Chapter 1

Introduction

Amorphous solids have been used as so-called glasses with various modifications in our life since more than 2 000 B.C., i.e., the earliest glass objects were beads, which have been found in Egypt, and glass was also actually made in earlier Mesopotamia. However, scientific investigations on amorphous solids only started in this century, particularly, about sixty years ago. Zachariasen (1932) proposed that the structure of vitreous SiO_2 can be described by a continuous random network (CRN) in which the SiO_4 tetrahedra joined at the corners are connected with each other to form a glassy solid. This idea is shown in the form of a hypothetical two-dimensional oxide, A_2O_3, in Fig. 1.1, where a regular lattice expressing its crystalline form is also shown for comparison. Each oxygen atom has twofold coordination, being corner-shared by two AO_3 triangles. As will be mentioned in more detail in Chapters 1 and 4, this structure exhibits a typical example of disordered solids.

The structure of amorphous solids is characterized as an irregular arrangement of atoms in contrast with crystalline solids whose structure has a periodic array of atoms, as seen in Fig. 1.1(a). Such a disordered structure manifests itself as a hollow pattern of electron diffraction. For example, the pattern for amorphous silicon (a-Si) is shown in Fig. 1.2(a). This is in contrast with that for crystalline silicon (c-Si) exhibiting the Laue spots (Fig. 1.2(b)). A detailed structure of amorphous solids varies with the nature

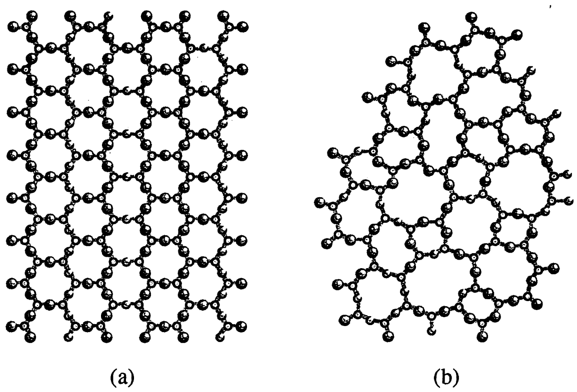
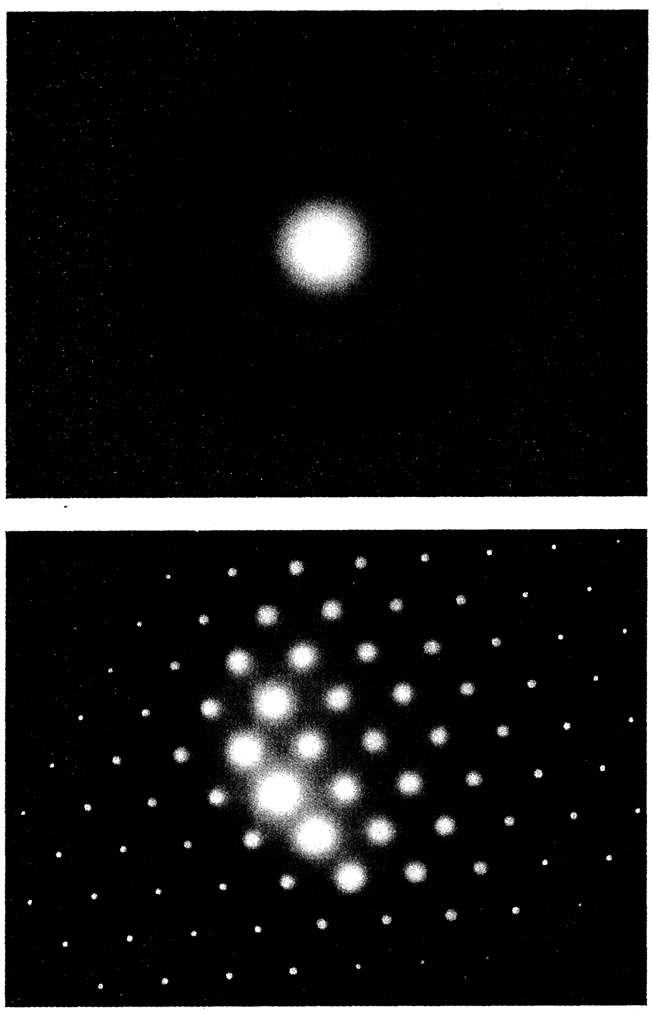


Figure 1.1. A hypothetical two dimensional oxide, A_2O_3: (a) crystalline form, (b) amorphous form.

of bonding schemes of constituent atoms. For amorphous covalent solids which are the main focus of this book, coordination of atoms retains short-range order. For example, for hypothetical two-dimensional oxide, A_2O_3, as shown in Fig. 1.1(b), atoms A have threefold coordination, while oxygen has twofold coordination. AO_3 tetrahedral units are very similar to those for crystalline counterparts. This means that short-range order is retained, although long-range order is broken. This feature of amorphous covalent solids is reflected in their electronic properties, as will be mentioned in detail in this book.

The other feature of amorphous solids is that they are in metastable states, i.e., in nonequilibrium states. Figure 1.3 shows the free energy versus atomic configuration diagram. Point C gives the minimum energy level corresponding to a crystalline state. On the other hand, A_1, A_2, and so on are quasi-minima or local minima corresponding to metastable states. Various points of local minima correspond to different metastable states which are brought out by different conditions during the formation process. These local minimum states are separated from the state C with some barriers. External perturbations such as thermal, optical, electrical and mechanical agitations etc., cause the metastable state, e.g., A1 to



(a)

(b)

Figure 1.2. Electron diffraction patterns: (a) amorphous silicon, (b) crystalline silicon.

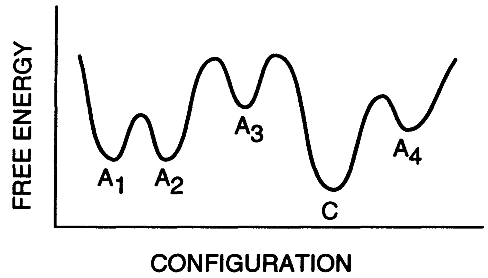


Figure 1.3. Schematic illustration of the free energy versus configuration curve.

be brought to the crystalline state C. Taking thermal agitation as an example of external perturbations, we have crystallization of amorphous solids which occurs by annealing at a certain temperature. The stability of amorphous solids depends on their detailed natures. Conventional oxide glasses such as those used for windows are quite stable, while amorphous Ge thin films prepared by vacuum evaporation can be crystallized by a mechanical shock, for example, the impact after falling onto the floor (Kikuchi, 1985). In Fig. 1.3, this depends on how low is the energy at the local minimum.

In this book, we deal with amorphous semiconductors which are constituted mainly from covalent bonds. They are classified into two types, i.e., *tetrahedrally-bonded amorphous semiconductors* such as Si and Ge and *chalcogenide glasses* such as Se and As_2Se_3. Typical materials for this classification are listed in Table 1.1. These materials are of particular interest from the viewpoints of physics and their applications. For the former viewpoint, they are typical examples of disordered systems for which basic theory has not been fully established, because the complex nature of this system is beyond the conventional solid state theory based on the periodic structure of solids, i.e., the Bloch theory. On the other hand, tetrahedrally-bonded amorphous semiconductors, particularly hydrogenated amorphous silicon, have a wider range of applications such as solar cells, thin film transistors, sensors

Table 1.1. Classification of amorphous semiconductors

Tetrahedrally-Bonded Semiconductors	
	C, Si, Ge,
	SiC, InSb, GaAs, GaSb
Chalcogenide Semiconductors	
	S, Se, Te,
	As_2S_3, As_2Se_3, As_2Te_3,
	Ge-Sb-Se, As-Se-Te

etc. while chalcogenide glasses are also used for optical memory devices. These applications are based on electronic properties of amorphous semiconductors. Thus, it is important to understand the electronic properties of amorphous semiconductors in order to achieve a breakthrough in developing novel applications with them.