Chapter 2
Structure

Abstract  Atomic and microscopic structures of chalcogenide glasses are discussed from theoretical and experimental points of view. Starting with discussion on an ideal glass structure, we will see continuous studies performed for grasping atomic structures in disordered materials. Experimental methods and deduced results for the short-range and medium-range structures (orders) in glasses are introduced. Structural defects, which are likely to produce localized states in the bandgap, are discussed. In addition to these atomic structures, we shed light upon inhomogeneity and nano-structures in chalcogenide glasses.

Keywords  Density · FSDP · Boson peak · Distorted layer · Wrong bond · Dangling bond · Homogeneity · Multi-layer

2.1 Ideal Structure

What is an ideal glass structure? For a crystal, we can envisage its ideal structure as one in which the structure is perfectly periodic with no defects at all (Fig. 2.1). The atomic position can be uniquely determined. Such a structure could conceptually be obtained through infinitely slow cooling of the corresponding melt to 0 K. In a simplified theory, crystal surfaces are tentatively neglected under the so-called periodic boundary condition, and the structure becomes a starting framework for analyses of macroscopic properties (Kittel 2005). Or, in the exact opposite, we can envisage a completely random atomic structure in an ideal gas. In this case, the atomic position can neither be predicted nor fixed. But, its property such as pressure at a given temperature can theoretically be evaluated through statistical mechanics for an assembly

Fig. 2.1  Two-dimensional views of (a) crystal (close packed), (b) liquid and glass (dense random packing), and (c) gas
of point-like substances (atom or molecule) having no interactions. The physical properties are uniquely fixed under a fixed temperature and volume. Having seen these ultimate examples, we are tempted to assume that the ideal should imply a uniquely defined structure, at least, in a statistical sense. *Ideal must be unique.* Can we imagine such an ideal structure for a glass?

It seems impossible to envisage the unique structure for a disordered lattice. For instance, in the two local structures illustrated in Fig. 2.2, both including fourfold coordinated one-kind atoms in (a) a 6-atom ring with a dangling bond and (b) a strained but completely bonded 5-atom ring, which has a smaller total (electron plus lattice) energy? The structure in (b) can be regarded as a part of the famous Polk model proposed for a-Si (Turnbull and Polk 1972), which contains no dangling bonds. Several authors may assume that such continuous random networks are ideal. But, the structure must be highly strained. And, even for such fully connected structures, a variety of atomic ring structures with different formation energies possibly exist. It seems that we cannot envisage an ideal glass structure.

Disorder implies a lot of varieties between the two ideal (ultimate) structures of crystal and gas. The amorphous structure is neither periodic, as that in a crystal, nor completely random, as that in an ideal gas. The non-crystalline structure spans a wide range between the completely perfect and the completely random structure: single crystal (periodic) ← non-crystal → ideal gas (completely random). We must consider a variety of intermediates. It should be noted, however, that liquid has also a disordered structure.

Then, what is the difference between a liquid and an amorphous material? In contrast to the liquid, which is thermodynamically equilibrated, the non-crystalline solid is in quasi-equilibrium, or is meta-stable. Strictly speaking, an amorphous material does not take a thermodynamically defined *phase*, but it takes just a spontaneous *state*, which necessarily changes with time. After infinitely long storage, the glass is believed to relax to a crystal. Actually, we know that a-Se films crystallize from surfaces within a few weeks when stored in humid atmospheres. We also know that the surface of glassy flakes, which are dug at prehistoric ruins, often appears micaceous or crystalline. In addition, a glass property depends upon preparation methods. Actually, as shown in Fig. 2.3, as-evaporated and annealed As$_2$S$_3$ films give markedly different x-ray diffraction patterns.

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**Fig. 2.2** Two bonding structures for fourfold coordinated atoms such as Si. (a) A 6-membered ring with a dangling bond, and (b) a strained 5-membered ring
Nevertheless, meta-stability has provided an unresolved problem on the uniqueness of glassy states. We here recall the so-called Kauzmann’s paradox, detailed in Section 3.2. The most stable glass may be obtained at the Kauzmann temperature \(T_K\), since the free energy can be uniquely defined. Kauzmann’s glass may be ideal. However, the idea is macroscopic, and we have never obtained the glass nor seen the atomic structure at the conceptual temperature \(T_K\).

### 2.2 Practical Structure

Determination of atomic bonding structures is a prerequisite in solid-state science. For crystals, the structure can be determined in principle through analyses of Bragg peaks in x-ray diffraction patterns. However, as exemplified in Figs. 2.3 and 2.4, the non-crystalline solid does not provide sharp Bragg peaks but gives...
only broad halos. Considering such observations, Zachariasen (1932) proposed the so-called continuous random network model for oxide glasses such as Si(Ge)O$_2$, while the real structure could not be determined. We here see fatal limitations of the traditional structural analysis. The limitation still remains, posing the biggest problem in science on non-crystalline materials. Then, how can we get insight into the atomic structure? We can see just the tip of an iceberg as described below.

A rough idea can be grasped from the macroscopic density (Fig. 2.5). It is known for simple glasses that the glass is less dense than the corresponding crystal by 10–20% (Thornburg 1973, Hobbs and Yuan 2000), which varies with preparation procedures and storage after preparation. This observation suggests that atomic packing in the glass and the crystal is not very different. More generally, the densities of a glass, the corresponding crystal, and the melt can be regarded roughly as the same in comparison with that in the gas, which has nearly completely random and time-varying atomic (molecular) structures with an average separation of ~5 nm at 1 atm (Fig. 2.1). Specifically, since the glass is produced from the melt, it is reasonable to envisage that the structures have some resemblances. We then assume that the atomic potential, which fixes the bond distance and atomic coordination, governs the density in all condensed matters.

To analyze the amorphous structure in atomic scales, we can classify it into two elements, as shown in Fig. 2.6: normal bonding structures and defective structures (Ovshinsky and Adler 1978). A normal bond can be defined as topologically

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**Fig. 2.6** A classification of amorphous atomic structures
the same atom connection with that existing in the corresponding crystal. In SiO$_2$ glass, it is SiO$_{4/2}$ ($\equiv$Si–O–) tetrahedral connections, as illustrated in Fig. 2.7a. The normal bonding structure can further be divided into the short ($\lesssim$0.5 nm) and the medium-range (0.5–3 nm) structure, as will be described later. On the other hand, the defective structure resembles a defect in practical crystals. The examples are an $E'$ center in g-SiO$_2$, which is a Si dangling bond ($\equiv$Si●), and a wrong bond (Halpern 1976), i.e., a Si homopolar bond ($\equiv$Si–Si$\equiv$), both non-existing in the ideal SiO$_2$ crystal. We here underline that these defective structures are point-like defect ($<$0.5 nm). Defects such as dislocations and stacking faults, which sometimes play important roles in crystals, do not exist in amorphous materials. We also note that the point-like defect is spatially isolated from each other in normal bonding matrices. The isolation may be a consequence arising from the non-existence of long-range atomic periodicity in the glass. If the Si wrong bonds would gather, the assembly might become a Si nano-crystal.

A note on small rings should be added. As known, c-SiO$_2$ takes a variety of atomic structures, in which the most common is the quartz, or $\beta$-quartz (the high-temperature form, Fig. 1.1). The crystal structure is hexagonal (Fig. 2.7d) consisting of SiO$_{4/2}$ tetrahedra, which contain 3 (6 atom)- and 6-membered (12 atom) rings. On the other hand, in g-SiO$_2$, it is plausible that a variety of rings exist. And, some researchers assume small rings such as 3- and 4-membered rings as defects. However, since the structure has spatial extension of $\sim$1 nm and the concentration may be greater than $\sim$1 at.% in some cases (Kohara and Suzuya 2005), it seems to be better to regard such small rings as strained normal bonds. As will be described later, the present classification is more useful to consideration of electronic structures, since the relaxed and strained normal bonds govern, respectively, the band and band-edge electronic states. On the other hand, the defects tend to produce mid-gap states.

In the following, we will see how the non-crystalline structure has been explored. In principle, the normal bonding structure has been investigated through structural
measurements using, e.g., x-ray diffraction and EXAFS (extended x-ray absorption fine structures) (Elliott 1990). We note here that, in these x-ray experiments, recent progress of synchrotron radiation sources can dramatically shorten the exposure time (∼40 ps) and increase the spatial resolution (∼100 nm) of the inspected area (Tanaka et al. 2009). In addition to these and other direct structural studies, versatile and circumstantial observations are also valuable for sketching the structure. For instance, pressure dependence of optical gaps (Fig. 1.25) gives insight into the amorphous structure, through comparing the result with those obtained for the corresponding crystal. Also, computer simulations have become valuable tools as described in Section 2.6.

2.3 Short-Range Structure

2.3.1 Experiments

Provided that a glass is homogeneous and has a simple composition, we can experimentally determine its short-range structure (Greaves and Sen 2007). Here, the short-range structure is determined by three parameters: the coordination number \(Z\) of atoms, the bond length \(r\), and the bond angle \(\theta\).

The short-range structure can be inferred from radial distribution function \(\rho(r)\), which can be calculated from x-ray (e-beam and neutron) diffraction patterns, an example being shown in Fig. 2.8. Let us assume an elementary system such as a-Se; the diffracted intensity \(I\) at an x-ray wavenumber \(Q\) can be written as (Elliott 1990)

\[
I(Q) \propto f(Q)^2 \int 4\pi r^2 [\rho(r) - \rho_0] (\sin Qr)/(Qr) \, dr \quad \text{with} \quad Q = \frac{4\pi}{\lambda} \sin \theta s / \lambda, \quad (2.1)
\]

where \(f\) is the atomic scattering factor, \(\rho_0\) an average atomic density, \(2\theta s\) the scattering angle, and \(\lambda\) the x-ray wavelength. Accordingly, from measured \(I(Q)\), we can calculate \(\rho(r)\), which provides \(Z\), \(r\), and \(\theta\), respectively, from the first-peak intensity,

![Fig. 2.8](image)

\(\text{Fig. 2.8} \quad \text{Diffracted x-ray intensity} \ I(Q) \text{ and calculated radial distribution function} \ \rho(r) \text{ of} \ \text{a-Se} \quad (\text{modified from Andonov (1982)})\)
Fig. 2.9 An illustration of a c-Se chain. The bond length is $\sim 0.24$ nm, bond angle $\sim 103^\circ$, and dihedral angle (the angle between the triangular planes defined by ABC and BCD atoms) $\pm 102^\circ$.

the first-peak position $r_1$, and the second-peak position $r_2$ with $r_1$ value. Note that this equation is useful also for crystals.

Debye equation gives a deduced form of the above equation for a pair of atoms which are randomly oriented, as those in gas, liquid, and glass (Elliott 1990):

$$I(Q) \propto \sum_{ij} f_{ij} \sin(Qr_{ij})/(Qr_{ij}), \quad (2.2)$$

where $r_{ij}$ is the distance between an atomic pair. We see that $I(Q)$ of disordered materials appears as a summation of sinc functions ($\sin x/x$), which provide broad halo patterns. Here, a straightforward analysis shows the following: Reflecting the functional shape, the halo at the smallest wavenumber gives the strongest peak at $Q_1$, which satisfies $Q_1r_{ij} \approx 7.7$. This relation is useful for estimating the responsible pair distance $r_{ij}$ (Tanaka 1990).

However, for multi-component glasses, direct applications of the above procedures are difficult. We cannot determine the structure from only one diffraction pattern, since $f$ changes with atom species. We may then utilize anomalous x-ray diffraction methods (Elliott 1990), in which $f$ becomes also a function of x-ray wavelengths. If a glass contains $n$ kinds of atoms, diffraction patterns using $n + 1$ x-ray wavelengths can give $n + 1$ simultaneous (coupled) equations:

$$I(Q, \lambda) \propto \sum_{ij} f_i(Q, \lambda)f_j(Q, \lambda) \int 4\pi r^2\left[\rho_{ij}(r) - \rho_0\right] (\sin Qr)/(Qr) \, dr, \quad (2.3)$$

which can uniquely determine $\rho_{ij}(r)$ for $ij$ pairs ($i$ and $j \leq n$). The isotope-substituted neutron diffraction follows a similar principle (Petri et al. 2000), in which $f$ changes with isotopes. Provided that the atomic discrimination is successful, these methods may give longer-range atomic correlation (Hosokawa et al. 2009) than that given by EXAFS, the principle being described below.

EXAFS may give more direct information for the structure in multi-component systems (Elliott 1990, Armand et al. 1992, Vaccari et al. 2009). In EXAFS experiments, x-ray transmittance (or absorbance) of a sample of interest is measured as a function of x-ray energy $E (= 2\pi ch/\lambda)$. As illustrated in Fig. 2.10, the absorbance abruptly changes at a core-electron excitation energy, e.g., at the K edge $E_K$, and
small intensity modulation “EXAFS” $\chi_i(E)$ appears just above this threshold energy at around $E - E_K \leq 500$ eV.

Why does such an oscillation appear? The oscillating EXAFS $\chi_i(k)$ can be regarded as an x-ray transmission spectrum which is modulated by the interference of x-ray excited electron waves with a wavenumber of $k = 2\pi/\lambda_e = (2m(E - E_K))^{1/2}/\hbar$, where $\lambda_e$ is the electron wavelength ($\sim0.2$ nm) and $m$ is the electron mass. In Fig. 2.10 (right), the electron wave spreading from the central atom and those being reflected back by surrounding (lower right) atoms interfere, which modulates x-ray transmittance through electron excitation efficiency. By scanning the x-ray energy $E$, the interference varies, and accordingly, the x-ray transmission spectrum has information of the surrounding atoms (atomic species, distance, number). Mathematically, at a slightly higher x-ray energy $E$ than a core-electron excitation energy $E_K$ of specified single atoms $i$, $\chi_i(k)$ contains a term as (Elliott 1990)

$$\chi_i(k) \propto \sum_j Z_{ij} \exp(-2r_{ij}/L) \sin(2kr_{ij} + \varphi_j(k)), \quad (2.4)$$

where $Z_{ij}$ is the number of atoms (coordination number) at a distance of $r_{ij}$ around a specified $i$ atom, $L$ is the electron mean free path, and $\varphi_j(k)$ is the phase change occurring when an excited electron is reflected at a neighboring atom $j$. If the phase change can be known using a reference material as related crystals, we can determine $r_{ij}$ from oscillating EXAFS spectra. (In other words, when analyzing EXAFS oscillations, we implicitly assume the species of neighboring atoms.) The amplitude of $\chi_i(k)$ is proportional to the coordination number $Z$ of the specified atom, i.e., the number of atoms reflecting the electron waves, which can also be determined with lower accuracy depending upon the value of $L$ and so on.

Note that, in the optical Fabry–Perot-type interference, the sinusoidal fringe in transmission spectra is produced by modulation of multiply-reflected light. For the EXAFS, we may use a metaphor: imagine that we (x-ray photons) are walking in a swimming pool, producing water waves (electron waves) and feeling reflected waves (electron waves) from pool sides (surrounding atoms). Our walk may be smooth or difficult, depending upon the interference by the waves.
2.3 Short-Range Structure

We underline three characteristics for the EXAFS. First, the EXAFS is useful specifically for multi-component systems. Since $E_K$ is fixed by an atom, we can determine peripheral structures around the specified atom $i$. Second, as imagined from the principle, Fig. 2.10 (right), it is more or less difficult to obtain a second nearest-neighbor peak in close-packed atomic structures from EXAFS spectra. Finally, as known from the principle, EXAFS experiments prefer x-ray beams having not characteristic peaks, but smooth and continuous spectra. Accordingly, the conventional x-ray tubes are less appropriate. Intense beams obtained as synchrotron orbital radiation are much effective to reduce exposure time and improve spatial resolution.

As an example, an EXAFS result around Ge in crystalline and glassy GeS$_2$ is shown in Fig. 2.11 (Armand et al. 1992). We see in the right figure the strong first peak at $\sim$0.2 nm (Ge–S distance) and two weaker peaks at $\sim$0.26 and $\sim$0.31 nm, the latter being identified to the two kinds of second-nearest Ge–S–Ge pairs (in edge- and corner-sharing tetrahedra) illustrated in the inset. The peak positions are very similar to those of the crystal, which evinces existence of the short-range structural order in this glass.

Direct images of amorphous structures can be obtained using two methods. Transmission electron microscopy is able to provide direct images and also diffraction patterns. For instance, Young and Thege (1971) take electron diffraction patterns of a-As$_2$S$_3$. However, the image for insulating materials such as sulfides and oxides tends to become blurred due to charge-up. To the authors’ knowledge, no atomic images have been obtained for such insulating glasses. On the other hand, scanning tunneling and atomic force microscopy have been applied for obtaining surface images (Tominaga et al. 1992, Ichikawa 1995). However, we may have some doubts about reliability and/or reproducibility of the surface-sensitive images. Nevertheless, atomic images obtained for Se films (Peled et al. 1995) and cleaved surfaces of oxide glasses (Poggemann et al. 2003) seem genuine. Specifically, Poggemann et al. (2003) take a histogram of obtained atomic images for a few glasses, as exemplified for g-SiO$_2$ in Fig. 2.12, which appears

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**Fig. 2.11** An EXAFS spectrum for Ge in c-GeS$_2$ (left) and RDFs for Ge in c- and g-GeS$_2$ (right). The inset in the right-hand side shows the distances corresponding to the three peaks (Armand et al. 1992, © Elsevier, reprinted with permission)
Fig. 2.12  An atomic force microscopy image of a vacuum-fractured surface of g-SiO$_2$ (left) and the distribution of atomic (white regions) distances (right) (Poggemann et al. 2003, © Elsevier, reprinted with permission), which is compared with an x-ray radial distribution function (RDF) reported by Kohara and Suzuki (2005).

to be consistent with the radial distribution function $\rho(r)$ deduced from x-ray patterns (Kohara and Suzuya 2005). Further studies including comparisons of surface structures of a glass and the corresponding crystal will be very interesting.

In addition to these direct structural experiments, there are less direct ones. Those are vibrational spectroscopy (infrared transmission, Raman scattering, and inelastic neutron scattering), several spin-related methods, and photoelectron spectroscopy.

Infrared and Raman spectroscopy measure the intensity and frequency (wavenumber) of vibrational modes (Elliott 1990). As known, the frequency is written as $\omega \sim (\kappa/M)^{1/2}$, where $\kappa$ is the force constant of a spring connecting a pair of atoms (or atomic units) and $M$ is the atomic mass. Accordingly, the peak frequency gives insight into the vibrational mode, which is an optical phonon in crystals (Kittel 2005) or a molecular vibration in disordered materials, e.g., vibrations of As$_3$S$_2$ in g-As$_2$S$_3$, as shown in Fig. 2.13. On the other hand, the spectral intensity $I(\omega, T)$ is written for disordered materials as (Shuker and Gammon 1970, Martin and Brenig 1974)

$$I(\omega, T) = g(\omega) C(\omega)[n(\omega, T) + 1]/\omega, \tag{2.5}$$

where $g(\omega)$ is the density of vibrational modes, $C(\omega)$ the opto-vibrational coupling constant, and $n(\omega, T)$ the Bose–Einstein (Planck) distribution. Here, it is known that infrared transmission and Raman scattering spectroscopy follow different selection rules in the coupling constant. However, disordered structures tend to make the selection rules loose. In addition, Raman scattering spectroscopy becomes experimentally more useful, due to the recent progress of lasers and imaging detectors at visible to near-infrared wavelengths. We can obtain not only the conventional Raman scattering spectra (Yannopoulos and Andrikopoulos 2004) in short exposure times for small probe areas ($\gtrsim 1 \mu m$), but also resonant (Tanaka and Yamaguchi 1998) and nonlinear (Klein et al. 1977) Raman scattering spectra. Therefore, Raman scattering spectroscopy becomes more commonly employed.
As an example, Fig. 2.13 shows Raman scattering spectra of glassy, as-evaporated, and crystalline As$_2$S$_3$. The broad and relatively sharp spectra of the glass and the as-evaporated film suggest that these are cross-linked and molecular, respectively (Lucovsky et al. 1975, Malyj and Griffiths 1987). On the other hand, the sharp peaks in the crystal correspond to optical phonons near the $\Gamma$ point in the Brillouin zone (Kittel 2005).

Spin-related methods can probe peripheral structures around a spin through its resonance frequency, peak width, etc. (Elliott 1990). Related studies for chalcogenide glasses include electron spin resonance (ESR) of Mn$^{2+}$ in Mn-doped As–Se(Te) (Watanabe et al. 1976), nuclear magnetic resonance (NMR) of $^{31}$P in P–Se (Lathrop and Eckert 1993) and $^{77}$Se in selenide compounds (Bureau et al. 2004, Gjersing et al. 2010, Kibalchenko et al. 2010), nuclear quadrupole resonance (NQR) of $^{75}$As in As–S(Se,Te) (Taylor et al. 2003), and Mössbauer spectroscopy of $^{125}$Te in As–Te (Tenhover et al. 1983). These studies owe more or less the specific samples and/or measuring instruments, and accordingly, fixed groups have published their results.

Finally, x-ray photoelectron spectroscopy (XPS) of core-electron states can probe the valence of constituent atoms through comparing with some references. It can discriminate Ge$^{4+}$ and Ge$^{2+}$ in Ge–S glasses (Takebe et al. 2001) and peripheral circumstances around Ge in a-Ge$_1$Sb$_2$Te$_4$ films (Klein et al. 2008) and Ge–Se glasses (Golovchak et al. 2009).

### 2.3.2 Observations

Direct and indirect experimental studies suggest that the short-range ($\leq 0.5$ nm) structure of a glass is similar to that in the corresponding crystal. An example for Se is summarized in Table 2.1. The coordination number $Z$ seems to satisfy the
Table 2.1 Comparison of atomic parameters in c-Se (hexagonal) and g-Se (Andonov 1982)

<table>
<thead>
<tr>
<th></th>
<th>Z</th>
<th>r (nm)</th>
<th>θ</th>
<th>Φ</th>
<th>ρ (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hex Se</td>
<td>2.0</td>
<td>0.23</td>
<td>105°</td>
<td>102°</td>
<td>4.80</td>
</tr>
<tr>
<td>g-Se</td>
<td>2.0 ± 0.04</td>
<td>0.23 ± 0.002</td>
<td>105±0.5°</td>
<td>70–110°</td>
<td>4.25</td>
</tr>
</tbody>
</table>

Z is the atomic coordination number, r the bond length, θ the bond angle, Φ the dihedral angle (see Fig. 2.9), ρ the density

Table 2.2 Bond lengths (in nm) and bond angles around the VIb atoms (in parentheses) in the VIb elemental materials (O, S, Se, and Te) and amorphous As₂O(S,Se,Te)₃ and GeO(S,Se,Te)₂. The bond angle in a-GeTe₂ is unclear

<table>
<thead>
<tr>
<th></th>
<th>O</th>
<th>S</th>
<th>Se</th>
<th>Te</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elemental</td>
<td>0.12 in O₂</td>
<td>0.21 (106°)</td>
<td>0.23 (105°)</td>
<td>0.29 (103°)</td>
</tr>
<tr>
<td>As-</td>
<td>0.18 (∼130°)</td>
<td>0.23 (∼100°)</td>
<td>0.24 (∼105°)</td>
<td>0.27 (∼90°)</td>
</tr>
<tr>
<td>Ge-</td>
<td>0.18 (∼105°)</td>
<td>0.22 (80–110°)</td>
<td>0.24 (80–100°)</td>
<td>0.26 (?)</td>
</tr>
</tbody>
</table>

so-called 8–N rule (Mott and Davis 1979), where N is the atomic group number in the previous IUPAC form, with an accuracy of ∼10%, which may reflect experimental uncertainty and effects of dangling bonds. The bond distance r is fixed with an accuracy of Δr/r ≈ 1%. The bond angle also shows a similar result in Se. However, for alloys (Table 2.2), it seems difficult to accurately determine the bond angle, which distributes roughly at Δθ/θ ≈ 5 – 10%, where θ is the angle for a group VIb atom such as the Si–O–Si angle. (Note that the angle is not uniquely fixed even in the crystal, which contains different kinds of atomic units.) On the other hand, experiments show that the cation angle, such as O–Si–O and S–As–S, is more tightly fixed due to steric restrictions. In short, we regard that there exists the short-range structural order in glasses. Note that the fluctuation ratios of r (∼1%) and θ (5–10%) imply comparable strain energies in bond distance and angle, k_r(Δr)^2 ≈ k_θ(Δθ)^2, since k_θ/k_r ≈ 1/10 in the force constants (Lucovsky et al. 1975). This result suggests that an energetic equilibrium is satisfied in the short-range scale.

In more detail, there exist some variations in the short-range structures. First, the coordination number, which is a direct consequence of the electron configuration s^2p^4 of the group VIb atoms, is modified when ionic and metallic characters are added. As described in Section 1.5, the metallic effect is appreciable in tellurides. Second, the bond length r increases in proportion to the period (2–5) in the periodic table, e.g., from 0.12 to 0.29 nm in the elements (Table 2.2), in accordance with the atomic size (Fig. 1.9). Third, and which should be underlined, we see that the bond angles are appreciably different between the oxide and the chalcogenide. As listed in Table 2.2, it is ∼130° in As₂O₃ and ∼100° in As₂S(Se,Te)₃, which may be approximated very roughly to 180° (ionic) and 90° (covalent). These characteristic angles
are favorable to produce the so-called corner-shared and edge-shared configurations (see Fig. 2.15), which will be connected to the medium-range structure.

Having seen the chemical bonding in elemental and stoichiometric binary glasses, we turn to more complicated glasses, including non-stoichiometric binary and ternary glasses. It was mentioned in Section 1.6 that the oxide can produce the mixtures, such as SiO$_2$–Na$_2$O, which consist of stoichiometric units, SiO$_2$ and Na$_2$O. Naturally, as shown in Fig. 1.13, the glass contains only Si–O bonds, which are relatively covalent, and Na–O ionic bonds. The homopolar bond such as O–O may be included in a defective level. In contrast, it is straightforward to prepare non-stoichiometric chalcogenide glasses, e.g., As(Ge)–S(Se,Te) in the limited glass-forming regions (see Fig. 1.17). As(Ge)-rich and As(Ge)-deficient glasses, which deviate from the stoichiometric compositions As$_2$S(Se,Te)$_3$ and GeS(Se)$_2$, necessarily contain homopolar bonds, As(Ge)–As(Ge) and S(Se,Te)–S(Se,Te), respectively, in addition to the heteropolar bond As(Ge)–S(Se,Te). And, As$_{15}$S$_{85}$ glass is demonstrated to be a mixture of As–S networks and S molecules (Tsuchihashi and Kawamoto 1971). Here, a principle on the atomic bonding seems to be the preference of heteropolar bonds (As–S, As–Te, Ge–S, etc.), since these have stronger bond energies than those of the homopolar bonds (As–As, S–S, etc.) (see Table 2.4).

In non-stoichiometric ternary alloys such as As–S–Se, Ge–Sb–Te, and Ag(Cu)–As–S, we will face more critical problems. For instance, in Ge–As–S, which bond is preferred between Ge–S and As–S? Difference of the bond energies is subtle as listed in Table 2.4. We may also wonder if a Ge–As–S glass possesses an intermediate property between those in Ge–S and As–S glasses. Universal understandings, which should take also the quasi-equilibriumness into account, have not been obtained.

As we have seen in this section, the short-range structure is determined by the chemical bonding, and accordingly, the existence of structural orders is plausible. Nevertheless, no further structural order could be envisaged, e.g., in the continuous random network model originally proposed by Zachariasen (1932). But, this view has been completely reformed as described below.

### 2.4 Medium-Range Structure

Historically, the first implication of a medium-range order in glasses is believed to have been presented by Vaipolin and Porai-Koshits (1963) for g-As$_2$S(Se,Te)$_3$. Successive studies have demonstrated the existence of some medium-range structural orders with scales of 0.5–3 nm, at least, in simple glasses. However, the “some” order remains controversial, because there are no experimental tools explicitly determining the atomic structure having such scales in disordered materials. This has become one of the biggest subjects covering structures and properties in glasses. In the following, we will see the present status of our understanding on the medium-range order from short to longer scales (Elliott 1991), not along a historical sequence.
2.4.1 Small Medium-Range Structure

The short side length of \(\sim 0.5\) nm of the medium-range structure must be connected to the short-range structure covering atomic structures up to the second nearest neighbors. We then envisage a position of the third nearest-neighbor atom, which is determined by the dihedral angle (see Fig. 2.9) in twofold coordinated structures, the simplest example being Se. In the hexagonal-type c-Se, the atomic connection is all \textit{trans}, being explicitly determined. On the other hand, the radial distribution function of a-Se gives no clear peaks corresponding to the third nearest neighbor (Fig. 2.8). This fact suggests that the dihedral angle is randomly distributed between \textit{trans} and \textit{cis} configurations (Andonov 1982), resulting in the so-called entangled chain structure (Fig. 2.7c). However, it is more or less difficult to experimentally distinguish between a long curled chain and a ring molecule. In the tetrahedral connection as in Si, we can envisage staggered and eclipsed conformations, illustrated in Fig. 2.14. As known, c-Si consists of only the staggered connection, while radial distribution functions of a-Si(:H) do not show a clear third-nearest peak, which suggests mixed structures with staggered, eclipsed, and intermediate configurations (Bodapati et al. 2006). In short, in a-Se and a-Si(:H), no third nearest-neighbor correlations seem to exist. However, such results are not universal as we see below.

We next see the fourth nearest neighbor, which is involved in the corner- and edge-shared connections of atomic units, as illustrated in Fig. 2.15. Here, it is interesting to compare the chalcogenide glasses, \(\text{As}_2\text{S(Se)}_3\) and \(\text{GeS(Se)}_2\), with the corresponding oxide glasses, \(\text{As}_2\text{O}_3\) and \(\text{Si(Ge)}\text{O}_2\). It has been demonstrated that, in the chalcogenide glass, the corner- and edge-shared units of \(\text{AsS(Se)}_{3/2}\) and \(\text{GeS(Se)}_{4/2}\) exist, while the oxide glass contains only corner-shared connections (Kohara and

![Fig. 2.14](image-url) Staggered and eclipsed conformations for tetrahedrally connected Si atoms

![Fig. 2.15](image-url) Edge- (left) and corner-shared (right) tetrahedra (GeS_{4/2}) in GeS_2. For As_2S(Se,Te)_3, envisage triangular pyramid structures without one S atom outside
Suzuya 2005). Pauling (1960) suggests that the corner- and edge-sharing can be related with the ionic and covalent bonds with the ideal bonding angles of 180° and 90°. Note that these connections of the atomic units automatically fix the third-neighbor distances.

Next to these scales, we may consider the ring statistics (Greaves and Sen 2007). Here, the edge-shared connection contains a 2-membered (4-atom) ring, which tends to define rigid and flat segmental planes. On the other hand, disordered corner-shared structures are likely to produce three-dimensional continuous random networks, which cannot fix the ring size. In a-S(Se), entangled long chains and ring molecules consisting of several atoms (Fig. 2.7) may co-exist. However, we do not have any convincing experimental methods which can explicitly determine the ring statics and the chain length. We can just envisage the structure with a combination of experimental results and computer simulations such as reverse Monte Carlo method, which is introduced in Section 2.6.

An exception, which has been partially resolved, is the ring statistics in g-SiO₂. Through comparisons between theoretical calculations and Raman scattering spectra in g-SiO₂, Galeener’s group has identified the so-called D₁ (495 cm⁻¹) and D₂ (606 cm⁻¹) peaks, indicated in Fig. 2.16, to vibrational modes of 4- and 3-membered rings, respectively (Barrio et al. 1993). These small rings are assumed to be fairly stable, and its density is estimated at ~1 at.%. (To the authors’ knowledge, the small rings do not produce any peaks in optical absorption spectra.) Similar studies have been done for B₂O₃ (Nicholas et al. 2004). Small rings are also pointed out for a-Si:H (Du and Zhang 2005).

We then wish to apply similar spectral analyses to other materials such as GeO(S,Se)₂ and As₂S(Se,Te)₃. Actually, Kotsalas and Raptis (2001) have offered a plausible interpretation for the so-called A₁ companion line, a small peak at ~374 cm⁻¹ above the main peak of 342 cm⁻¹, in g-GeS₂. However, Raman scattering spectra in heavier atomic systems shift to lower wavenumbers, consequently resulting in substantial overlaps of characteristic peaks, and the spectra make the peak identification difficult. More detailed analyses seem to be needed for obtaining convincing insights.

![Fig. 2.16 Raman scattering spectra (HH and HV) of g-SiO₂ (Barrio et al. 1993, © American Physical Society, reprinted with permission)]
2.4.2 First Sharp Diffraction Peak

We then come to the big problem concerning the first (lowest wavenumber) sharp diffraction peak (FSDP). Vaipolin and Porai-Koshits (1963) discovered, as shown in Fig. 2.17, using the Cu Kα x-ray line that g-As₂S(Se)₃ present relatively sharp halo peaks, referred to as the FSDPs, at θ ≈ 14° (Q_{FSDP} = 4π sin θ/λ ≈ 10 nm⁻¹ = 1 Å⁻¹) with a peak width Δθ of ~5°. In As₂Te₃, the peak merges into a shoulder. Provided that the Bragg equation is applicable to the peak position, we obtain a structural period of ~0.6 nm. They also noticed that the FSDP position is similar to that of a Bragg peak appearing in As₂S(Se)₃ layer crystals (Fig. 1.16). In addition, the Scherrer equation \( D \approx \frac{\lambda}{(\Delta \theta \cos \theta)} \), being derived for polycrystalline materials, suggests a correlated domain size \( D \) of 2–3 nm. Taking these results into account, they have proposed the so-called distorted layer model for the glasses, i.e., deformed covalent layers with somewhat correlated interlayer distances of ~0.6 nm (see Fig. 2.7b). The layer may be a “raft,” in which the edge is terminated by chalcogen dimers, in a structural model proposed by Phillips (1979). Note that these models are different from polycrystalline structures, in which the domains are crystallites.

At first glance, the existence of such large correlated regions of 2–3 nm in the glass appeared anomalous. We may assume that the application of the Scherrer equation is problematic. On the other hand, a variety of experiments have been done for the FSDP. The experiments cover many kinds of chalcogenide glasses with different preparations and under varied temperatures and pressures (Busse 1984, Cervinka 1988, Elliott 1991). Through these studies, we tried to grasp atomic structures...
2.4 Medium-Range Structure

giving rise to the FSDP. However, in short, the results have given an impetus of continuing controversy. We also underline that, before ~1985, the FSDP had been assumed to be located at $Q_{\text{FSDP}} \approx 10 \text{ nm}^{-1}$, and that the peak was inherent to the chalcogenide glasses such as As$_2$S$_3$ and GeSe$_2$. No one might assume that the oxide glass possesses a FSDP, since its first peak is located at $Q \approx 16 \text{ nm}^{-1}$.

However, Wright et al. (1985) have presented a different definition. They noticed, as shown in Fig. 2.18, that the FSDP in the chalcogenide glasses satisfies a condition of $Q_{\text{FSDP}r'} \approx 2 - 3$, where $r$ is the nearest-neighbor distance, and this criterion meets also the first, but not so sharp, diffraction peak in $g$-SiO$_2$. The FSDP was re-defined as "$Q_{\text{FSDP}r'} \approx 2 - 3$," and this definition has been applied to many oxide, halide, chalcogenide, and elemental glasses (Moss and Price 1985). Then, several researchers have tried to obtain unified understandings of this seemingly more universal criterion, $Q_{\text{FSDP}r'} \approx 2 - 3$. We should, however, note that the half-width of the peak in Si(Ge)O$_2$ suggests a correlation distance of $1 - 2$ nm (Greaves and Sen 2007, Lucovsky and Phillips 2009), substantially shorter than that in the chalcogenides.

Since then, considerable studies have been performed for the FSDP in oxide glasses, specifically Si(Ge)O$_2$ (Kohara and Suzuya 2005, Greaves and Sen 2007). It has been amply demonstrated that $g$-Si(Ge)O$_2$ has continuous random network structures, and some researchers make efforts in answering the question "Why does the continuous random network exhibit such a peak?" Studies on complicated oxide glasses have also been performed. Gaskell et al. (1991) demonstrate a cation distribution order persisting over $\sim 1$ nm in CaO–SiO$_2$ glass. Other materials such as

---

**Fig. 2.18** Comparison of x-ray structure curves $S$ of (a) SiO$_2$ and (b) GeSe$_2$ in horizontal scales of $Q$ (lower) and $Qr$ (upper) (modified from Wright et al. 1985)
glassy ZnCl$_2$ (Salmon et al. 2005), a-As (Tanaka 1988), and a-P (Zaug et al. 2008) also present the FSDPs.

In short, there seems to be a consensus that some kinds of medium-range orders with scales of 1–3 nm exist in simple glasses, while the real atomic structure is controversial. For the group VIb stoichiometric glasses such as Si(Ge)O$_2$ and As$_2$S(Se)$_3$, there are roughly two ideas. One insists, taking $Q_{FSDP} \approx 2 – 3$ seriously, that the oxide and the chalcogenide possess qualitatively the same medium-range order, in which three-dimensional network structures have been presumed as a starting concept (Zaug et al. 2008, Massobrio and Pasquarello 2008, Lucovsky and Phillips 2009), the model hereafter referred to as a three-dimensional view. The others, including Zallen (1983), Cervinka (1988), and Bradaczek and Popescu (2000), assume that the oxide has three-dimensional and the chalcogenide has two-dimensional structures, the idea being consistent with the original view by Vaipolin and Porai-Koshit (1963). The present authors believe that this dimensional view is more intuitive and instructive, at least with the following three reasons.

First, the dimensional view is consistent with interpretations made for zero-dimensional (point-like) and one-dimensional molecular materials. Examples of the zero-dimensional materials are molecular CCl$_4$ liquids (Salmon et al. 2005) and as-evaporated As$_2$S$_3$ films (consisting of molecules such as As$_4$S$_4$) (DeNeufville et al. 1973, Wright et al. 1985), and those of one-dimensional molecules are organic polymers such as polyethylene (Fischer and Dettenmaier 1978) and polysilane (Tanaka and Nitta 1989). These zero- and one-dimensional molecules exhibit clear FSDPs, as exemplified in Fig. 2.19, which are ascribed without any ambiguity to intermolecular correlation of van der Waals-type bonding. The fact that a-Se consisting of Se chains does not show a clear FSDP, but a shoulder, is ascribed to the short inter-chain distance (~0.4 nm), which is similar to the second-nearest intra-chain distance of ~0.37 nm (Andonov 1982). Extrapolating these insights, we can assume that the two-dimensional (layer) structure gives the FSDP, which reflects the van der Waals-type correlation, in the chalcogenide glass. The peak in three-dimensional glasses should be ascribed to different origins. Also consistent with
the different origins of the first peaks are the appreciably different correlation

distances, ~2 and ~1 nm, estimated from the FSDP widths in chalcogenide and oxide

Second, the dimensional view is consistent with the material variation in the VIb
glasses. We saw in Fig. 1.12b that the density in As₂O(S,Se,Te)₃ and GeO(S,Se)₂
does not monotonically change, showing clear minima at the sulfides. The density
minimum at the sulfides can be understood by taking the dimensional view into
account, including longer van der Waals distances (~0.5 nm) than the covalent bond
(0.2–0.3 nm), as described in Section 4.10.

The third reason is posed from pressure dependence. Upon hydrostatic com-
pression, the position of FSDPs in polyethylene (Yamamoto et al. 1977) and
chalcogenide glasses (Tanaka 1998) dramatically shifts to lower diffraction angles,
while that in Si(Ge)O₂ is more or less intact (Guthrie et al. 2004). In addition, as
illustrated in Fig. 2.20, it should be noted that pressure behaviors of the FSDP in
g-GeS₂ and the interlayer distance in layer-type c-GeS₂ are similar (Tanaka 1986).
We may imagine compression of crumpled (glass) and stacked (crystal) papers
(covalent layers) here, in which the paper separations give the diffraction peaks.
It should also be mentioned that pressure dependence of optical absorption edges
(Fig. 1.25) is consistent with the dimensional view (Zallen 1983).

In short, the authors’ standpoint can be summarized as follows: What is impor-
tant in disordered materials science is an intuitive description of seemingly vague
observations in terms of “simple pictures.” The picture should be useful also for
understanding macroscopic properties of many kinds as possible. In this con-
text, the dimensional view seems to be more instructive. Controversy between
the dimensional and the three-dimensional view may arise from the terminology
or the definition of FSDP: \( Q ≈ 10 \, \text{nm}^{-1} \) and \( Q_{\text{FSDP}} r ≈ 2 – 3 \). The universal-
sity \( Q_{\text{FSDP}} r ≈ 2 – 3 \) may be coincidental, which arises from the fact that
the van der Waals distance is approximately equal to twice the covalent bond

\[ \text{Fig. 2.20} \quad \text{Comparison of atomic distances } d \text{ in g-GeS}_2 \]
\[ \text{glass (●) and the layer-type } \]
c-GeS₂ (○) under hydrostatic compression. The distance \( d \)
is calculated for the glass
from the FSDP position and
for the crystal from the
interlayer x-ray peak.
Fractional change \( \Delta l/l \) in
macroscopic linear
compressibility for the glass
is also shown by a dotted line
with an error bar (Tanaka
1986, © Elsevier, reprinted
with permission)
distance. Note that the two models are in agreement for g-SiO$_2$ and also a-Si:H, the structure being grasped unambiguously as three-dimensional continuous random networks.

### 2.4.3 Boson Peak

Probably related with the FSDP is the so-called *Boson peak* in Raman scattering spectra, a broad peak appearing at 20–50 cm$^{-1}$ (0.6–1.5 THz, $\sim$5 meV), which is lower than the conventional vibrational modes by an order. Krishnan (1953) may have been the first who noticed this anomalous low-frequency peak in a glass, SiO$_2$. (Note that such a low-frequency broad peak has never appeared in c-SiO$_2$ and similar crystals, since the optical phonon is located at higher frequencies.) For the peak in chalcogenide glasses, Nemanich (1977) performed a comprehensive study, who gave the name of “Boson peak,” the reason being that the spectral shape at low-frequency limits appears to be governed by the Bose factor, $\{n(\omega, T)+1\}/\omega \simeq \omega^{-2}$.

Since then, many studies have been published for the peak in oxide and chalcogenide glasses (Greaves and Sen 2007) and even in proteins (Ciliberti et al. 2006). Because of this universal feature being inherent to disordered materials, a variety of characteristics have been investigated. For instance, in g-As$_2$S$_3$, the peak becomes smaller under hydrostatic compression (Fig. 2.21; Andrikopoulos et al. 2006) and is intensified by temperature rise (Yasuoka et al. 1986). The peak position depends upon preparation conditions of the glass ingot, such as quenching rate of the melt (Tanaka 1987). We also add that far-infrared absorption spectroscopy detects a similar peak (Ohsaka and Ihara 1994).

Several models have been proposed for the origin of the Boson peak. The vibrational wavenumber $k$ is given as $k = (1/s)(\kappa/M)^{1/2}$, where $s$ is the sound velocity,
2.4 Medium-Range Structure

\[ \kappa \] a force constant, and \( M \) a reduced mass. Accordingly, we can ascribe the low wavenumber of Boson peaks to some vibrations of nearly-free atomic units having small \( \kappa \), which may be related with van der Waals forces. Phillips (1981) followed this view, proposing that the Boson peak is a kind of rigid-layer modes, which are vibrations of crystalline layers held together by van der Waals forces. Or, the low wavenumber may be due to atomic clusters having large masses, which may be related with medium-range structures. Martin and Brenig (1974), assuming inhomogeneous cluster structures with the Gaussian-type correlation function characterized by a spatial scale \( \sigma \), derived a peak shape for an acoustic Raman scattering mode in disordered materials as

\[
I(k) \sim (\sigma^3 k^3 / s^5)(n(k) + 1) \exp (-k^2 \sigma^2 / s^2),
\]

(2.6)

where \( n(k) \) is the Bose factor. This equation gives the position of Boson peaks at \( \Omega_{\text{max}} \sim s / \sigma \). Nemanich (1977) followed this idea, obtaining \( \sigma \approx 0.7 \) nm in \( \text{As}_2\text{S(Se)}_3 \), which is substantially smaller than the correlated scale of 2–3 nm inferred from the FSDP.

Researches on the Boson peak appear to follow labyrinths as those of the FSDP. Malinovsky and Sokolov (1986) demonstrated, as shown in Fig. 2.22, that the shapes of Boson peaks of many glasses are the same if the spectrum is normalized with the peak frequency \( \Omega_{\text{max}} \), or the corresponding energy \( E_{\text{max}} \). Novikov and Sokolov (1991) found a proportionality between the normalized FSDP position and the Boson peak wavenumber, \( Q_{\text{FSDP}} \propto \Omega_{\text{max}} c / s \), where \( c \) is the velocity of light. Afterward, the problem was extended to universal understandings of the FSDP and the Boson peak. Later, such studies have been further extended to understanding

**Fig. 2.22** Boson peaks in several glasses, normalized by the peak energy \( E_{\text{max}} \).

1. \( \text{As}_2\text{S}_3 \) with \( E_{\text{max}} = 26 \text{ cm}^{-1} \),
2. \( \text{Bi}_4\text{Si}_3\text{O}_{12} \) with \( 34 \text{ cm}^{-1} \),
3. \( \text{SiO}_2 \) with \( 52 \text{ cm}^{-1} \),
4. \( \text{B}_2\text{O}_3 \) with \( 28 \text{ cm}^{-1} \),
5. \( \text{B}_2\text{O}_3-\text{Li}_2\text{O} \) with \( 88 \text{ cm}^{-1} \),
6. \( \text{GeS}_2 \) with \( 22 \text{ cm}^{-1} \),

(Malinovsky and Sokolov 1986, © Elsevier, reprinted with permission)
correlations between the Boson peak, the FSDP, and thermal properties including the known low-temperature anomalies (Section 3.4) and glass transition parameters (Sokolov et al. 1993). The final elucidation remains (Grigera et al. 2003, Taraskin et al. 2006, Ruocco 2008, Baldi et al. 2010).

2.5 Defect

Defect structures are also controversial. At the outset, we may recall what the defect is in disordered structures (see Section 2.2). In crystals, it is traditional to assume an ideal structure, and some deviations from that can be regarded as the defects, which are classified into point defects (color center in NaCl, etc.), line defects (dislocation, etc.), stacking faults, grain boundaries, etc. (Kittel 2005). However, since we cannot envisage the ideal amorphous structure, the definition of defects becomes necessarily vague. On the other hand, it is reasonable to assume that only point-like defects can exist in glasses, since the other defects require some long-range atomic correlations, which must be lacking in non-crystals.

We define the defect in a non-crystalline solid as a connected or disconnected atomic bond, or a point defect-like structure, which cannot exist in the corresponding ideal crystal. This definition implicitly assumes that the defect arises in the short-range scale. Naturally, if the corresponding crystal does not exist, e.g., non-stoichiometric glasses such as Ge-doped g-SiO$_2$, this definition is meaningless. Otherwise, since the defect is a deviated structure from the normal bonding network, the defective site should be rare, e.g., being smaller than $\sim 1\%$ of the total bonds. A dangling bond and an ill-coordinated bond are typical defects. Note that the density of $\sim 1\%$ can be neglected in structural properties such as the elastic constant and heat capacity at room temperature, while the defect may provide substantial effects upon electronic properties if it produces a mid-gap state, which is more or less common.

Is it possible to detect such a few point-like defects in disordered structures? X-ray measurements, including diffraction and EXAFS, seem to be insufficient in sensitivity ($\gtrsim 5\text{ at.}\%$), so that we usually employ two methods. One is the Raman scattering spectroscopy, while its sensitivity seems to be, at the best, $\sim 1\text{ at.}\%$. The other is the electron spin resonance (ESR), which seems to have a sensitivity of ppm (Griscom 2000). However, the method can detect only unpaired electrons, such as $E'$ centers in silica glasses and $D^0$ defects in chalcogenide glasses. In addition to these methods, there are some non-direct methods. An example is the comparison of experimental optical spectra with some calculations, which may predict that a defect produces mid-gap absorption and/or photoluminescence peaks. Such optical investigations are more useful in the oxide than in the chalcogenide, since the former has a wider optical gap and the defect peak is likely to appear in the visible wavelength region, which can easily be detected. In the following, we will examine Si(Ge)O$_2$ and As$_2$S$_3$ (and Se) as examples of the oxide and the chalcogenide glass (Table 2.3). Ge-chalcogenides such as g-GeS(Se)$_2$ are likely to possess intermediate properties between these materials.
Defects in g-Si(Ge)O$_2$ can be divided into Si(Ge) related and O related (Pacchioni et al. 2000). The most famous Si(Ge)-related defect is a kind of dangling bond, E' center ($\equiv$Si•), which is ESR active, and accordingly, it can be easily detected. On the other hand, ESR-inactive defects are twofold coordinated Si (–Si–) and Si homopolar bond ($\equiv$Si–Si$\equiv$); the latter can be regarded as a kind of oxygen-deficient center (ODC). Existence of these defects is suggested from optical studies. The O-related defect includes non-bridging oxygen hole center (NBOHC; oxygen dangling bond, –O•) and per-oxy radical (POR; –O–O•), which are ESR active, and per-oxy linkage (POL; oxygen wrong bond, –O–O–), which is ESR inactive. In addition, oxygen molecules, O$_2$ and O$_3$, seem to be produced by radiation. It is plausible that the density of these defects, typically $\sim 10^{18}$ cm$^{-3}$, depends upon samples.

For the chalcogenide glass, many kinds of defects have been proposed (Ovshinsky and Adler 1978), while experimentally confirmed ones are a few. Since the chalcogenide glass is covalent, it is straightforward to envisage the wrong bonds (Halpern 1976) or like-atom (homopolar) bonds in stoichiometric compositions. The wrong bond is neutral in charge in covalent materials, and because of this character the defect becomes appreciable in density. Actually, the wrong bonds, As–As and S–S (Fig. 2.23), in g-As$_2$S$_3$ with concentrations of $\sim$1% are inferred from chemical analyses (Kosek et al. 1983) and Raman scattering studies (Tanaka 1987). In addition, Vanderbilt and Joannopoulos (1981) suggest the wrong-bond density of $\sim$0.5% in g-As$_2$Se$_3$ using a canonical factor, $\exp(-\Delta E/kT_g)$, where $\Delta E$ is the energy difference between hetero and homopolar bonds. In such calculations, however, we should be careful about the selection of bond energies, which depend upon the sources, as listed in Table 2.4. For g-GeSe$_2$, Zhou et al. (1991) did not detect any wrong bonds using EXAFS, while Petri et al. (2000) have found substantial numbers ($\sim$4%) of wrong bonds using isotope-substituted neutron diffraction. The

### Table 2.3 Defects in SiO$_2$ and As$_2$S$_3$ glasses

<table>
<thead>
<tr>
<th>Related atoms</th>
<th>Normal bonding</th>
<th>D$^0$</th>
<th>Wrong bond</th>
<th>Coordinational</th>
<th>Molecular</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>$\equiv$Si–</td>
<td>$\equiv$Si• (E’)</td>
<td>$\equiv$Si–Si$\equiv$ (ODC)</td>
<td>–Si– (ODC)</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>–O–</td>
<td>–O• (NBOHC), –O–O• (POR)</td>
<td>–O–O– (POL)</td>
<td>O$_2$, O$_3$</td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>=As–</td>
<td>=As• under exc.*</td>
<td>=As–As$\equiv$</td>
<td>=As (P$_2$)</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>–S– (C$_2$)</td>
<td>–S• under exc.*</td>
<td>–S–S–</td>
<td>=S– (C$_3$)</td>
<td></td>
</tr>
</tbody>
</table>

A covalent and a dangling bond are represented by – and •, respectively. NBOHC stands for non-bridging oxygen hole center, ODC for oxygen-deficient center, POR for per-oxy radical, and POL for per-oxy linkage. P and C stand for pnictogen and chalcogen, respectively. In As$_2$S$_3$, ESR signal in the dark is below a detection limit ($\sim 10^{15}$ cm$^{-3}$), appearing only under light excitation (*) at low temperatures.
Fig. 2.23 Wrong bonds, As−As and S−S, in g-As$_2$S$_3$.
The gray lobes attached to S depict lone-pair electrons.

Table 2.4 Bond energies of interest in units of kcal/mol, selected for As−S (Pauling 1960, Tsuchihashi and Kawamoto 1971, Popescu 2001) and Ge−S (Kawamoto and Tsuchihashi 1971, Popescu 2001) glasses

<table>
<thead>
<tr>
<th></th>
<th>As−S</th>
<th>As−As</th>
<th>S−S</th>
<th>Ge−Ge</th>
<th>Ge−S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pauling</td>
<td>47</td>
<td>32</td>
<td>51</td>
<td>38</td>
<td>56</td>
</tr>
<tr>
<td>Tsuchihashi–Kawamoto</td>
<td>61</td>
<td>32</td>
<td>51</td>
<td>38</td>
<td>56</td>
</tr>
<tr>
<td>Popescu</td>
<td>62</td>
<td>48</td>
<td>67</td>
<td>63</td>
<td></td>
</tr>
</tbody>
</table>

The values selected by Pauling may be obtained from related gases with different atomic coordination from that in the glasses, and accordingly, the value seems to provide unreasonable estimates in the present purpose.

difference may be attributed to different sample preparations and/or experimental methods.

The dangling bond is a known defect. However, in the chalcogenide glass, the common dangling bond having an unpaired electron, D$^0$ in Mott’s notation, appears only in Ge−S(Se) (Arai and Namikawa 1973, Elliott 1990). Pure Se and As-chalcogenides present no ESR signals ($<10^{16}$ cm$^{-3}$) in the dark, which means that there are no neutral dangling bonds having unpaired electrons. In these materials, the ESR signal appears only under illumination at low temperatures (see Section 6.3.10). Mott and many researchers have related the appearance of D$^0$ under illumination to the presence of charged dangling bonds (D$^+$ and D$^-$) in the dark, the idea being discussed in Section 4.4.

Note that here we neglect impurities, such as O in a-Se and Fe in g-As$_2$S$_3$ (Churbanov and Plotrichenko 2004), and intentionally doped atoms such as H, F, and Cl in g-SiO$_2$ (Pacchioni et al. 2000). Due to the disordered structure, however, it is common that a glass contains comparatively larger amounts of impurities than those in the corresponding crystal. Actually, a difficulty of studying g-SiO$_2$ is that, in addition to small deviations from the 1:2 stoichiometric ratio, the glass is likely
2.6 Computer Simulations

Since the non-crystalline structure cannot be determined explicitly, structural modeling has played an important role. In early studies, the modeling employed physical “balls-and-sticks,” a known example being the so-called Polk model for a-Si (Turnbull and Polk 1972). Such approaches may still be valuable for obtaining intuitive ideas, since the model can be deformed by hand (Tanaka 1998).

Gradually, computer simulations have become indispensable. A lot of studies have employed classical molecular dynamics (MD) calculations and other methods, which rely upon Newton’s equation and empirical potentials. For instance, Brabec (1991) and Antonio et al. (1992) have simulated, respectively, bonding structures of $\text{As}_2\text{S}_3$ and $\text{SiSe}_2$ glasses having 1790 and 5184 atoms.

At present, most studies perform the so-called ab initio MD calculation. It is based upon Schrödinger’s equation taking all relevant wavefunctions into account. However, the calculation is limited to a system having 200–300 atoms contained in nanometer-sized cubes, which may be imposed on the periodic boundary condition (Greaves and Sen 2007, Drabold and Estreichen 2007). The simulation follows the “cook-and-quench” type, in which a liquid having a fixed atomic composition is first equilibrated, e.g., at 1000 K, followed by a thermal quench to 300 K. We expect that these ab initio calculations can reproduce not only the atomic structure but also a variety of macroscopic properties (Fig. 2.24).

However, at present, the ab initio calculation seems to be valuable but with limited scope. It can reproduce experimental radial distribution functions and vibrational spectra, which characterize the short-range structure. However, the number of atoms 200–300, which corresponds to a cubic side number of $\sim$5 atoms, is still insufficient for obtaining insights into the medium-range structure. In addition, the...
biggest problem may be liquid quenching. In all MD simulations for glasses, the quenching rate from a melt is enormously fast, e.g., $10^{11} - 10^{14}$ K/s, which is governed by needed computational times, and as a result, a simulated glass is likely to contain too many defects. Therefore, MD calculations may predict what kinds of defects can exist in the amorphous material, but it is nearly impossible to estimate the defect density in real samples.

There are other computational methods. Specifically, the reverse Monte Carlo method is frequently utilized in analyses of experimentally obtained structural data (Kohara and Suzuya 2005, Greaves and Sen 2007, Itoh and Fukunaga 2009, Cliffe et al. 2010). In this method, we first distribute finite numbers ($\leq 5000$) of atoms in a cube having a volume, which gives an appropriate atomic density, and then move the atoms randomly until the resultant structure agrees satisfactorily with experimental data in wavenumber and/or real spaces. Otherwise, novel calculation methods as a statistical computation method, which is not limited by the time scale, may be more promising, while the system is limited to, e.g., 64 Se atoms (Mauro and Loucks 2007).

### 2.7 Homogeneity

Up to now, we have implicitly assumed that the amorphous structure is continuous and homogeneous. Is this assumption justified? It should be kept in mind that almost all of the structural measurements described above, except real space measurements such as transmission electron microscopy and atomic force microscopy, presume structural homogeneity. Unfortunately, the present x-ray methods, Raman scattering spectroscopy, etc., cannot have spatial resolution better than $\sim 100$ nm. These methods present structural information averaged over the probed area. However, the structural inhomogeneity is likely to arise, at least, from two origins: density fluctuations and chemical factors.

Glass necessarily contains density fluctuations. This is because the glass is quenched from the corresponding melt, which undergoes time-varying density fluctuations. The fluctuating amplitude $\Delta \rho / \rho$ of a few percent is theoretically derived (see Section 7.2). Experimentally, the amplitude and spatial scale ($\sim 2$ nm in silica) can be probed using small-angle x-ray and light scatterings (Greaves and Sen 2007). The density fluctuation is a critical problem in preparations of optical fibers and so forth. In addition, recent studies suggest that, during aging processes at temperatures below the glass transition temperature, so-called dynamic heterogeneity appears, which may lead to crystalline nucleation (Yunker et al. 2009).

Apart from the density fluctuation, the reported microscopic views are not conclusive. Structural homogeneity in atomic bonding can be conjectured in the elemental a-Se (Andonov 1982), having entangled chain and ring structures. Simple stoichiometric glasses such as $\text{As}_2\text{S}_3$ provide no small-angle x-ray scattering signals (Bishop and Shevchik 1974), suggesting certain homogeneity. Hosokawa et al. (2008) draw a similar conclusion for $\text{As}_2\text{S}_3$ from inelastic x-ray scattering.
However, a more sensitive method, positron lifetime spectroscopy, detects microvoids of \( \sim 0.5 \) nm in diameter with a volume fraction of \( 10^{-5} - 10^{-2}\% \) in g-As\(_2\)Se\(_3\) (Jensen et al. 1994). As references, we note that a-Si:H and similar films present marked signals indicating the existence of small voids (Muramatsu et al. 1989).

However, the glass structure critically depends upon preparation procedures and storage conditions, which are likely to govern homo and heterogeneity. Actually, Ležal et al. (1993) demonstrate that light scattering characteristics in g-As\(_2\)S\(_3\) depend upon the quenching rate of melts. Boolchand et al. (2001) assert that GeS(Se)\(_2\) is phase-separated in nano-scales through self-organization (Chen et al. 2008). Non-stoichiometric glasses such as As(Ge)-S(Se) tend to phase-separate (Tichý et al. 1984, Bychkov et al. 2006). More complicated glasses may be inhomogeneous, the examples being Ag-chalcogenide glasses (Mitkova et al. 1999) and modifier-mixed oxide glasses such as Na\(_2\)O(PbO)-SiO\(_2\) illustrated in Fig. 2.25, which is in contrast to a homogeneous structure, Fig. 1.13. Spinodal decomposition in multi-component oxide glasses has been well known (Doremus 1994). An oxy-chalcogenide glass GeO\(_2\)-GeS\(_2\) appears to be heterogeneous in electron microscopy images (Terakado and Tanaka 2008). Finally, it should be mentioned that partially

![Fig. 2.25](image1.png)

**Fig. 2.25** A schematic illustration of an oxide glass consisting of phase-separated network former (gray) and modifier (white) regions (Greaves 1985, © Elsevier, reprinted with permission)

![Fig. 2.26](image2.png)

**Fig. 2.26** A scanning-electron microscopy image of an obliquely deposited 1 \( \mu \)m-thick As\(_2\)S\(_3\) film (Starbov et al. 1992, © Elsevier, reprinted with permission)
controlled inhomogeneity, a kind of nano-structures, can be produced by oblique evaporation, the examples being given for Se (Kriščiūnas et al. 1983) and As$_2$S$_3$ in Fig. 2.26 (Starbov et al. 1992).

2.8 Surface and Nano-structures

The surface gives a special problem in solid-state science. Particularly, in crystals, atomic periodicity is broken at the surface, and accordingly, surface atoms necessarily produce unique surface structures. In c-Si, the ideal surface must have many dangling bonds, while practical surfaces have undergone surface reconstruction or oxidation. In contrast, it is likely that, in amorphous materials, the surface has smaller roles than those in single crystals, since the interior atomic structure is already disordered.

Despite such speculations, some surface effects have been reported for amorphous materials. Isobe et al. (1986) and Mamontova et al. (1988) demonstrate that surface structures affect photoconductive and electrical properties in (As-)Se. Inam and Drabold (2008) theoretically predict that oxidation changes surface conductance of Ge$_2$Sb$_2$Te$_5$ films. In silica glass, it is well known that the surface is terminated by Si–OH groups (Doremus 1994).

Recently, nano-structured materials have attracted substantial interest, as reviewed for chalcogenide by Tanaka (2004). Among the many topics, focus has been placed on surface manipulation. Here, we should note a characteristic difference of the surface manipulation in crystalline and non-crystalline solids. As known, using scanning tunneling microscopes, Eigler and Schweizer (1990) have manipulated single atoms on atomically flat surfaces of single crystals. However, such atomic manipulation seems to be difficult in amorphous materials, due to the existence of medium-range (2–3 nm) orders. In non-crystalline solids, the smallest structural unit which can be artificially manipulated may be attained not at the atomic scale, but at the nano-scale.

The multi-layer system has been the most extensively studied nano-structure from a fundamental and technological point of view. And, notable studies have been reported for amorphous chalcogenide semiconductors. Nesheva et al. (2005) have comprehensively studied variations of the glass transition temperature, the optical gap, etc., as functions of layer thicknesses for GeS$_2$/CdSe multi-layers. However, as summarized in Fig. 2.27 (Tanaka 2004), thickness dependences of reported studies are not reproducible.

In addition, we should be careful in interpretations. With a decrease in layer thickness, a blue shift of optical absorption edges (or optical gap $E_g$) tends to appear, which is often interpreted as a quantum-well effect. However, the effect can appear only when the mean free path of electrons and/or holes is longer than the layer thickness (Kittel 2005). Nevertheless, the mean free path of electrons, e.g., in a-Si:H films is reported to be $\sim 1$ nm (Okamoto et al. 1991), and accordingly, the quantum-well interpretation may be misleading. The blue shift possibly appears as a
result of vague layer boundaries, which are likely to govern macroscopic properties in thinner layer structures, since material diffusion becomes more evident in such systems (Adarsh et al. 2005).

Finally, it may be valuable to refer to some related studies. Regarding technological developments, we note a pioneering study by Maruyama (1982) on multi-layered chalcogenide films for vidicon targets. Chong et al. (2008) have studied crystalline–amorphous multi-layers using GeTe/Sb$_2$Te$_3$ stacks. We also mention that substantial studies have been done for ultrathin films (Tanaka 2004, Raoux et al. 2008) and chalcogen-impregnated zeolites (Poborchii et al. 2002, Tanaka and Saitoh 2009), which provide nano-dot and/or single-chain structures.

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