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Technological Applications of Chalcogenide Glasses

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ABSTRACT: Among material science fields, the field of amorphous semiconductors is much attractive to researchers due to its contribution in various technological devices such as in memory, telecommunication, linear and nonlinear optical devices and in switching devices. In chalcogenide based materials, the freedom from the constraint of atomic periodicity permits a wide range of material compositions to be prepared. The composition dependent reliability is the greatest advantage of chalcogenide glasses that helps to design materials for specific requirements. The applications such as Phase-change memory, Thermal imaging, xerography, optical fibers are discussed in this paper.

Keywords: Chalcogenide glasses; optical fibers; phase-change memory; thermal imaging; xerography

INTRODUCTION

In the present scenario technology demands advanced materials such as light weight gazettes having fastest speed and optical fibres for rapid communication. Hence, the research in material science is progressing day by day. Every field of material science has vital role for developing the technological fields of science to meet the need of society. Among material science fields, the field of amorphous semiconductors is much attractive to researchers due to its contribution in various technological devices such as in memory, telecommunication, linear and non-linear optical devices and in switching devices [1-3]. In these materials, the freedom from the constraint of atomic periodicity permits a wide range of material compositions to be prepared. These semiconductors mainly have three classifications as; tetrahedral amorphous semiconductors (TAS), tetrahedral glasses (TG) and chalcogenide glasses(ChG) on the basis of their chemical properties. Chalcogenide glasses are of great interest due to presence of lone pair electrons in them. The glasses which contain one or more of the chalcogen elements (S, Se, Te) as alloy elements are known as chalcogenide glasses (ChG). The most important elemental constituents of ChG are group [IV] (Si, Ge), group [V](P, As, Sb) and group [VI] (Se, S, Te). They behave as semiconductors, i.e. they exhibit semiconductor behavior with band gap varying from 0.7 to 3.24 eV [4]. They have very interesting physical properties and can be prepared in the bulk as well as thin film forms. Chalcogenide glasses possess properties intermediate between those of organic polymers and oxide glasses. Due to two fold co-ordinated structure of chalcogenide glasses, they can be prepared in wide range of stoichiometric as well as non-stoichiometric compositions. The composition dependent reliability is the greatest advantage of these glasses that helps to design materials for specific requirements such as a good thermal stable glass possessing high T_g offers its applications in high temperature applications. Chalcogenide glasses form an important class of materials. Glass which was previously considered as an optical, dielectric or passive material can now be used to construct phase change materials, optical fibres, memory devices, laser devices, telecommunication devices, detector devices, solar cells, catalysts, television tubes etc. due to heavy research on glasses in the recent years [5-12].

Applications and Discussion: Chalcogenide glasses having at least one element as chalcogen (S, Se, Te) contain several unique properties which create interest in them as compared to other materials for their technological applications [13-15]. The properties such as high refractive index, high nonlinearity and low phonon energy of chalcogenide glasses make them ideal for many active devices such as lasers, photonic integrated circuits, fibre amplifiers etc. Due towide range of compositions as well as doping with varity of additional elements to chalcogenide glasses, these materials have a large scope in fabrication of technological devices. Due to compositional dependence of properties they find a place in almost every field of material science and technology. Now Chalcogenide materials have been used in a wide range of applications due to large transparency region. Some applications or devices in which chalcogenide glasses being used today are; Phase change memory (PCM): Phase-change memory (PCM) is a form of random-access memory that stores data by altering the state of matter rapidly back and forth between amorphous and crystalline on a microscopic scale. Recently PCM is an emerging technology of data storage that combines the unique properties of phase change materials such as fast access time, large electrical contrast, non-volatility, and high scalability. The stability of

chalcogenide materials in both amorphous as well as crystalline phase at moderate temperature and fast transition rate from one phase to another makes these materials useful in memory applications. The amorphous and crystalline phase have contrast optical and electrical properties i.e. amorphous phase has low reflectivity and high resistivity known as reset state while crystalline phase is highly reflective and low resistive known as set state. The switching between these two states is achieved by the application of current pulse. Switching from the high-resistance or reset state occurs when a current pulse is applied that heats the amorphous material above the crystallization temperature for a sufficiently long time for the material to crystallize. Switching from the low resistance or set state is achieved by a high current pulse with a very short trailing edge. This current pulse heats the material above melting temperature and enables very fast cooling (melt quenching) such that the material solidifies in the amorphous state. The resistance state of the memory cell can be read with a sufficiently small current pulse, which does not alter the state of the memory cell. GST (Ge-Sb-Te) is commercially used material for memory. Now these days the emphasis is on multilevel storage chalcogenide materials for high storage with programming [16].

Threshold switching: In threshold switching device the material goes from high resistance (OFF state) to a low resistance state (ON state) at threshold voltage in a very short interval of time and they do not have a stable operating point between the OFF state and the ON state. In threshold switching materials, the ON state requires a small threshold current (I_t) and voltage (V_t) to sustain it i.e. if the current is above threshold current only then the device is in ON state. Once the switching current is below threshold current, the material reverts back to the low conducting OFF state in contrast to the memory switching devices in which ON state is restrained even after the removal of the applied field i.e. even when current reaches zero and application of suitable current pulse will restore the original OFF state. The quaternary systems like Si-Te-As-Ge (STAG) [17] and Al-Ge-As-Te[18] have been found toexhibit threshold switching. However, the threshold behavior is limited to a narrow composition range, while the other compositions of the series lead to memory switching behavior. Such devices are important in manufacturing solid state digital electronic devices and in power control devices. They are nonpermanent or volatile as they always revert to the OFF state in the absence of an appropriate current.

Thermal imaging: Thermal imaging based on the principal that all materials having temperature above 0°K can emit infrared energy. The infrared energy emitted from the object is then converted into an electrical signal by the thermal lens in the camera and displayed on a monitor as a monochrome thermal image in dark environment. The living objects emit infrared radiation having wavelength up to 12 μ m, so the lens of camera should be made up of material having transparent to these infrared rays. Ge-Se-Sb glass family is one of the most promising families in chalcogenide glasses having low transmission loss and high transparency in the infrared region $2-16 \,\mu\text{m}$ [19]. Thus the lenses made of chalcogenide glasses are used in thermal imaging.

X-ray imaging: The chalcogenide materials are also suitable to replace the conventional semiconductor crystals in X-ray detection. The X-ray imaging employs conversion of X-ray photon to charge signal using photoconductor which can detect the X-ray photons. There have been devised integrated radiographic systems in which X-ray induced charge images are produced on photoconductors of amorphous thin films at high fields [20]. At high fields electron-hole pair creation energy decreases which lead to an improved X-ray to charge conversion. In these X-ray sensitive amorphous thin films, the image sequences are taken at short time intervals and also act as image receptor. Amorphous Se thin films of suitable thickness and large homogeneous area are easy to form, hence suitable for detecting the X-ray photons with accuracy. Also a-Se at sufficiently high fields exhibits avalanche multiplication which increases the quality of image. Recently flat-panel displays technologies are there to capture the whole X-ray image and provide output in digital form. A flat panel X-ray image detector based on selenium has been devised [21-22] which is used in fluoroscopy i.e. real-time interactive Xray imaging. In fluoroscopy, a video image on a monitor enables the radiologist to see a moving Xray picture of the inside of the human body instead of still X-ray image.

Xerography: The copying of documents on normal paper by an electrophotographic dry process is called xerography. This process uses no any liquid chemical for photocoping the document. In xerography the chalcogenide glassy material is essen-

tial element because they are good photoconductors and thin films of large homogeneous area can be easily formed. The thin film of chalcogenide material have longer stability, chemical inertness to the environment of a corona discharge, good mechanical strength, reproducible physical properties and rendered flexibility which offers a variety of different typed and sized machine configurations. The film of chalcogenide glass acts as a photoreceptor which is formed by evaporation technique on the substrate. During a xerographic cycle the photoreceptor is charged by corona up to 700V. The charged photoreceptor is then exposed to light reflected from a document and illuminated surface potential of the photoreceptor is discharged and electrostatic image is formed. The latent image is then developed by use of fine toner particles. The latent image is then transferred to a sheet of paper which has been oppositely charged by a corona to that of the toner and then the image is fixed permanently on paper by fusing process. Xerography is the first industrial scale electronic application of amorphous semiconductors glasses such as a-Se or As₂Se₃ [23].

Photolithography: The photoinduced changes when exposed to photons in the structure and solubility of chalcogenide thin films make a new platform for chalcogenide glasses. The interest increased when photo-doping of these glasses with metals like silver, chromium, aluminium etc make them highly insoluble into alkaline solutions. The chalcogenide glasses also show strong durability against acid solutions. Hence all these properties of chalcogenide glasses make them efficient to produce high-resolution images and resists which are the necessary parts of photolithography. Photolithography with chalcogenide glass use inorganic resist [24] in contrast to lithography which uses conventional organic-resist [25]. The inorganic resist have many advantages over organic resist for example; 1) Thin films of chalcogenide material of very small thickness (micro meter) can be easily deposited on substrate by using sputtering, chemical vapor deposition or evaporation method. 2) Uniformity on large areas which ensure the accurate results. Photolithography of chalcogenide material uses micro-fabrication of patterns on a substrate by following process; A thin film of chalcogenide glass is deposited on the substrate after that a thin layer of desired metal is deposited over this film to make a photoresist. The sample is exposed to radiation through the desired geometric pattern. This step

transfers the desired pattern from photo mask to light-sensitive photoresist on the substrate by doping the metal ions to the exposed area of photoresist. The undoped material can be removed with wet or dry etching leaving behind a negative resist. Now chalcogenide photoresist can be manufactured successfully for making precise diffraction gratings, frasnel lenses and phase zone plates in optics.

Solar cell: Now these days, there is tremendous increase in energy consumption due to increasing demand. Due to excessive demand a new and scientifically based technology, thin film study of solar cells have gained momentum in the last decade. Non-renewable energy resources like fossil fuels are being depleted and do not have attention due to increasing cost, air pollution and greenhouse effect. Some other alternative sources of energy such as water or wind are limited to areas with windy environments or flowing rivers. Hence utilization of energy from the sun is the only way to solve the worldwide energy problem because solar energy is largely abundant, cost free, environmentally safe and will exist for billions of years. So the interest increases in the development of the systems for deposition of thin films which are capable of converting and storing the solar energy. The metal chalcogenide thin films are very useful for this purpose as they have potential applications in solar cell, light emitting diode (LED), thermoelectric coolers, optoelectronics and heterojunction based devices due to easy fabrication of large area glassy semiconducting stable films with low cost and high absorption coefficient. Binary and multinary compound thin films of chalcogenide of II-VI, IV-VI, III-V, V-VI and VI-VI groups have emerged as potential candidates having low production cost and good performance in energy conversion[26] in comparison to conventional solar cell. A thin film solar cell can be fabricated using different materials deposited in thin film form. In general, thin film solar cell consists of a substrate, absorber layer, antireflection coating and metal contact. Chalcogenide compounds are used in solar cell components due to their suitable band gap for solar energy conversion. Cd-Te combination is the best available combination in group II-VI for solar energy conversion [27]. Now a days thin film modules based on $Cu(In-Ga)Se_2$ are used due to enhanced performance and high efficiency [28].

Infrared detectors: An infrared detector is a device that reacts to infrared radiation. A solid

emits electrons when it is subjected to suitable radiation. This phenomenon is utilised for producing systems for electron amplification and used in detector. These detectors can be used in counting and burglar alarm and other security and scientific applications [29-30] because they offer the possibility of higher energy resolution than conventionally used scintillation detectors. From the group of materials with secondary electron emission properties, semiconducting glasses are mostely used due to simple fabrication procedure, the lack of chemical reactivity and broad range of characteristic properties. Detectors fabricated from the ternary compound having one chalcogen atom shows well resolved spectroscopic features at room temperature, indicating its potential as a radiation detector [31]. The wide bandgap of thallium gallium selenide (TlGaSe₂) is promising for X-ray and γ -ray detection [32].

Radiation sensors: Chalcogenide based sensors or detectors have find a different platform in various fields like environment monitoring, remote sensing of chemical and biological species and medical diagnosis due to their unique properties such as wide transmission window (1-20 µm), high refractive indices, dependence on composition and concentration of large portion of the light outside the core material. Wide transmission window in IR region is the basic need of sensors where most of molecules vibrate and the vibrational spectra of each molecule are unique which allows highly specific recognition of chemical species. A chemical sensor is an analytical device which can provide quantitative information about the chemical composition of its environment in terms of measurable physical signal, related to concentration of a certain chemical species. If a sensor is based on recognition of biological material then it is known as biosensor. The chalcogenide sensors are even employed to differentiate and classify different beverages i.e. mineral water, wine, tea, milk, juice etc and industrial waste. In environmental change or pollutant monitoring measurements exposure of few days whereas in biomedical analysis i.e. a diseased tissues minute exposure is required [33-34]. The chemical stability and toxicity of Te-As-Se fiber is used for biosensing applications that involve direct contact with live cultivated human cells [35].

CONCLUSIONS

Chalcogenide glasses have immense importance as they find applications in almost every field of technology such as in civil, electrical, optical as well as in medical to produce industrially electrical switches, xerographic and thermoplastic media, photoresistant and holographic media, optical filters, optical sensors, thin films waveguides, photo resist for lithography, nonlinear elements for telecommunications etc. Applications of chalcogenide glasses in infra-red optics include energy management, night vision, thermal fault detection and temperature monitoring. Due to high transparency in the mid to far infrared region, they originally attract technological and commercial interest for use in IR optics. ChG fibers find applications in various fields due to their high bandgap, long wavelength multi-phonon edge and low optical attenuation.

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