Introduction

- Definition
- General characteristics
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- Fabrication
Applications of chalcogenide materials

IT
- Optical memory
- PRAM
- X-ray digital imaging
- Chemical sensor
- Optical fiber
- IR optics
- Thin film switching device
- Flexible sensor
- Solution-processed TFT

Energy
- TE generation
- Solar cell
- Thin film battery
- FIC

Commercialized
- DVD / Blu-ray discs
- Optical fiber
- Solar cell

Under development
- PRAM
- Solution-processed TFT
- Flexible sensor
- Optical memory
Characteristics of chalcogenide materials

- **Resistivity** \( (\Omega \text{cm}) \)
  - \( 10^{18} \) insulator
  - \( 10^{10} \)
  - \( 10^{3} \)
  - \( 10^{-1} \) to \( 10^{-1} \)
  - \( 10^{-8} \) conductor

- **Mobility** \( (\text{cm}^2/\text{Vs}) \)
  - \( 0.1 \sim 1 \)
  - \( 20 \sim 30 \)
  - \( \sim 600 \)
  - \( 1400 \)

- **Bandgap** \( (\text{eV}) \)
  - \( 0.5 \)
  - \( 0.7 \)
  - \( 1.0 \)
  - \( 1.8 \)

- **Absorption** @500~600nm
  - \( 10^3 \) c-Si
  - \( 10^5 \) a-Si

- **Ionic Conduction of Li** [S/cm]
  - Liquid electrolyte
  - Polymer gel electrolyte
  - Chalcogenide

- **TE Coeff. (mV/K)**
  - \( \text{Pb} \)
  - \( 4.0 \)
  - \( \text{Ca}_3\text{Co}_4\text{O}_9 \)
  - \( 230 \)
  - \( \text{Si} \)
  - \( 440 \)

- **Processing Temp (C)**
  - \( \text{SnS(Se}, \ n-\text{Ge}_2\text{Sb}_2\text{Te}_5) \)
  - \( \text{PI}_T \): 385
  - \( \text{PA}_T \): 330
  - \( \text{PES}_T \): 228
  - \( \text{PC}_T \): 150
Chalcogenides are chameleon compounds: they can be crystalline or amorphous, metallic or semiconducting, and conductors of ions or electrons.

“Thus, a unified approach to the study of chalcogenides, assessing the roles of atoms, ions and electrons, may prove crucial for both device performance and reliability.”
Glass consisting of the Group VI elements (S, Se, Te), as major constituents, and others (usually Group IV and/or V elements)
Covalent amorphous solids

✓ The chemical bond nature of inorganic glasses
  - Ionic bond: fluoride and halide glasses
  - Covalent bond: chalcogenide glasses (S-, Se-, or Te-based)
  - Metallic bond: amorphous metals
  - Mixed (ionic + covalent) bond: oxide glasses

✓ Relatively strong covalent bonds in ChG
  - Semiconducting but can’t be doped: the empirical 8-N rule
  - Presence of the homopolar bonds
  - Similar electronegativity of constituent atoms
  - Relatively well-defined intermediate range order
  - Presence of (various kinds of) electronic defects
Some characteristics of chalcogenide glasses

✓ Good transmittance in the infrared region (~20 μm)
  ➢ IR optical devices

✓ Low phonon energy (~200 cm\(^{-1}\) for selenide glass)
  ➢ Host for ion-doped laser and amplifier

✓ High $\chi^{(3)}$ optical nonlinearity (~10\(^3\) higher than a-SiO\(_2\))
  ➢ Ultrafast all optical switching for optical communications

✓ Semiconducting
  ➢ Photocopying machines, digital x-ray imaging, PCM

✓ Fast ion conducting
  ➢ Thin film battery, ionics devices

✓ Photo-induced phenomena
  ➢ Photolithography, Optical waveguide
Classification

✓ Amorphous covalent solid
  ➢ Glassy semiconductor
  ➢ Lone-pair semiconductor

✓ Strong covalent glass
  ➢ Obeying the 8-N rule
  ➢ Ge, Si, As, Sb…
  ➢ Electronic conductor

✓ Weak covalent glass
  ➢ Violating the 8-N rule
  ➢ Ga, In, Na, Ag…
  ➢ Ionic conductor

✓ Bulk or film?

* Figure taken from K. Tanaka, Optoelectronic Mater. Devices 1 (2004) 43.
Surface of fresh cut of glass vs freshly deposited thin film

**Bulk As$_2$S$_3$**

- S$_2$p core level
- As$_2$S$_3$ bulk
- 84% AsS$_{3/2}$
- 16% within S-S

**Freshly deposited As$_2$S$_3$ film**

- Binding energy, eV
- As$_2$S$_3$ bulk
- As$_3$d core level
- As-As
- As$_{3/2}$

*Slide provided by Dr A. Kovalskiy*
Chemical bonds

Brief history

- The earliest experimental data on an oxygen-free glass have been published by Schulz-Sellack in 1870 [1].
- Later on, Wood in 1902 [2], as well as Meier in 1910 [3] carried out the first researches on the optical properties of vitreous selenium.
- In 1950, Frerichs [4] published the paper: “New optical glasses transparent in infrared up to 12 μm”
- Glaze and co-workers [5] developed in 1957 the first method for the preparation of the glass at the industrial scale.
- A research group lead by Kolomiets and Goriunova discovered the first semiconducting glass, TlAsSe$_2$ [7].
- In 1968, Ovshinsky [8] discovered the memory and switching effects of some chalcogenide glasses.

E9. New Optical Glasses Transparent in the Infra-red up to 12μ.* R. Frerichs, Northwestern University.—According to Zachariasen\(^1\) in oxide glasses polyhedra of oxygen atoms around the cations form an extended unperiodic network of open structure. The glass-forming oxides are found under the small ions of the fourth and fifth column of the periodical table. The majority of these oxides have been observed in the glassy state, but very little is known about other glass-forming compounds. Arsenic tri-sulfide forms a perfectly clear, stable red glass which has remarkable optical properties hitherto unknown. 2.6 mm of As\(_2\)S\(_3\) pass 45 percent radiation between the red and 8μ, and this amount decreases to 21 percent at 12μ. 0.15 mm transmit 65 percent throughout this region, indicating high reflection losses due to a high index of refraction. The index of refraction \(N_{Li(\text{red})}\) is about 2.5. The glass softens at 300°C, distills without decomposition at 500°C, and is non-hygroscopic. It can be melted in Pyrex tubes and forms binary glasses with different sulfides. An investigation of this group of sulfide glasses, which have optical properties not realized in oxide glasses, is planned.

* This work was sponsored by the U. S. Navy, Bureau of Ships.
\(^1\) W. H. Zachariasen, J. Am. Chem. Soc. 54, 3841 (1932).
REVERSIBLE ELECTRICAL SWITCHING PHENOMENA IN DISORDERED STRUCTURES

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(Received 23 August 1968)

A rapid and reversible transition between a highly resistive and conductive state effected by an electric field, which we have observed in various types of disordered semiconducting material, is described in detail. The switching parameters and chemical composition of a typical material are presented, and microscopic mechanisms for the conduction phenomena are suggested.

We describe here a rapid and reversible transition between a highly resistive and a conductive state effected by an electric field which we have observed in various types of disordered materials, particularly amorphous semiconductors\textsuperscript{1,2} covering a wide range of compositions. These include oxide- and boron-based glasses and materials which contain the elements tellurium and/or arsenic combined with other elements such as those of groups III, IV, and VI.

The material used: amorphous AsSiGeTe
Fabrication

✓ Melt-quenching

* Photo provided by D. Zhao

<table>
<thead>
<tr>
<th>Cooling rate $q$ (K s$^{-1}$)</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-5}$</td>
<td>Annealing of large telescope mirrors</td>
</tr>
<tr>
<td>approx. $2 \times 10^{-4}$</td>
<td>Annealing of optical glasses</td>
</tr>
<tr>
<td>$10^{-3} - 10^{-2}$</td>
<td>Annealing of ordinary glasses</td>
</tr>
<tr>
<td>$1 - 2$</td>
<td>Air exposure of chalcogenide melts of 10–20 g in quartz ampoules (wall thickness 2 mm)</td>
</tr>
<tr>
<td>$8 - 10$</td>
<td>In water at 273 K</td>
</tr>
<tr>
<td>35</td>
<td>1 g (ampoule wall thickness 0.5 mm) in water</td>
</tr>
<tr>
<td>approx. 180</td>
<td>0.015 g in thin-wall ampoule in water [2.23]</td>
</tr>
<tr>
<td>approx. $10^3$</td>
<td>Spray-cooling of melts</td>
</tr>
<tr>
<td>$10^5 - 10^6$</td>
<td>Melt-spinning methods</td>
</tr>
<tr>
<td>$10^6 - 10^7$</td>
<td>Piston-and-anvil technique</td>
</tr>
<tr>
<td>$10^6 - 10^{10}$</td>
<td>Splat-cooling methods</td>
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* Feltz book, p. 16.
Spin-coated amorphous chalcogenide films

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Preliminary investigations have shown that a family of chalcogenides may be deposited in technologically useful thin film form by an inexpensive technique of spin deposition from solution. The materials which are amorphous and microstructure free retain many of the properties of the solute (e.g., As$_2$S$_3$, As$_2$S$_2$, As$_2$Se$_3$, As$_2$Te$_3$, or GeSe) from which they are prepared. Some of the materials have been demonstrated to be potentially useful for high resolution pattern replication in particular for microlithography.
On the other hand, there are compounds with stoichiometric composition which always occur in amorphous form after precipitation from aqueous solutions, such as the sulphides As$_2$S$_3$, As$_2$S$_5$, Sb$_2$S$_3$, Sb$_2$S$_5$ or GeS$_2$. These can even be used for the gravimetric determination of As, Sb or Ge owing to their sparing solubility and stoichiometry. As$_2$S$_5$ and Sb$_2$S$_5$ are so far only known as amorphous compounds; the same also applies to MoS$_3$, MoSe$_3$, WS$_3$, WSe$_3$, and V$_2$S$_5$. Ge$_2$S$_3$ and Ge$_2$Se$_3$ are obtained as amorphous precipitates from solutions of thiohypodigermanate and selenohypodigermanate, but can also be obtained as vitreous compounds from the melt (see Sections 3.2.2.4, 3.2.2.5, and 3.2.4).

Amorphous precipitates of defined composition M$_2$SnTe$_4$ (M = Cr, Mn, Fe, Co) have recently been reported. They can be obtained from the combination of anhydrous M$^{2+}$ and SnTe$_4^{4-}$ solutions, and they show metallic conductivity after compaction by pressing [2.456].

PVD (Evaporation)

- Thermal and/or e-beam

Fig. 2.5. Experimental arrangement for deposition of amorphous layers by thermal evaporation in vacuum according to [2.37]; (a) complete arrangement with rotatable substrate holder and masks; (b) details of mask.

1. boat of Ta sheet; 2. substance; 3. preheated Cu block with opening


Many different variants of evaporator arrangements have been described [2.36]. A possible arrangement for investigating the evaporation of vitreous Ge$_2$Se$_3$ and polycrystalline mixtures of GeSe and GeSe$_2$ is shown in Figure 2.5 a. The rotatable substrate plate (Fig. 2.5 b) has different masks and allows sample contacting in the same vacuum to insert (1); (4) current supplies, thermocouples; (5) rotatable vapour jet screen; (6) quartz crystal oscillator monitor; (7) stationary substrate block with interchangeable substrate holder (8); (9) rotatable plate with thin-film mask for base contact (10), chalcogenide glass layer (11), and cover contact (12); (13) substrate temperature control; (14) substrate holder and (15) masks for analysis of layers; (16) mask plate locking mechanism.
PVD (Sputtering)
- DC or RF magnetron

Fig. 2.8. Cathode sputtering, with diode arrangement (a) and triode arrangement (b).

The investigation of layers of chalcogenide glasses, such as the relatively complicated composition of $\text{As}_{0.30}\text{Si}_{0.12}\text{Ge}_{0.12}\text{Te}_{0.48}$, which can be produced by this method with

The comparison of Ag–As$_{33}$S$_{67}$ films prepared by thermal evaporation (TE), spin-coating (SC) and a pulsed laser deposition (PLD)

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for preparation of As$_{33}$S$_{67}$ thin films. The PLD system consisted of a vacuum chamber and a near-UV laser. A KrF excimer laser (Lambda Physik COMPex 102), operating at 248 nm with a constant output energy of 290 mJ pulse$^{-1}$, a pulse duration of 30 ns and a repetition rate of 20 Hz was used. The energy density of the laser beam on the target was 1 J cm$^{-2}$. The laser beam hit a bulk chalcogenide glass target at an angle of 45°. The target and substrate rotated, and their distance from each other was about 5 cm.

Fig. 1. The X-ray pattern of As$_{33}$S$_{67}$ bulk glass and as-deposited thin films prepared by techniques TE, SC and PLD.
Mechanical milling

20 μm. The glasses were also prepared by the mechanochemical method using a planetary ball mill apparatus (Fritsch Pulverisette 7). The mechanochemical treatment using an Al₂O₃ pot and balls was performed for the mixture of Li₂S and P₂S₅ crystals. Fine glassy powders were obtained after mechanical milling for several hours at a constant rotation speed of 370 rpm. All the processes were carried out at room temperature in a dry Ar-filled glove box. Glass-ceramic materials were prepared by heating the mechanically milled glasses over their crystallization temperatures.

To prepare powdered amorphous materials by mechanical milling, stoichiometric amounts (3 g) of crystalline Li₂S and GeO₂ and glassy GeS₂ were placed into the sample container (zirconium oxide) with 10 zirconium oxide balls (3 g in weight and 10 mm in diameter) inside a N₂ glove box. The sample container was then sealed using a rubber O-ring and placed in a high-energy planetary mono mill (Model Pulverisett 6, Fritsch). The mechanical milling was performed with 300 rpm at room temperature for increasing periods of time, 0 to 100 h.

Recent progress of glass and glass-ceramics as solid electrolytes for lithium secondary batteries

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Ionic conductivities of various GeS₂-based oxy-sulfide amorphous materials prepared by melt-quenching and mechanical milling methods

Youngsik Kim, Steve W. Martin *