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Chalcogenide Glasses Opto-Electronic Applications

Neelam Sinha
Associate professor
Dept. of Physics
S.D. College, Muzaffarnagar, U.P., India

Abstract

Chalcogenide glasses (ChGs) are of great interest for the researchers because of their novel and promising properties. Chalcogens are technologically very important materials which contain at least one chalcogen element as a major constituent. The utilization of ChGs is in a vast range, from Infrared (IR) optical applications to phase-change, optical-electrical data recording applications.

ChGs possess several extraordinary properties making them interesting materials, when compared to other kinds, especially for the opto-electronic applications[1]. This chapter is dedicated to the discussion of the optical, electronic and optoelectronics properties of ChGs with their applications in sensing devices in different areas depending upon the transmission in IR spectral region.

Key words: Chalcogenide glass (ChGs), fiber, Infrared (IR), chalcogen (Ch), opto-electronic.

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Introduction

Chalcogen elements can be found in the 6th group of the periodic table, consisting of O, S, Se, Te and Po. “Char.s” has been derived from the Greek word *chalkós* (ore formers). “Chalcogenides (Ch)” referring to their compounds have metallic character. O and S are non-metals, unlike Se, Te being metalloids and Po is a metal.

ChGs. can be produced by mixing the chalcogen elements such as S, Se and Te with Ga, In, Si, Ge, Sn, As Sb and Bi, Ag, Cd, Zn etc. belonging to an important class of amorphous solids[2]. Glass being an amorphous and isotropic material, can also be defined as an organic fusion product cooled down to a rigid form without any crystallization.

Optical Properties of Chalcogenide glasses and fibers

ChGs have been known as optical materials for about the last sixty five years. The applications of Ch as materials for fiber optics especially for the mid-IR range has been observed during the past 30 to 35 years[3]. The ChGs are made from chalcogen elements sulfur, selenium and tellurium alloyed with the III-V group elements such as germanium, arsenic and antimony[4]. These glasses typically possess a broad range of IR transparency, low optical attenuation, limited visible transparency, high optical nonlinearity, large refractive index and are generally chemically stable to atmospheric moisture. Ch are widely used in windows, lenses and fibers for IR and beyond 2 micrometer wavelengths. These can be divided into two groups called active and

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passive fibers. In active fibers the 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. Fiber lasers, amplifiers, bright sources, grating and non-linear effects are examples of active fibers. The fibers are used for the transmission of light from one location to another without interacting with the light and without much losses other than that due to absorption scattering, end face reflection etc. losses associated with the fiber.

Electronic and Optoelectronic Properties

The silicates and quartz glasses are of the importance which transmit the radiation in visible range in the electromagnetic spectrum. The demand for Chs which can transmit radiation in IR region up to the wavelength of the order of 2 micrometer is increased in the application of optics, photonic and optoelectronics. These Chs which are called special glasses, can be divided into 3 groups:

1. Fluoride glasses – made of ZrF_4, Hf F_4 etc.,
2. ChGs – based on Chalcogen (S, Se, Te) e.g. As-S, As-Se, As – Se – Te, Ge-Se-Te, Ge-As-Se
3. Heavy metal oxide e.g., GeO_2 – PbO, TeO_2 – PbO, TeO_2 –ZnO etc.,

Nowadays special glasses especially ChGs are of immense interest due to their promising properties as transmission in middle and far IR regions of electromagnetic spectrum.

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It was shown that amorphous ChGs are semiconductors and also found that the band gap depends on the existence of short-range order of the lattice and suggested that the first coordination number of the corresponding crystal is preserved in the amorphous structure.

Chalcogens are known as perspective materials of optoelectronics with a high optical transparency in the infrared region of telecommunication windows 3-5 m and 8-12m. It is observed that due to the addition of the Talinum quantity in the Ge-Te-Se system the IR transparency window of ChGs increases towards a longer wavelength up to 20meter. The problems regarding global warming or greenhouse effect can be resolved by using ChGs in the far IR region.

The main disadvantage of ChGs is their natural physical aging that may be up to 20 years.

Applications of Active ChGs fibers

ChGs adopted with rare earth ions[5] possess characteristic electronic energy levels which can only be slightly influenced by the original matrix due to the screening effect of the electrons. When given with appropriate energy, the electrons get excited into upper levels from which they subsequently decay to lower levels. In this process certain transitions become increasingly more efficient in longer wavelengths. Transmitting hosts such as the ChGs due to less multiphoton quenching and IR fluorescence emissions beyond 2 micrometers are only seen in ChGs not in Silica. In Table (1)[2] the applications of active ChGs fibers in different

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fields with composition is shown. It is seen that in only Nd ChGs laser oscillations are observed at 1.08-meter wavelength while amplification has been observed at 1.08 micrometer. These are the results obtained in sulfide glass hosts. For the telecommunications' purpose 1.3meter wavelength is of interest.

Table 1[2]

Sensor	Glass composition	Year	Developer
Cell potential on pH	Lithium silicate glass	1906	Cremer
Glass electrode	$Na_2O – Al_2O_2 – SiO_2$	1957	Eisenman
Semiconductor gas sensor	SnO_2	1962	Sugiyama, Taguchi
Ion exchange membrane	Calcium selective electrodes	1967	Ross
Potentiometric biosensor	Asparagine, glutamine, urea, leucine, D- and L-tyrosine and	1969	Gibault, Montalvo

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	proline		
PVC based ISEs	Polyvinyl chloride	1971	Moody, Thomas
Gas FET	Carbon nanotube	1975	Lundstrom
First Commercial ISFET-EMI Microsensor	ISFET based	1986	Thorn
Electronic Noise	Cu doped Tin Oxide	1982	Persaud, Dodd
Taste Sensor	Polymer based	1992	Toko
Electronic tongue	Cu based chalcogenide glasses	1995	Vlasov, Di Natale, Legin
Radiation sensor	Ge-Sb-Se	2006	A Ganjoo, J.V. Ryan, H. Jain, C.G. Pantano, R. Song, J. Irudayaraj, C.Yu, Y.J. Ding

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Nitrogen di-oxide gas sensing	Ge-Se	2012	Ping Chen, Dmitri A. Tenne, Maria Mitkova, Kasandra Wolf, Lazar Vergov, Velichka Georgieva
Radiation Sensor for nuclear wastes	Ge-Se	2014	M.S. Ailavajhala, M. Mitkova, Y. Gonzalez Velo, C.D. Poweleit, M.N. Kozicki, H.J. Barnaby, D.P. Butt
Chemical sensor	Ge-Se-Te	2015	Xin Jiang, Animesh Jha
Biosensor for detection of human tissue	Ge-As-Se	2018	Anuj K. Sharma, Jyoti Gupta, Rikmantra Basu

The rare earth doped ChGs fibers emit in the region 2 - 5 micrometer wavelength[6] hence they are attractive alternatives to black body sources for many applications. InSb[7] is an example of arrays of the fibers that can be used

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for IR seen simulation for characterization of local plane array detectors. The emission spectrum of a Pr-doped selenide glass fiber demonstrated broadband emission between 3 - 5 micrometer wavelength. Prototype bundles have been fabricated and mid I-R emission measured from the pixels. Black body temperatures up to 2400K have been simulated in single pixel pumping, indicating that these fibers are capable of providing bright sources in the Infra-red region.

ChGs based optical fiber are the suitable materials for preparing solid membranes for various types of sensors which can be developed both as low-selective sensors and high-selective sensors. Due to their good transparency in IR region 0.6 – 2.0 micrometer, low optical losses, low phonon energy 200-300 cm^{-1}, good chemical stability, high nonlinearity of optical properties, ChGs have the probability to produce long length fibres[8]. It has been a challenge to find out the membrane materials for sensors which could respond to the concentration of molecules.

ChGs sensors have larger efficiency in transforming the photoelectric effect and may form a junction when contacted with metal hence they can be used as Image sensors as these possess photo conductive property.

A respiratory sensor is used in detecting carbon dioxide in the exhalation of a patient. The chalcogenide material AS2S3 is used for this sensor can be operated in the temperature range 7^0C to 127^0C. These sensors have low cost due to its small size hence suitable for respiratory sensors.

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The biomedical sensor is a graphene based three-layer sensor with ChGs composition As4OS6O for core and Ge20GasSb10S65 for cladding. These sensors are used in analyzing hemoglobin concentration in human blood because of its chemical stability. Biomedical sensors can detect the extremely small level of hemoglobin concentration.

Applications of Passive ChGs fibers

Passive ChGs fibers are enabling numerous applications in many areas for example laser power delivery, chemical sensing, near-field microscopy etc.,

Laser Power Delivery

High Power carbon monoxide and carbon dioxide lasers operate at 5.4 micrometer and 10.6 micrometers can be used for industrial welding and cutting. Transmitting the laser power through fibers enables remote operation.

Small core diameter fibers less than 200 micrometer fibers have demonstrated tolerance to power densities of the order of 125 $KWcm^{-2}$ at 5.4 micrometer and 5.4 $KWcm^{-2}$ at 10.6 micrometer without damage. The arsenic sulfide fibers transmit in the atmospheric 2-5 micrometer region and can be used for transmission of laser power in the region. Medical free electron laser (MFEL) operating between 2-10 micrometer through ChGs fiber is of interest also. MFEL can emit more than 10 MW of power in fermi second pulse that relates to an average power of greater than 10W.

Chemical sensing

One of the important sensors is Chemical Sensor.

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The important parameters for this sensor are response time, selectively and cross sensitivity, lifetime, potential stability and the concentration limit and ph-value region. The ion-selective sensors are based on the ChGs having long term stability with study potential at the time of continuous measurements[11]. This solid-state design has low detection limits, high stability in strong acids and also in corrosive media, high sensitivity and long lifetime. For this purpose, ChGs show easier shaping, higher chemical durability and stability over time, thus it can be used in sensor applications. Another reason ChGs fiber is used in Chemical sensing is that its most molecular species vibrate in the IR region. ChGs fibers may be used in fiber optic chemical sensor systems for quantitative remote detection and identification. Examples of different chemical sensing techniques include ATR (attenuated total reflectance) diffuse reflectance and absorption spectroscopy. The diffuse reflectance and evanescent / ATR techniques are useful for samples that scatter IR wavelengths or opaque to IR wavelengths. Many species have been studied and detected including aqueous, non-aqueous and toxic liquids as well as solids. Examples include soap, oil, Freon, paint polymer curing reactions, benzene and derivatives, glucose, water, alcohols, carboxylic acid, aqueous acids, chlorinated hydrocarbons, perfumes and pharmaceutical products.

Near-field microscopy

The high-quality single mode and multimode ChGs fibers and recently used to demonstrate about 20nm

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topographic resolution and about 200 nm spectral resolution for different samples such as pancreatic cells, polycrystalline diamond, biofilms and semiconductor samples. This is a promising technique for imaging and biological samples with sub-micron resolution.

Some of the ChGs based sensors are shown in table (2).

Table 2

Passive Application	**Active Applications**
Laser power delivery	Rare – earth doped fibers
5 4 m (CO)	Fiber lasers: 1.08m (Nd)
10.6 m (CO_2)	Amplifiers
Atmospheric 2-5 m region	1.08m (Nd)
Medical free electron laser (2-10 m)	1.34m (Pr)
Anti-reflection (AR) costings	1.34m (Dy)
Chemical sensing	Infrared scene simulation (IRSS)
Aqueous, non-aqueous,	Chemical sensing
toxic-chemicals	Gratings: 1.5m
Polymers,paints,	Non-linear
pharmaceuticals	Optical switching
Condition based maintenance (CBM)	Second harmonic

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Cone penetrometer system Active coatings Bio-medical Temperature monitoring Grinding ceramics **Thermal imaging and hyperspectral imaging:** Coherent fiber bundles Near-field microscopy Imaging and spectroscopy Fiber multiplexing Fiber couples	generation Frequency mixing Electrical poling Raman amplification

Applications of ChGs in Optics and in Optoelectronics

ChGs exhibit several types of photo induced phenomenon e.g., photo crystallization, photo-polymerization, photo-decomposition, photo-vaporization, photo-contraction, photo-dissolution of metals and light induced changes in local atomic configuration. These changes occur due to the change in optical band gap and optical constant. The Chalcogenide atom have double bond structure and possess a lone pair of electrons (non-bounded) which can alter the bond number when illuminated. These photo induced effects are used in the

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formation of various components of waveguides and surface grating[9].

A new technology for the deposition of ChGs material as thin film onto a given SI substrate has been developed in the last two decades called Pulse Laser Deposition Technique (PLD). With the discovery of high temperature semiconductors, the PLD technique became an important tool for the preparation of a wide spectrum of fundamental materials e.g., diamond like C.

Another field for PLD is the fabrication of optical waveguides having low optical losses and the realization of complex oxides for the fabrication of high temperature superconducting quantum interference detectors[10].

Conclusion

The arsenic chalcogenides are of permanent scientific and applied interest as these show high optical transparency in mid IR range, low tendency to crystallization, low concentration of limiting impurities and also low optical losses. Hence a number of technical problems in optics and opto-electronics are efficiently solved through the use of Ch fibers with low optical losses. Several research groups from different countries are now at work on Chs fibers.

Enormous progress has been made in reducing the optical losses of the chalcogenide glass fibers in the past several years resulting in many fold applications. It seems that IR fiber optics will become increasingly more important in future as further improvements are made to enhance the

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quality of the fibers and develop new compositions.

One of the most exciting developments in future is in the area of rare earth ion doping of fibers for IR sources. Using this method, the development of IR lasers and amplifiers will be very useful in civil, medical and military applications. Remote IR spectroscopy and imaging using flexible fibers are used in medical and military applications.

With the development of high quality, low loss and high strength Ch fibers will definitely improve the capabilities of existing technologies as well as enable new technologies.

Hence one can say that the future of ChGs and the fibers look very bright.

References

1. *Bekir, Karasu et.al., Chalcogenide Glasses, Journal of Science and Engineering, Vol. 6, No. 3, 2019 (428-457)*
2. *J. Sanghera et. Al. Applications of ChGs optical fibers Elsevier, Vol. 5, Issue 873-883, 12 Dec. 2002*
3. *Katsuyama and Matsumura, 1988; Devyatykh et.al., 1991; Nishii and Yamashita, 1998*
4. *J. Sanghera, Gibson in Chalcogenide Glasses, 2014*
5. *J. Heo et.al. Rare earth-doped ChGs for laser and amplifier 2014*
6. *B.B. Harbison et.al. US Patent No. 5, 846, 889, 1998*
7. *L.B. Shaw et. Al. SPIE 3368, 1998, 42*
8. *8Johann et.al. "Chalcogenide micro structured optical fibers for mid I-R applications" C.R. Physique, Vol. 18,*

ISBN: 978-81-951728-4-9

P. 19-23, 2017

9. *Galsatyan et.al. J. Light Wave Technol. 1997, 15, 1343*
10. *Saenger et. Al. pulsed laser deposition's part I a review of process characteristics and capabilities, Proc. of Adv. Mat. 1993; 3:1*
11. *K. Richardon et. al. "Progress on the fabrication of on chip integrated chalcogenide (CHG) – based sensors" J. of Non-opt. Phy. & Mat. Vol. 19, no. 1, pp. 75-99 2010*