

# Introduction

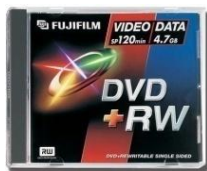


- ✓ Definition
- ✓ General characteristics
- ✓ Brief history
- ✓ Fabrication

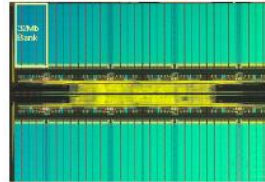


# Applications of chalcogenide materials

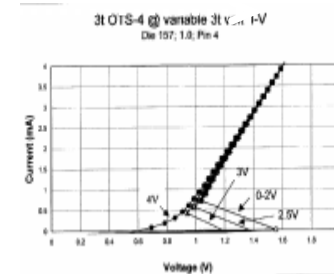
IT



Optical memory



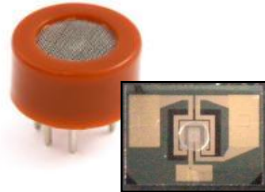
PRAM



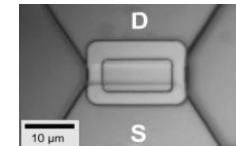
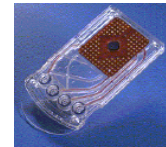
Thin film switching device



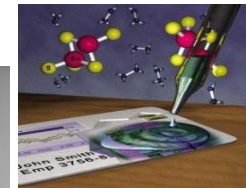
X-ray digital imaging



Chemical sensor



Flexible sensor



Solution-processed TFT



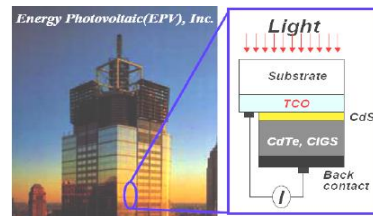
Optical fiber



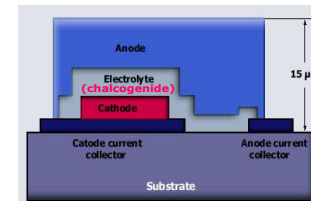
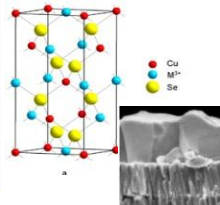
IR optics



TE generation



Solar cell



Thin film battery



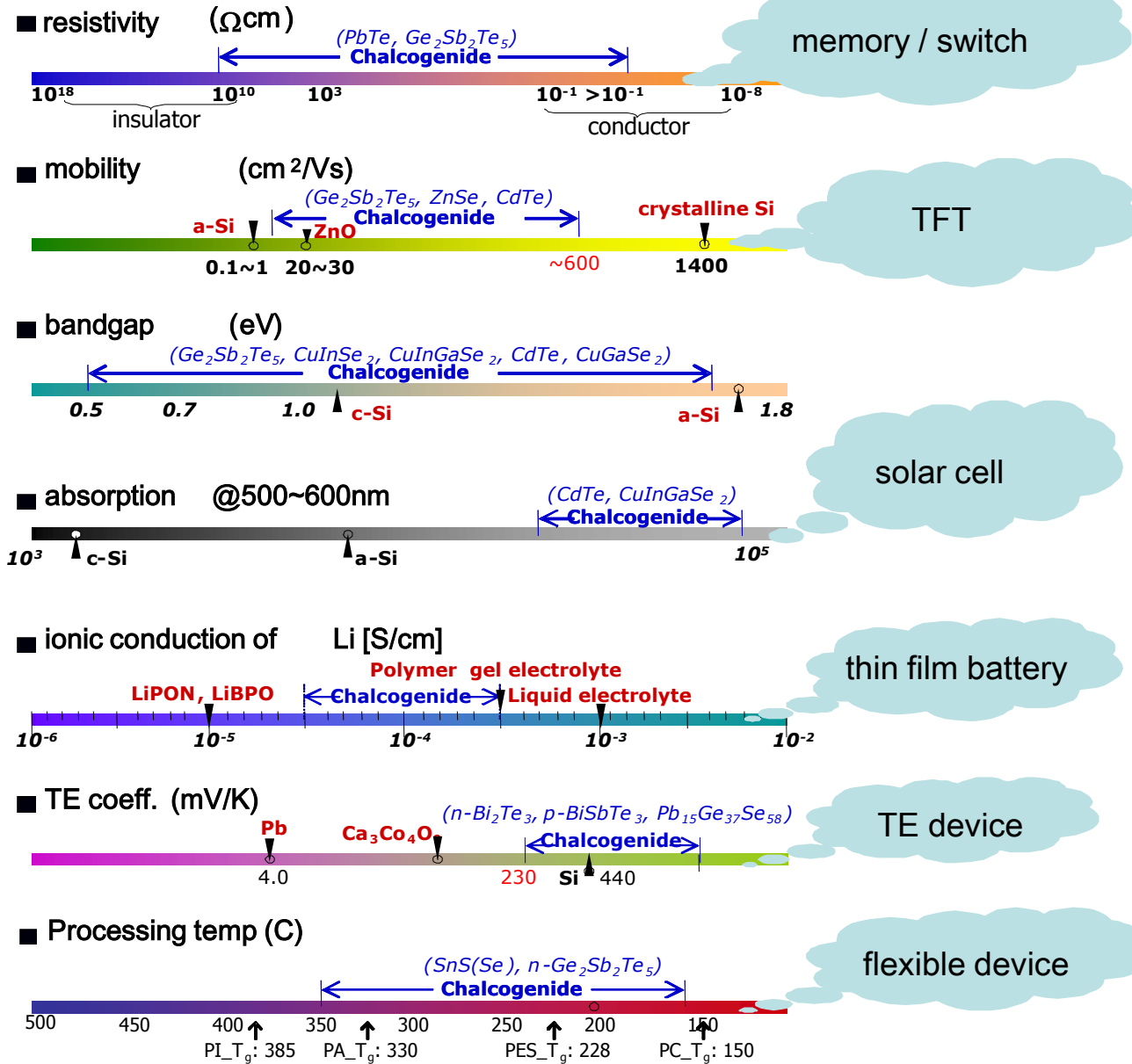
FIC

commercialized

under development

Energy

# Characteristics of chalcogenide materials



## MATERIALS SCIENCE

# Changing face of the chameleon

A. Lindsay Greer and Neil Mathur

Chalcogenide materials form the basis of CD and DVD technologies. But an identity crisis looms in the wider field: what role do atomic reconfiguration, electronic processes and ionic movement play in these materials?



- “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.”

# Chalcogenide glass?

Periodic Table of the Elements

	IA 1											IIA 2											IIIA 13	IVA 14	VA 15	VIA 16	VIIA 17	VIIIA 18	
1	1.0 1 H											9.0 4 Be											10.8 5 B	12.0 6 C	14.0 7 N	16.0 8 O	19.0 9 F	4.0 2 He	
2	6.9 3 Li											24.3 12 Mg											27.0 13 Al	28.1 14 Si	31.0 15 P	32.1 16 S	35.5 17 Cl	20.2 10 Ne	
3	23.0 11 Na											24.3 12 Mg											27.0 13 Al	28.1 14 Si	31.0 15 P	32.1 16 S	35.5 17 Cl	39.9 18 Ar	
4	39.1 19 K											40.1 20 Ca											69.7 31 Ga	72.6 32 Ge	74.9 33 As	79.0 34 Se	79.9 35 Br	83.8 36 Kr	
5	85.5 37 Rb											87.6 38 Sr											106.4 46 Pd	107.9 47 Ag	112.4 48 Cd	127.6 52 Te	126.9 53 I	131.3 54 Xe	
6	132.9 55 Cs											137.3 56 Ba											195.1 78 Pt	197.0 79 Au	200.6 80 Hg	209 84 Po	210 85 At	222 86 Rn	
7	223 87 Fr											226 88 Ra											208 108 Hs	269 109 Mt	272 111	277 112			

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Dépot légal 3<sup>e</sup> trimestre 1992, Bibliothèque Nationale du Québec, Bibliothèque Nationale du Canada  
Printed in Canada

- 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**

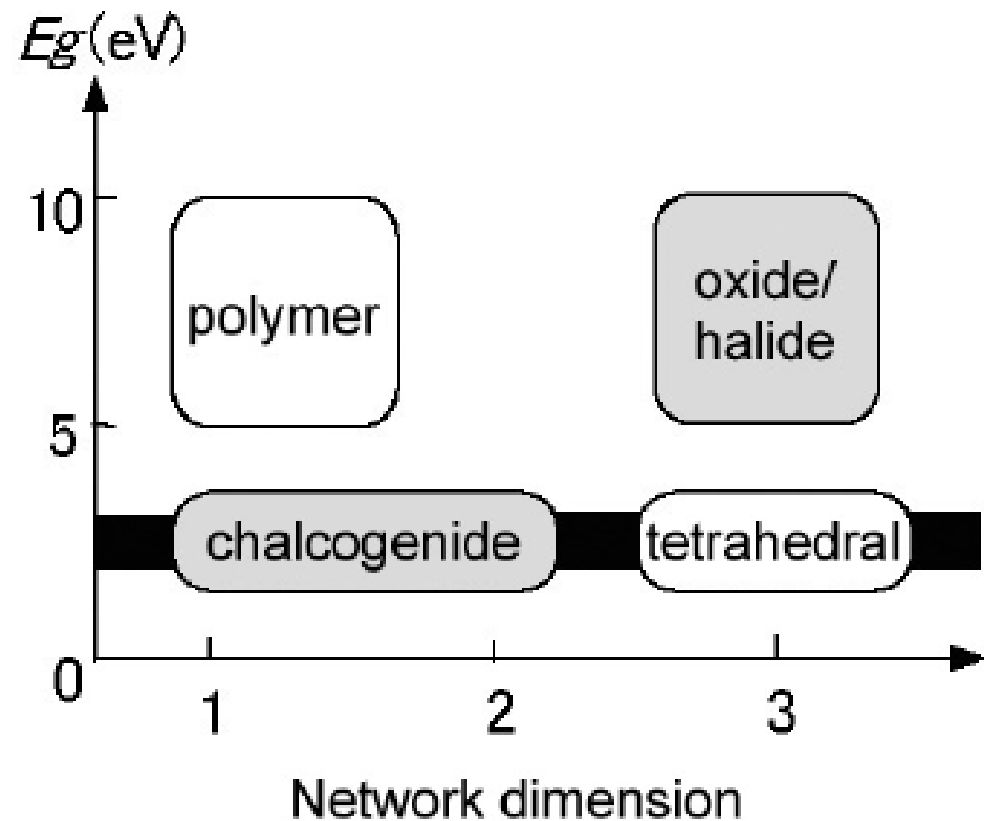
- Semiconducting but can't be doped: the empirical  $8-N$  rule
- Presence of the homopolar bonds
- Similar electronegativity of constituent atoms
- Relatively well-defined intermediate range order
- Presence of (various kinds of) electronic defects

# Some characteristics of chalcogenide glasses

- ✓ **Good transmittance in the infrared region** ( $\sim 20 \mu\text{m}$ )
  - IR optical devices
- ✓ **Low phonon energy** ( $\sim 200 \text{ cm}^{-1}$  for selenide glass)
  - Host for ion-doped laser and amplifier
- ✓ **High  $\chi^{(3)}$  optical nonlinearity** ( $\sim 10^3$  higher than  $a\text{-SiO}_2$ )
  - 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

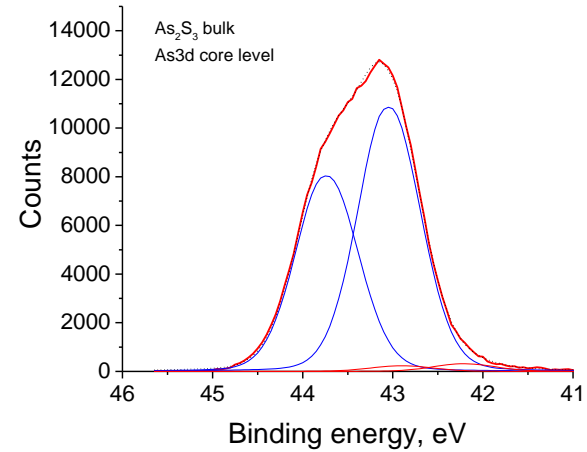
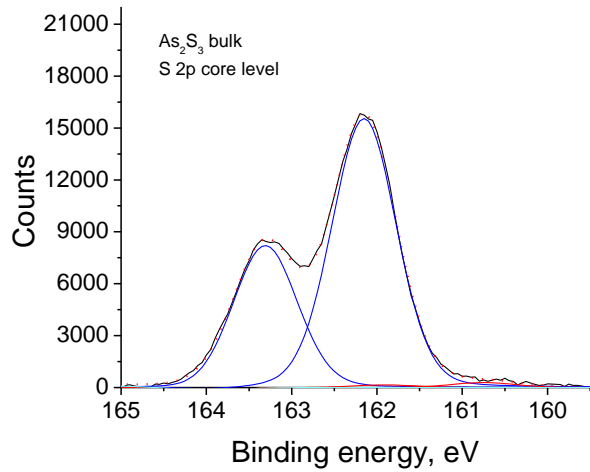
- ✓ Amorphous covalent solid
  - Glassy semiconductor
  - Lone-pair semiconductor
- ✓ **Strong covalent glass**
  - Obeying the 8-*N* rule
  - Ge, Si, As, Sb...
  - Electronic conductor
- ✓ **Weak covalent glass**
  - Violating the 8-*N* rule
  - Ga, In, Na, Ag...
  - Ionic conductor
- ✓ Bulk or film?



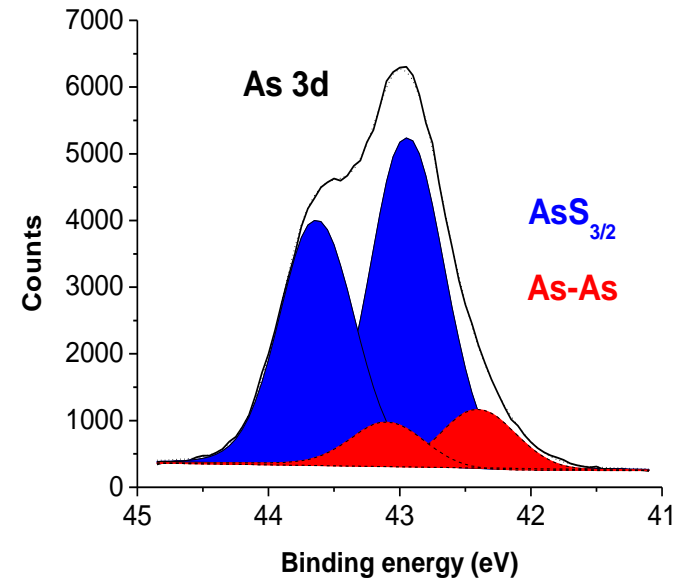
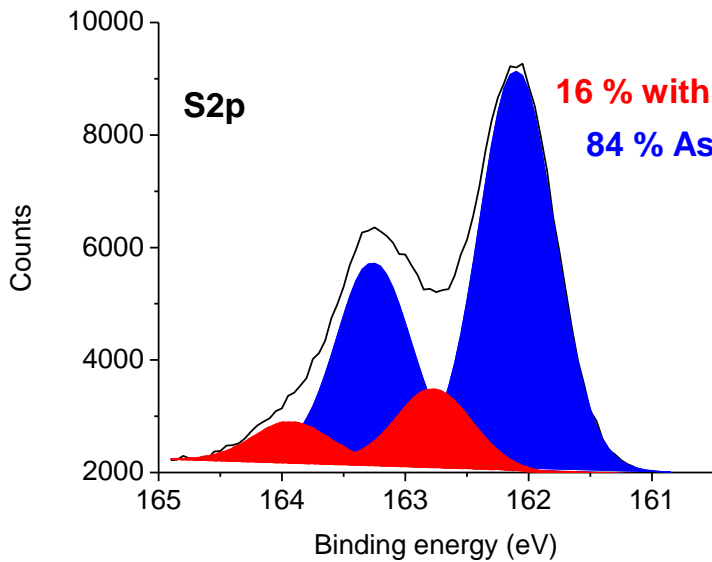
\* Figure taken from K. Tanaka, Optoelectronic Mater. Devices 1 (2004) 43.



# Surface of fresh cut of glass vs freshly deposited thin film



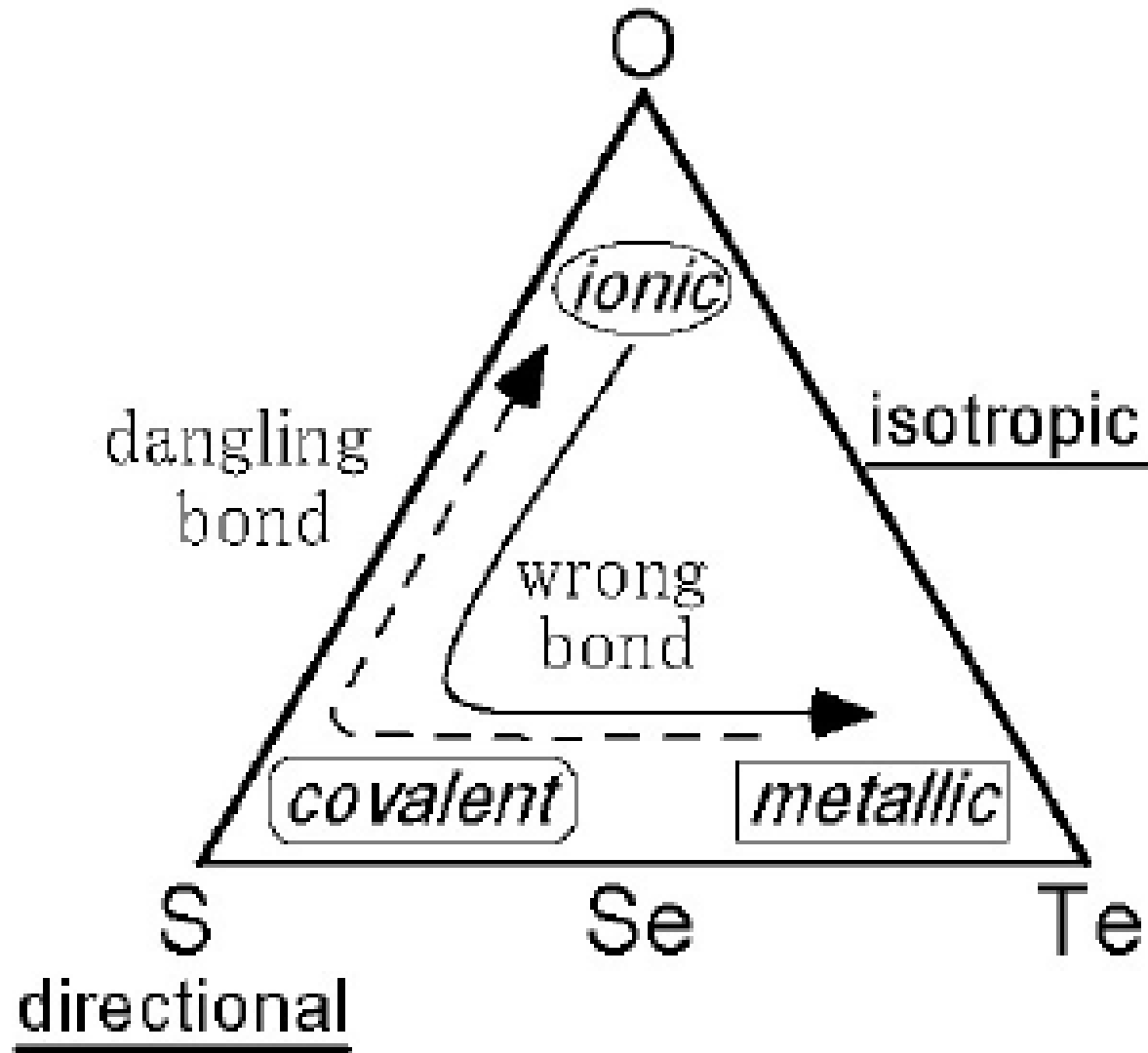
**Bulk  $As_2S_3$**



**Freshly deposited  $As_2S_3$  film**

\* 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  $\mu\text{m}$ ”
- Glaze and co-workers [5] developed in 1957 the first method for the preparation of the glass at the industrial scale.
- Winter-Klein [6] published reports on numerous chalcogenides prepared in the vitreous state.
- A research group lead by Kolomiets and Goriunova discovered the first semiconducting glass,  $\text{TlAsSe}_2$  [7].
- In 1968, Ovshinsky [8] discovered the memory and switching effects of some chalcogenide glasses.

1. C. Shultz-Sellack, Ann. Phys. 139, 182 (1870).
2. R. W. Wood, Phil. Mag. 3, 607 (1902).
3. W. Meier, Ann. Phys. 31, 1017 (1910).
4. R. Frerichs, Phys. Rev. 78, 643 (1950).
5. F. W. Glaze, D. H. Blackburn, J. S. Osmalov, D. Hubbard, M. H. Black, J. Res. Nat. Bur. Standards 59, 83 (1957).
6. A. Winter-Klein, Verres et Refractaires 9, 147 (1955).
7. N. A. Goriunova, B. T. Kolomiets, Zhurnal Tekhnicheskoi Fiziki (Russ.) 25, 2069 (1955).
8. S. R. Ovshinsky, Phys. Rev. Lett. 21, 1450 (1968)

**E9. New Optical Glasses Transparent in the Infra-red up to 12 $\mu$ .**\* R. FRERICHS, *Northwestern University*.—According to Zachariasen<sup>1</sup> 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<sub>2</sub>S<sub>3</sub> pass 45 percent radiation between the red and 8 $\mu$ , and this amount decreases to 21 percent at 12 $\mu$ . 0.15 mm transmit 65 percent throughout this region, indicating high reflection losses due to a high index of refraction. The index of refraction  $N_{Li(red)}$  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.

<sup>1</sup> W. H. Zachariasen, *J. Am. Chem. Soc.* **54**, 3841 (1932).

# REVERSIBLE ELECTRICAL SWITCHING PHENOMENA IN DISORDERED STRUCTURES

Stanford R. Ovshinsky

Energy Conversion Devices, Inc., Troy, Michigan

(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<sup>1,2</sup> 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.

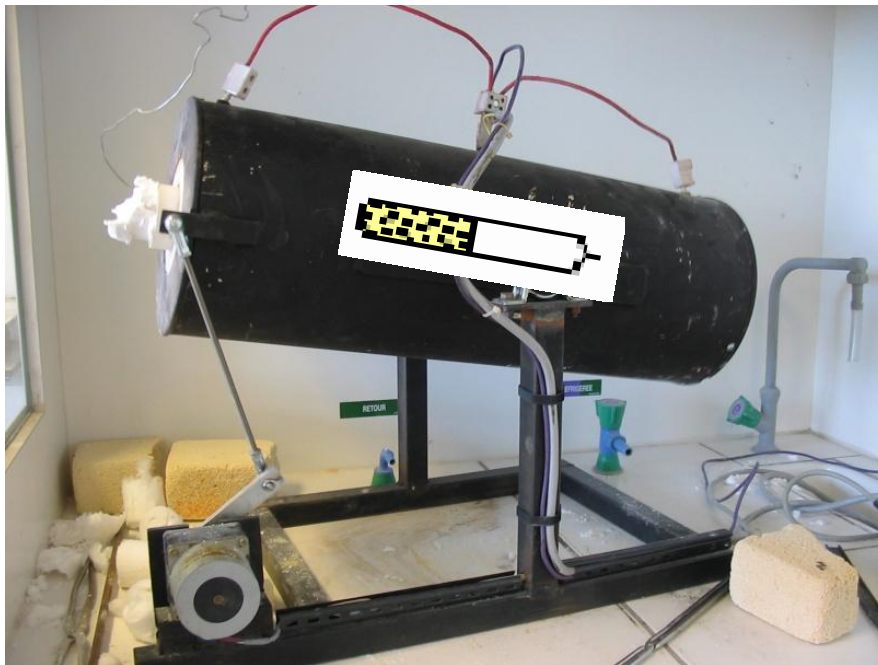
ing (in atomic percent) 48 at.% tellurium, 30 at.% arsenic, 12 at.% silicon, and 10 at.% germanium. The specimen was an evaporated film,  $5 \times 10^{-5}$  cm thick, between two carbon electrodes with a contact area of about  $10^{-4}$  cm<sup>2</sup>. This material has a resistivity at 300°K of  $\rho = 2 \times 10^7$   $\Omega$  cm,  $\Delta E = 1.0$  eV, and a positive thermopower.

Figure 1 shows oscilloscope pictures of (a) the  $I$ - $V$  characteristic, (b) the voltage  $V$  across the unit, and (c) the current  $I$  passing through the

➤ The material used: amorphous AsSiGeTe

# Fabrication

## ✓ Melt-quenching



\* Photo provided by D. Zhao

Table 2.3. Typical cooling rates of glass melts.

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

\* Feltz book, p. 16.

- ✓ Low-temp. wet process
  - Solution process

## **Spin-coated amorphous chalcogenide films**

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(Received 6 May 1982; accepted for publication 11 June 1982)

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.,  $\text{As}_2\text{S}_3$ ,  $\text{As}_2\text{S}_2$ ,  $\text{As}_2\text{Se}_3$ ,  $\text{As}_2\text{Te}_3$ , or  $\text{GeSe}$ ) 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.

6979

J. Appl. Phys. **53**(10), October 1982

- ✓ Low-temp. wet process
  - Sol-gel

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  $As_2S_3$ ,  $As_2S_5$ ,  $Sb_2S_3$ ,  $Sb_2S_5$  or  $GeS_2$ . These can even be used for the gravimetric determination of As, Sb or Ge owing to their sparing solubility and stoichiometry.  $As_2S_5$  and  $Sb_2S_5$  are so far only known as amorphous compounds; the same also applies to  $MoS_3$ ,  $MoSe_3$ ,  $WS_3$ ,  $WSe_3$ , and  $V_2S_5$ .  $Ge_2S_3$  and  $Ge_2Se_3$  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).

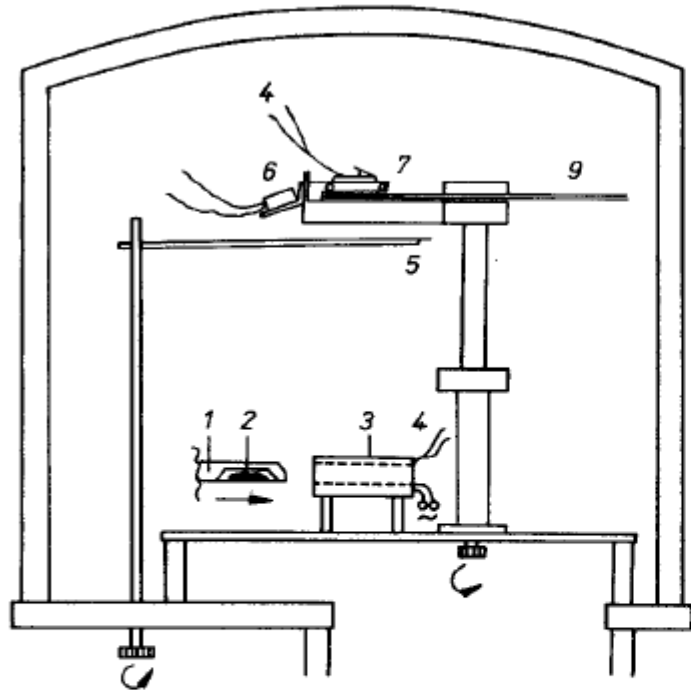
Amorphous precipitates of defined composition  $M_2SnTe_4$  ( $M = Cr, Mn, Fe, Co$ ) have recently been reported. They can be obtained from the combination of anhydrous  $M^{2+}$  and  $SnTe_4^{4-}$  solutions, and they show metallic conductivity after compaction by pressing [2.456].

\* Feltz book, p. 19.

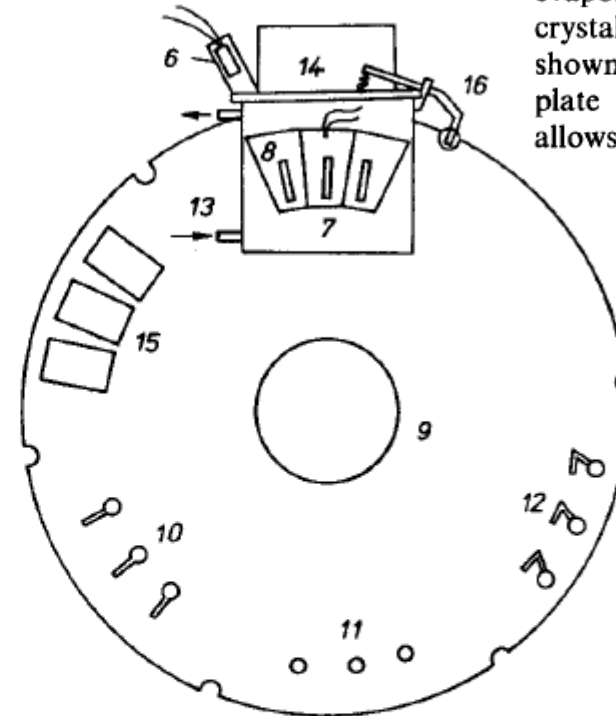


✓ PVD (Evaporation)

➤ Thermal and/or e-beam



(a)



(b)

Many different variants of evaporator arrangements have been described [2.36]. A possible arrangement for investigating the evaporation of vitreous  $\text{Ge}_2\text{Se}_3$  and polycrystalline mixtures of  $\text{GeSe}$  and  $\text{GeSe}_2$  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

**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

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.

\* Feltz book, p. 22.

- ✓ PVD (Sputtering)
- DC or RF magnetron

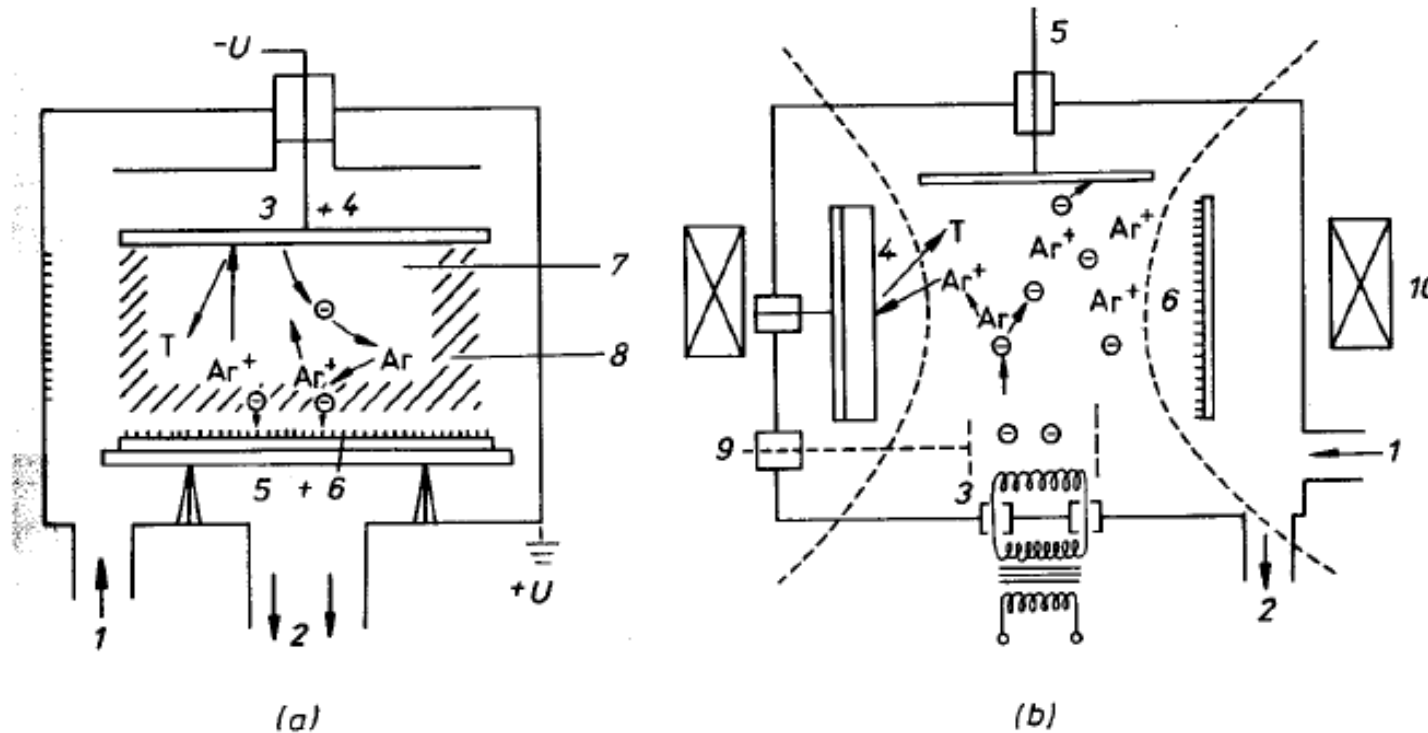


Fig. 2.8. Cathode sputtering, with diode arrangement (a) and triode arrangement (b).

(1) gas supply; (2) pump; (3) cathode; (4) target; (5) anode; (6) deposited layer; (7) cathode dark space; (8) positive column; (9) auxiliary anode; (10) magnetic coil and constriction of plasma.

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

\* Feltz book, p. 25.

# ✓ PVD (PLD)

## ➤ Laser ablation

ELSEVIER

Journal of Physics and Chemistry of Solids 68 (2007) 953–957

[www.elsevier.com/locate/jpcs](http://www.elsevier.com/locate/jpcs)

The comparison of Ag–As<sub>33</sub>S<sub>67</sub> films prepared by thermal evaporation (TE), spin-coating (SC) and a pulsed laser deposition (PLD)

M. Krbal\*, T. Wagner, T. Kohoutek, P. Nemeč, J. Orava, M. Frumar

*Department of General and Inorganic Chemistry, University of Pardubice, Czech Republic*

for preparation of As<sub>33</sub>S<sub>67</sub> 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<sup>-1</sup>, 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<sup>-2</sup>. 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.

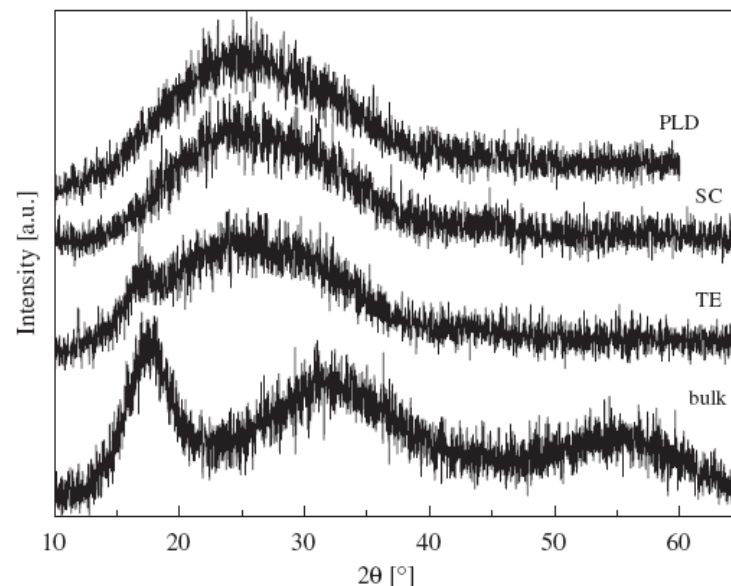


Fig. 1. The X-ray pattern of As<sub>33</sub>S<sub>67</sub> bulk glass and as-deposited thin films prepared by techniques TE, SC and PLD.

# ✓ Mechanical milling

20  $\mu\text{m}$ . The glasses were also prepared by the mechanochemical method using a planetary ball mill apparatus (Fritsch Pulverisette 7). The mechanochemical treatment using an  $\text{Al}_2\text{O}_3$  pot and balls was performed for the mixture of  $\text{Li}_2\text{S}$  and  $\text{P}_2\text{S}_5$  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.

IER

Solid State Ionics 177 (2006) 2715–2720



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

Tsutomu Minami \*, Akitoshi Hayashi, Masahiro Tatsumisago

To prepare powdered amorphous materials by mechanical milling, stoichiometric amounts (3 g) of crystalline  $\text{Li}_2\text{S}$  and  $\text{GeO}_2$  and glassy  $\text{GeS}_2$  were placed into the sample container (zirconium oxide) with 10 zirconium oxide balls (3 g in weight and 10 mm in diameter) inside a  $\text{N}_2$  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.

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Solid State Ionics 177 (2006) 2881–2887

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Ionic conductivities of various  $\text{GeS}_2$ -based oxy-sulfide amorphous materials prepared by melt-quenching and mechanical milling methods

Youngsik Kim, Steve W. Martin \*