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Kazuo Morigaki Sándor Kugler Koichi Shimakawa

Amorphous Semiconductors

Structural, Optical, and Electronic Properties





Amorphous Semiconductors

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Amorphous Semiconductors

Structural, Optical, and Electronic Properties

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Series Preface

Wiley Series in Materials for Electronic and Optoelectronic Applications

This book series is devoted to the rapidly developing class of materials used for electronic and optoelectronic applications. It is designed to provide much-needed information on the fundamental scientific principles of these materials, together with how these are employed in technological applications. The books are aimed at (postgraduate) students, researchers and technologists, engaged in research, development and the study of materials in electronics and photonics, and industrial scientists developing new materials, devices and circuits for the electronic, optoelectronic and communications industries.

The development of new electronic and optoelectronic materials depends not only on materials engineering at a practical level, but also on a clear understanding of the properties of materials, and the fundamental science behind these properties. It is the properties of a material that eventually determine its usefulness in an application. The series therefore also includes such titles as electrical conduction in solids, optical properties, thermal properties, and so on, all with applications and examples of materials in electronics and optoelectronics.

The characterization of materials is also covered within the series in as much as it is impossible to develop new materials without the proper characterization of their structure and properties. Structure–property relationships have always been fundamentally and intrinsically important to materials science and engineering.

Materials science is well known for being one of the most interdisciplinary sciences. It is the interdisciplinary aspect of materials science that has led to many exciting discoveries, new materials and new applications. It is not

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unusual to find scientists with a chemical engineering background working on materials projects with applications in electronics. In selecting titles for the series, we have tried to maintain the interdisciplinary aspect of the field, and hence its excitement to researchers in this field.

> Arthur Willoughby Peter Capper Safa Kasap

Preface

This book deals with amorphous semiconductors, which are typical disordered systems. Many textbooks and monographs concerning amorphous semiconductors have already been published. In this book, we treat their structural, optical, and electronic properties; in particular, recent developments in these areas are included and are emphasized as features of the book, because since amorphous semiconductors exhibit a disordered nature, there exist difficult problems to be resolved in the interpretation of experimental results. So, we attempt to present recent experimental data and interpretations in order to help in obtaining a deeper understanding of these properties.

The book is composed of eight chapters. The basic ideas for understanding the properties of amorphous semiconductors mentioned above are presented in these chapters, particularly preparation techniques in Chapter 2 and theoretical fundamentals in Chapter 4. In Chapter 3, structural properties are treated, with particular emphasis on neutron diffraction measurements and structural modeling of computer simulations. In Chapter 5, hydrogenated amorphous silicon is treated and emphasis is put on recent developments in the nature of shallow and deep states and of light-induced defects, particularly as investigated by magnetic resonance measurements. In Chapter 6, amorphous chalcogenides are treated, with particular emphasis on their basic glass science, their unique properties, and light-induced effects in them. In Chapter 7, other amorphous materials are treated, particularly amorphous carbon and amorphous semiconducting oxides. In Chapter 8, applications of amorphous semiconductors are mentioned, particularly those of hydrogenated amorphous silicon and amorphous chalcogenides. The eight chapters were written by the authors as follows: Kazuo Morigaki (KM) wrote Chapters 1 and 5 (except for Section 5.4.2, by (KS)), Sándor Kugler (SK) wrote Chapters 3 and 4, and Koichi Shimakawa (KS) wrote Chapters 2, 6, 7 (with contributions from SK), and 8. We hope that the book will be useful for students in physics, chemistry, and materials science as well as for researchers and engineers interested in amorphous semiconductors.

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Kazuo Morigaki Sándor Kugler Koichi Shimakawa 1

Introduction

1.1 General Aspects of Amorphous Semiconductors

Amorphous solids are typical disordered systems. Two classes of disorder can be defined, namely, compositional disorder as seen in crystalline binary alloys and topological disorder as seen in liquids. Amorphous solids have topological disorder. However, short-range order, that is, chemical bonding of constituent atoms, exists in amorphous covalent semiconductors. Spatial fluctuations in the bond lengths, bond angles, and dihedral angles (Figure 1.1) give rise to tail states in the band gap region, that is, below the edge of the conduction band and above the edge of the valence band. The edges of the conduction and valence bands are called mobility edges and the band gap is called a mobility gap. These edges are the boundaries between delocalized and localized states. This is illustrated in Figure 1.2. Such boundaries are caused by disorder; this is called Anderson localization. In an amorphous network, translational order does not exist, so the Bloch theory of crystalline solids is not applicable, but the tight-binding model, the Hartree-Fock approximation or the density functional method can be applied for understanding the electronic properties of amorphous semiconductors, as shown in Chapter 4.

Although the above considerations are based on a continuous random network, actual samples have a structure deviating from an ideal random network, that is, the coordination of the constituent atoms deviates from the normal coordination following the 8 - N rule [1], where N denotes the relevant column number in the periodic table. Here, we consider elements only in columns IV– VI of the periodic table. An additional rule can be given as follows: Z (the valency) = N if N < 4. For instance, the normal coordination of amorphous silicon is fourfold, but threefold-coordinated silicon atoms are also present. These are called structural defects. For amorphous selenium, since the normal coordinated selenium atoms. The band tails and structural defects affect the optical and

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Figure 1.2 Schematic illustration of density of states in an amorphous semiconductor. See text for details.

electronic properties of amorphous semiconductors. Thus it is very important to elucidate the electronic structures of these states in order to understand these properties. An important experimental means of doing this is magnetic resonance. For instance, the electronic structures of these localized states can be elucidated from electron spin resonance (ESR); that is, their symmetry can be determined from a *g*-value measurement. However, the principal axes of symmetry are randomly oriented in an amorphous network, and that it makes more difficult to identify defects in amorphous semiconductors than in crystals. This identification is normally performed by comparison between observed ESR spectra and computer-simulated spectra. In addition, electron– nuclear double resonance (ENDOR) provides us with a powerful means for identification of defects, as shown in Chapter 5, in which pulsed electron magnetic resonance measurements in particular are presented in detail.

In this book, we consider two types of material as examples of amorphous semiconductors, namely, amorphous silicon and other column IV elemental semiconductors, and amorphous chalcogenides, including amorphous metal chalcogenides. Their preparation, structure, and optical and electronic properties are presented in Chapters 2, 3, 5, 6, and 7. In Chapter 3, definitions of crystalline and noncrystalline structures are given, and the structures of amorphous silicon, hydrogenated amorphous silicon (a-Si:H), and amorphous selenium are treated theoretically and experimentally in more detail.

1.2 Chalcogenide Glasses

Amorphous chalcogenides are also known as chalcogenide glasses, because they exhibit a glass transition. The details of the glass transition and the structural, optical, and electronic properties of these material are dealt with in Chapter 6.

1.3 Applications of Amorphous Semiconductors

Amorphous semiconductors are widely today used as device materials. Devices using a-Si:H include, for example, solar cells and thin-film transistors. Devices using amorphous chalcogenides include, for example, phase-change memories, direct x-ray image sensors for medical use, high-gain avalanche rushing amorphous semiconductor vidicons, and optical fibers and waveguides. These are treated in Chapter 8.

There are several comprehensive books about amorphous semiconductors [1-5], as well as books about hydrogenated amorphous silicon [6] and amorphous chalcogenides [7].

References

- 1 Mott, N.F. and Davis, E.A. (1979) *Electronic Processes in Non-Crystalline Materials*, 2nd edn, Clarendon Press, Oxford.
- 2 Elliott, S.R. (1990) *Physics of Amorphous Materials*, Longman Scientific and Technical, Harlow.
- **3** Morigaki, K. (1999) *Physics of Amorphous Semiconductors*, World Scientific, Singapore and Imperial College Press, London.
- 4 Singh, J. and Shimakawa, K. (2003) *Advances in Amorphous Semiconductors*, Taylor & Francis, London and New York.
- **5** Kugler, S. and Shimakawa, K. (2015) *Amorphous Semiconductors*, Cambridge University Press, Cambridge.
- **6** Street, R.A. (1991) *Hydrogenated Amorphous Silicon*, Cambridge University Press, Cambridge.
- 7 Tanaka, K. and Shimakawa, K. (2011) *Amorphous Chalcogenide Semiconductors* and *Related Materials*, Springer, New York.

2

Preparation Techniques

There are many preparation techniques, depending on what kind of material is needed. Quenching from the liquid state, also termed melt-quenching (MQ), is a popular technique for so-called glasses. To meet the requirements of thin-film forms, a variety of techniques such as evaporation, sputtering, and chemical vapor deposition (CVD) are adopted. Ion bombardment and the use of powerful light on crystalline solids can also produce amorphous materials. Here we briefly summarize the principal methods for preparing hydrogenated amorphous silicon (a-Si:H) films and amorphous chalcogenides.

2.1 Growth of a-Si:H Films

a-Si:H films, as well as a-Ge:H, a-C:H, and related compound films, are prepared only by condensation from the gas phase. The most popular preparation techniques for these films belong to the class of CVD techniques. Two CVD techniques are known: one is *glow-discharge deposition*, which is now also called *plasma-enhanced chemical vapor deposition* (PECVD), and the other is *hot-wire chemical vapor deposition* (HWCVD), as described in the following.

2.1.1 PECVD Technique

This was previously called glow-discharge deposition, when a-Si:H films were deposited by decomposition of SiH₄ gas with the help of a glow discharge [1]. It is now termed plasma-enhanced chemical vapor deposition [2]. The application of an RF field (usually at 13.6 MHz; RF PECVD) generates a plasma in a reaction chamber. By introducing PH₃ or B₂H₆ gas into the SiH₄, n- or p-type Si:H films can be prepared [1]. RF PECVD provides high-quality uniform films, but the deposition rate can be slow as 0.3 nm/s. The development of

this technique, with control of the gas pressure (0.05-2 Torr), RF power $(10-100 \,\text{mW/cm}^2)$, substrate temperature $(150-350 \,^\circ\text{C})$, and so on, has led to a huge range of commercial applications, such as large-area photovoltaics and thin-film transistors.

To improve the deposition rate, PECVD with a very high-frequency field (40–100 MHz), called VHF PECVD, has been employed, and the deposition rate has reached 2 nm/s [3]. VHF PECVD also provides high-quality films. However, its poor uniformity is still a problem. Microwave PECVD (MW PECVD) with a 2.45 GHz field provides a significantly enhanced deposition rate, reaching 10 nm/s, but device quality films are not easy to obtain [4]. It is known, however, that VHF PECVD and MW PECVD are very useful means for preparing microcrystalline Si films (μ c-Si:H), as well as a-Ge:H films [5], whereas the deposition rate of RF PECVD for μ c-Si:H is very low. A high deposition rate is a necessary condition for cost-effective performance in large-scale production.

2.1.2 HWCVD Technique

When we are interested in a very high deposition rate of a-Si:H and related films, HWCVD can be a promising technique, and the deposition rate for this technique has reached 15–30 nm/s [6]. The setup for an HWCVD system is similar to that for RF PECVD except that the RF electrode is replaced with a heated filament (Pt, W, Ta, etc.). This technique is thus *thermal deposition*, in principle. The gas introduced into a chamber is catalytically excited or decomposed into radicals or ions by a metal filament heated to around 1800–2000 °C. Then Si radicals diffuse inside the chamber and are deposited onto a substrate, kept at a relatively high temperature (150–450 °C). Although device quality films can be obtained with a high deposition rate by this technique, a drawback is poor uniformity of the deposited films, and great efforts are being made to overcome this.

2.2 Growth of Amorphous Chalcogenides

Strictly speaking, the term *glass* usually refers to materials prepared from the liquid state. On the other hand, the term *amorphous* is used for materials made by quenching from the gas phase. However, the actual structural and electronic properties are not very different, and hence these two terms are frequently used without distinguishing between them. We shall thus simply use the terms "amorphous chalcogenides" and "chalcogenide glasses" interchangeably. Although many preparation techniques are possible for these materials, depending on what kinds of material are required, the most popular one is quenching from the liquid state (melt-quenching, MQ). So-called glasses and

glass fibers are prepared by this method. When thin films are required, techniques such as evaporation (EV), sputtering (SP), and pulsed laser deposition (PLD) are adopted. In the following, we briefly explain the above-mentioned techniques:

- 1) Quenching from the liquid state. Most chalcogenide, as well as oxide, glasses are prepared by the MQ method. When the temperature of the melt decreases, the melt becomes a supercooled liquid. A further decrease in temperature below the glass transition temperature T_g produces a glassy material. Thus, glasses prepared by the MQ method undergo a glass transition. It is of interest to note that the empirical relation $T_g \approx 2T_m/3$ holds for most glasses, where T_m is the melting temperature. Chalcogenide materials are sealed in quartz ampoules at 10^{-6} Torr and heated beyond their melting temperature. The samples are agitated by rotation or vibration and then cooled quickly by immersion in cold water or air at ambient temperature. Glasses are formed owing to the relatively high cooling rate. Details will be discussed in Chapter 6, and Figure 6.1 may help in understanding glass formation.
- 2) *Evaporation*. This is the most conventional method of preparing films. The films are simply condensed at an arbitrary temperature onto a substrate, directly from the gas phase. Thus the T_g used for MQ materials does not have any physical meaning for EV materials. The starting material comprises ingots or powder mounted in a boat and is heated above the melting temperature in a vacuum chamber at around 10^{-6} Torr (~ 10^{-4} Pa). The deposition rate (~10 nm/s) is controllable and depends on the boat temperature. The thickness of the film is usually controlled by the deposition time. Some well-known amorphous chalcogenides, for example Se, As₂Se(S)₃, and GeSe(S)₂, are prepared using this technique. Evaporation of multiple compounds is not easy and hence so-called *flash evaporation* techniques are often employed, in which powdered components are poured into a heated boat. The main disadvantage of EV films is that the composition of the resulting film is not always the same as that of the starting material. Device quality a-Se thick films (more than 1 mm thick), which are utilized commercially in direct X-ray image detectors [7] and high-gain avalanche rushing amorphous photoconductor (HARP) vidicon TV cameras [8], can be prepared by the EV technique.
- 3) *Sputtering*. In the sputtering process, a strong RF electric field (a frequency of 13 MHz is usually used) is applied between a target made from the source material and electrodes made from the substrate. A sputtering gas, for example Ar or N, is introduced into the chamber and kept at a pressure of 0.13–2.7 Pa. Positively ionized gas produced by the RF field supplies kinetic energy to the surface of the source material target. Atoms or molecules dissociated from the target are deposited onto the substrate. The deposition

8 2 Preparation Techniques

rate (~1 nm/s) is lower than that for the EV method (~10 nm/s), although it depends strongly on the sputtering conditions. SP is superior to EV for multicomponent systems; the composition of the resulting films is almost the same as that of the target material because the sputtering rates of different elements are of the same order. When a magnetic field is applied, the deposition rate is significantly enhanced. This is due to confinement of the ionized gas in a spiral motion by the Lorentz force produced by the magnetic field. This method is called *magnetron sputtering* (MSP). The MSP method is suitable for large-scale production. So-called phase-change materials, such as the Ge₂Sb₂Te₅ films used in optical memory devices (DVDs) and electrical memory devices (phase-change random access memory, PRAM) are usually prepared using the MSP technique (Section 6.6).

4) Pulsed laser deposition. PLD is very simple technique compared with SP. A pulsed high-power laser beam is focused onto a target material in a vacuum chamber, causing vaporization of the source material. This technique resembles the EV method. In PLD, however, a directional plasma plume is created by the absorption of photons, and hence this method is distinct from simple thermal evaporation [9]. The pulse energy, 300–600 mJ/ pulse, induces an instantaneous power density of around 10⁹ W/cm². Excimer gas (KrF or ArF) lasers are used for this purpose. Stoichiometric transfer of atoms from multicomponent source materials to the substrate can be performed by the PLD technique, and hence this technique can be useful for preparing device quality phase-change chalcogenides such as Ge₂Sb₂Te₅ films.

We have discussed only *physical* deposition techniques for amorphous chalcogenides here. However, there are other techniques, for example chemical deposition techniques such as CVD, that are suitable for a-Si:H. The CVD technique is not popular for amorphous chalcogenides.

References

- 1 Spear, W.E. and Le Comber, P.G. (1975) Substitutional doping of amorphous silicon. *Solid State Commun.*, **17**, 1193–1196.
- 2 Shiff, E.A., Hegedus, S., and Deng. X. (2010) Amorphous silicon-based solar cells, in *Handbook of Photovoltaic Science and Engineering*, 2nd edn (eds A. Luque, S. Hegedus, and W. Shire), John Wiley & Sons, Inc., Hoboken, NJ, pp. 487–545.
- 3 Chen, Y., Wang, J., Liu, J., Zheng, W., Gu, J., Yang, S, and Gao, X. (2008) Microcrystalline silicon grown by VHF PECVD and the fabrication of solar cells. *Solar Energy*, 82, 1083–1087.

- 4 Mejia, S.R., McLeod, R.D., Kao, K.C., and Card, H.C. (1983) The effects of deposition parameters on a-Si:H films fabricated by microwave glow discharge techniques. *J. Non-Cryst. Solids*, **59&60**, 727–730.
- 5 Aoki, T., Kato, S., Hirose, M., and Nishikawa, Y. (1989) DC bias effects on growth of a-Ge:H in coaxial type ECR plasma. *Japan. J. Appl. Phys.*, **28**, 849–855.
- **6** Mahan, A., Xu, Y., Nelson, B., Crandal, R., Cohen, J.D., Palinginis, K., and Gallagher, A. (2001) Saturated defect densities of hydrogenated amorphous silicon grown by hot-wire chemical vapour deposition at rates up to 150 Å. *Appl. Phys. Lett.*, **78**, 3788–3790.
- 7 Rawlands, J.A. and Kasap, S.O. (1997) Amorphous semiconductors usher in digital X-ray imaging. *Phys. Today*, **50**, 24–31.
- 8 Tanioka, K. (2007) The ultra sensitive TV pickup tube from conception to recent development. *J. Mater. Sci.*, **18**, S321–S325.
- 9 Delahoy, A.E. and Guo, S. (2010) Transparent conducting oxides for photovoltaics, in *Handbook of Photovoltaic Science and Engineering*, 2nd edn (eds A. Luque, S. Hegedus, and W. Shire), John Wiley & Sons, Inc., Hoboken, NJ, pp. 716–796.

Structural Properties of Amorphous Silicon and Amorphous Chalcogenides

3.1 General Aspects

Amorphous materials are not new. People have been preparing glassy materials (i.e., SiO₂) for thousands of years. The earliest glaze known is one on stone beads from the Badarian age in Egypt, from about 12 000 BC. Green glaze was applied to powdered quartz for making small figures in about 9000 BC. The oldest pure glass is an amulet of deep lapis lazuli color, from about 7000 BC. In the last century, iron-rich siliceous glassy materials estimated to be a billion years old were recovered from the Moon! Amorphous materials have been applied in electrophotography, or xerography (from the Greek for "dry writing"). In the first machines, in the 1930s, a metal cylinder called the drum was coated with amorphous selenium.

The start of a period of very intensive research on amorphous semiconductors, including the structure of these materials, can be traced to work carried out by Chittick, Alexander, and Sterling in 1969 [1] at Standard Telephone Laboratories, Harlow, UK, and by Spear and Le Comber in 1975 [2] in Dundee, UK. These authors demonstrated that amorphous silicon can be doped. From that point on, amorphous silicon became the basis of a multibillion-dollar market, with diverse applications including solar cells, electrophotography, and liquid crystal TV displays.

3.1.1 Definitions of Crystalline and Noncrystalline

There is a considerable amount of confusion in the scientific literature concerning the terms "noncrystalline," "amorphous," "glassy," "vitreous," "randomness," "disorder," "liquid," and even "crystalline." The first question we put is whether an atomic structure is crystalline or noncrystalline. A perfect crystal is one in which atoms or groups of atoms are arranged periodically in three dimensions and has an infinite extent. This model of the atomic configuration provides us with simple methods for calculating various properties of such

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condensed matter. Unfortunately, these methods are useless in the amorphous case. A more realistic arrangement, an imperfect crystal, is one where the atoms are found in a pattern that repeats periodically but only has a finite extent. Real crystals are not only finite in size but also contain imperfections such as vacancies, interstitial (foreign or self-) atoms, dislocations, impurities, and distortions associated with the surface. Furthermore, at finite temperature the random motion of the atoms about their equilibrium position destroys the perfect periodicity in a snapshot of the crystal. These defects cause distortion in the crystal lattice, but we do not consider such crystals to be amorphous solids.

Until 1992, a crystal was defined by the International Union of Crystallography as "a substance, in which the constituent atoms, molecules, or ions are packed in a regularly ordered, repeating three-dimensional pattern." In 1984 Shechtman *et al.* published a paper [3] on rapidly solidified alloys of Al with 10–14% Mn that possessed icosahedral symmetry in combination with long-range order; these were named quasicrystals. Since this discovery, hundreds of materials with similar atomic structures have been synthesized in laboratories. The International Union of Crystallography had to modify their statement, and the new and broader definition of a crystal became "any solid having an essentially discrete diffraction diagram." Now a possible definition of amorphous materials can be given as follows: *Amorphous materials are in the condensed phase and do not possess long-range translational order (periodicity) in the atomic sites. They have no essentially discrete diffraction diagram.*

In this terminology, the set of amorphous materials has a fundamental subset called glasses. A glass is an amorphous solid which exhibits a glass transition. If a liquid (melt) is cooled very rapidly so that crystallization is bypassed, then a disordered structure can be frozen in. This disordered condensed phase is known as a glass. Such a glass-forming process involves supercooling of a liquid below its normal freezing point. The transformation from a melt to a glassy phase is a transition where a discontinuity can be observed in the second-order thermodynamic variables, such as the calorimetric heat capacity at constant pressure, $C_p = T(dS/dT)_p = -T(d^2G/dT^2)_p$, where *G* is the Gibbs free energy; G(T, p, N) = E - TS + pV.

3.2 Optical Spectroscopy

3.2.1 Raman Scattering

Raman scattering measurements provide us with useful information about the degree of disorder and about chemical bonding. Figure 3.1 shows the Raman spectrum of hydrogenated amorphous silicon (a-Si:H), where the Raman spectrum of crystalline silicon (c-Si) is also shown for comparison. A peak at



Figure 3.1 Raman spectra of a-Si:H and crystalline silicon. Source: R.A. Street 1991 [5].

 480 cm^{-1} is associated with the transverse optical (TO) mode of the network vibration and corresponds to a peak at 520 cm^{-1} in c-Si. The shift of the TO band peak in a-Si:H to a lower frequency and its broadening compared with c-Si are related to the relaxation of the momentum selection rule caused by disorder in the network. A quantitative measure of the disorder can be obtained from the shift and broadening of the TO band compared with c-Si [4]. Raman spectroscopic measurements and Hartree–Fock *ab initio* calculations of Raman spectra have been carried out for amorphous selenium in order to identify the characteristic vibrational mode due to sigma bonds [5]. In these Raman spectra, the peaks around a wavenumber of 250 cm^{-1} correspond to vibrational modes of 0.234 nm covalent bonds in the amorphous material, as displayed in Figure 3.2.

3.2.2 Infrared Absorption

Infrared (IR) absorption measurements can be used to estimate the hydrogen content and the Si–H bonding scheme in a-Si:H. The Si–H bonding scheme, that is, the content of SiH, SiH₂, and SiH₃ groups, is obtained by observing IR absorption bands associated with vibration modes, that is, stretching, bending (rocking or wagging), and scissor bending modes, as shown in Figure 3.3 [6]. The vibration frequencies of each mode are illustrated in Figure 3.4. The IR absorption intensities depend on the characteristics of the samples, as shown in Figure 3.3. The device quality sample exhibits only IR vibrations due to SiH