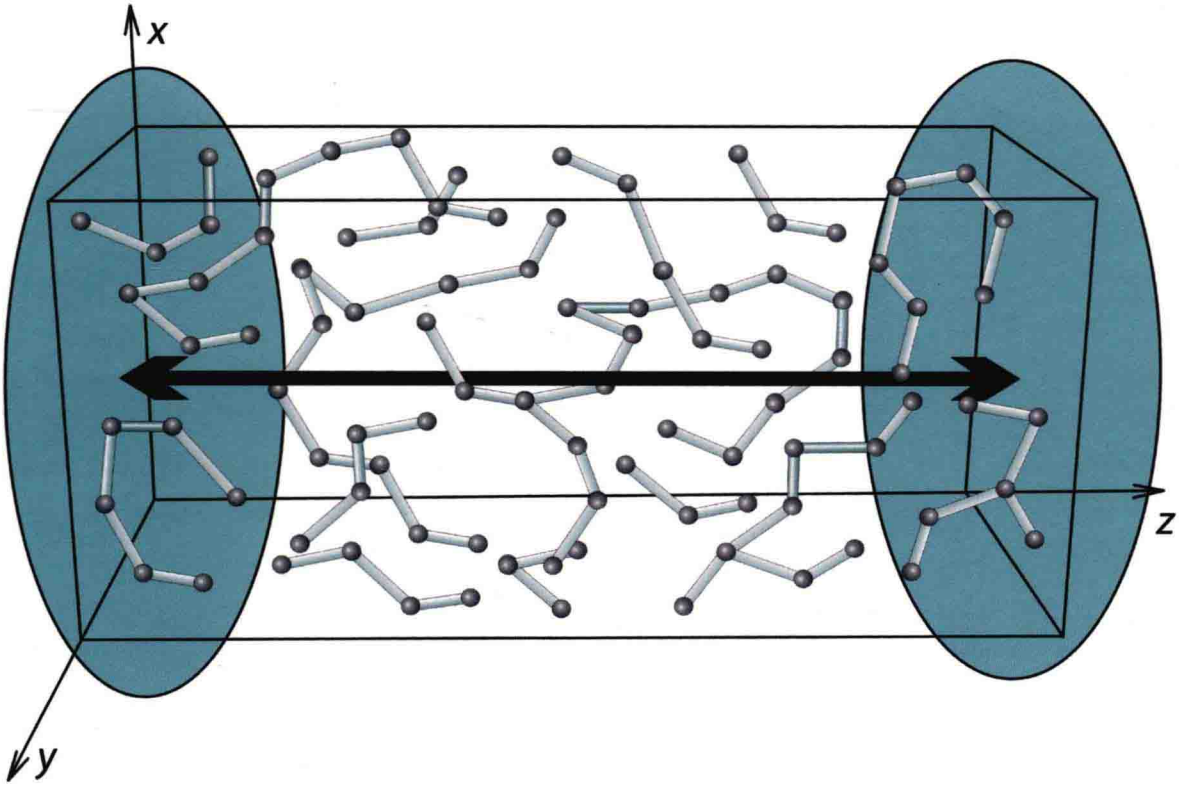
Amorphous Semiconductors

Sándor Kugler and Koichi Shimakawa



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SÁNDOR KUGLER
Budapest University of Technology and Economics, Hungary

KOICHI SHIMAKAWA
University of Pardubice, Czech Republic

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AMORPHOUS SEMICONDUCTORS

Understanding the structural unit of crystalline solids is vital in determining their optical and electronic properties. However, the disordered nature of amorphous semiconductors, where no long-range order is retained, makes it difficult to determine their structure using traditional methods. This book shows how computer modeling can be used to overcome the difficulties that arise in the atomic-scale identification of amorphous semiconductors.

The book explains how to generate a random structure using computer modeling, providing readers with the techniques to construct realistic material structures. It shows how their optical and electronic properties are related to random structures. Readers will be able to understand the characteristic features of disordered semiconductors. The structural and electronic modifications by photon irradiation are also discussed in detail. This book is ideal for both physicists and engineers working in solid state physics, semiconductor engineering, and electrical engineering.

SÁNDOR KUGLER is an Associate Professor at Budapest University of Technology and Economics, Hungary, and Guest Professor at Tokyo Polytechnic University, Japan. He is an overseas editor for the *Japanese Journal of Applied Physics*, and is a well-known expert in amorphous semiconductors and chalcogenide glasses.

KOICHI SHIMAKAWA is a Professor at the University of Pardubice, Czech Republic, a Fellow and Emeritus Professor of Gifu University, Japan, and Senior Researcher at Nagoya Industrial Science Research Institute, Japan. He is an internationally recognized researcher in the field of amorphous solids.

To my wife, Szabina, and our children, Szilvia and Zsófia

SK

To my wife, Akiko, and our children, Tetsuro, Shoko, and Ryo

KS

Preface

Understanding the structural unit of crystalline solids is vital in determining their optical and electronic properties. Determination of the structure of a condensed phase without periodicity is not an easy task. An important objective of the book is to provide an introduction to the reader of how to construct computer modeling of realistic random structures of amorphous IV- and VI-column-element semiconductors and their alloys. Both the merits and drawbacks of the techniques currently used to generate structures using powerful computers are discussed. Furthermore, the structural, electronic, and optical properties of mostly sigma-bonded amorphous semiconductors can be learned.

The basis of this monograph was a course given by Sándor Kugler (SK) during several years at Budapest University of Technology and Economics (and other universities in Europe and Japan), with an extension by Koichi Shimakawa (KS). Our common research experience with amorphous semiconductors extends back more than twenty years. The book is aimed at final-year university students and PhD students in physics, materials science, and chemistry who have already completed introductory courses on quantum mechanics and solid state physics. This book will be useful for both physicists and engineers working in solid state physics, semiconductor engineering, and electrical engineering. For most of the text, no high-level mathematics is needed. This book provides a much wider literature overview than is usual for most handbooks.

A historical overview and a detailed summary of applications are given in the first part of Chapter 1. Readers are informed how to develop further the current technology (photovoltaic cells, thin-film transistors, DVDs, and direct x-ray image detectors for medical use, etc.) using amorphous semiconductors. The rest of the chapter analyzes and answers one of the most exciting questions in the field: what are amorphous semiconductors?

This is followed by a discussion of preparation techniques in Chapter 2. As the glass-transition temperature determines most of the physical properties of glasses, it is briefly discussed, together with Phillip's constraint theory of glassy materials, at the end of the chapter.

The third and longest chapter begins with an important topic, namely how to determine experimentally whether a sample has an amorphous or crystalline phase. The chapter describes atomic-scale computer modeling, including atomic interactions, different simulation methods, and models obtained by structure simulation. The final part of Chapter 3 introduces readers to the most successful commercialized product of chalcogenide glasses, the phase-change materials.

Chapter 4 deals with the electronic behavior of covalently bonded amorphous semiconductors, including defect-free systems and deviation from the ideal networks, i.e. defects. Optical properties of amorphous semiconductors are also described in this chapter.

Chapter 5 presents experimental results of photoinduced changes. It is shown that the structural studies by means of atomic-scale computer simulations are very useful for understanding the experimental results. The photoinduced changes observed in both amorphous chalcogenides and hydrogenated amorphous silicon films are discussed.

We, SK and KS, would like to thank Kazuo Morigaki for introducing us to the physics of amorphous semiconductors. Thanks are also due to Jai Singh (University of Charles Darwin), S.O. Kasap (University of Saskatchewan), Keiji Tanaka (Hokkaido University), Ted Davis (University of Leicester), Stephen Elliott (University of Cambridge), and Takeshi Aoki (Tokyo Polytechnic University) for their powerful discussions. We must also thank Tokyo Polytechnic University (formerly the Tokyo Institute of Polytechnics) for allowing us to use their computing facilities for our large-scale computer simulations.

SK is indebted to many of his colleagues at the Budapest University of Technology and Economics, but he is especially grateful to his four PhD students, Krisztina Kádas (Uppsala University), Krisztián Koháry (University of Exeter), József Hegedüs (University of Helsinki), and Rozália Lukács (Norwegian University of Life Sciences). Furthermore, SK extends his thanks to István László and László Pusztai, with whom he has had the pleasure of working on diverse aspects of research on amorphous semiconductors. Special thanks are also due to Károly Härtlein (Budapest University of Technology and Economics) for his careful work in drawing some of the figures.

KS wishes to thank his colleagues at Gifu University, Shuichi Nonomura and Takashi Itoh, for discussions, and also his PhD student, Yutaka Ikeda (YM systems, Company Executive), who developed a precise measurement system for the photoinduced volume change observed in amorphous chalcogenides. Discussions with Alex Kolobov (Advanced Institute of Industrial Science, Tsukuba), Hiroyoshi Naito (Osaka Prefecture University), Hideo Hosono (Tokyo Institute of Technology), Takashi Uchino (Kobe University), Masaru Aniya (Kumamoto University), and Sergei Baranovskii (University of Marburg) were also very fruitful and enjoyable in promoting our subjects.

Tomas Wagner and Miloslav Frumar (University of Pardubice) provided KS with the opportunity to continue the research work at the Department of General and Inorganic Chemistry (University of Pardubice), after his retirement from Gifu University, supported by grant project CZ.1.07/2.3.00/20/0254 *ReAdMat* financed by the European Union. KS wishes to express his thanks for this opportunity.

Contents

1

Introduction

We present a brief historical overview of amorphous semiconductors including their definition.

1.1 Historical overview: science and applications

It is important to include a historical overview of the science and successful applications of amorphous semiconductors in the market in order to understand the current situation. Although science and technology are closely connected, we would venture that some applications have proceeded *without* secure scientific knowledge. This may be a characteristic feature of the field of material science. It is thus a good idea to begin by giving some examples of successful applications.

(1) **Chalcogenides**. Electrophotography (or so-called xerography, a Greek word, meaning "dry writing") has been one of the most successful applications of amorphous selenium (a-Se). The process was demonstrated by C.F. Carlson and O. Kornei in 1938, and modern xerographic processes are the same as those proposed at that time (Pai and Springett, 1993). The Hungarian scientist Pal Selényi first proposed the concept of the photographic process in the 1930s. His pioneering work in electrostatic picture recording formed the basis of xerography. In fact, Selényi published and patented several fundamental ideas of electrography and produced high-quality electrographic copies well before Carlson's proposal (Selényi, 1935a, 1935b, 1936). Films of a-Se have the following unique features: (i) high resistivity (it is a good insulator), and (ii) high photoconductivity. These properties are useful for electronic charging in the dark state and discharging in the photoilluminated state. These technologies

were later applied to laser printers. More recently, a-Se has been replaced by organic polymers for xerography (Weiss and Abkowitz, 2006). The main reason for this is that organic materials cost less.

Most people would recognize the acronym "DVD" (digital versatile disk). The basic operation of the DVD was first proposed by Feinleib *et al.* (1971), although the material $Ge_2Sb_2Te_5$ (also known as GST) has been employed commercially by the Panasonic group in Japan (Yamada *et al.*, 1991). A DVD operates via optically induced phase changes (and hence changes in the reflection coefficient) between amorphous and crystalline states. Using GST, DVDs can be rewritten in excess of one million times, with a crystallization time of less than 50 ns achieved during each rewriting process. The DVD system currently has a memory capacity exceeding 50 GB per disk using a blue semiconductor laser. In the near future, rewritable electrical memory devices will be commercially available that use a phase-change random access memory (PRAM), following the memory switching devices proposed by Ovshinsky (1968). In addition, phase-change materials offer a promising route for the practical realization of new forms of general-purpose and "brain-like" computers that could learn, adapt, and change over time (Wright *et al.*, 2011).

As a-Se is a very sensitive photoconductor, especially for x-rays, due to its high atomic weight, it has been possible to realize a direct x-ray imaging device for use in the medical field. The image of a human hand by Rowlands and Kasap (1997) recalls Wilhelm Röntgen's first x-ray photograph of his wife's hand. This device incorporates a large area of thick (1 mm) a-Se evaporated onto a thin-film transistor (TFT) made from a hydrogenated amorphous silicon (a-Si:H) active matrix array (AMA). The x-ray-induced carriers in a-Se travel along the electric field lines and are collected at their respective biased electrode and storage capacitor. The stored images are then sent directly to the medical specialist's computer. This type of x-ray image sensor is used widely in mammography.

The Japan Broadcasting Corporation, NHK, has utilized the "avalanche photomultiplication" effect in a-Se (Juška, Arlauskas, and Montrimas, 1987; Tanioka, 2007) to create a powerful broadcasting tool. High-gain avalanche rushing amorphous photoconductor (HARP) vidicon tubes have been developed by K. Tanioka and his collaborators, leading to the construction of a HARP vidicon TV camera that is over 100 times more sensitive than a CCD camera.

(2) **Hydrogenated amorphous silicon (a-Si:H)**. In the early 1970s, the oil crisis in the Middle East led to the serious consideration of using photovoltaic (PV) cells as an alternative source of energy. To use PV cells as a viable power

source requires a large area and low cost. Consequently, the first a-Si:H solar cells were fabricated by Carlson and Wronski (1976) at RCA Laboratories in Princeton, NJ. Later, Y. Kuwano's group at Sanyo Co. Ltd. (Japan) was the first to market the PV devices. Common structures comprise p-i-n type heterojunctions. There are several types of PV cells available, the most common being tandem (with dual and triple junctions) a-Si:H configurations, for which more than 10% efficiency is achieved in large-area commercial devices (Carlson *et al.*, 1996). People have recognized the importance of developing PV devices following the Fukushima nuclear power station disaster caused by the earthquake and subsequent tsunami on 11 March 2011.

Thin-film transistors (TFTs) using a-Si:H were first developed in the form of field effect transistors (Powell, 1984; Spear and LeComber, 1984). Two of the most important requirements for TFTs are a high ON/OFF current ratio and a small gate voltage; these are achieved by using a-Si:H. These characteristics mean that TFTs are suitable for use as switching transistors in a liquid crystal display (TFT-LCD), which has completely replaced the former cathode ray tube. Following subsequent improvements in TFT-LCDs, flat-panel displays (FPDs) now produce the clear and large (over 100 cm) images used in TVs and monitors.

(3) **Oxides**. The high demand for flexible and optically transparent TFTs for use in the next-generation FPDs led to the realization of transparent conductive oxides (TCOs) by H. Hosono's group in 1996 (see, for example, Hosono (2006)). Transparent TFTs were developed using ionic oxides such as a-$InGaZnO_4$ (known as a-IGZO). The electron mobility of a-IZGO is larger than that of a-Si:H, and the TFT stability is excellent. Samsung's group in Korea developed the a-IGZO TFT-LCD display that is used commercially in the iPad 3 (Apple Inc.). The high quality and stability of a-IGZO TFT-LCD large-area displays may dominate the "display world" in the near future.

It should be noted that two great discoveries – the amorphous chalcogenides (known as a-chalcogenides or a-Chs) used in electrical memory (Ovshinsky, 1968) and switching devices, and device-quality hydrogenated amorphous silicon (a-Si:H) (Spear and LeComber, 1975) – initiated a vast field of science, which will be briefly reviewed in the following.

The most important scientific issue that resulted from work on amorphous semiconductors was the structural information gained from experiment and theory (in the form of modeling), because the fundamental physical and chemical properties are principally determined by their structure. For tetrahedrally bonded

materials such as amorphous germanium (a-Ge) and a-Si, a hand-built random network model was first proposed by Polk (1971), in which 440 atoms and bonds were modeled. Later, computer-generated structures of threefold-coordinated amorphous arsenic (a-As) and twofold-coordinated a-Se were generated by Greaves and Davis (1974) and Long *et al.* (1976), respectively. Molecular dynamic (MD) simulations are now very popular and are used to understand microscopic structures (see, for example, Greaves and Sen (2007)). The average coordination number Z of bonding atoms plays a role in structural properties, and Phillips (1979) proposed a topological constraint model using Z. The magic number $Z_c = 2.4$ (Phillips, 1979) or 2.67 (Tanaka, 1989) may dominate optical and electronic properties in multicomponent glasses. A MD simulation has been also used for the study of photoinduced structural transformation in a-Se (Drabold, Zhang, and Li, 2003; Hegedüs *et al.*, 2005).

A model of the electronic density of states (DOS) for non-crystalline semiconductors was proposed by Cohen, Fritzshe, and Ovshinsky (1969). The DOS separated by a bandgap is not sharp, and extends into the bandgap (where it is known as the band tail). The valence band (VB) originates from the bonding states in a-Si as it does in crystalline Si. However, the VB in a-Chs is formed from a lone-pair band. Amorphous chalcogenides are therefore called lone-pair (LP) semiconductors (Kastner, 1972). In this case, the tailing DOS should be localized, and hence it is known as the "band tail (localized) states." The concept of the mobility edge, which separates the extended and localized states, was then proposed (see, for example, Mott and Davis, 1979; Mott, 1992). It is believed that the localized tail states originate mainly from the distortion of the bond angle, which produces a lack of long-range structural order.

In addition to the localized tail states, there are bonding *defects* that may produce midgap states. In a-Si:H, these defects are identified by Si dangling bonds. These are electronically neutral states. However, in a-Chs, they are believed to be charged dangling bonds, which may be over- or under-coordinated (Street and Mott, 1975; Kastner, Adler, and Fritzshe, 1976).

Optical and electronic transport properties are primarily determined by the electronic DOS. There are no obvious edges to the DOS, and therefore the bandgap is not easy to define. Tauc (1968) defined the bandgap using optical absorption with energy space (without using wave vectors), which has led to it being called the "optical gap" or sometimes the "Tauc gap." In binary and ternary a-Chs, a composition-dependent optical gap was found to be well described using an analogy with mixed crystals (Shimakawa, 1981). Photoluminescence (PL)