Structure and Properties of Amorphous Silica and Its Related Materials: Recent Developments and Future Directions

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Amorphous silica and related silica-based materials have been widely developed in optoelectronics and optical telecommunications technology. Despite comprehensive research for over the decades, the subject of amorphous silica continues to excite the interest of researchers in the field of chemistry, physics, and geology. This paper reviews some of the recent experimental and theoretical developments in the field, including medium-range order, structural changes under pressures, vibrational and thermodynamic anomalies, and photoluminescence properties.

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1. Introduction

Despite the intensive studies over the past fifty years, the subject of amorphous and crystalline silicon dioxide (silica) have still attracted considerable interest in the field of technologies and basic researches. As for the crystalline phases of silicon dioxide, the structure is defined in terms of a unit cell, and the related electronic states and optical properties can rather be well understood. However, the structure and properties of amorphous silica ($a$-SiO$_2$) or silica glass remain to be solved and still continue to mystify us.

Although we are far from the goal of complete understanding, the last decade has witnessed a number of experimental and theoretical approaches to the possibility of revealing structure and bonding in amorphous silica. In particular, recent advances in theoretical and computational techniques have made it possible to address the problems of such complex systems. Ab initio or first principal studies of crystalline and amorphous silicon dioxide have become practical within the past 5–10 years and are shedding new light on the properties of random silica network. Point defects and imperfections in amorphous silica are also the subject of theoretical calculations, and several new structural models of defect centers have been recently proposed on the basis of the calculated results.

In addition to bulk silicon dioxide, porous silica, silica nanoparticles, and amorphous silicon suboxides ($a$-SiO$_x$, $x < 2.0$) have been increasingly studied in view of their bright photoluminescence (PL) and electroluminescence (EL). Studies on these silica-related light-emissive materials were originally motivated by the discovery of visible light emission from porous silicon by Canham. Following Canham's initial report of porous silicon there has been an explosion of interest into its novel silicon-based light emitting materials, and indeed surprisingly efficient PL has been reported from such an indirect gap material. However, the recognized instability of porous silica may not be suitable for practical use. Thus, a related silicon-rich silica or $a$-SiO$_2$ has recently begun to generate increasing interest. $a$-SiO$_2$ is arguably a more robust material than porous silicon and has been shown to exhibit similar emission properties. To understand the origin of the PL from $a$-SiO$_2$, a knowledge about point defects in amorphous silica is indispensable although a quantum confinement effect also plays a role in showing such efficient PL emission from silicon-rich silica.

Thus, we believe that studies on amorphous silica and silica-related materials are still active and fascinating, which may allow us to call it “innovative ceramics.” In this account, recent development of our understanding of electronic and structural properties of $a$-SiO$_2$ is emphasized. We also review the recent progress of silica-based light-emitting materials and highlight possible future directions. However, we do not deal with photosensitivity and photoinduced structural changes in silica, which are also a recent topic in the field of silica-based oxide glasses,

2. Structure of $a$-SiO$_2$

Traditionally, the structural order in a glass has been divided into three length scales: short-, medium- and long-range structures. Properties of glasses are governed by the structure of a specific length scale as illustrated in Fig. 1. Of particular interest in $a$-SiO$_2$ is medium-range order (MRO), which refers to specific structural ordering at length scale ($\sim 5 < r < 50$Å) beyond that characteristic of short-range order (SRO, $r \sim 3$Å), or SiO$_4$ tetrahedral units (see also Fig. 2). It has been demonstrated that MRO and the related dynamics are associated with some interesting but challenging characteristics of $a$-SiO$_2$, including the first sharp diffraction peak (FSDP) in the structure factor $S(Q)$, the excess vibrational modes in the low-frequency range (10–100 cm$^{-1}$ or 1 THz) often called the boson peak, and the hump in the temperature dependence of the heat capacity, plotted as $C_v/T^3$ vs $T$, in the range $T \sim 10–30$ K. Thus, in what follows, we will mainly focus our interest on MRO among other structural orders in $a$-SiO$_2$. Experimental and theoretical investigations of the changes in MRO at elevated pressure are also addressed.

2.1 Theories and models of $a$-SiO$_2$

As mentioned earlier, MRO is associated with non-random correlations between neighboring SiO$_4$ tetrahedra. Usual diffraction techniques such as neutron and X-ray diffraction techniques, in which three-dimensional information on the
glass network is projected onto one-dimensional space, are not useful to get a detailed picture of MRO. Thus, a number of molecular dynamics (MD) simulations have been carried out to obtain a better model of the three dimensional structure of $a$-SiO$_2$.

In the late 1980s and early 1990s, the usual computational approach to generate $a$-SiO$_2$ structure was performed within the framework of classical MD. Since classical MD simulations can deal with more than ~100 000 atoms, the methods are indispensable to gain atomistic insights into the structure and dynamics of $a$-SiO$_2$. However, the resulting structure and dynamical behaviors are dependent on the potential functions used. From the late 1990s, first-principles approaches has becoming an alternative tool for MD simulations of $a$-SiO$_2$. In 1995, Saranthe, Pasquarello, and Car have reported a first-principle MD study of liquid and amorphous silica using the Car–Parrinello method. Although the number of atoms used in their simulations is not quite large ($N = 72$), the total neutron structure factor $S(Q)$ of $a$-SiO$_2$ was adequately modeled by the calculations. The simulated model showed that Si–Si, O–O, and Si–O correlations contribute to the FSDP, in basically agreement with the results of previous classical MD simulations, although the real-space structural origin of the FSDP is still the subject of controversy as well be shown below. The ab initio model of amorphous silica generated by Saranthe, Pasquarello, and Car further succeeded in reproducing the observed vibrational density of states and infrared absorption spectrum, demonstrating that the observed high-frequency doublet cannot be ascribed to a longitudinal-optic–transverse-optic (LO–TO) effect but results from different local motions of the SiO$_4$ subunits. The calculations also demonstrated that the two Raman features at 495 and 606 cm$^{-1}$, known as “defect” lines $D_1$ and $D_2$, result from the motion of the oxygen atoms in four- and three-membered rings in the $a$-SiO$_2$ network, as was originally suggest-
ed by Galeener.20 The Galeener’s assignments were confirmed independently by Uchino, Tokuda and Yoko21 by using ab initio quantum chemical cluster calculations. Recently, Car-Parrinello MD simulations based on density-functional perturbation theory (DFPT) have been applied to the problem of photoelasticity of crystalline and amorphous silica. Donadio et al.22 have shown that the ab initio DFPT framework has provided a phenomenological model of the dielectric properties transferable to several crystalline and amorphous polymorphs.

In addition to MD simulations, the structure of a-SiO2 has been modeled by a Monte Carlo method. One drawback of MD simulations is the high cooling rate, often resulting in structures with a higher strain or a larger spread in bond lengths and bond angles than observed in experiments. This drawback can be overcome by a Monte Carlo scheme using an artificial dynamics consisting of bond transpositions. Recently, Vink and Barkema23 have generated large and well-relaxed amorphous silica network composed of 300 000 atoms. It has been shown that the resultant three-dimensional structure can perfectly reproduce the observed total correlation functions and interference functions.

2.2 Structural changes under pressure

It has been well documented that an experimental manifestation of MRO is the FSDP, which is a characteristic feature of the measured structure factor S(Q) for many disordered systems. Although several interpretations have been proposed as for the origin or the real space structural correlations of FSDP,24-26 the subject still continues to be controversial.27 One method to gain insight into the real space information concerning the FSDP of a-SiO2 is the structure modification under pressure. The intensity, position, and width of the FSDP in reciprocal space are expected to be modified by applied pressure, and the comparison between the observed features in reciprocal space and those in real space may clarify the structural origin of the FSDP. Thus, to get the information about the correlation between FSDP and MRO, various high-pressure studies on a-SiO2 have been previously carried out.28-30 According to in situ high-pressure X-ray diffraction measurements on a-SiO2,28-30 the FSDP (≈1.52 Å−1) shifts in position to higher values of Q as a function of increasing pressure from −2 GPa, whereas the other peaks in S(Q) to lower values of Q. On the other hand, the intensity of FSDP shows a gradual decrease with increasing pressure, accompanied by an emergence of a new peak at ≈3.2 Å−1 at pressures in excess of ≈10 GPa.28,30 It has also been demonstrated that a-SiO2 exhibits an irreversible densification after being subjected to pressures above ≈10 GPa. The densified samples show similar changes in FSDP,29 e.g., shift in the position to a larger-Q value, reduction in its intensity, and increase in its width, as those observed under high-pressures. Thus, the characteristics of FSDP, including the position, intensity and width, can be changed by applying pressure indeed, and this change also accompanies the modification and creation of the other peaks in S(Q) as mentioned above. This indicates that the structural changes induced by pressure are not confined to the length scale associated with the FSDP but will extend over a whole range of the glass structure (see also Fig. 1), transforming to a pressure-densified amorphous phase often called a high-pressure amorphous polymorph.31

A pressure-induced amorphous-amorphous transition in glasses and liquids is one of the recent active topics in the field of physical chemistry of condensed matters. It has been demonstrated that the pressure-induced transformation observed in H2O is first order and occurs with a discontinuous volume change.32 On the other hand, previous high pressure experiments on a-SiO2 have not revealed a first-order-type behavior of the pressure induced structural changes of a-SiO2.33,34 However, it has recently been suggested from a thermodynamic analysis of the pressurized a-SiO2 that there must exist a first-order phase transition around 3 GPa.34 This prediction was later argued in the literature,35,36 but was confirmed by an experiment showing that an apparently first-order phase transition from the low density amorphous phase to the high density amorphous phase with a discontinuous volume change of about 20% at 3.6 GPa and 680°C.37 In a recent classical MD study on pressurized a-SiO2 by Trachenko and Dove,31,38 it has been proposed that structural changes start to develop in the pressure window between 3 and 5 GPa. That is, the structure is compressible without need to break the tetrahedral topology up to about 3 GPa; only fourfold Si coordinations are present in the structure and no rebonding take place before 3 GPa. As the pressure increases beyond 3 GPa, further deformation of the network necessarily involves the appearance of increased coordinations, leading re-bonding and modifications in MRO. The idea of the pressure window may shed new light on the observed compressibility anomaly at pressures exceeding 5 GPa. Another classical MD simulations by Dávila et al.40 have shown that the ring size distribution remains practically unchanged during elastic compression but varies continuously after the transition to the plastic regime. During the plastic regime, it has been shown that there is a continuous decrease in the number of rings of size 5 and 6 and an increase in the number of both smaller and larger rings. The result is consistent with Raman measurements of compressed silica showing that the enhancements of the D1 and D2 lines associated with 4- and 3-membered rings, respectively.31,33

2.3 Boson peak and related problems

The early experimental evidence for boson peak was derived from Raman scattering measurements.41 The boson peak is generally more pronounced in strong glass formers such as SiO2 and B2O3 and is located at higher frequencies than in fragile glasses.42 Later, these low-frequency excess vibrations were also seen in the vibrational density of states (DOS) measurements in inelastic neutron scattering.43 This anomalous low-frequency feature shows no appreciable dependence on the scattering angle,45 suggesting a localized nature of the vibrations. This also means that the length scale contributing to the boson peak is much shorter than the light wavelength that they scatter incoherently.

In discussing the problem of boson peak, we have to take into account of the effect of acoustic modes, i.e. propagating plane waves in the continuum limit. At frequencies up to 300 GHz, it has been shown that there exist quasi-plane waves that can propagate in the a-SiO2 network although they are slightly damped in space or time.46 The point is the fate of acoustic modes at higher frequencies where the boson peak begins to dominate. Unfortunately, however, there is no definite experiments that can settle the problem. Recent MD simulations by Taraskin and Elliott47 show that propagating waves are not valid approximations of eigenmodes beyond a certain crossover. The crossover between weak- and strong-scattering regimes is often called the Ioffe-Regel crossover, i.e., the frequency at which vibrational modes change from being propagating to diffusive-type modes.48 According to the results of Taraskin and Elliott,47 the Ioffe-Regel crossover occurs at ≈1 THz, in harmony with the value obtained from combined inelastic neutron scattering and inelastic X-ray scattering.49-51 This implies that acoustic waves show strong
scattering and must cease to propagate beyond this crossover frequency. For typical sound velocities $v \sim 3000$ m/s, this corresponds to a wavelength $\sim 5$ nm, suggesting that $\alpha$-SiO$_2$ is no more homogeneous in this length scale at least in view of acoustic phonons.

We now turn to the boson peak. In amorphous silica, the frequency of the boson peak maximum is compared with the observed Ioffe–Regel crossovers of acoustic modes mentioned above. However, the relation between the acoustic modes and the boson peaks remains to be solved.\textsuperscript{52–54} Is the boson peak simply the scattering from localized acoustic excitations? Does propagating nature of acoustic modes still play a vital role in showing the boson peak? Although the true nature of the boson peak is far from being well understood, it has been becoming a general consensus that coupled rotations of SiO$_4$ tetrahedra are related to the motions contributing to the boson peak.\textsuperscript{55–60} As for the problem of the coupling between such coupled rotations SiO$_4$ tetrahedra and acoustic modes, we have to await further investigations.

2.4 Size dependence of the structure and properties

In previous subsections, we have shown that the structure of $\alpha$-SiO$_2$ is not homogeneous in terms not only of the atomic configurations but also of the propagation of acoustic modes. As the length scale of the glass structure of interest becomes shorter, such an inhomogeneous nature of the glass structure will dominate the related glass properties. It is hence interesting to investigate the sized dependence of the structure and properties of $\alpha$-SiO$_2$.

Thus far the size dependence of the structure and properties of crystalline materials have been extensively studied.\textsuperscript{61} This is because the structure of crystalline materials is well defined, and the effect of particle size on the structure can be interpreted in terms of the changes in the thermodynamics and kinetics of phase transformation. Furthermore, it has often been shown that the structure and properties of crystalline materials with reduced dimensions differ dramatically from those of the bulk because of the surface and quantum-confinement effects. On the other hand, the analysis of the sized dependence of the structure and properties of glassy materials is a challenging task owing to the random nature of the structure and hence has hardly been carried out.

Recently, Uchino \textit{et al.}\textsuperscript{52–64} have performed a series of studies on the structure and properties of nanometer-sized silica fine particles called fumed silica. Fumed silica is widely used in industry as active filler for reinforcement of elastomers, as a rheological additive in fluids and as a free flow agent in powders. Fumed silica is produced in a hydrothermal process by burning silicon tetrachloride in an oxygen-hydrogen flame in the temperature range of about 1200–1800°C, forming a synthetic amorphous form of silicon dioxide having the size of primary particles $\sim 10–20$ nm.\textsuperscript{65} It is known that each primary particle is nonporous but a dense form of amorphous silicon dioxide since the true density of fumed silica is identical to that of the corresponding bulk (2.20 g/cm$^3$).\textsuperscript{66}

Although the surface properties and reactivity of fumed silica have been extensively studied in the past decades,\textsuperscript{66–69} the structure especially in the medium-range length scale has not been thoroughly investigated. As mentioned earlier, one powerful method to investigate MRO of $\alpha$-SiO$_2$ is a Raman scattering technique. However, when Raman spectra of fumed silica are measured with a conventional dispersive Raman spectrometer using an excitation wavelength in the visible range, one inevitably observes strong scattering resulting from the nanometer-sized characteristics of fumed silica. Uchino \textit{et al.}\textsuperscript{64} found that this problem was virtually eliminated using FT-Raman spectroscopy since it employs a near-infrared (1064 nm) laser for excitation and can hence suppress the effect of scattering. They reported that the intensities of the $D_1$ and $D_2$ Raman bands in fumed silica are substantially higher than those in bulk $\alpha$-SiO$_2$, indicating that three- and four-membered rings are more frequent in fumed silica than in the corresponding bulk (see Fig. 3). Such an abundance of small-membered rings in fumed silica was also confirmed by high energy X-ray diffraction measurements using synchrotron radiation\textsuperscript{68} and a recent MD simulation.\textsuperscript{70} Uchino \textit{et al.}\textsuperscript{52,64} further found that fumed silica exhibits a unique structural modification under pressure. That is, fumed silica has a lower pressure threshold ($\sim 2$ GPa) for irreversible compaction than bulk $\alpha$-SiO$_2$ ($\sim 10$ GPa). This result is interesting in that the pressure window mentioned in Sec. 2.1 may depend on the particle size or the ring size distributions, implying that MRO affects the compressibility of the $\alpha$-SiO$_2$ network. This is not surprising since the pressure window reflects the degree of reordering and reformation of atoms in the length scale of MRO. We should also note that the ring size distributions in $\alpha$-SiO$_2$ are also affected by the thermal history of glasses or a fictive temperature.\textsuperscript{71–73} It is hence natural to assume that the structure and properties of $\alpha$-SiO$_2$ are a function of a fictive temperature as well.\textsuperscript{74} Furthermore, it has been shown that the optical properties of point-defect-free $\alpha$-SiO$_2$ in the vacuum ultraviolet region is primarily governed by the populations of three- and four-membered rings.\textsuperscript{75} Thus, we would like to stress once again that MRO, or a network connectivity in the length scale of $\sim 0.5–1$ nm, plays a vital role in determining the entire structure and properties of $\alpha$-SiO$_2$. This is certainly a peculiar nature of glassy solids that cannot be found in the corresponding crystalline polymorphs.

3. Defect structures of $\alpha$-SiO$_2$—models of the $E'$ centers

It has been well documented that in $\alpha$-SiO$_2$ there exist a large variety of point defects both on the intrinsic and extrinsic origins.\textsuperscript{76–78} Since the optical properties of $\alpha$-SiO$_2$ are strongly affected by the electronic states of point defects, considerable efforts have been made in the past decades to understand the structural, optical and electronic properties of point defects in $\alpha$-SiO$_2$. Among other defect centers in $\alpha$-SiO$_2$, $E'$ centers have...
been most widely investigated since the $E'$ centers are the major oxygen-deficiency-related paramagnetic defect in $a$-SiO$_2$. Thus far, at least four different types of $E'$ centers, $E'_1$, $E'_2$, $E'_3$, and $E'_4$, have been observed in $a$-SiO$_2$ with the only common feature being an unpaired electron on threefold coordinated silicon. These $E'$-center variants will differ from each other in the second-coordination environments around the respective paramagnetic Si atoms, although their local structures have not been fully understood yet.

Until recently, it was generally assumed that the $E'_1$ center was analogous to the $E'_1$ center of crystalline $a$-quartz. That is, it was assumed that the local structural model of the $E'_1$ center is basically the same as that of the $E'_1$ center, which was originally proposed by Feilg, Fowler, and Yip (FFY).$^{77}$ According to the FFY model, a positive hole, $h^+$, trapped at a neutral oxygen monovacancy can be localized on one silicon atom and then lower its energy by relaxing back into the place of its three remaining oxygen neighbors. This reaction can be expressed as follows:

$$\equiv \text{Si-Si} \equiv + h^+ \rightarrow \equiv \text{Si} \cdot (E'_1) + \text{Si} \equiv,$$

where and $\equiv$ represent an unpaired electron and three Si-O bonds, respectively. This model was subsequently refined by Rudra and Fowler,$^{79}$ who suggested that the relaxation of the positively charged silicon is further stabilized by forming additional Si-O bond with a nearby oxygen atom, making the oxygen atom threefold coordinated (see also Fig. 4). However, this model for the $E'_1$ center cannot account satisfactorily for certain experimental characteristics observed for this paramagnetic center,$^{79,80}$ suggesting that the FFY model is not appropriate for explaining the microscopic structure of the $E'_1$ center in $a$-SiO$_2$.

Recently, Uchino, Takahashi and Yoko (UTY)$^{79,80}$ put forward an alternative model that can also be capable of explaining the basic experimental feature of the $E'_1$ center. The model proposed by UTY is an oxygen-bridged structure, called a bridged hole-trapping oxygen-deficiency center (BHODC, see Fig. 4). UTY assumed that a possible precursor of the BHODC is a neutral epoxide-like structure, which can be formed by removing one of the two oxygens in the edge-sharing structure. Furthermore, UTY showed that the BHODC structure could act as a switching oxide trap through a process forming part of a set of transformations (see Fig. 5).$^{81}$ (2) A precursor of the peryoxy radical defect by capturing an electron and diffusing O$_2$ and (3) a precursor of the $E'_1$ center by capturing an electron and atomic hydrogen.$^{80}$ The UTY’s scheme for the formation of the $E'_1$ center has been supported independently by recent ab initio MD simulations.$^{83}$ In addition, a new experimental result on the $E'_1$ center supporting the UTY model has been reported.$^{54}$

As for the structural model of the $E'_1$ center, however, the discussion is still continuing.$^{55,66}$

In $a$-SiO$_2$, there exist other defect centers whose structural origins are also of a matter of concern. As for recent models of the other defect centers, interested readers can refer to a recent review$^{5}$ given by the present author.

4. Photoluminescence properties of $a$-SiO$_x$, $a$-SiO$_2$ and the related materials

The optical properties of $a$-SiO$_2$ are of great importance for its use in modern optoelectronic technologies. Unwanted absorption and photoluminescence (PL) bands in optical fibers and ultraviolet (UV) lenses could degrade the quality of the
related devices, and the formation process to obtain extremely pure $a$-$SiO$_2 has been pursued for over the decades. As a result, studies on optically active defect centers in bulk forms $a$-$SiO$_2 have advanced remarkably as reviewed by Skuja.87

As mentioned in the Introduction, the observation of strong visible PL from porous silicon at room temperature87 stimulated substantial activity in the field of preparation of Si-based materials. Later, intense visible PL has been reported not only from porous silicon but also from SiO$_2$ thin films containing crystallites or amorphous silicon nanoparticles.88,89 It is believed that this PL emission is attributed to radiative recombination of photogenerated carriers confined in Si nanoparticles, namely quantum confinement effects in Si nanoparticles.88,89

However, it has also been proposed that particular surface states on SiO$_2$ and Si/SiO$_2$ interface are responsible for the PL emission.90 Thus, the PL emission from SiO$_2$-related materials has attracted a renewed interest in terms of novel photonic materials.

4.1 PL from porous silicon and $a$-$SiO$_2$ films

Although the detailed knowledge about defect states of the PL in porous silicon and SiO$_2$ films is still lacking, one possible candidate for the PL center is silanolene, $Si=O$ groups.92 From time-dependent excitation spectroscopy using pulsed UV laser excitation, Gole et al.93 proposed that the visible PL emission from porous silicon results from the pumping of an excited-state manifold for a molecular-like species followed by rapid relaxation via nonradiative transitions down to the manifold and the subsequent emission of radiation at longer (visible) wavelengths. Further quantum chemical modeling supports this interpretation and suggests a correlation to changes in the bonding associated with electronic transitions associated with silanolene-like ground electronic singlet state and their low-lying triplet excitons.94 Chabal et al.95 also demonstrated from infrared absorption measurements that the initial oxidation of clean Si(100) - (2×1) by $O_2$ indeed involves the formation of a metastable silanolene intermediate structure. Later Wolkin et al.96 presented evidence that the electronic states that are responsible for the PL emission of silicon quantum dots in porous silicon are those of a silanolene bond. In addition to the PL emission from porous silicon, it has been suggested that PL from SiO$_2$ films result from the silanolene bonds as well.92 Pavesi et al.97 proposed that the emission from the silanolene bonds at the interface between the nanocrystalline silicon and the SiO$_2$ matrix can lead to the amplified spontaneous emission. The technique used to measure the optical gain from silicon nanocrystals by Pavesi and coworkers92 was later argued,98,99 but it is interesting to say that such a localized center has a possibility to show population inversion for the stimulated emission.

It should also be worth mentioning that SiO$_2$ films show electroluminescence (EL), which will potentially open up new applications of silicon optronics. Sopinskyy and Khomchenko98 recently gave a nice review for EL in SiO$_2$ films and SiO$_2$-film-based systems.

4.2 PL from silica aerogels

Silica aerogels is expected to possess several microstructural characteristics suitable for a luminescent material. However, it was not until recently that the PL properties of silica aerogels were systematically investigated. In what follows, we show some PL properties of undoped silica aerogels, in which no metal phosphors and/or fluorophors are added to exhibit the PL emission.

Ayers and Hund80 reported that treatment of silica aerogels with microwave-energized reducing gases induces permanent visible PL in the material. They showed that aerogel samples treated with $H_2$ exhibited brighter PL at the exterior surface of the monoliths, while those treated with NH$_3$ gave more uniform intensity throughout. The observed PL requires an excitation wavelength of 300–400 nm, and the observed PL maxima for the $H_2$ and NH$_3$ treated samples are located at 490 and 460 nm, respectively. It was assumed that the PL observed in these samples result from localized oxygen deficiencies induced within the materials.

Recently, it was further demonstrated that aerogels produced by sol–gel hydrolysis and condensation of alkoxysilane in H$_2$O-alcohol solution shows PL mainly in the UV region without any reduction treatment.100,101 Chiodini et al.100 found that the PL spectra from porous silica heat treated at ~500°C are dominated by a 3.7 eV (335 nm) emission similar to the UV emission of oxidized porous Si and Si nanocrystals. They also found the samples show weaker PL bands located at 2.9 (427), 3.8 (326), and 4.2 eV (295 nm). All the observed PL emissions were characterized by decay times of a few nanoseconds. Since the PL intensity especially at 3.7 eV was dependent on the specific surface area of the samples,101 it is likely that the PL emission results from some surface defect states. It should also be worth mentioning that none of these PL activity matches known emissions of bulk silica, implying that the observed PL emissions result from microstructural characteristics of the porous materials. Anedda et al.102 suggested that the surface OH groups are related to the UV PL emission from porous silica, but currently no accepted assignments for the PL centers have yet been given.

4.3 PL from silica fine particles

In addition to silica aerogels, silica fine particles have attracted recent attention in terms of unique sintering behavior and PL characteristics. Yong-Taeg, Fujino, and Morinaga105 recently reported that highly transparent hydroxyl-free silica glass can be prepared by sintering a green compact prepared by micrometer-sized silica powders in a high vacuum environment. El-Shell et al.106 produced silica nanoparticles by laser-vaporization of polycrystalline silicon in a He/O$_2$ or Ar/O$_2$ atmosphere in a diffusion cloud chamber. Using this technique, a weiblike agglomeration of silica nanoparticles was obtained. The resulting PL consists of two peaks at 2.64 eV (467 nm) and 2.94 eV (422 nm). El-Shell et al.106 suggested that the PL from the silica nanoparticles are attributed to a divalent Si defect, however it appears that no further experiments to confirm the assignment, e.g. decay time measurements and quenching studies, have yet been performed.

PL measurements of another class of silica nanoparticles, fumed silica mentioned in Sec. 2.4, were carried out by Glinka and co-workers.105-107 They found that UV and visible PL emissions were induced by a focused pulsed UV laser beam of ArF laser [193 nm] or Nd:YAG laser [266 nm]. They observed the PL bands at 2.37 eV (523 nm) and 1.9 eV (652 nm) which are excited by ArF and Nd:YAG laser lights. They also observed the PL at (2.8 eV (443 nm) excited only by ArF laser light and showed that this PL emission results from the two-photon process. From the time-resolved PL measurements, Glinka et al.106 demonstrated that the 1.9-, 2.37- and 2.8-eV bands are attributed to nonbridging oxygen hole centers (NBOHCs), hydrogen-related defects and self-trapped excitons (STEs), respectively. They further demonstrated that the PL properties of silica nanoparticles are closely analogous to those of bulk $a$-SiO$_2$ as far as the focused pulsed UV lasers are used for excitation.107

Quite recently, Uchino and Yamada108 have reported that bulk transparent $a$-SiO$_2$ prepared from solid-phase sintering of fumed silica exhibits intriguing PL properties under excita-
where $I(t)$ and $I_0$ are the PL intensity during the decay and $t = 0$, respectively, $\tau$ an effective decay time, and $\beta$ a dispersion factor. In general, $\beta < 1$ represents a distribution of independent single exponentials with different lifetimes. This decay law is commonly observed in disordered and/or low-dimensional semiconductors\cite{109-113} and the phenomenon is believed to result from the complicated diffusion dynamics of the photoexcited carriers.\cite{114-118} From the temperature dependence of the PL data, Uchino and Yamada\cite{119} have found that at low temperatures ($\sim 200 \text{ K}$), the thermally activated formation process of an electron-hole pair dominates the quantum yield of the PL emission. At high temperatures ($\sim 200 \text{ K}$), the radiative decay of the electron-hole pair begins to compete with nonradiative decay channels, and a simultaneous decrease of $\tau$ and $I(t)$ is observed. This is probably the first observation of the PL emission arising from the trapping-controlled migration of photoexcited carriers in $a$-$\text{SiO}_2$ through below the band gap excitation. They\cite{119} suggest that highly deformed siloxane linkages that are created during the sintering process are responsible for the present PL phenomena. It is likely that such highly deformed bonds result solely from solid-phase sintering of nanometer-sized silica particles since the sintering of sol-gel derived porous silica does show a PL behavior as seen in the present sample. Although the true origin of the PL has yet not been clarified yet, the transparent $a$-$\text{SiO}_2$ reported by Uchino and Yamada may open up a new practical application in the field of lighting products and related optoelectronic and display technologies.

5. Conclusions

As for the structure, one of the most interesting and challenging problems is homogenity in terms of static and dynamical structures. The problem is highly related to the universal anomalies of glassy and amorphous solids, including excess in the density of states, low-temperature transport and thermodynamic properties, the fate of acoustic modes at higher frequencies, and an Ioffe–Regel crossover. Recent inelastic X-ray scattering studies appear to give a new insight into the problem;\cite{119-52} however, a general consensus on the characteristics of the observed excitations is still lacking.

Photoluminescence from $a$-$\text{SiO}_2$ and the related Si/$\text{SiO}_2$ materials are becoming increasing interest in the field of optoelectronic and lighting technologies. In particular, the PL from silicon nanoparticles embedded in $a$-$\text{SiO}_2$, films show interesting properties such as the amplified spontaneous emission.\cite{121} The mechanism of the emission from $a$-$\text{SiO}_2$-based materials has not been fully understood; however, the surface defect states, e.g. silane bonds, along with the quantum confinement effects play a vital role in showing the PL emission.

Finally, nanostructured $a$-$\text{SiO}_2$ materials are also attractive in their own right. We should note that such materials show UV/visible PL emissions without incorporating any metal-based phosphors and/or fluorophors, indicating a diversified nature of the Si–O bond in the silica network. If one can control the atomic arrangements of the nanostructured materials in the length scale of the MRO, SRO and atomic bonds, one can possibly obtain novel luminescent materials.

Thus, structure and properties of $a$-$\text{SiO}_2$ is far from being a mature field of research in spite of extensive studies over the decades. Further advances both in experimental and theoretical methods will make it possible to obtain much more detailed information on the dynamical, optical and electronic properties of $a$-$\text{SiO}_2$ and related materials. We believe silica is still a mysterious, fascinating and innovative material.
(1975).
69) Gallas, J. P., Lavallely, J. C., Burmea, A. and Barres, O., Langmuir,
72) Chemarin, C., Champagnon, B. and Panczer, G., J. Non-
75) Hosono, H., Ikuta, Y., Kinoshita, T., Kajihara, K. and
Hirano, M., Phys. Rev. Lett., Vol. 87, article no. 175501
76) Griscom, D. L., J. Ceram. Soc. Japan (Seramikkusu
64, article no. 081310(R) (2001).
83) Alemany, M. G. and Chelikowsky, J. R., Phys. Rev. B,
Vol. 68, article no. 054026 (2003).
84) Agnello, S., Bascaino, R., Buscaino, G., Bausch, M. and
Gelardi, F. M., Phys. Rev. B, Vol. 66, article no. 113201
(2002).
86) Lu, Z. Y., Nicklaw, C. J., Fleetwood, D. M., Selmpl, R. D.,
Pantelides, S. T., Phys. Rev. Lett., Vol. 89, article no. 285305
(2002).
(1994).
91) Wolkin, M. V., Jorne, J., Fauchet, P. M., Allan, G. and
92) Pavesi, L., Dal Negro, L., Mazzoleni, C., Franzó, G. and
93) Cole, J. L., Dudel, F. P., Grantier, D. and Dixon, D. A.,
95) Chabal, Y. J., Raghavachari, K., Zhang, X. and Garfunkel,
97) Dal Negro, L., Cazzanelli, M., Pavesi, L., Ossicini, S.,
Pacifici, D., Franzó, G., Priolo, F. and Iacono, F., Appl.
100) Chiadini, N., Mearani, F., Morazzeno, F., Paleari, Scotti, R.
(2000).
102) Anedda, A., Carbonaro, C. M., Clemente, F., Corpino, R.,
104) El-Shell, M. S., Li, S., Turkki, T., Graiver, D., Pernz, U. C.
66, article no. 035404 (2002).
111) Ventura, P. J., de Camo, M. C. and O’Donnell, K. P., J.
112) Pophristic, M., Long, F. H., Tran, C., Ferguson, I. T. and
114) Scher, H., Schlesinger, M. F. and Bendler, J. T., Phys.
(1978).
(1996).
119) Uchino, T. and Yamada, T., unpublished data.