STUDY ON THE GLASSES WITH CHALCOGENIDES

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Abstract: Chalcogenide glasses can be regarded as glassy semiconductors, and the level of our present understanding can be summarized as follows. For the atomic structural components, listed at the left-hand side in Figure 11, we have obtained relatively firm knowledge of the short-range structure, which covers the coordination number, the bond length, and the bond angle. Also, dependence on atomic compositions, which are practically possible only in covalent glasses, has added valuable insights into the chalcogenide-glass science. Now, the problem is shifting to the identification of medium-range structures, density fluctuations, and defects. For these structures, however, there are few effective experimental techniques available at present. In addition, the quasi-stability, which is an inherent character to glasses, also makes the problem intricate. Under such situations, we may employ computer simulations and/or refine simple structural models which can interpret as many observations as possible. It may be fair to say that, at the present stage, because of the incomplete structural knowledge, the chalcogenide-glass science is far behind the one constructed for single crystalline semiconductors.

Introduction:

Chalcogenide glasses can be regarded as glassy semiconductors. For the atomic configuration, more-or-less firm insights have been obtained into the short-range structure, which covers the coordination number, the bond length, and the bond angle. Now, the problem is shifting to the identification of medium-range structures and defect structures. However, for these problems, there are no effective experimental techniques at present. Under such situations, we may employ computer simulation and/or refinement of simple structural models which can interpret as many observations as possible. In addition, studies of atomic composition dependence, which are practically possible only in covalent glasses, may add new insights into the chalcogenide-glass science. At the present stage, because of the incomplete structural knowledge, it is far behind the science constructed for single crystalline semiconductors.

Many problems, fundamental and simple, remain unresolved. For instance, the glass transition may be a common problem and also the biggest problem in glass science. On the other hand, electronic behaviors near the band edge and in the bandgap are also important problems both fundamentally and in applications. For instance, no one can give a convincing answer to such a simple question as ''Why in chalcogenide glasses are holes more mobile than electrons?'' Readers may refer to an issue of *Semiconductors* 1998, **32**(8), which discusses some problems.

Chalcogenide glasses have been known as optical materials for about 50 years (Frerics, 1953). The first report on their applications in fiber optics was published in the 1960s (Kapany and Simms, 1965). The most intensive research on chalcogenide glasses as materials for fiber optics for the mid-IR range has been carried out during the past 15–20 years (Katsujama and Matsumura, 1988; Devyatykh et al., 1991a; Nishii and Yamashita, 1998), and research included the testing of a set of chalcogenide glasses made from III–V group elements for prospective optical fibers production. The most promising results were obtained from the glasses based on arsenic chalcogenides. Their properties include a wide transparency range, low optical losses within 2–12 μm range, and stability to atmospheric moisture.

The transparency range of glasses measured at the absorption level of 1 cm^{-1} is 0.62–11.5 μm for As_2S_3, 0.8–17.5 μm for As_2Se_3, and 0.75–12.25 μm for $As_2Se_{1.5}S_{1.5}$. Minimum optical losses in AS_2S_3 and As_2Se_3 are evaluated as $(6-7) \times 10^{-2}$ dB km^{-1} at 4–6 μm range (Lines, 1984). For this reason the vitreous arsenic chalcogenides are attractive and applicable for optical fiber manufacturing. Moreover, a number of technical problems in optics and optoelectronics may be efficiently solved through the use of chalcogenide glass fibers with low optical losses.

As a result, there is a permanent scientific and applied interest to chalcogenide glass fibers. Several research groups from different countries are now at work. The results of investigation and different aspects of chalcogenide glass fibers are considered in original papers and reviews. This chapter presents the current status of high-purity chalcogenide glasses and fibers based on arsenic chalcogenide glasses.

The name chalcogenide originates from the Greek word "chalcos" meaning ore and "gen" meaning formation, thus the term chalcogenide is generally considered to mean ore former [1]. The elements of group sixteen of the periodic table is known as the chalcogens. The group consists of oxygen, sulphur, selenium, tellurium and polonium though oxygen is not included in the chalcogenide category. Though oxide materials are the oldest known glass forming systems it has become traditional to treat them separately from more recently discovered chalcogenide compounds. Chalcogenide glasses are a recognized group of inorganic glassy materials which always contain one or more of the chalcogen elements. Scientifically oxide materials behave rather differently from other chalcogenides, in particular their widely different band gaps contribute to very dissimilar optical and electrical properties [2-5]. Energy Conversion Devices have used this particular alloy to develop a phase-change memory technology used in commercially available re-writeable CD and DVD disks [5-12]. This phase-change technology uses a thermally activated, rapid, reversible change in the structure of the alloy to store data. Since the binary information is represented by two different phases of the material it is inherently non-volatile, requiring no energy to keep the material in either of its two stable structural states. The two structural states of the chalcogenide alloys are an amorphous state and a polycrystalline state. Relative to the amorphous state, the polycrystalline state shows a dramatic increase in free electron density, similar to a metal. This difference in free electron density gives rise to a difference in reflectivity and resistivity. In the case of the re-writeable CD and DVD disk technology, a laser is used to heat the material to change states. The state of the memory is read by directing a low power laser at the material and detecting the difference in reflectivity between the two phases.

Chalcogenide glasses are based on the chalcogen elements S, Se, and Te. These glasses are formed by the addition of other elements such as Ge, As, Sb, Ga, etc. They are low-phonon-energy materials and are generally transparent from the visible up to the infrared. Chalcogenide glasses can be doped by rare-earth elements, such as Er, Nd, Pr, etc., and hence numerous applications of active optical devices have been proposed. Since chalcogenide-glass

fibers transmit in the IR, there are numerous potential applications in the civil, medical, and military areas. Passive applications utilize chalcogenide fibers as a light conduit from one location to another point without changing the optical properties, other than those due to scattering, absorption, and reflection. These glasses are optically highly nonlinear and could therefore be useful for all-optical switching (AOS). Chalcogenide glasses are sensitive to the absorption of electromagnetic radiation and show a variety of photo induced effects as a result of illumination. Various models have been put forward to explain these effects which can be used to fabricate diffractive, waveguide and fiber structures. Next-generation devices for telecommunication and related applications will rely on the development of materials which possess optimized physical properties that are compatible with packaging requirements for systems in planar or fiber form. This allows suitable integration to existing fiber-based applications, and hence requires appropriate consideration as to material choice, stability, and long-term aging behavior. The aim of this short review is to describe the highlight and to the potential applications.

Structure of Chalcogenide Glasses

Solids are a particular state of condensed matter characterized by strong interactions between the constituent particles (atoms, molecules). Solids can be found or prepared either in an ordered (crystalline) state or in a disordered (noncrystalline) state. An ideal crystal corresponds to a regular arrangement of atoms in a lattice with well-defined symmetry, and a structural unit called the unit cell can be defined. Translation of the unit cell along the three coordinate axes reproduces the whole assembly of atoms. A real crystal does not exhibit perfect periodicity in space and contains various kinds of imperfections or defects. Solids which lack the periodicity of the atoms are called noncrystalline solids or amorphous, vitreous or glassy solids. While crystals possess long-range order (LRO), in amorphous materials short-range order (SRO) still exists. Although the first and second nearest-neighbor coordination shells are well defined, atoms in the third coordination sphere start to become uncorrelated with those in the first one. The ideal noncrystalline network is difficult to define. Particularly, different thermal treatments lead to various noncrystalline arrangements of atoms. A continuous random network might be considered to be an ideal noncrystalline network for covalent solids. The structure of chalcogenide glasses, however, cannot be described by means of a continuous random network which is isotropic in three dimensions, as in the case of amorphous silicon for example. As_2S_3, As_2Se_3, GeS_2, and $GeSe_2$ can be locally layer-like, while pure S and Se are chain like. For all these

materials, there is considerable flexibility of the structure as a result of the weak van der Waal's bonding between layers or chains, so that changes in the structure can be relatively easily accommodated. The chemical bonding of the matrix is usually directional and covalent and halogens act as chain or network terminators. The chalcogenide glasses are bandgap semiconductors and are infrared transmitting. The model of a binary glass forming chalcogenide is considered to be analogous to silica; there are two group 16 chalcogen elements bonded to a single group 14 elements. Another common class of chalcogenides has glass forming regions where three chalcogens are bonded to two group 15 elements. Most stable binary chalcogenide glasses are compounds of a chalcogen and a group 14 or 15 element. This allows a wide range of atomic ratios. Ternary glasses allow a larger variety of atoms to be incorporated into the glass structure; thus giving greater engineering capacity [14]. Although chalcogenides can exist over a wide range of compositions, not all of which exist in glassy form, it is often possible to find materials with which these non-glass forming compositions can be alloyed in order to form a glass. An example of this is gallium sulphide based glasses. Gallium sulphide on its own is not a known glass former however it readily bonds with sodium or lanthanum sulphides to form a glass, gallium lanthanum sulphide (GLS). Amorphous chalcogenide materials can be broadly classed by the type of atoms to which they bond to form amorphous systems. One of the more wellknown chalcogenide glasses is based on arsenic trisulphide, an example of a stable binary glass which preferentially exists in a glassy phase. In contrast, compounds based on heavier chalcogenides, for example tellurium based materials are more likely to exist as a crystal.

Electrical Properties of Chalcogenide Glasses

Chalcogenide glasses can be characterized as being variously covalent, metallic, and ionic. In covalent chalcogenide glasses such as Se and As_2S_3, the so-called 8-N rule applies to the coordination number of the constituent atoms, e.g. the coordination number of chalcogens is generally 2 since the total number of valence electrons is $N = 6$. The magnitude of the band gap is 1–3 eV depending on the composition, the band gap increases in the series Te $\rightarrow$ Se $\rightarrow$ S. Electrical conduction in many chalcogenide glasses is governed by holes. Accordingly, these glasses can be regarded as amorphous semiconductors. However, in a glass containing large amounts of Te, the band gap decreases (~1 eV), and the metallic character increases. Electrical switching in chalcogenide semiconductors emerged in the 1960s, when the amorphous chalcogenide $Te_{48}As_{30}Si_{12}Ge_{10}$ was found to exhibit sharp,

reversible transitions in electrical resistance above a threshold voltage. The switching mechanism would appear initiated by fast purely electronic processes. If current is allowed to persist in the non-crystalline material, it heats up and changes to crystalline form. This is equivalent to information being written on it. A crystalline region may be melted by exposure to a brief, intense pulse of heat. Subsequent rapid cooling then sends the melted region back through the glass transition. Conversely, a lower-intensity heat pulse of longer duration will crystallize an amorphous region. Attempts to induce the glassy–crystal transformation of chalcogenides by electrical means form the basis of phase-change random-access memory (PC-RAM). This emerging technology is on the brink of commercial application. For write operations, an electric current supplies the heat pulse. The read process is performed at sub-threshold voltages by utilizing the relatively large difference in electrical resistance between the glassy and crystalline states. Although the electronic structural transitions relevant to both optical discs and PC-RAM were featured strongly, contributions from ions were not considered even though amorphous chalcogenides can have significant ionic conductivities. However, it is shown that ionic transport can also be useful for data storage in a solid chalcogenide electrolyte. At the nanoscale, this electrolyte consists of crystalline metallic islands of silver selenide (Ag_2Se) dispersed in an amorphous semiconducting matrix of germanium selenide (Ge_2Se_3).

Applications of Chalcogenide Glasses

The first chalcogenide glass to be commercially developed was A_2S_3, produced for passive, bulk optical components for the mid-IR in the 1950s. The modern technological applications of chalcogenide glasses are widespread. Examples include infrared detectors, mouldable infrared optics such as lenses, and infrared optical fibers, with the main advantage being that these materials transmit across a wide range of the infrared electromagnetic spectrum. The physical properties of chalcogenide glasses (high refractive index, low phonon energy, high nonlinearity) also make them ideal for incorporation into lasers, planar optics, photonic integrated circuits, and other active devices especially if doped with rare earth ions. Many chalcogenide glasses exhibit several non-linear optical effects such as photon-induced refraction [4], and electron-induced permittivity modification. Some chalcogenide materials experience thermally driven amorphous crystalline phase changes. This makes them useful for encoding binary information on thin films of chalcogenides and forms the basis of rewritable optical discs and non-volatile memory devices such as PC-

RAM. All of these technologies present exciting opportunities that are not restricted to memory, but include cognitive computing and reconfigurable logic circuits. It is too early to conclude which technology will be selected for which application. But scientific interest alone should drive the continuing research. For example, the migration of dissolved ions is required in the electrolytic case, but could limit the performance of a phasechange device. Diffusion of both electrons and ions participate in electromigration widely studied as a degradation mechanism of the electrical conductors used in modern integrated circuits. Thus, a unified approach to the study of chalcogenides, assessing the collective roles of atoms, ions and electrons, may prove essential for both device performance and reliability [16, 17].

During the last two decades, other sulphide and selenide glasses were developed, as well as selenidetelluride glasses for optical components for the far infrared which have since been exploited commercially [18, 19]. Applications of infrared optics include energy management, thermal fault detection, electronic circuit detection, temperature monitoring and night vision [20]. As an example of the latter, the blackbody radiation emitted by room temperature objects such as the human body is in the 8-12 p.m regions where selenidetelluride-based glasses are applicable for thermal imaging. In the 1970s, chalcogenide glasses were researched to assess their suitability as active electronic device components in photocopying and switching applications. However, a lot of activity in threshold memory and thin film telluride glass electronic switches in fact did not lead to any commercial production [19]. Far-IR chalcogenide glasses, when suitably formulated to optimize the acousto-optic figure of merit, are attractive for operation at 10.6 µm [21]. Ga-La-S glasses have been investigated for shorter optical wavelength operation [22]. The metal photodissolution effect in chalcogenides has features desirable for image creation and storage. Up to 30-40 at.% Ag can be driven into an As-S amorphous film, forming an embedded structure with up to a 0.5 absolute change in refractive index [23]. On removal of the illumination at ambient temperatures, there is no further movement of the metal ions and hence no degradation of the image. Further, a surface relief structure can be formed by removing undoped material with an alkali etchant. Applications are possible in the production of inorganic resists for VLSI lithography [24]. The surface relief structures achievable by metal photodoping are attractive for making bulk components for infrared diffractive optics and also for small scale integrated optics [25]. Diffractive optical elements are essentially planar devices which operate by diffraction rather than by reflection or refraction

and are more lightweight than conventional bulk elements such as mirrors, lenses and filters. The photoinduced phase transition amorphous crystalline, and vice versa, in chalcogenide glasses could be the basis for optical mass memory applications. Thus a focused laser writes information by inducing a localised phase transition, and data are read by utilising the difference in reflectance between the amorphous and crystalline phases. Antimony- based chalcogenide glasses appear to be the most suitable [26]. The wide IR window of chalcogenides and the high resolution of Fourier transform infrared spectrometry together permit remote sensing of gases and liquids using absorption due to the fundamental vibrational modes, for instance by means of fibre-optic evanescent field spectroscopy [27]. The third order non-linear susceptibility of chalcogenides is 2.2×10^{-12} esu for A2S3 glasses [28], which is 100 times higher than for silica, with the possibility of a fast response time [29]. This opens up possibilities for their use as the active element in all-optical switching devices. Chalcogenide fibers are well-suited for chemical-sensing applications, since most molecular species vibrate in the infrared region. Chalcogenide fibers can be used in fiber-optic chemical-sensor systems for quantitative remote detection and identification, as well as detecting chemicals in mixtures. Different sensing techniques including attenuated total reflectance (ATR), diffuse reflectance, and absorption spectroscopy have been introduced. Numerous systems have been studied which include oil, freon, soap, paints, polymer-curing reactions, glucose/water, benzene and derivatives, chlorinated hydrocarbons, alcohols, carboxylic acids, aqueous acids, perfumes, and pharmaceutical products.

Conclusion

Chalcogenide glasses are low-phonon-energy materials and are generally transparent from the visible to the infrared. Doping chalcogenide glasses by rare-earth elements has opened up numerous applications of active optical devices. Because of their large nonlinearities, chalcogenide glasses are promising candidates for alloptical switching (AOS) applications. Doping chalcogenide glasses with rare-earth elements has allowed the possibility of using these glasses for active applications such as amplifiers and lasers. Since chalcogenide glass fibers transmit in the IR, there are numerous potential applications in the civil, medical and military areas. Chalcogenide fibers are well-suited for chemical-sensor applications, such as fiber-optic chemical sensor systems for quantitative remote detection and identification as well as detecting chemicals in mixtures. Different techniques have been used to measure the optical constants of chalcogenide glasses and films, such as optical transmission and

reflection, ellipsometry, prism coupling, etc. While, up to now, evaporated and sputtered films have been used for producing films of chalcogenide glasses, pulsed laser-deposition of these films has proved useful. They have been used in fabricating many devices, such as waveguides, fiber Bragg gratings, nonlinear directional couplers, etc. using light-induced photostructural changes.

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