Photonic, electronic, and photo-electric applications of non-crystalline solids are rapidly growing in recent years. Such growth seems to synchronize with the development of oxide glass fibers and related devices for optical communications, which started near the end of the last century. Otherwise, we can trace its growth back to the use of amorphous Se films at around 1950 as xerographic photoreceptors in copying machines. In addition, recent applications of thin films, including Ge–Sb–Te to digital versatile disks (DVDs) and amorphous hydrogenated Si (a-Si:H) to solar cells and thin-film transistors (TFTs), are remarkable. On the other hand, we also know that fundamental studies on amorphous chalcogenide semiconductor have yielded several universal and revolutionary concepts such as “mobility edge” and “magic coordination number,” and some of these concepts have been applied to other materials. The authors therefore believe that, to study fundamentals and applications of non-crystalline insulators and semiconductors, *amorphous chalcogenides* such as Se, As$_2$S$_3$, and Ge–Sb–Te continue to be instructive and valuable substances.

The aim of this monograph is to be an introductory textbook in amorphous chalcogenide and related materials. This text will be suitable for graduate students. Actually, KT has used this text (unpublished versions) in seminars for graduate students, who start to study amorphous materials in the departments of applied physics, inorganic chemistry, and electronics. The present text will also be valuable to researchers working on related materials such as oxides, a-Si:H films, and organic semiconductors. This book also serves in comparative understandings of amorphous and crystalline semiconductors. The readers will see that, for such purposes, chalcogenide could be a good bridging material, since some simple compounds can be obtained in both crystalline and non-crystalline forms. Of course, for materials and topics dealt with in this book, several excellent books, listed at the end of the Preface, are already available. However, those are more or less difficult or detailed for students and research beginners. Zallen’s book (1983) gives a good introduction

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1These terminologies are defined in Section 1.1.

2Oxford English Dictionary defines “chalco” as a stem, which is a combining form of Greek χαλκός (copper and brass), and “gen” as an adjective suffix giving the sense “born in a certain place or condition.” We know that minerals such as Cu$_2$S may be an origin of “chalcogen.”
for students and researchers, while the content is focused on some fundamental subjects. The authors, therefore, have tried to write a book on glassy semiconductor on the level of the book *Introduction to Solid State Physics* by Kittel.

The present book treats disordered solids, exemplified in Fig. 1, and its related applications in Table 1. To keep the total page into an appropriate length, we will proceed as follows: Experimental methods may be briefly sketched. We then look at fundamental observations, trying to grasp their interpretations from unified standpoints and to draw simple pictures as possible. We will try to bridge atomic structures and physical properties (Fig. 2). In such ways, relationships among different macroscopic properties can be understood. The authors have also tried to point out the remaining and controversial problems.

We will consider the amorphous chalcogenide material from two standpoints: One is as a kind of glass. At present, we utilize at least three kinds of photonic (highly pure) glasses, which are the oxide, chalcogenide, and halide, all these being treated as (semi-)transparent insulators. In these three kinds of glasses, both

\[
\begin{align*}
\text{Si(Ge)} & \\
\text{Si(Ge)O}_2 & \text{– As}_2\text{O}_3 \\
\text{GeS(Se)}_2 & \text{– As}_2\text{S(Se,Te)}_3 \quad \text{– S(Se,Te)} \\
\text{Ge-Sb-Te, Ag(Cu)-As-S(Se)} \\
\end{align*}
\]

![Fig. 1](image1.png)

**Fig. 1** Relationships between materials of interest. Si(Ge) is tetrahedrally coordinated, producing three-dimensional networks. Inserting O to \(\equiv\text{Si}–\equiv\) bonds produces \(\equiv\text{Si}–\text{O}–\equiv\) connections, giving three-dimensional continuous random SiO\(_2\) networks. GeO\(_2\) has structures similar to that in SiO\(_2\). O can be changed to S, Se, and Te, producing GeS(Se,Te)\(_2\). With a change in the cation from Ge to As, the atomic coordination number decreases from 4 to 3, giving As\(_2\)O(S,Se,Te)\(_3\). And, in pure S(Se,Te), the structure is molecular as rings and polymeric chains

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Typical materials and related applications described in this text. For abbreviations, see the text</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Film</strong></td>
<td><strong>Bulk</strong></td>
</tr>
<tr>
<td>Insulator</td>
<td>SiO(_2) (fiber)</td>
</tr>
<tr>
<td>Semiconductor</td>
<td>Se (vidicon, x-ray imager)</td>
</tr>
<tr>
<td></td>
<td>Ge(_2)Sb(_2)Te(_5) (DVD)</td>
</tr>
<tr>
<td></td>
<td>a-Si:H (solar cell, TFT)</td>
</tr>
</tbody>
</table>

![Fig. 2](image2.png)

**Fig. 2** A goal of solid-state science, which intends to give universal understandings of macroscopic properties through simple theories on the basis of known atomic structures
oxygen (O) and chalcogens (S, Se, and Te) belong to the group VIb (16) atoms in the periodic table. Accordingly, the oxide and chalcogenide glasses possess many common features, which will be understood from a unified point of view. In addition, in these glasses, simple compositions such as SiO$_2$ and As$_2$Se$_3$, which also solidify into crystals, are available. And, for the crystal we have had firmer scientific knowledge. Therefore, the group VIb glass can be an interesting target for understanding the glass property through comparisons with that of the corresponding crystal. We also mention here that the chalcogenide glass containing group I (1 and 11) atoms such as Li and Ag also exhibits (super)ionic conduction.

The other aspect of chalcogenide is as a kind of amorphous semiconductor. As an amorphous semiconductor (or photoconductor), we had utilized a-Se photoreceptors in copying machines, although it has now been taken over by organic photoconductors. We have also developed phase-change memories using Ge–Sb–Te films. In fundamentals, a lot of concepts such as the mobility edge, charged defects, and Phillip’s magic number have been proposed. Applications of these concepts to other materials will extend our total understanding of the solid-state science. Nevertheless, amorphous semiconductor physics has remained far behind that of crystalline. Actually, famous texts on solid-state physics, by Kittel for example, deal mostly with single crystals.

The reader may notice that the first (glass) and the second (amorphous semiconductor) viewpoints mentioned above have been taken mainly by chemists and physicists, respectively. They also tend to employ different words for pointing nearly the same concepts, e.g., LUMO (lowest unoccupied molecular orbital)–HOMO (highest occupied molecular orbital) in molecular chemistry and conduction–valence bands in physics. However, an important fact here is the interplay between bond and band, developed by Phillips in the famous book, *Bonds and Bands in Semiconductors*. We will try to take such an approach in the present text.

We list several books published in the present and related fields.

**Written by Physicists**

Written by Chemists


Edited Volumes

R. Fairman and B. Ushkov (Eds.), *Semiconducting Chalcogenide Glass* (Elsevier, Amsterdam, 2004). *I (Glass Formation, Structure, and Stimulated Transformations in C.G.), II (Properties of Chalcogenide Glasses), and III (Applications of Chalcogenide Glasses).*

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