

Applications of chalcogenide glasses in electronics and optoelectronics: A review

N Mehta*

Department of Physics, Pranveer Singh Institute of Technology, Kanpur

Received 16 December 2005; accepted 08 June 2006

Following the development of the glassy chalcogenide field, new optoelectronic materials based on these materials have been discovered. Several non-oxide glasses have been prepared and investigated in the last several decades, thus widening the groups of chalcogen materials used in various optical, electronic and optoelectronic glasses. This paper reviews the development of chalcogenide glasses, their physical properties and applications in electronics and optoelectronics. The glassy, amorphous and disordered chalcogenide materials, important for optoelectronic applications, are discussed. The main electronic and optoelectronic phenomena, specific to these materials are described, and the applications based on these phenomena are evidenced.

Keywords: Amorphous semiconductors, Chalcogenide glasses, Ovonic materials

IPC Code: C03C1/04

Introduction

Most studies about glasses were carried out on silicate and quartz glasses, which transmit the radiation in visible range of the electromagnetic spectra. The application in optics, photonic, optoelectronics increased the demand in glasses, which can transmit a radiation in infrared range up to the wavelength $\sim 2 \mu\text{m}$. Chemical and physical properties of these, so-called special glasses will complete the ones of silicate glasses. Special glasses can be divided into three groups: i) Fluoride glasses based on ZrF_4 or HfF_4 ; ii) Chalcogenide glasses (CG)-glasses based on chalcogens (S, Se, Te) such as As-S, As-Se, As-Se-Te, Ge-Se-Te, Ge-As-Se; and iii) Heavy metal oxide (HMO) glasses such as GeO_2 -PbO, TeO_2 -PbO, TeO_2 -ZnO, etc.

There is a growing interest in the family of special glasses involving fluoride, chalcogenide and HMO glasses due to their promising properties such as transmission in middle and far infrared regions of spectra, lower values of phonon energies and higher values of refractive indices as compared to SiO_2 . Research¹ on special glasses includes preparation procedure of high purity glasses, diagnostic of their properties (chemical and physical properties) and applications (Fig. 1, Table 1). Glasses, which fulfill

necessary chemical and physical requirements, are used to draw optical fibers².

In 1955, Goryunova & Kolomiets³ showed that amorphous CGs are semiconductors. In 1960, Ioffe & Regel⁴ realized that the band gap depends on the existence of short-range order rather than on the long-range order of the lattice and suggested that the first coordination number of the corresponding crystal (if it exists) is preserved in the amorphous structure. In his effort to explain hopping conduction on compensated crystalline semiconductors, Anderson⁵ introduced the concept of localization. Mott & Twose⁶ showed that, as soon as disorder was introduced, all states in one-dimensional energy band became localized. Thus the concept of a sharp 'mobility edge', that separates a range of localized energy states from the extended electronic states, was first introduced by Cohen *et al*⁷ (Fig. 2). This model represents an ideal covalent random network structure having extended states with extended wave function. The localized states exist in the gap between the valence band (E_V) and the conduction band (E_C). The Fermi level lies near the centre of the gap. There exist various deviations from ideal covalent random network as vacancies, dangling bonds, chain ends. These deviations lead to localized states having various energies giving rise to curve of non-monotonic density of localized states. At E_C and E_V , the electron and hole mobility drops sharply from

*E-mail: neeraj_mehta28@yahoo.com

Table 1—Some physical properties of selected special glasses

| Glass | Phonon energy cm^{-1} | Transmission energy μm | Refractive index | Hardness kgf.mm^{-2} | Thermal expansion $10^{-7}/^\circ\text{C}$ |
|--------------|-----------------------------------|--------------------------------------|------------------|----------------------------------|---|
| Chalcogenide | 330-380 | 0.5-10.0 | 2.3-2.7 | 100-200 | 240-250 |
| Fluoride | 440-650 | 0.25-6.50 | 1.52 | 225-250 | 150-180 |
| HMO | 590-850 | 0.4-7.0 | 2.65 | 600 | 120-180 |

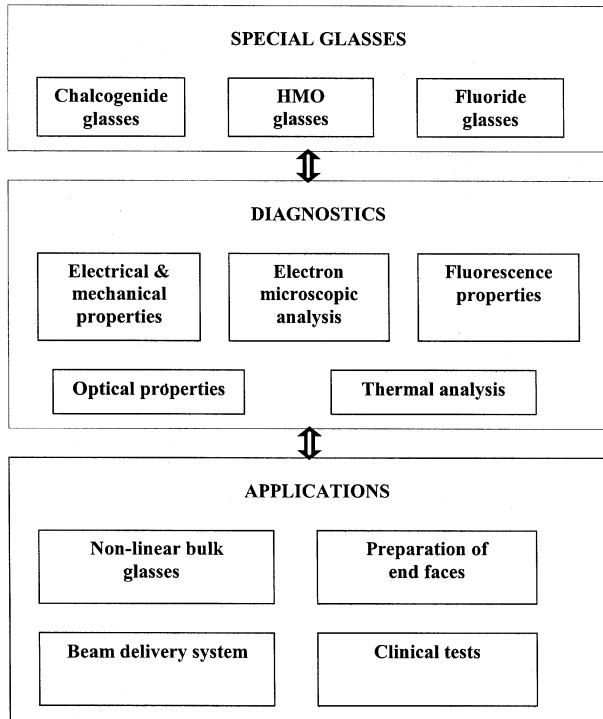


Fig. 1—General overview of chalcogenide glasses with the other special glasses

a low mobility band transport having finite mobility at $T=0$ to a thermally activated tunneling between the localized gap states that disappears at $T=0$. The wave function changes at critical energies E_C and E_V separating the extended and localized states. The mobility edge causes a 'mobility gap' (E_C-E_V) containing only the localized states.

In contrast, Davis & Mott⁸ suggested a model where geometrical disorder of the material, forms a short range of localized states at the band edges while the neutral dangling bonds give rise a well-separated narrow band of localized states, at the centre of the gap where the E_F lies. In the case of charge dangling bonds⁹, two narrow bands are formed, proportional to the concentration of the D+ and D- centres that are located around E_F (Fig. 2b). The mobility edges for electrons and holes are at E_C and E_V respectively. The localized states originate due to lack of long-range

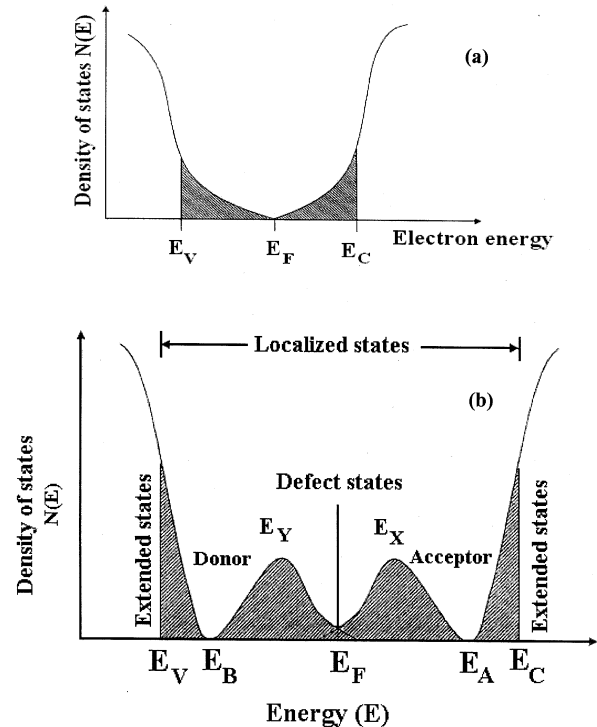


Fig. 2—Energy band models for chalcogenide glasses

order, while the defect states are due to various kinds of defects in the structure. The first type of localized states extend only from E_C to E_A and from E_V to E_B in the mobility edge and the other defect states form longer tails but of insufficient energy to pin the Fermi level.

Ovshinsky¹⁰ led the fabrication of the Ovonic Electrically Erasable Programmable Read Only Memory for computer data storage. The device is continuously developed and Ovshinsky's goal for the near future is to fabricate a single device, called Ovonic Unified Memory, in order to replace the multiple memory types of devices used in today's personal computers¹¹. In the early 70's, sensitivity of the chalcogenide alloys to the light have been already recognized^{12,13} and Xerography was widely used¹⁴. CGs in bulk and thin film forms are prepared by following different techniques¹⁵.

Preparation Techniques of Chalcogenide Glasses

Quenching Technique

Chalcogenide materials are prepared by rapid cooling from the melt. For preparation of glasses, required composition is prepared by weighing the constituent elements in desired atomic percentages and then sealed in quartz ampoules under high vacuum. Sealed ampoules are kept in a furnace at a temperature for components to melt. Inside furnace, ampoules are frequently rocked for 12 h to make the melt homogeneous. Quenching is done by dropping the quartz ampoules suddenly in ice-cooled water or liquid nitrogen depending upon the requirement. In some cases, air quenching is sufficient where an air blower blows air on the heated ampoules. Not all the materials can be made in glassy form even at the fastest cooling rates. In case of alloys also, there are certain range of constituent elements in which they can be glassy. A systematic study is made to find out phase diagram for a specific series for making glassy alloys by preparing small amount of sample and checking glassy nature by X-ray diffraction.

Thermal Evaporation Technique

Chalcogenide materials are made amorphous in the form of thin films by creating high vacuum in the bell jar and heating the filament containing the material by passing electricity. Substrate used may be glass or any other suitable material. Substrate temperature can also be varied by mounting a heater inside the bell jar. Standard coating units are available in the market for making thin films by this technique.

Flash Evaporation Technique

This technique is similar to Thermal Evaporation except that the material is dropped on already heated filament. In addition to the coating unit, an AC magnetic field is established to produce vibration in a magnetic strip containing material.

Sputtering Technique

It consists bombardment of a target by energetic ions from low-pressure plasma, causing erosion of material, either atom by atom or as clusters of atoms, and subsequently depositing of film on the substrates. Simplest way to induce sputtering is to apply a high negative voltage to the target surface, thereby attracting positive ions from the plasma. However, DC sputtering process is feasible only when target is sufficiently conducting so that target can act as electrode.

Glow Discharge Decomposition Technique

This technique, like sputtering, relies on the production of plasma in a low-pressure gas, but instead of ions from the plasma ejecting material from the target, a chemical decomposition of the gas itself takes place, leading the deposition of a solid film on a substrate kept in the plasma. The plasma is produced by the application of an r.f. field, either using inductive coupling or capacitive coupling. The films deposited depend upon gas pressure, flow rate, substrate temperature and chamber geometry.

Chemical Vapor Deposition Technique

It is analogous to the glow discharge method in that both depend on the decomposition of a vapor species. This method relies on the thermal energy for the decomposition and the applied r.f. field simply serves to heat up the substrate upon which the vapor decomposes.

Some Physical Properties of Chalcogenide Glasses

Structural Properties

Crystalline solid state is characterized by strict order in the position of atoms even at large atomic distances. CGs could be characterized by short-range order (SRO) and partially by intermediate range order (IRO). That means that after changing the crystalline state of a crystal in vitreous or amorphous state, the shortest distance between neighboring atoms is almost the same as in the crystal, may be, only with small distortion, which certainly leads to destroying of the long-range order (LRO). For example, the first atomic coordination in the crystals and glasses of As_2S_3 and As_2Se_3 are almost the same¹⁶. Of course, this is not characteristic for all materials. The germinate glasses (Ge_xCh_{1-x} , where $Ch=Se, Te, S$) are a typical example of different SRO in crystals and glasses of the same composition^{17,18}.

CGs bear some similarity to oxide glasses, since both oxygen and chalcogen belong to group VI in the Periodic Table. A CG can be regarded a kind of 'soft semiconductor', soft because its atomic structure is flexible and viscous (due to two-fold coordination of chalcogen atoms) and a semiconductor because it possesses a band gap energy (~2 eV) characteristic of semiconductor materials (1-3 eV). Accordingly, a CG may be characterized as being in between an oxide glass composed of three-dimensional networks and an organic polymer possessing one-dimensional chain structure¹⁹. Atomic bonding is, therefore, more rigid in CGs than that of organic polymers and more

flexible that of oxide glasses (Fig. 3). Atomic structure and related properties in CGs depend upon preparation methods and history after preparation^{20,21}.

Electronic Properties

CGs possess electrical and optical band gaps of 1-3 eV and accordingly they can be regarded as amorphous semiconductors. Gap decreases in the sequence of S, Se and Te, reflecting enhanced metallic character. As a semiconductor, overall property of CGs can be grasped as the vertical sequence (Fig. 3). That is, with the change from organic semiconductors, chalcogenides, hydrogenated amorphous silicon films, to crystalline semiconductors, the electronic mobility becomes higher and a faster response is available. The material also becomes more rigid. Instead, material prices seem to increase with this sequence, which may reflect their typical preparation methods (coating, evaporation, glow discharge, and crystal-growth techniques).

Electrically, CGs exhibit smaller conductivities than the corresponding crystals^{20,21}. This is because the electronic mobility is suppressed by band tail and gap states, which are manifestations of disordered structures. Glass can be regarded as a p-type semiconductor or, more exactly, hole conduction is greater than electron conduction^{20, 21}. In selenium at room temperature, holes exhibit conventional Gaussian transport with a mobility of $0.1 \text{ cm}^2 (\text{Vs})^{-1}$. However, at low temperatures and, in several materials, at room temperature, holes exhibit so-called dispersive transport, and the effective mobility decreases to $10^{-5} \text{ cm}^2 (\text{Vs})^{-1}$ or even less. Such hole motions are described in terms of multiple trapping

with band-tail states or hopping transport in gap states. In general, the position of Fermi energy, which may be located near the center of the band gap, cannot be controlled by impurity doping. However, there are a few exceptions, such as Bi-Ge-Se, Pb-Ge-Se and Pb-In-Se, in which thermo power indicates n-type conduction²²⁻²⁸.

Optical Properties

Extensive studies have been made on photo-induced phenomena in CGs^{29,30}. At least seven distinct photo-induced phenomena are observed in amorphous chalcogenides but not usually in crystalline chalcogenides. Photo-induced phenomena observed in CGs can be classified into two groups (Fig. 4): i) It includes heat-mode phenomena, in which the heat generated through non-radiative recombination of photo-excited carriers triggers atomic structural changes; and ii) Photon-mode, which can further be divided into the phenomena observed under illumination and after illumination. The best-known heat-mode phenomenon may be the optical phase change, or the optical Ovonic effect²⁹. This phenomenon appears in tellurium compounds, which undergo thermal crystallization. A light pulse heats the film sample above crystallization temperature, resulting transformation from amorphous to crystalline phases. In some materials, this change is reversible. That is, a more intense light pulse heats the sample above melting temperature, and a successive temperature quenching can reproduce original amorphous structure.

As for the photon-mode phenomena, reversible photo-darkening and related changes have been extensively studied^{29,30}. Here, light illumination induces a red shift of the optical absorption edge, so that the sample becomes darker, while the red shift can be reversed with annealing at the glass-transition temperature. Refractive index in transparent wavelength regions increases with the red shift, which is consistent with the expectation obtained from the Kramers-Kronig relation. Sample volume, elastic, and chemical properties also change with illumination and recover with annealing. As for the light, band gap illumination ($h\nu = E_g$) has been assumed to be effective. However, sub-gap light with photon energy lying in Urbach-tail region also produces some changes, which can be more prominent than those induced by band gap light²⁹.

Photo-darkening phenomenon continues to attract extensive interest, since this is a simple bulk

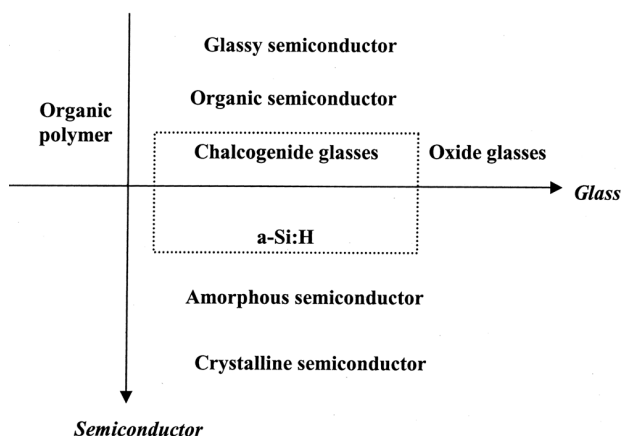


Fig. 3—Characterization of chalcogenide glasses as glasses and semiconductors in comparison with other materials

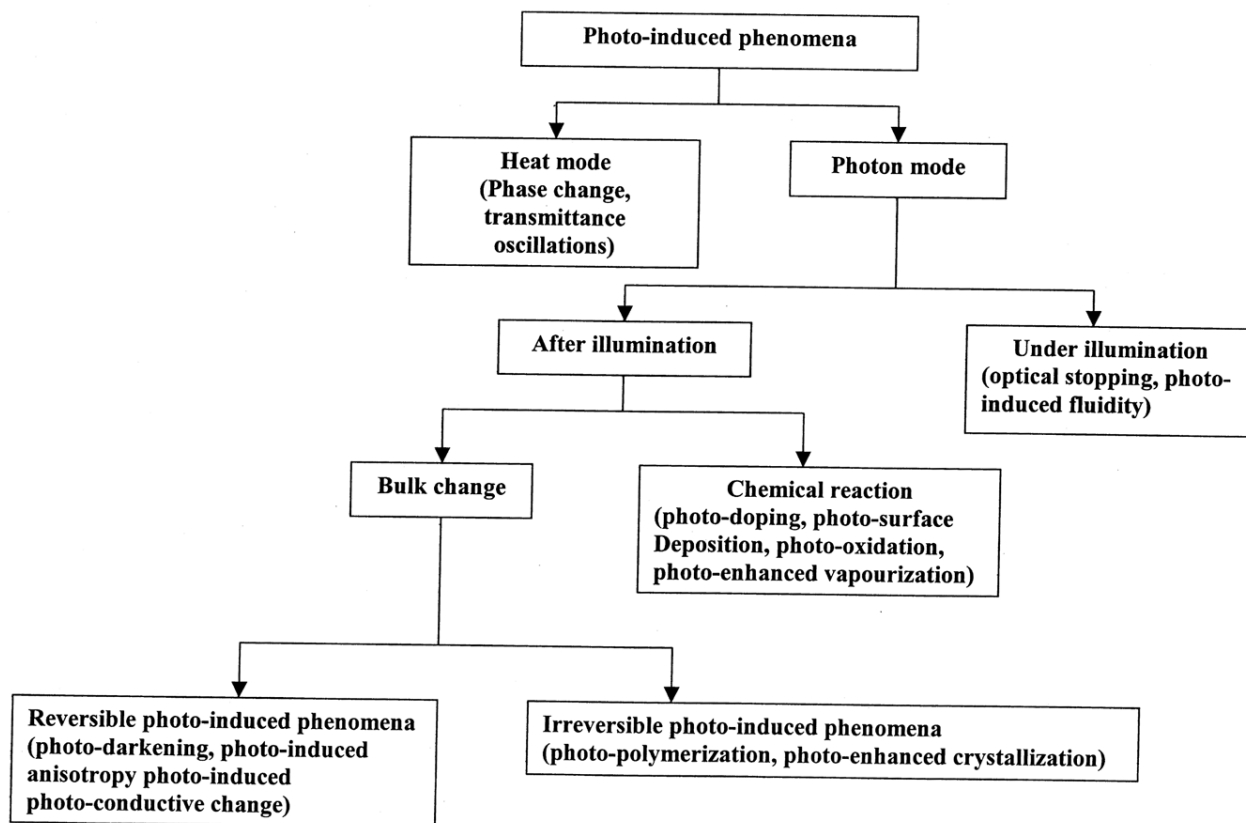


Fig. 4—Flow chart of photo-induced phenomena in chalcogenide glasses

phenomenon, which is characteristic of CG. That is, it does not appear in the corresponding crystal. Some structural studies have demonstrated that the amorphous structure becomes more disordered with illumination. However, it is difficult to identify explicitly the structural change in amorphous phases, and the mechanism is not yet elucidated. An example of photo-thermal bulk phenomena is the photo-induced anisotropy originally discovered by Fritzsche²⁹. Macroscopically, untreated glasses are generally isotropic, while illumination with linearly polarized light can add some anisotropy such as dichroism, birefringence, and axial strains. Even unpolarized light can induce anisotropy if the light irradiates a side surface of a sample²⁹.

Photo-doping is a famous photo-thermal chemical reaction²⁹. Consider a bilayer structure consisting of silver and AsS₂ films. When this bilayer is exposed to light, the silver film dissolves rapidly into the AsS₂. For instance, if the silver film is 10 nm in thickness, and the exposure is provided from the semitransparent silver side using a 100 W ultrahigh-pressure mercury lamp, the silver film will dissolve within few minutes.

Since the reaction becomes slower if the sample is illuminated at lower temperatures, this can be regarded as a photo-thermal phenomenon. However, it should be mentioned that temperature rise induced by illumination is not essential.

There are also several irreversible and transitory changes. Examples are photo-polymerization and photo-induced fluidity²⁹. Not only photons but also other excitations such as electrons can give rise to a variety of structural changes³¹. Some of these are similar to, but others are dissimilar from, the corresponding photon effects. For instance, electron beams can enhance silver doping into chalcogenide films like photons³¹, while the beam can suppress crystallization of Se, in contrast to the photo-crystallization phenomenon. Studies using scanning tunneling microscopes etc. demonstrate nanometer scale structural changes in CGs.

Thermal Properties

Many properties, especially that are time dependent, can be described from the enthalpic / temperature diagram (Fig. 5). When a CG is obtained

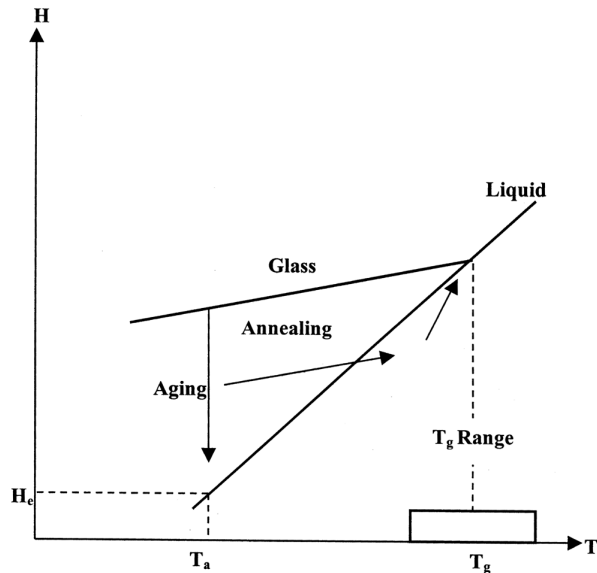


Fig. 5—A typical plot of enthalpy against temperature for chalcogenide glasses

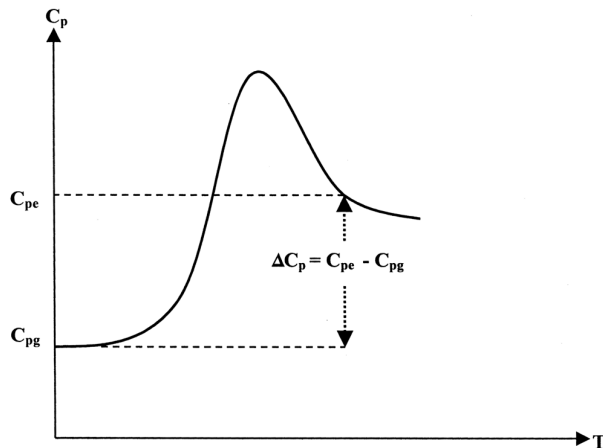


Fig. 6—Temperature dependence of specific heat in chalcogenide glasses

from the liquid state and the cooling rate is high enough, enthalpy will follow the extrapolated liquid equilibrium curve and for a critical temperature, called the fictive equilibrium temperature (T_f), viscosity will increase drastically and enthalpy will leave the equilibrium curve and will reach a non-equilibrium state characterized by an excess of enthalpy³². This last state corresponds to the glassy state. Because of the lack of thermodynamic equilibrium, which characterizes these materials, two important phenomena will appear: i) Heating of a glass will lead to the appearance of a new transition called the glass transition, where the glass upon heating softens at a characteristic temperature, known

as the glass transition temperature, T_g , when molar volumes (V) and enthalpy (H) undergo a qualitative change; and ii) When the glass is maintained at a temperature lower than T_g , it will undergo structural relaxation (physical aging), observed by an enthalpic decrease.

T_g represents temperature above which an amorphous matrix can attain various structural configurations and below which the matrix is frozen into a structure, which cannot easily change to another structure. Therefore, it is reasonable to assume that T_g must be related to the magnitude of cohesive forces within the network since these forces must be overcome to allow for atom movement. Predictions of the T_g are generally based on simple models, in which it is assumed that T_g is proportional to another material parameter, which strongly depends on the cohesive forces or the rigidity of the network. Examples found in the literature of such parameters are average coordination number, enthalpy of atomization, overall mean bond energy, band gap or the average group number³³⁻³⁵. T_g is related to the average co-ordination number $\langle z \rangle$. This relationship can be an exponential function as in³⁶ or follow the modified Gibbs-DiMarzio equation³⁷, which gives a reasonably good prediction of the T_g of CGs especially at low average coordination numbers. Physical quantities (melting temperature, magnitude of photo-darkening, mean atomic volume and width of the band tails in CGs) are also related with T_g ³⁸⁻⁴³.

Specific heat is another important thermal property of CGs, which is useful to understand the thermal relaxation process in these glasses. Specific heat is very sensitive to the way in which atoms or molecules are dynamically bound in a solid⁴⁴. Thus measurement of such parameter like heat capacity will lead to an effective test for characterizing material as glassy substance. An abrupt change in specific heat at the glass transition is characteristic of the all CGs.

Below glass transition temperature, C_p is weakly temperature dependent (Fig. 6). However, near glass transition temperature, C_p increases drastically with increase of temperature and shows maxima at glass transition temperature. After glass transition temperature, C_p attains a stable value, which is slightly higher as compared to C_p below glass transition temperature. The sudden jump in C_p value for each alloy at glass transition can be attributed⁴⁵ to anharmonic contribution to the specific heat. Overshoot in C_p at the upper end of “ C_p jump” at

glass transition is due to the relaxation effects. The time scale⁴⁶ for structural relaxation is highly dependent both on temperature and on the instantaneous structure itself. The observed peak in C_p at T_g may be due to the fact that the structural relaxation times at this temperature becomes of the same order as the time scale of experiment. Specific heat values after glass transition (equilibrium liquid specific heat, C_{pe}) and before glass transition (glass specific heat, C_{pg}) and their difference (ΔC_p) are found useful for study of thermal relaxation in a particular CG.

Applications of Chalcogenide Glasses

CGs find applications in civil, medical and military areas (Fig. 7) to produce industrially electrical switches, xerographic and thermoplastic media, photo-resistant and holographic media, optical filters, optical sensors, thin films waveguides, nonlinear elements, etc.

The first CG to be commercially developed was As_2S_3 , produced for passive, bulk optical components for the mid-IR in the 1950's. During the next two decades, other S and Se glasses were developed, as well as Se-Te glasses for optical components for the far infrared, which have since been exploited commercially^{47,48}. In 1960's, attention was paid to threshold switching elements, which were able under the pulse of voltage to pass from the state OFF with a very high resistivity to the state ON with low resistivity⁴⁹. Industrial technology was started by S R Ovshinsky who named his optimized element as

ovonic threshold switching^{49,50}. The switching acts in the very short time (< 10 nanosec). A great success was utilization of thin films of CGs as target in vidicon image tube (for TV camera).

Application of CGs in IR optics includes energy management, thermal fault detection temperature monitoring and night vision⁵¹. Black body radiation emitted by room temperature objects such as the human body is in the 8-12 μm region, where Se-Te-based glasses are applicable for thermal imaging. In 1970s, CGs were assessed for 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 production⁴⁷. Though in 1980s, attention was focused on fabrication of ultra-low loss IR fibres for telecom signal transmission to compete with silica optical fibres^{52,53}. Compact fibre-optic systems based on CG fibres have been found suitable for low power transmission, which has applications for industrial welding operations and also for microsurgery in medical and biological conditions^{54,55}. Infrared CG fibers have found useful for bio-sensing experiments on liver metabolism, tumor detection, serum analysis and IR fingerprints of human lung cells in different metabolic conditions.

Photo-induced phenomena in CG fibers were utilized in order to propose a novel type of variable fiber optic attenuator (VFOA)⁵⁶. It can be used in visible and near IR range of spectrum for continuous change of light intensity in fiber optic circuits. Thin films of CGs are promising materials for the integrated optic devices such as lenses, gratings, optical filters, multiplexers and demultiplexors, optical scanners and printer heads, multiple output logical elements etc⁵⁶. A wide variety of light-induced and electron beam changes in CGs allow fabricate on basis of these effects planar and three-dimensional optical waveguides as well as gratings for integrated optics⁵⁶. Other commercial and the today's most promising application for CGs concerns optical lenses for IR radiometry. Recently, moulding technology has been developed, making possible the economical production of very complex and high efficient lenses, which are necessary for thermal imaging application. IR cameras have been made with exclusively CG lenses. Optical performance of the system is the same as the ones using germanium optics which are much

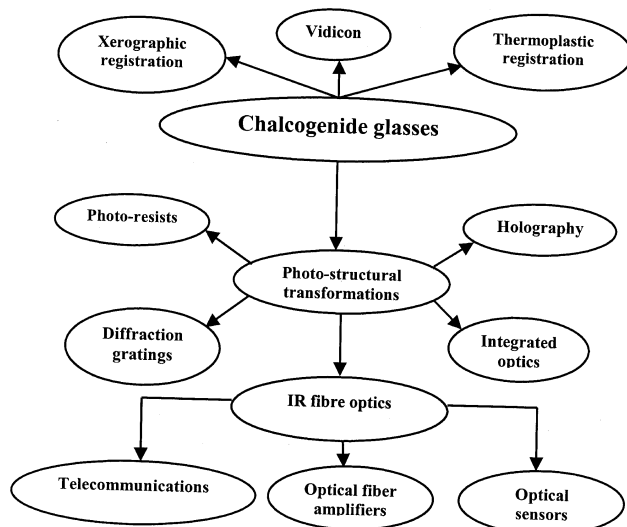


Fig. 7— Applications of chalcogenide glasses in different fields

more expensive. An exceptional resistance to devitrification, especially when large samples of glasses are concerned (Fig. 8). In such samples the presence of small crystallites in the heart of the rod, which is a slow-cooling region, would be detrimental for the optical properties of the lenses.

Optoelectronic methods for processing of information in form of the images, holograms and bits are of great interest for application in the development of the new generation equipment of computers with a great processing speed of the information and in other fields of techniques, such as TV etc. Reversible optoelectronic devices based on metal (Me)-CG semiconductors (ChGS)-dielectric(D)-semiconductor(S)-(ChGSDS) structures were developed and used for writing and readout of the optical images, as a new type sensor of radiation in wide range of energy, and as X-ray solid state image devices⁵⁶.

The progress of science and engineering presents new requirements to holographic recording media: diminishing of the recording time, high stability and possibility of recording over large areas. These requirements are partially satisfied by registration media based on CG semiconductors. At the same time, modern development of the holographic techniques requires recording holograms and reconstruction of images in real time. New recording structures based on CGs and new methods of holographic recording are proposed⁵⁶. The metal photo-dissolution in CGs has features desirable for image creation and storage. Wide IR window of chalcogenides and the high resolution of Fourier transform infrared spectroscopy together permit remote sensing of gases/liquids⁵⁷. Acousto-optical devices based on CGs are proposed, which can rapidly modulate the amplitude and direction of a laser beam⁵⁸.

Photo-induced amorphous to crystalline phase transition and crystalline to amorphous phase transition in CGs could be the basis for optical memory applications. These materials can be reversibly switched between amorphous and crystalline phases and find applications in rewritable optical recording⁵⁹⁻⁶⁵ and in electrically programmable non-volatile memories⁶⁶.

Conclusions

Non-crystalline semiconductors and especially CG semiconductors (ChGS) are important materials that are used/can be used in electronics and

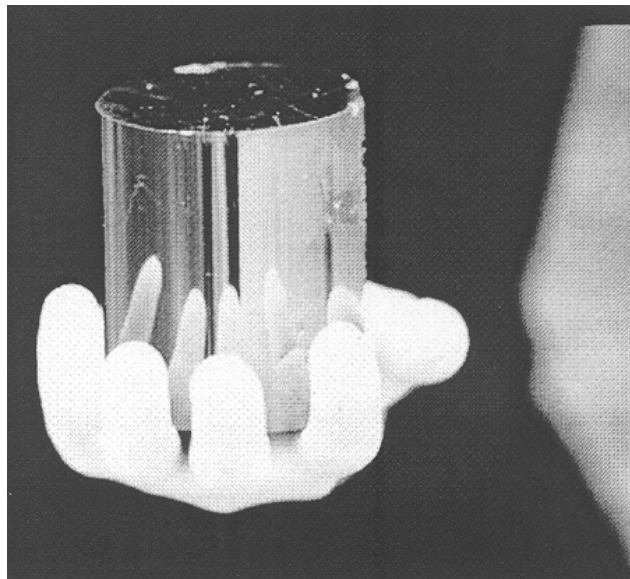


Fig. 8—Chalcogenide glass rod

optoelectronics. These materials contain one or more chalcogen elements, S, Se and/or Te. Advantages of these disordered materials are simple preparation procedures, low sensitivity to impurities, low cost, and possibility to produce large area films of various thickness in classical systems for deposition in systems for evaporation in vacuum, magnetron systems, flash, spin-coating systems, sol-gel systems etc.

Acknowledgement

Author thanks Prof A Kumar, Harcourt Butler Technological Institute, Kanpur for useful suggestions and discussions on the physics of chalcogenide glasses.

References

- 1 Lezal D & Macko P, *Non-Crystalline Semiconductors* (ALFA, Bratislava) 1989.
- 2 Poulain M, *Fluoride Glass Fiber Optics* (Academic Press, Inc., Boston) 1991.
- 3 Goryunova N A & Kolomiets B T, New vitreous semiconductors, *Zhurn Techn Fiz*, **25** (1955) 984-1015.
- 4 Ioffe A F & Regel A R, Non-crystalline, amorphous and liquid electronic semiconductors, *Progr Semiconductors*, **4** (1960) 237-291.
- 5 Anderson P W, Absence of diffusion in certain random lattices, *Phys Rev*, **109** (1958) 1492-1505.
- 6 Mott N F & Twose W D, The theory of impurity conduction, *Adv Phys*, **10** (1961) 107-163.
- 7 Cohen M H, Fritzsche H & Ovshinsky S R, Simple band model for amorphous semiconducting alloys, *Phys Rev Lett*, **22** (1969) 1065.
- 8 Davis E A & Mott N F, Conduction in non-crystalline systems, *Phil Mag*, **22** (1970) 903-927.

- 9 Street R A & Mott N F, States in the gap in glassy semiconductors, *Phys Rev Lett*, **35** (1975) 1293-1296.
- 10 Ovshinsky S R, An introduction to ovonic research, *J Non-Cryst Solids*, **2** (1970) 99-106.
- 11 Ovshinsky S R, in *Physical Properties of Amorphous Materials*, edited by D Adler, B B Schwartz & M C Steele (Institute of Amorphous Studies Series, Plenum Press, N Y) 1985, 105.
- 12 Ovshinsky S R & Klose P H, Imaging in amorphous materials by structural alteration, *J Non-Cryst Solids*, **8-10** (1972) 892-898.
- 13 Tanaka K, Reversible photostructural change: Mechanisms, properties and applications, *J Non-Cryst Solids*, **35-36** (1980) 1023-1034.
- 14 Mott N F & Davis E A, *Electron Processes in Non-Crystalline Materials* (Clarendon Press, Oxford) 1979.
- 15 Lezal D, Pedilkova J, Zavadil J, Kostka P & Poulain M, Preparation and characterization of sulfide, selenide and telluride glasses, *J Non-Cryst Solids*, **326 & 327** (2003) 47-52.
- 16 Lucovsky G, Optic modes in amorphous As_2S_3 and As_2Se_3 , *Physical Rev B*, **6** (1972) 1480-1489.
- 17 Fisher G B & Tauc Y, *Proc 5th Int Conf Amorphous and Liquid Semiconductors*, edited by I Stuke & W Brenig (Taylor & Francis, London) 1974, 1259.
- 18 Popescu M, Stotzel H & Vescan L, *Proc Int Conf Amorp Semicond'80*, 1, 44, Chisinau, 1980.
- 19 Zallen R, *The Physics of Amorphous Solids* (John Willey & Sons, New York) 1983.
- 20 Elliot S R, in *Chalcogenide Glasses*, edited by J Zarzycki (Materials Science and Technology, VCH, New York) 1991.
- 21 Feltz A, *Amorphous Inorganic Materials and Glasses* (VCH, Weinheim, Germany) 1993.
- 22 Morigaki K, *Physics of Amorphous Semiconductors* (Imperial College Press, London) 1999.
- 23 Tohge N, Minami T & Tanaka M, Electrical transport in n-type semiconducting $Ge_{120}Bi_xSe_{70-x}Te_{10}$ glasses, *J Non-Cryst Solids*, **37** (1980) 23-30.
- 24 Nagel P, Ticha H, Tichy L & Triska A, Electrical properties of glasses in the Ge-Bi-Sb-Se and Ge-Bi-S systems, *J Non-Cryst Solids*, **59-60** (1983) 1015-1018.
- 25 Tohge N, Matsuo H & Minami T, Electrical properties of n-type semiconducting chalcogenide glasses in the system Pb-Ge-Se, *J Non-Cryst Solids*, **95-96** (1987) 809-816.
- 26 Bhatia K L, Parthasarathy G, Gopal E S R & Sharma A K, Study of effects of dopants on structure of vitreous semiconductors $(GeSe_{3.5})_{100-x}M_x$ (M=Bi, Sb) using high pressure techniques, *Solid State Commun*, **51** (1984) 739-742.
- 27 Bhatia K L, Parthasarathy G, Gosain D P & Gopal E S R, Role of dopants in pressure-induced effects in glassy $GeSe_{3.5}$ containing Bi and Sb, *Phil Mag B*, **51** (1985) L63-L68.
- 28 Kohli S, Sachdeva V K, Mehra R M & Mathur P C, High pressure studies on n-type Se-In-Pb chalcogenide glasses, *Phys Stat Sol (b)*, **209** (1998) 389-394.
- 29 Fritzsche H, Light induced effects in glasses, in *Insulating and Semiconducting Glasses*, edited by P Boolchand (World Scientific, Singapore) 1993.
- 30 Shimakawa K, Kolobov A & Elliott S R, Photoinduced effects and metastability in amorphous semiconductors and insulators, *Adv Phys*, **44** (1995) 475-588.
- 31 Kolobov A & Elliott S R, Photodoping of amorphous chalcogenide glasses, *Adv Phys*, **40** (1991) 625-684.
- 32 Tool A Q & Eichlin C, Variations caused in the heating curves of glass by heat treatment, *J Am Ceram Soc*, **14** (1931) 276-308.
- 33 DeNeufville J P, Rockstad H K, Stuke J & Brenig W, in *Proc 5th Int Conf Amorphous and Liquid Semiconductors*, Edited by Stuke J & Brenig W, 1974, 419.
- 34 Lasocka M, Thermal evidence of overlapping effects of glass transition and crystallization, derived from two different glassy phases in the phase-separated system $Te_{80}Ge_{12.5}Pb_{7.5}$, *J Mater Sci*, **13** (1978) 2055-2059.
- 35 Tichy L & Ticha H, Covalent bond approach to the activation energy of the glass-transition temperature of chalcogenide glasses, *J Non-Cryst Solids*, **189** (1995) 141-146.
- 36 Tanaka K, Glass transition of covalent glasses, *Solid State Commun*, **54** (1985) 867-869.
- 37 Sreeram A N, Varshneya A K & Swiler D R, Microhardness and indentation toughness versus average coordination number in isostructural chalcogenide glass systems, *J Non-Cryst Solids*, **130** (1991) 225-235.
- 38 Mahadevan S & Giridhar A, Copper as an additive in the $As_{0.4}Se_{0.3}Te_{0.3}$ glass: Mean atomic volume and T_g , *J Non-Cryst Solids*, **221** (1997) 281-289.
- 39 Mahadevan S & Giridhar A, Mean atomic volume, T_g and electrical conductivity of $Cu_x(As_{0.4}Te_{0.6})_{100-x}$ glasses, *J Non-Cryst Solids*, **238** (1998) 225-233.
- 40 Rabinal M K, Chemical ordering in $Ge_{20}Se_{80-x}In_x$ glasses, *J Non-Cryst Solids*, **188** (1995) 98-106.
- 41 Giridhar A & Mahadevan S, Cu as an additive in the $As_{0.4}Se_{0.2}Te_{0.4}$ glass: Mean atomic volume and T_g , *J Non-Cryst Solids*, **248** (1999) 253-256.
- 42 Giridhar A & Mahadevan S, Mean atomic volume and T_g of $Ag_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ glasses, *J Non-Cryst Solids*, **258** (1999) 207-215.
- 43 Mahadevan S & Giridhar A, Mean atomic volume and T_g of Cu-Ge-As-Se glasses, *J Non-Cryst Solids*, **275** (2000) 147-152.
- 44 Tiwari R S, Mehta N, Agarwal P, Shukla R K & Kumar A, Specific heat studies in glassy $Se_{78}Ge_{22}$ and $Se_{68}Ge_{22}M_{10}$ (M=Cd, In, Pb) alloys, *Indian J Pure Appl Phys*, **43** (2005) 363-368.
- 45 Mahadevan S, Giridhar A & Singh A K, Calorimetric measurements on As-Sb-Se glasses, *J Non-Cryst Solids*, **88** (1986) 11-34.
- 46 Ma H L, Zhang X H & Lucas J, Relaxation near room temperature in tellurium chalcogenide glasses, *J Non-Cryst Solids*, **140** (1992) 209-214.
- 47 Savage J A, *Infrared Optical Materials and their Antireflection Coatings* (Adam Hilger, Bristol), 1985.
- 48 Hilton A R, Jones C E & Brau M, Non-oxide IV-VA-VIA chalcogenide glasses, *Phys Chem Glasses*, **7** (1966) 105-126.
- 49 Ovshinsky S R, *Proc 20th Int Semicond Conf CAS'97* (IEEE publications, Sinaia, Romania) 1997, 33.
- 50 Ovshinsky S R, in *Homage Book*, edited by M Popescu (INOE & INFIM Publishing House, Bucharest, Romania) 1999, 15.
- 51 Johnson R B, Proc Soc Photo-Optical Instrumentation Engrs, *SPIE*, **915** (1998) 106.
- 52 Katsuyama T & Matsumura H, *Infrared Optical Fibres* (Adam Hilger, Bristol) 1989.

- 53 Parker J M & Seddon A B, *High Performance Glasses*, edited by M Cable & J M Parker (Blackie, London) 1992.
- 54 Keirsse J, Boussard-Pledel C, Loreal O, Sire O, Bureau B, Leroyer P, Turlin B & Lucas J, Chalcogenide glass fibers used as biosensors, *J Non-Cryst Solids*, **326-327** (2003) 430-433.
- 55 Keirsse J, Boussard-Pledel C, Loreal O, Sire O, Bureau B, Leroyer P, Turlin B & Lucas J, IR optical fiber sensor for biomedical applications, *Vib Spectrosc*, **32** (2003) 23-32.
- 56 Andriesh A M, Iovu M S & Shutov S D, Chalcogenide non-crystalline semiconductors in optoelectronics, *J Optoelectron Adv Mater*, **4** (2002) 631-647.
- 57 Nishi J, Morimoto S, Inagawa I, Iizuka R, Yamashita T & Yamagishi T, Recent advances and trends in chalcogenide glass fiber technology: a review, *J Non-Cryst Solids*, **140** (1992) 199-208.
- 58 Seddon A B & Laine M J, Chalcogenide glasses for acousto-optic devices. II. As-Ge-Se systems, *J Non-Cryst Solids*, **213 & 214** (1997) 168-173.
- 59 Ohta T, Phase-change optical memory promotes the DVD optical disk, *J Optoelectron Adv Mater*, **3** (2001) 609-626.
- 60 Zhou Gou-Fu, Materials Aspects in phase change optical recording, *Mater Sci Engin A*, **304-306** (2001) 73-80.
- 61 Lankhorst M H R, Modelling glass transition temperature of chalcogenide glasses applied to phase-change optical recording materials, *J Non-Cryst Solids*, **297** (2002) 210-219.
- 62 Kolobov A V & Tominaga J, Chalcogenide glasses in optical recording: Recent progress, *J Optoelectron Adv Mater*, **4** (2002) 679-686.
- 63 Bureau B, Zhang X H, Smektala F, Adam J, Troles J, Ma H, Boussard-Pledel C, Lucas J, Lucas P, Coq D L, Riley M R & Simmons J H, Recent Advances in chalcogenide glasses, *J Non-Cryst Solids*, **345 & 346** (2004) 276-283.
- 64 Popescu M, Disordered chalcogenide optoelectronic materials: Phenomena and applications, *J Optoelectron Adv Mater*, **7** (2005) 2189-2210.
- 65 Lezal D, Zavadil J & Prochazka M, Sulfide, selenide and telluride glassy systems for optoelectronic applications, *J Optoelectron Adv Mater*, **7** (2005) 2281-2291.
- 66 Ovshinsky S R, *Proc CAS 1* (IEEE publications, Sinaia, Romania) 1998, 33.