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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

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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 More recently, a-Se has been replaced by organic polymers for xerography (Weiss and Abkowitz, 2006).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

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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

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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)

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is dominated by the DOS. Street (1976) initiated work on PL in this field, and recently the technique of PL with wide-lifetime distribution (in the nanosecond to millisecond range) has become well established (Aoki, 2012).

Thermally activated band-type electronic transport occurs in both a-Si:H and amorphous chalcogenides near room temperature. The Meyer–Neldel compensation law for thermally activated processes has been discussed with reference to disordered matter; however, this compensation law is not clearly understood from a theoretical standpoint (Yelon, Movaghar, and Crandall, 2006). At low temperatures, or in defect-dominated materials, transport through localized states is dominant. Mott (1969) developed the variable-range-hopping (VRH) model for a single-phonon carrier hopping process. The importance of small polarons has been pointed out in disordered materials (Emin, 1975), in which multiphonon processes dominate transport. Whether multiphonon or single-phonon processes dominate in amorphous semiconductors is still a matter of debate (Shimakawa and Miyake, 1988; Emin, 2008). Recent results in hydrogenated amorphous/nanocrystalline Si suggest that this factor will depend on temperature (Wienkes, Blackwell, and Kakalios, 2012). Alternating current (ac) transport studies, initiated by Pollak and Gegalle (1961) in crystalline Si, provide information on localized states. Theories involving the continuous time random walk (CTRW) of carriers have developed well, and apply to hopping systems (Dyre and Schröder, 2000).

Time-of-flight measurements developed by Spear and Adams (1966) were applied to crystalline sulfur. In amorphous semiconductors, this technology has been applied to many systems involving a-Si:H and a-Chs to study the drift mobility of both electrons and holes. In most cases, non-Gaussian transport has been discovered. This opened the door for studying dispersive transport in disordered matter (Pfister and Scher, 1978).

The illumination of amorphous semiconductors, effectively with bandgap light, induces various changes on structural and electronic properties. In amorphous chalcogenides, the bandgap decreases with illumination; this is referred to as *photodarkening*, which was first reported by DeNeufville, Moss, and Ovshinsky (1973/1974), and it was confirmed that photodarkening accompanied volume changes (Hamanaka *et al.*, 1976). These effects are of interest in scientific applications, and hence a huge amount of work has been devoted to these topics (see the reviews by Tanaka (1990), Pfeiffer, Paesler, and Agarwal (1991), and Shimakawa, Kolobov, and Elliott (1995)). Photoinduced volume changes in a-Se films have been discussed using MD simulations (Hegedüs *et al.*, 2005). Giant photoexpansion (Hisakuni and Tanaka, 1995) and photodeformations (Tanaka and Mikami, 2009) have produced the interesting terms *photofluidity* and *optical force*, respectively.

A decrease in the photoconductivity of a-Si:H after photoillumination was first discovered by Staebler and Wronski (1977), and is called the Staebler–Wronski (SW) effect. This effect is problematic for applications and hence it is also called *photodegradation*. Photodegradation is attributed to defect creation, and understanding it is a very important subject (see, for example, Street (1991), Redfield and Bube (1996), Morigaki (1999), and Singh and Shimakawa (2003)). Similar effects on photoconductivity have also been found in amorphous chalcogenides (Shimakawa, 1986).

1.2 Definitions

Crystalline and non-crystalline structure

For the reader unfamiliar with amorphous semiconductors, we present here a brief explanation of the most essential definitions. Firstly, we must stress that there is a considerable amount of confusion in the scientific literature concerning the terms non-crystalline, amorphous, glassy, vitreous, randomness, disorder, liquid, and even crystalline. A first important question is whether an atomic structure is crystalline or non-crystalline (amorphous). A perfect crystal is one in which the atoms, or a group of atoms, are arranged periodically in three dimensions to an infinite extent and are rigidly fixed at their thermal equilibrium. This mathematical model of atomic configurations provides us with a relatively easy method for calculating the different properties of condensed matter, which may be found in books on theoretical solid state physics.

A more realistic arrangement is an imperfect crystal in which the atoms form a pattern that repeats periodically only to a finite extent. In fact, this may seem more realistic, but we still have a serious problem in that this type of imperfect crystal behaves counter to thermodynamics. This is because, at nonzero temperatures, defects form in any atomic configuration when the crystals are in their equilibrium states. Real crystals are, of course, not only finite in size, but also contain imperfections such as vacancies, interstitial (foreign or self) atoms, dislocations, impurities, distortions associated with the surface, etc. Furthermore, another effect must be taken into account at finite temperature. The random motion of atoms at their equilibrium positions also weakly destroys the perfect periodicity at any given moment in time. These defects cause distortions in the crystal lattice, but we do not consider these real crystals to be amorphous solids. Translational symmetry more or less remains.

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 (two years after their discovery), Shechtman *et al*. (1984) published a paper on rapidly solidified alloys of aluminum with 10–14% manganese that possess icosahedral symmetry in combination with long-range order, named *quasicrystals*, in clear violation of the above definition of a crystal. Since this discovery, hundreds of similar atomic structures have been synthesized in laboratories around the world. Recently, the naturally occurring quasicrystalline mineral icosahedrite has been identified in a sample from the Khatyrka river in Chukotskii Autonomous Okrug, Far-Eastern Region, Russia. The International Union of Crystallography has had to modify their declaration, and the new and broader definition of crystal became "any solid having an essentially discrete diffraction diagram."

Other types of deviation from perfection occur in crystals. Consider a perfect lattice, but one in which each atomic site possesses a randomly oriented spin or other magnetic moment. Another partially ordered arrangement is possible in materials built up of large near-spherical molecules. Molecular centers of mass can be found in crystalline sites where the directions of molecular axes are randomly distributed. A typical example of the so-called *plastic crystals* is the solid crystalline phase of C_{60} molecules. A similar example occurs when a binary (ternary) alloy has two (three) different, randomly distributed atoms inside a perfect lattice. Are they crystalline or non-crystalline? This issue does not occur for amorphous materials.

A *liquid crystal* is a state of matter that has properties between those of a conventional liquid and those of a solid crystal. Rigid rod-shaped or disc-like molecules develop in a well-defined direction. The centers of mass of the molecules are distributed randomly in two or three dimensions. How does one distinguish between the condensed phase and the liquid phase? A solid is a phase whose shear viscosity exceeds $10^{13.6}$ Pa s (N s m^{-2}), although this threshold is rather arbitrary. Values for the viscosity of common liquids at room temperature are on the order of 10^{-3} Pa s. For some examples, see Table 1.1. Liquid crystals are anisotropic fluids.

A *granular material* is a collection of distinct macroscopic particles with randomly distributed centers of mass, such as sand or peanuts in a container. There is a weak interaction between macroscopic particles. Their behavior is

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Table 1.1. *Shear viscosity values for some materials.*

Substance	Temperature (°C)	Shear viscosity (Pa s)
Water	90	0.31
Water	10	1.31
Honey	room temperature	2–10
Bitumen	20	10^8
Ice	–13	15×10^{12}
Window glass	room temperature	10^{40}

differently from that of solids, liquids, and gases, and this has led many to characterize granular materials as a new form of matter. A similar topology can be observed in the "microworld." Polycrystalline materials (poly is a Greek word meaning "many") consist solely of crystalline grains, separated by grain boundaries, and the interaction between them is strong. Furthermore, in some cases crystalline grains do not touch each other; rather, they are embedded into a disordered atomic environment. The grain size determines whether these materials are named *nanocrystalline* or *microcrystalline* materials.

Amorphous, glassy materials

After our brief overview, we can provide the following definition for amorphous materials: amorphous materials exist in the condensed phase and do not possess the long-range translational order (periodicity) of atomic structures. By "long range" we mean over 10 nm. We may also talk about short-range order (also called "local order," below 1 nm) and medium-range order (in the range 1–10 nm). Following the discovery of quasicrystals, another sentence must be added to the previous definition of amorphous materials.

Amorphous materials exist in the condensed phase and do not possess the long-range translational order (periodicity) of atomic structures. They do not exhibit a discrete diffraction pattern.

Using this terminology, the set of amorphous materials has within it a fundamental subset *glasses*, where a glass is an amorphous solid that exhibits a glass transition. If a liquid (melt) is cooled very rapidly so that crystallization can be bypassed, the disordered structure can be frozen-in. This disordered condensed phase is known as a glass. Such a glass-forming process involves the

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supercooling of a liquid below its normal freezing point. The freezing of a crystalline solid is a first-order thermodynamic phase transition; there are discontinuities in first-order thermodynamic variables such as entropy, $S = -(dG/dT)_p$, or volume, $V = (dG/dp)_T$, at the transition (where G is the Gibbs free energy, $G(T, p, N) = E - TS + pV$). The transformation from a melt to the glassy phase is a transition in which there is no discontinuity in first-order thermodynamic variables at the glass-transition temperature, T_g. However, in second-order thermodynamic variables, such as the calorimetric heat capacity at constant pressure, $C_p = T(dS/dT)_p = -T(d^2G/dT^2)_p$, a discontinuity can be observed.

Groups IV and VI elements and their alloys

For us, the most interesting class of materials comprises the amorphous semiconductors. An important task therefore is to define a semiconductor. A simple definition would be that a semiconductor belongs to a class of materials that have an energy gap of 1–2 eV in their electronic DOS and whose resistivity values fall between that of an insulator and a good conductor. A more accurate definition of crystalline semiconductors is associated with the temperature dependence of resistivity:

$$\rho(T) = \rho_0 \exp(\varepsilon_0 / k_B T), \tag{1.1}$$

where ρ_0 and ε_0 are constants, k_B is the Boltzmann factor, and T is the temperature. Note that ρ decreases with increasing T, which is opposite to the case for conventional metals (where ρ is proportional to T). Most chalcogenide glasses and hydrogenated a-Si follow the above equation, whereas pure a-Si and a-Ge do not.

Atomic structure is one of the main features that distinguish between different electronic transport properties. Carbon provides us with a simple example. The diamond crystal arrangement of carbon atoms creates a good insulator, with about a 5.5 eV gap in the electronic DOS. However, the non-crystalline configuration of carbon displays semiconductor properties, and the graphitic atomic structure is a conductor. Furthermore, superconductivity at 30 K in caesium-doped C_{60} has been observed.

Pure amorphous semiconductor materials are located in the even-numbered groups of the periodic table, such as group IV (carbon, silicon, and germanium)

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and group VI (selenium and tellurium). In group VI, stable allotropes of sulfur are excellent electrical insulators.

The basis of this structure was formulated by Sir Nevill Francis Mott (Mott, 1969), who concluded via his famous $(8-N)$ rule that there are no dangling bonds inside such a material. This is explained as follows. In a glass, any atom appears in such a way that it retains its natural coordination. The number of covalent bonds $Z = 8 - N$, where N is the number of valence electrons. (We consider elements only in groups IV, V, and VI.) Further, an additional rule states that $Z = N$ if $N < 4$. The most important consequence of this was that amorphous semiconductors *cannot* be doped. Today, however, we know this is not the case.

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