at 77 K,⁴⁷⁾ although F_2 laser light directly excites a weak

VUV optical absorption band of SiCl groups above ~ 7.5 eV.⁵²⁾ Some chlorine-doped silica glasses even show better hardness to ArF laser light than chlorine-free silica glasses.⁵³⁾ These observations may indicate that SiCl groups show a good stability to DUV–VUV light in the absence of interstitial chemical species.

SiF groups do not exhibit measurable optical absorption within the band gap of silica glass^{46),54),55)} and are much more stable than SiCl groups. These properties primarily originate from the large Si–F bonding energy, which is even larger than the Si–O bonding energy. In contrast to SiCl groups, SiF groups do not react with O_2 and H_2O to form F_2 and HF molecules, respectively.⁵⁶⁾ Furthermore, formation of fluorine atoms (F^0) via the cleavage of Si–F bonds has not been observed.¹⁵⁾

C. Interstitial hydrogenous species

Silica glass is a low density oxide (2.2 g cm^{-3}) compared to the related crystalline form of silica (e.g. α -quartz, 2.65 g cm^{-3}) and other light metal oxides of analogous formula weight (e.g. MgO , 3.6 g cm^{-3} ; Al_2O_3 , 3.97 g cm^{-3}). Hence, it contains a lot of interstitial voids that enable dissolution and diffusion of small chemical species.^{57),58)} These interstitial chemical species often play a key role in photochemical reactions in silica glasses. Reactions involving interstitial hydrogenous species are particularly important because they are mobile and reactive at room temperature.

Interstitial hydrogen in silica glass includes hydrogen atom (H^0) and molecule (H_2). H^0 is paramagnetic and detectable by EPR. It is a transient species created mainly by the cleavage of SiO–H and Si–H bonds [Eqs. (2) and (3)]. It becomes mobile in silica glass above $\sim 50 \text{ K}$,^{34),35),59)} and quickly disappears above $\sim 160 \text{ K}$ through dimerization or reactions with other chemical species. Interstitial H_2 originates from glass manufacturing in oxygen-hydrogen combustion flame,^{34),35)} dimerization of H^0 s,^{34),35),60)} and thermal annealing in H_2 atmosphere.^{61),62)} It becomes mobile in silica glass above $\sim 200 \text{ K}$.^{34),35),60),63),64)} Diffusion coefficients of H^0 and H_2 in silica glass are summarized in Fig. 4.³⁵⁾ Since H^0 and H_2 migrate through interstitial voids of various sizes and shapes, the diffusion coefficients are significantly distributed.

Because of the large mobility and reactivity at room temperature, H^0 and H_2 are involved in various photochemical reactions, although they do not exhibit optical absorption within the band gap of silica glass. They convert E' centers to SiH groups,^{65)–74)}

and transform NBOHCs into SiOH groups,^{34),35),60),65)–67),69),72)}

On the other hand, possible formation of E' centers via the cracking of SiH groups by H^0 ,

is suggested.⁷²⁾ A similar reaction, cracking of SiCl groups by H^0 [Eq. (6)], is observed in F_2 -laser-irradiated silica glasses containing both SiCl and SiOH groups.⁴⁷⁾

Other significant reactions include cracking of Si–O bonds with mobile hydrogen. Interstitial H_2 slowly dissociates Si–O–Si bonds in silica glass,^{75)–78)}

Fig. 4. (Top) Time-dependent decay of the normalized NBOHC concentration in silica glasses containing SiOH groups and exposed to a single F₂ laser pulse at $t = 0$ s.^{34),35)} NBOHCs are generated by the F₂ laser photolysis of SiO–H bonds [Eq. (2)], and subsequently annihilated by recombinations with H⁰ [Eq. (9)] and H₂ [Eq. (10)]. H₂ molecules are formed by the dimerization of H⁰s. Open symbols denote simulated decay curves, calculated based on the diffusion-limited reaction theory with considering distributions in diffusion activation energies of H⁰ and H₂. Ranges I, II, and III are due to reactions with free H⁰, trapped H⁰, and H₂, respectively. (Bottom) Arrhenius plots of the diffusion coefficients of H⁰ and H₂ evaluated from the diffusion-limited recombination with NBOHCs.³⁵⁾ The diffusion coefficients are distributed because of the structural disorder of silica glass (see Fig. 2). The diffusion coefficients at the distribution maxima correspond to solid lines and those between the two half maximum points define the shaded areas. The diffusion coefficient of H₂ obtained by this method agrees well with those determined by the permeation method at high temperatures (dashed line). The right ordinate denotes the approximate diffusion distance during 1 s, given by $\sqrt{Dt}$.

Formation of SiOH groups by this mechanism is responsible for the “hydrogen corrosion” problem in optical telecommunication fibers.^{64),79)–82)} The cracking reaction is modified when the glass network is photoexcited: besides reaction Eq. (12)^{83),84)} photoexcited Si–O–Si bonds are reduced to Si–Si bonds,⁸⁵⁾

Si–Si bonds exhibit an intense absorption band at 7.6 eV^{86)–88)} and significantly decrease the VUV transmittance of silica glass. Furthermore, reaction Eq. (13) is accompanied by formation of macroscopic cracks,⁸⁹⁾ which occurs probably due

to stress corrosion^{90),91)} of the silica network by the resultant H₂O. In silica glasses containing SiOH groups and exposed to F₂ laser light at 77 K, H⁰s generated by reaction Eq. (2) have a long life time and they cleave photoexcited Si–O–Si bonds as^{92),93)}

Concentrations of persistent E' centers and NBOHCs created by reactions Eqs. (14) and (15) are one order of magnitude larger than those formed by room temperature irradiations.

3. Point defect control to improve deep-ultraviolet and vacuum-ultraviolet transparency

In the previous sections structures and properties of point defects found in commercial synthetic silica glasses are described. To obtain better transmittance and hardness to DUV–VUV light, it is necessary to optimize the type and concentrations of point defects, because some defects have positive effects in improving the DUV–VUV optical properties of silica glasses. Two examples, incorporation of network modifiers and optimal loading with interstitial H₂, are described.^{2),94)}

As described in Sec. 2 A, strained Si–O–Si bonds arising from the distribution of the Si–O–Si angle cause the VUV optical loss near the absorption edge and become a major source of the radiation-induced point defects. Thus, the strained Si–O–Si bonds must be removed to improve the transmittance and radiation hardness of silica glass. A possible approach is to relax the glass structure by thermal annealing at low temperatures (“physical annealing”). However, this method is not practical because the structural relaxation takes a long time at low temperatures because of a large activation energy of viscous flow (~ 5 eV).^{95)–97)}

A promising way to eliminate the strained Si–O–Si bonds is to incorporate network modifiers such as SiF, SiCl, SiOH, and SiH groups that dissociate Si–O–Si glass network (“chemical annealing”). These functional groups reduce the viscosity,⁹⁵⁾ facilitating the structural relaxation.^{98),99)} Both SiOH and SiCl groups exhibit optical absorption only above ~ 7 eV (Sec. 2 B), and can be used to improve radiation hardness of silica glasses against KrF and ArF lasers.^{53),100)} Nevertheless, excess incorporation of these functional groups would be unfavorable,²⁾ because they participate in various defect processes described in Sec. 2 B, which can be caused by two photon absorption of KrF and ArF laser light. Silica glasses containing SiOH and SiCl groups are not transparent above ~ 7 –7.5 eV. The best choice in this spectral range is silica glasses doped with SiF groups, which are quite stable and transparent below ~ 8 eV (Sec. 2 B). As shown in Fig. 5, the transparency near the VUV absorption edge is improved only by a small amount of SiF groups (≤ 1 –0.1%), whereas further fluorine doping is insignificant for the improvement.^{2),55),101),102)} Thus, the main reason for the increase in the VUV transparency is evidently the structural relaxation, and is not the simple band gap widening that is expected to be proportional to the fluorine concentration. Silica glasses containing SiH groups may also be usable above ~ 7 –7.5 eV but the possible radiation-induced cleavage of Si–H bonds [Eq. (3)] can be problematic.

Another key factor is the presence of interstitial H₂. Figure 6 shows effects of H₂ loading on optical absorption induced by ArF or F₂ laser light. H₂ loading is quite important in maintaining the transparency of silica glasses at ~ 4.7 eV^{39),65),69),103),104)} because interstitial H₂ removes E' centers

Fig. 5. Transmission spectra of 5 mm-thick SiF-free and 1 mol% SiF-doped silica glasses. The inset shows relation between the location of the VUV absorption "edge" (wavelength at which the absorption coefficient reaches 5 cm^{-1}) and the SiF content.¹⁰¹⁾

Fig. 6. Effects of H_2 loading on photoinduced absorption in an SiF-free, SiOH-doped silica glass exposed to ArF laser light (10^7 pulses at $\sim 30 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$) (a), and in an SiF-doped, SiOH-free silica glass exposed to F_2 laser light (2.88×10^6 pulses at $\sim 6 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$) (b).⁸⁵⁾

and NBOHCs that dominate the optical absorption in this spectral range [Sec. 2 C, Eqs. (7)–(10)]. In contrast, H_2 loading enhances the formation of Si-Si bonds [Eq. (13)] and it is detrimental for applications above $\sim 7 \text{ eV}$. Thus, the concentration of interstitial H_2 needs to be optimized depending on the application of silica glasses.

4. Practical applications

A. Silica glasses for F_2 laser photolithography

In the initial development state of F_2 laser photolithography, silica glass was not thought to be transparent enough for F_2 laser light.¹⁰⁵⁾ However, as described in previous sections, optical loss at 7.9 eV is not due to the intrinsic interband transition, but mainly due to point defects such as SiOH groups, Si-Si bonds and strained Si-O-Si bonds. The concentration of these point defects is the lowest in fluorine-doped silica glasses. Indeed, fluorine-doped silica glasses show good 7.9 eV transparency. To suppress the photoinduced formation of Si-Si bonds H_2 loading is not performed. This type of silica

Fig. 7. Transmission spectra of as-drawn and H_2 -loaded DUV optical fibers, before and after exposure to ArF laser light (10^5 pulses at $\sim 50 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$). The inset shows the optical loss spectrum of a DUV optical fiber.⁷³⁾

glass, which is often termed "modified silica," is suitable for photomask substrates in F_2 laser photolithography.^{106), 107)}

B. Deep-ultraviolet optical fibers

DUV-VUV optical fibers are one of the best uses of silica glass, which is of good DUV-VUV transparency and shape workability. However, conventional optical telecommunication fibers are not DUV transparent because of the optical absorption associated with metal cations (e.g. Ge) intentionally added to the fiber core to increase the refractive index. It is also necessary to remove strained Si-O-Si bonds and dangling bonds, which are generated by the large deformation at high temperature and are subsequently frozen in the resultant fibers by rapid quenching. Furthermore, transmittance of optical fibers with long optical path lengths is easily degraded even by a small amount of point defects. These factors make it difficult to develop optical fibers of good DUV-VUV transparency.

These problems can be solved by fluorine doping and H_2 loading. Viscosity reduction by the fluorine doping is effective in enhancing the structural relaxation to suppress the formation of drawing-induced defects and strained Si-O-Si bonds. In addition, since the fluorine doping decreases the refractive index, the core-cladding interface is formed by incorporating much more SiF groups in the cladding than in the core. H_2 loading to the resultant fiber is effective in maintaining the DUV transparency, because H_2 quickly terminates E' centers [Eqs. (7), (8)], which are the main radiation-induced point defects in this type of fibers. As shown in Fig. 7, a DUV optical fiber developed in this way exhibits a good transmittance and hardness to ArF laser light ($T \sim 70\%$ at $h\nu = 6.4 \text{ eV}$).^{73), 108)} In addition, this optical fiber shows good transparency from near IR to DUV spectral region, which is quite attractive for various spectroscopic applications.

5. Summary

Influence of point defects on deep-ultraviolet (DUV) and vacuum-ultraviolet (VUV) transparency of synthetic silica glass is described. Strained Si-O-Si bonds decrease transparency near the absorption edge and radiation hardness to DUV-VUV laser light. Doping with network modifiers that relax the glass structure is effective in eliminating the strained Si-O-Si bonds. Interstitial hydrogen molecules (H_2) are use-

ful in removing photoinduced dangling bonds. However, they enhance the formation of oxygen vacancies by photoreducing the silica network. Consequently, fluorine-doped H₂-free silica glass is the best choice at photon energies ≥ 7 eV, whereas network-modified H₂-loaded silica glasses give better results at ≤ 7 eV. These findings make it possible to develop photomask substrates for F₂ laser ($h\nu = 7.9$ eV) photolithography and DUV optical fibers for ArF laser ($h\nu = 6.4$ eV) transmission.

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References

- Griscom, D. L., *J. Ceram. Soc. Japan*, Vol. 99, pp. 923–942 (1991).
- Skujia, L., Hosono, H., Hirano, M. and Kajihara, K., *Proc. SPIE*, Vol. 5122, pp. 1–14 (2003).
- Mozzi, R. L. and Warren, B. E., *J. Appl. Cryst.*, Vol. 2, pp. 164–172 (1969).
- Dupree, R. and Pettifer, R. F., *Nature*, Vol. 308, pp. 523–525 (1984).
- Mukhopadhyay, S., Sushko, P. V., Stoneham, A. M. and Shluger, A. L., *Phys. Rev. B*, Vol. 70, 195203 (2004).
- Sushko, P. V., Mukhopadhyay, S., Mysovsky, A. S., Vladimir, B., Sulimov, A. T. and Shluger, A. L., *J. Phys. Condens. Matter*, Vol. 17, pp. S2115–S2140 (2005).
- Godmanis, I. T., Trukhin, A. N. and Hübner, K., *Phys. Status Solidi B*, Vol. 116, pp. 279–287 (1983).
- Kitamura, N., Fukumi, K., Kadono, K., Yamashita, H. and Suito, K., *Phys. Rev. B*, Vol. 50, pp. 132–135 (1994).
- Devine, R. A. B. and Arndt, J., *Phys. Rev. B*, Vol. 35, pp. 9376–9379 (1987).
- Geissberger, A. E. and Galeener, F. L., *Phys. Rev. B*, Vol. 28, pp. 3266–3271 (1983).
- Hosono, H., Ikuta, Y., Kinoshita, T., Kajihara, K. and Hirano, M., *Phys. Rev. Lett.*, Vol. 87, 175501 (2001).
- Galeener, F. L., *J. Non-Cryst. Solids*, Vol. 49, pp. 53–62 (1982).
- Devine, R. A. B. and Arndt, J., *Phys. Rev. B*, Vol. 39, pp. 5132–5137 (1989).
- Devine, R. A. B. and Arndt, J., *Phys. Rev. B*, Vol. 42, pp. 2617–2620 (1990).
- Arai, K., Imai, H., Isoya, J., Hosono, H., Abe, Y. and Imagawa, H., *Phys. Rev. B*, Vol. 45, pp. 10818–10821 (1992).
- Galeener, F. L., Kerwin, D. B., Miller, A. J. and Mikkelsen, J. C., Jr., *Phys. Rev. B*, Vol. 47, pp. 7760–7779 (1993).
- Devine, R. A. B., *Phys. Rev. B*, Vol. 35, pp. 9783–9789 (1987).
- Kajihara, K., Ikuta, Y., Hirano, M. and Hosono, H., *Appl. Phys. Lett.*, Vol. 81, pp. 3164–3166 (2002).
- Kajihara, K., Ikuta, Y., Hirano, M. and Hosono, H., *J. Non-Cryst. Solids*, Vol. 322, pp. 73–77 (2003).
- Hosono, H., Kajihara, K., Suzuki, T., Ikuta, Y., Skujia, L. and Hirano, M., *Solid State Commun.*, Vol. 122, pp. 117–120 (2002).
- Cannas, M. and Gelardi, F. M., *Phys. Rev. B*, Vol. 69, 153201 (2004).
- Suzuki, T., Skujia, L., Kajihara, K., Hirano, M., Kamiya, T. and Hosono, H., *Phys. Rev. Lett.*, Vol. 90, 186404 (2003).
- Walrafen, G. E. and Samanta, S. R., *J. Chem. Phys.*, Vol. 69, pp. 493–495 (1978).
- Davis, K. M. and Tomozawa, M., *J. Non-Cryst. Solids*, Vol. 201, pp. 177–198 (1996).
- Kajihara, K., Hirano, M., Skujia, L. and Hosono, H., *J. Non-Cryst. Solids*, Vol. 352, pp. 2307–2310 (2006).
- Kajihara, K., Ikuta, Y., Hirano, M., Ichimura, T. and Hosono, H., *J. Chem. Phys.*, Vol. 115, pp. 9473–9476 (2001).
- Shelby, J. E., *J. Non-Cryst. Solids*, Vol. 179, pp. 138–147 (1994).
- Kakiuchida, H., Saito, K. and Ikushima, A. J., *Jpn. J. Appl. Phys.*, Vol. 41, pp. 2993–2998 (2002).
- Imai, H., Arai, K., Saito, T., Ichimura, S., Nonaka, H., Vigouroux, J. P., Imagawa, H., Hosono, H. and Abe, Y., “The Physics and Technology of Amorphous SiO₂,” Ed. by Devine, R. A. B., Plenum Press, New York (1988) pp. 153–159.
- Awazu, K. and Kawazoe, H., *J. Non-Cryst. Solids*, Vol. 179, pp. 214–225 (1994).
- Morimoto, Y., Nozawa, S. and Hosono, H., *Phys. Rev. B*, Vol. 59, pp. 4066–4073 (1999).
- Kajihara, K., Hirano, M., Skujia, L. and Hosono, H., *Phys. Rev. B*, Vol. 72, 214112 (2005).
- Kajihara, K., Skujia, L., Hirano, M. and Hosono, H., *Appl. Phys. Lett.*, Vol. 79, pp. 1757–1759 (2001).
- Kajihara, K., Skujia, L., Hirano, M. and Hosono, H., *Phys. Rev. Lett.*, Vol. 89, 135507 (2002).
- Kajihara, K., Skujia, L., Hirano, M. and Hosono, H., *Phys. Rev. B*, Vol. 74, 094202 (2006).
- Imai, H., Arai, K., Hosono, H., Abe, Y., Arai, T. and Imagawa, H., *Phys. Rev. B*, Vol. 44, pp. 4812–4818 (1991).
- Pacchioni, G. and Ierano, G., *Phys. Rev. B*, Vol. 57, pp. 818–832 (1998).
- Skujia, L., Kajihara, K., Hirano, M. and Hosono, H., *J. Non-Cryst. Solids* (in press).
- Smith, C. M., Borrelli, N. F. and Araujo, R. J., *Appl. Opt.*, Vol. 39, pp. 5778–5784 (2000).
- Ikuta, Y., Kikugawa, S., Hirano, M. and Hosono, H., *Proc. SPIE*, Vol. 4347, pp. 187–194 (2001).
- Messina, F. and Cannas, M., *J. Phys. Condens. Matter*, Vol. 17, pp. 3837–3842 (2005).
- Youngman, R. E. and Sen, S., *J. Non-Cryst. Solids*, Vol. 337, pp. 182–186 (2004).
- Dumas, P., Corset, J., Carvalho, W., Levy, Y. and Neuman, Y., *J. Non-Cryst. Solids*, Vol. 47, pp. 239–242 (1982).
- Dumas, P., Corset, J., Levy, Y. and Newman, V., *J. Raman Spectrosc.*, Vol. 13, pp. 134–138 (1982).
- Mulder, C. A. M., *J. Non-Cryst. Solids*, Vol. 95 & 96, pp. 303–310 (1987).
- Awazu, K., Kawazoe, H. and Muta, K., *J. Appl. Phys.*, Vol. 69, pp. 4183–4186 (1991).
- Kajihara, K., Hirano, M., Skujia, L. and Hosono, H., *J. Appl. Phys.*, Vol. 98, 043515 (2005).
- Imai, H. and Hirashima, H., *J. Non-Cryst. Solids*, Vol. 179, pp. 202–213 (1994).
- Kawaguchi, Y. and Kuzuu, N., *J. Appl. Phys.*, Vol. 80, pp. 5633–5638 (1996).
- Nishikawa, H., Nakamura, R., Ohki, Y., Nagasawa, K. and Hama, Y., *Phys. Rev. B*, Vol. 46, pp. 8073–8079 (1992).
- Griscom, D. L. and Friebele, E. J., *Phys. Rev. B*, Vol. 34, pp. 7524–7533 (1986).
- Awazu, K., Kawazoe, H., Muta, K., Ibuki, T., Tabayashi, K. and Shobatake, K., *J. Appl. Phys.*, Vol. 69, pp. 1849–1852 (1991).
- Kuzuu, N., Taga, T. and Kamisugi, N., *J. Appl. Phys.*, Vol. 81, pp. 8011–8017 (1997).
- Kyoto, M., Ohoga, Y., Ishikawa, S. and Ishiguro, Y., *J. Mater. Sci.*, Vol. 28, pp. 2738–2744 (1993).
- Skujia, L., Kajihara, K., Ikuta, Y., Hirano, M. and Hosono, H., *J. Non-Cryst. Solids*, Vol. 345 & 346, pp. 328–331 (2004).
- Kajihara, K., Hirano, M., Skujia, L. and Hosono, H., *J. Non-Cryst. Solids* (in press).
- Doremus, R. H., “Diffusion of Reactive Molecules in Solids and Melts,” John Wiley & Sons, New York (2002).
- Shelby, J. E., “Handbook of Gas Diffusion in Solids and Melts,” ASM International, Materials Park (1996).
- Brower, K. L., Lenahan, P. M. and Dressendorfer, P. V.,

- Appl. Phys. Lett.*, Vol. 41, pp. 251–253 (1982).
- 60) Griscom, D. L., *J. Non-Cryst. Solids*, Vol. 68, pp. 301–325 (1984).
 - 61) Shackelford, J. F., Studt, P. L. and Fulrath, R. M., *J. Appl. Phys.*, Vol. 43, pp. 1619–1626 (1972).
 - 62) Hartwig, C. M., *J. Chem. Phys.*, Vol. 47, pp. 956–958 (1976).
 - 63) Shelby, J. E., *J. Appl. Phys.*, Vol. 48, pp. 3387–3394 (1977).
 - 64) Noguchi, K., Shibata, N., Uesugi, N. and Negishi, Y., *J. Lightwave Technol.*, Vol. LT-3, pp. 236–243 (1985).
 - 65) Faile, S. P. and Roy, D. M., *Mater. Res. Bull.*, Vol. 5, pp. 385–389 (1970).
 - 66) Hartwig, C. M., *J. Chem. Phys.*, Vol. 66, pp. 227–238 (1977).
 - 67) Shelby, J. E., *J. Appl. Phys.*, Vol. 50, pp. 3702–3706 (1979).
 - 68) Li, Z., Fonash, S. J., Poindexter, E. H., Harmatz, M., Rong, F. and Buchwald, W. R., *J. Non-Cryst. Solids*, Vol. 126, pp. 172–176 (1990).
 - 69) Yamagata, S., *Miner. J.*, Vol. 15, pp. 333–342 (1991).
 - 70) Radzig, V. A., Bagratashvili, V. N., Tsypina, S. I., Chernov, P. V. and Rybaltovskii, A. O., *J. Phys. Chem.*, Vol. 99, pp. 6640–6647 (1995).
 - 71) Edwards, A. H., *J. Non-Cryst. Solids*, Vol. 187, pp. 232–243 (1995).
 - 72) Vitiello, M., Lopez, N., Illas, F. and Pacchioni, G., *J. Phys. Chem. A*, Vol. 104, pp. 4674–4684 (2000).
 - 73) Oto, M., Kikugawa, S., Sarukura, N., Hirano, M. and Hosono, H., *IEEE Photon. Technol. Lett.*, Vol. 13, pp. 978–980 (2001).
 - 74) Cannas, M., Costa, S., Boscaino, R. and Gelardi, F. M., *J. Non-Cryst. Solids*, Vol. 337, pp. 9–14 (2004).
 - 75) Faile, S. P. and Roy, D. M., *J. Am. Ceram. Soc.*, Vol. 54, pp. 533–534 (1971).
 - 76) Bell, T., Hetherington, G. and Jack, K. H., *Phys. Chem. Glasses*, Vol. 3, pp. 141–146 (1962).
 - 77) Wiesenfeld, J. M., Stone, J., Marcuse, D., Burrus, C. A. and Yang, S., *J. Appl. Phys.*, Vol. 61, pp. 5447–5454 (1987).
 - 78) Schmidt, B. C., Holtz, F. M. and Beny, J.-M., *J. Non-Cryst. Solids*, Vol. 240, pp. 91–103 (1998).
 - 79) Mochizuki, K., Namihira, Y. and Yamamoto, H., *Electron. Lett.*, Vol. 19, pp. 743–745 (1983).
 - 80) Uesugi, N., Murakami, Y., Tanaka, C., Ishida, Y., Mitsunaga, Y., Negishi, Y. and Uchida, N., *Electron. Lett.*, Vol. 19, pp. 762–764 (1983).
 - 81) Tanifuji, T., Matsumoto, M., Tokuda, M. and Miyauchi, M., *Electron. Lett.*, Vol. 20, pp. 13–14 (1984).
 - 82) Stone, J., *J. Lightwave Technol.*, Vol. LT-5, pp. 712–733 (1987).
 - 83) Mizuguchi, M., Skuja, L., Hosono, H. and Ogawa, T., *Opt. Lett.*, Vol. 24, pp. 863–865 (1999).
 - 84) Nishii, J., Kintaka, K., Nishiyama, H., Sano, T., Ohmura, E. and Miyamoto, I., *Appl. Phys. Lett.*, Vol. 81, pp. 2364–2366 (2002).
 - 85) Ikuta, Y., Kajihara, K., Hirano, M., Kikugawa, S. and Hosono, H., *Appl. Phys. Lett.*, Vol. 80, pp. 3916–3918 (2002).
 - 86) Imai, H., Arai, K., Imagawa, H., Hosono, H. and Abe, Y., *Phys. Rev. B*, Vol. 38, pp. 12772–12775 (1988).
 - 87) Hosono, H., Abe, Y., Imagawa, H., Imai, H. and Arai, K., *Phys. Rev. B*, Vol. 44, pp. 12043–12045 (1991).
 - 88) Mukhopadhyay, S., Sushko, P. V., Stoneham, A. M. and Shluger, A. L., *Phys. Rev. B*, Vol. 71, 235204 (2005).
 - 89) Ikuta, Y., Kajihara, K., Hirano, M. and Hosono, H., *Appl. Opt.*, Vol. 43, pp. 2332–2336 (2004).
 - 90) Michalske, T. A. and Freiman, S. W., *J. Am. Ceram. Soc.*, Vol. 66, pp. 284–288 (1983).
 - 91) Bunker, B. C., *J. Non-Cryst. Solids*, Vol. 179, pp. 300–308 (1994).
 - 92) Skuja, L., Kajihara, K., Hirano, M. and Hosono, H., *Proceedings of the 20th International Congress on Glass*, Kyoto (2004) O-14-052.
 - 93) Skuja, L., Kajihara, K., Hirano, M., Saitoh, A. and Hosono, H., *J. Non-Cryst. Solids*, Vol. 352, pp. 2297–2302 (2006).
 - 94) Kajihara, K., Ikuta, Y., Oto, M., Hirano, M., Skuja, L. and Hosono, H., *Nucl. Instrum. Methods Phys. Res. B*, Vol. 218, pp. 323–331 (2004).
 - 95) Hetherington, G., Jack, K. H. and Kennedy, J. C., *Phys. Chem. Glasses*, Vol. 5, pp. 130–136 (1964).
 - 96) Mikkelsen, J. C., Jr. and Galeener, F. L., *J. Non-Cryst. Solids*, Vol. 37, pp. 71–84 (1980).
 - 97) Kakiuchida, H., Saito, K. and Ikushima, A. J., *J. Appl. Phys.*, Vol. 93, pp. 777–779 (2003).
 - 98) Saito, K. and Ikushima, A. J., *Appl. Phys. Lett.*, Vol. 73, pp. 1209–1211 (1998).
 - 99) Ikushima, A. J., Fujiwara, T. and Saito, K., *J. Appl. Phys.*, Vol. 88, pp. 1201–1213 (2000).
 - 100) Shimbo, M. and Sato, K., *Jpn. J. Appl. Phys.*, Vol. 34, pp. 5640–5643 (1995).
 - 101) Hosono, H. and Ikuta, Y., *Nucl. Instrum. Methods Phys. Res. B*, Vol. 166–167, pp. 691–697 (2000).
 - 102) Saito, K. and Ikushima, A. J., *J. Appl. Phys.*, Vol. 91, pp. 4886–4890 (2002).
 - 103) Sempolinski, D. R., Seward, T. P., Smith, C., Borrelli, N. and Rosplock, C., *J. Non-Cryst. Solids*, Vol. 203, pp. 69–77 (1996).
 - 104) Shimbo, M., Nakajima, T., Tsuji, N., Kakuno, T. and Obara, T., *Jpn. J. Appl. Phys.*, Vol. 38, pp. L848–L850 (1999).
 - 105) Bloomstein, T. M., Horn, M. W., Rothschild, M., Kunz, R. R., Palmacci, S. T. and Goodman, R. B., *J. Vac. Sci. Technol. B*, Vol. 15, pp. 2112–2116 (1997).
 - 106) Hosono, H., Mizuguchi, M., Kawazoe, H. and Ogawa, T., *Appl. Phys. Lett.*, Vol. 74, pp. 2755–2757 (1999).
 - 107) Mizuguchi, M., Skuja, L., Hosono, H. and Ogawa, T., *J. Vac. Sci. Technol. B*, Vol. 17, pp. 3280–3284 (1999).
 - 108) Oto, M., Kikugawa, S., Miura, T., Hirano, M. and Hosono, H., *J. Non-Cryst. Solids*, Vol. 349, pp. 133–138 (2004).

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