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Review Article

Physical Properties and Applications of Chalcogenide Glasses - A Brief Study

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ABSTRACT

Chalcogenide glasses based on sulfide, selenide and telluride alloys in binary or multi-component systems are very promising materials for various optical and photonic applications in the spectral range 0.6 to 15 mm. These glasses are being studied mostly for applications as passive devices but these glasses are also attractive for preparation of active devices such as laser fibre amplifiers and non-linear components. 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. Recently, a new technology for the deposition of chalcogenide glass materials as thin films onto a given silicon substrate could be introduced, namely the pulsed laser deposition technique. Chalcogenidefibers are well suited for chemical sensing applications since practically most molecular species vibrate in the infrared region. The chalcogenidefibers can be used in fiber optic chemical sensor systems for quantitative remote detection and identification as well as detecting chemicals in mixtures.

Keywords: Glasses, Chalcogenide, Fibers, Properties, Applications.

1.INTRODUCTION

In conjunction with more electropositive elements most 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. These glasses are low-phonon energy materials and are generally transparent from the visible up to 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. These glasses are optically highly non-linear and could therefore be useful for all optical switching. 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 fiberstructures[1].When a liquid is cooled below its melting temperature very slowly, it is supposed to undergo crystallization. However, quite often the system freezes into states other than a crystal. Such states are categorized generally as glass. However, the feature that distinguishes glasses from other states of matter is that a glassy state generally depends on how it is formed, and lowering the temperature is just one of numerous means of forming a glass. This means that a glassy state cannot be uniquely specified by giving thermodynamic variables of that state like pressure and temperature. In other words, a glass is not in a thermodynamic equilibrium state. This is the source of all the difficulties in constructing a theory of glass[2].

The glass-forming ability of chalcogens or pseudochalcogens combinations has been known for several decades but compared to oxide glasses, especially silicates; this class of vitreous materials is just emerging from their infancy. The main attention paid to these materials relies on their large optical window extending in the mid-infrared and covering usually the two atmospheric windows lying from 3 to 5 and 8 to 12lm. These low-phonon materials have to be considered as heavy anion glasses since sulfur, S, selenium, Se and even tellurium, Te, are the main constituents of their compositions. This situation leads to fundamental vibrational materials modes shifted far in the IR, and rending these glasses interesting for the fabrication of thermal-imaging systems[3]. This exceptional transparency, associated with suitable viscosity/temperature dependence, creates a good opportunity for the development of molded optics for low-cost infrared cameras. It must be noticed that these chalcogenide glasses also exhibit unique properties, such as photo-darkening, giant photo-expansion as well as photo-fluidity when irradiated by appropriate light. These photo-induced phenomena will not be discussed here. Therefore, these glasses, which contain large polarizable atoms associated with external lone-pair electrons, are prone to exceptional non-linear optical properties when irradiated by an electromagnetic field[4].

Chalcogenide glasses always contain one or more chalcogen element, sulphur, selenium or tellurium in combination with elements from IV, V or VI group of the periodic system of elements. Glasses are solids with covalent bonds, maximum of ionic conductivity is 9% and their properties are significantly different from oxide glasses on the base of SiO_2. Chalcogenide glasses based on sulfide, selenide and telluride alloys in binary or multi-component systems are very promising materials for various optical and photonic applications in the spectral range 0.6 to 15 mm. These glasses are being studied mostly for applications as passive devices but these glasses are also attractive for preparation of active devices such as laser fibre amplifiers and non-linear components. Since the chalcogenide glasses transmit to longer wavelengths in the IR than silica and fluoride glasses, there are numerous potential applications in the civil, medical and military areas. These can be essentially divided into two groups, namely “passive” and “active” applications. The passive applications utilize chalcogenidefibers as a light conduit from one location to another without changing the optical properties, other than that due to scattering, absorption and end face reflection losses associated with the fiber. Active applications of chalcogenide glass fibers are where the initial light propagating through the fiber is modified by a process other than that due to scattering, absorption and end face reflection losses associated with the fiber. Examples of these include fiber lasers, amplifiers, bright sources, gratings and non-linear effects.

2.PROPERTIES

2.1 Chemical structure properties

Chalcogenide glasses are based on the chalcogen elements S, Se and Te combined with network-forming elements, such as Ge, As, P, Sband Si. The resulting glass exhibits a number of amorphous semiconductors like properties. The glass structure consists of covalently bonded molecules, as opposed to the ionic bonding of other glasses and these are weakly bound together via a combination of covalent and Van der Waals-like attraction. Chalcogenide glasses may form with a wide range of compositions as both hetropolar and homopolar bonds may form. In the case of the As-S glass system, the atomic ratio of arsenic to sulfur can be varied between 1.5 and 9. As a result, the composition of the chalcogenide glasses can be adjusted to tune particular properties. For a given chalcogenide glass system, increasing the relative atomic mass of the chalcogen or its proportion in the glass reduces the average bond strength. The weaker bonds of chalcogenide glasses contribute to them being generally less robust than oxide glasses. For example they have lower softening temperatures and hardness, and higher thermal expansion coefficients[5].

2.2 Refractive index and dispersion

Chalcogenide glasses possess relatively large refractive indices between 2 to greater than 3. The refractive index increases as sulfur is replaced by the more polarizable selenium and tellurium. The high refractive index is advantageous for strong optical field confinement which allows small waveguide bend radii and enhanced optical intensities. In addition, the large index contrast relative to air can potentially provide a complete band-gap for photonic crystals. The zero dispersion wavelengths for chalcogenide glasses lie well in the mid IR. At communication wavelengths around 1.55 µm these materials exhibit strong normal dispersion. This is not necessarily detrimental to performance as typical device lengths are short, of the order of centimetres and the dispersion sign ensures that possibility of using waveguide dispersion to engineer the chromatic dispersion, similar to what has been achieved in silicon[6].

2.3 Linear loss mechanisms

For chalcogenide glasses the long wavelength cut-off lies in the mid infrared due to large atomic masses and relatively weak bond strengths resulting in low phonon energies. As a rule of thumb, the transparency edge is 12 µm for sulfide based glasses, 15 µm for selenide glasses and 20 µm for telluride glasses. In the absence of extrinsic attenuation mechanisms, Rayleigh scattering defines the minimum attenuation of the glass within the electronic and multiphoton absorption window. Free carrier absorption is generally negligible in Chalcogenide glasses. While most chalcogenide glasses have small band gaps, they also exhibit low carrier mobility. As the magnitude of the free carriers in solids in the low mobility case is proportional to the carrier mobility, free carrier absorption is not important in chalcogenide glasses. However chemical impurities, particularly oxygen can result in a drastic reduction in infrared transmission. Typically ultra pure chemicals must be further purified, for example by hydrogen distillation, before being melted either under vacuum or within a nitrogen environment to create bulk glasses[7].

2.4 Photo-induced phenomena

Chalcogenide glasses exhibit several types of photo-induced phenomena including: photocrystallisation, photo-polymerization, photodecomposition, photo-contraction, photovaporisation, photo-dissolution of metals and light-induced changes in local atomic configuration. These changes are accompanied by changes in the optical band gap and thus optical constants. Chalcogenide glasses exhibit strong photo-induced properties because of their inherent structural flexibility. The usually double covalent bonded chalcogen atom possesses a lone pair of non-binding electrons that under illumination can alter the bond number. These photo induced effects have been used for the formation of various components including waveguides and surface gratings[8].

3. APPLICATIONS

Recently, a new technology for the deposition of chalcogenide glass materials as thin films onto a given silicon substrate could be introduced, namely the pulsed laser deposition technique. This technique became its “breakthrough” in the end of the eighties. Due to the discovery of high temperature superconductors, the PLD represents an important tool for the preparation of a wide spectrum of functional materials, like e.g. diamond-like carbon. Another field for PLD is the fabrication of optical wave guides with low optical losses and the realization of complex oxides for the fabrication of high-temperature superconducting quantum interference detectors[9]. The advantage of the PLD is the stoichiometric transfer of even complex materials, e.g. chalcogenide glasses, to be deposited into their thin-film state, an easy set-up and short process times]. Different chalcogenide glass systems ($PbSAgIAs_2S_3$, $CdSAgIAs_2S_3$, CuAgAsSeTe and TlAgAsIS) have been prepared as thin-film sensors for the detection of heavy metals (Pb^{2+}, Cd^{2+}, Cu^{2+} and Tl^{+}) in aqueous media. The integration of different chalcogenide glass-based thin films onto one sensor chip offers the possibility to realize multi-sensor systems. As a first step, three different chalcogenide glass materials for the detection of Pb^{2+}-, Cd^{2+}- and Cu^{2+}-ions in aqueous solution have been integrated onto one silicon chip. The thin films have been physically characterized by means of Rutherford backscattering spectrometry, scanning electron microscopy and video microscopy[10]. The electrochemical sensor characterization has been performed by means of ion-selective potentiometry and impedance spectroscopy.

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 also make them ideal for incorporation into lasers and other active devices especially if doped with rare earth ions. 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 PRAM. Examples of such phase change materials are GeSbTe and AgInSbTe. In optical discs, the phase change layer is usually sandwiched between dielectric layers of $ZnS\text{-}SiO_2$, sometimes with a layer of a crystallization promoting film. Other less common such materials are InSe, SbSe, SbTe, InSbSe, InSbTe, GeSbSe, GeSbTeSe and AgInSbSeTe. 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.

Chalcogenidefibers are well suited for chemical sensing applications since practically most molecular species vibrate in the infrared region. The chalcogenidefibers can be used in fiber optic chemical sensor systems for quantitative remote detection and identification as well as detecting chemicals in mixtures. Examples of different sensing techniques include evanescent/ATR, diffuse reflectance and absorption spectroscopy. The diffuse reflectance and evanescent/ATR techniques are useful for samples that scatter or are opaque at the IR wavelengths. Numerous systems have been studied and many species have been detected including aqueous, non-aqueous and toxic liquids as well as solids[11]. Examples include oil, freon, soap, paints, polymer curing reactions, glucose/water, benzene and derivatives, chlorinated hydrocarbons, alcohols, carboxylic acids, aqueous acids, perfumes and pharmaceutical products. A fiber optic dipstick probe could potentially monitor the quality of the oil and consequently save large amounts of money in preventing unnecessary oil changes in the military and civil sector. For example, there is an additive package used to inhibit viscosity breakdown of engine oil. Unfortunately, the environmental breakdown of the additive package occurs and leads to viscosity breakdown of the oil.

Optical amplification at 1.083 lm with neodymium doped chalcogenidefibers was observed in a glass composition of Ge–As–Ga–Sb–S. A maximum internal gain of 6.8 dB was achieved for a pump power of 180 mW. The first amplified spontaneous emission in a chalcogenide glass fiber was also reported. A selenide glass has been developed that can be doped with rare-earth ions and is stable against crystallization during fiberization[12]. The glass is based on GeAsGaSe and can be doped with Pr3+ and Dy3+ for near- and mid-IR applications. The doped glasses have been fiberized with core only losses of 0.8 dB/m at 6 lm and 1.5 dB/m at 2.5 lm. Single-mode fibers have been drawn with a measured core loss of 3 dB/m at 1.55 lm.

4.CONCLUSIONS

In conjunction with more electropositive elements most 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. These glasses are low-phonon energy materials and are generally transparent from the visible up to 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. These glasses are optically highly non-linear and could therefore be useful for all optical switching. Chalcogenide glasses are sensitive to the absorption of electromagnetic radiation and show a variety of photo induced effects as a result of illumination. Chalcogenidefibers are well suited for chemical sensing applications since practically most molecular species vibrate in the infrared region. 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.

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