Ion diffusion in chalcogenide glasses
Application in ionics and optics

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**Chalcogenide Glasses**

*Chalcogenide glasses are glasses containing chalcogens (Se, S, Te).*

*Chalcogenide homologous of oxide glasses*

\[
\text{SiO}_2 \; ; \; \text{GeO}_2 \; \rightarrow \; \text{SiS(e)}_2 \; ; \; \text{GeS(e)}_2
\]
Chalcogenide Glasses

Presence of S, Se, Te → polarisable environment with lone-pair (LP)

↓

Specific property of chalcogenide glasses compared to oxide ones

They exhibit semiconductor properties and thus form a large group of amorphous semiconductors

Intrinsically metastable, they can undergo various structural transformations under the action of external stimuli, in particular light.

Specific property of chalcogenide glasses compared to oxide ones

Semiconductor

As$_2$S$_3$ glass
\( \sigma \sim 10^{-14} \text{ Scm}^{-1} \)

Eg \( \sim 2.15 \text{ eV} \)

Photoinduced phenomena

\( h\nu \rightarrow \) hole-electron pair \( \rightarrow \) change in n

Ovshinsky effect

(amorphous state \( \leftrightarrow \) crystalline state)

Transparency in the IR
Application of ion diffusion in chalcogenide glasses

- Interface ion exchange
  - Ion sensors
- Diffusion under $E$
  - Electrochemical energy storage: batteries
- Diffusion under photons $\nu$
  - Photoinduced phenomena
- Diffusion under $\tilde{E}$ and $\nu$
  - PMC memories
Principle of a sensor

**CHEMICAL or PHYSICAL SENSOR**

- Analyte
- Sensitive part
- Membrane
- Potentiometric FET
- Transducer
- Electrical signal
- Analysis and treatment system

**Ion exchange: Chemical Sensor**

*Sensitivity, reversibility, selectivity and stability*
Potentiometric analysis of a chemical sensor depends on the relationship between the concentration of the species and the e.m.f. The ideal relationship is known as the Nernst equation:

$$E = E_0 + \frac{RT}{z_i F} \log a_i$$

**Typical calibration curve of an ion-selective electrode obtained with the well known addition method.**
Development of ISE chemical microsensors

Analytical device for Cu\(^{2+}\) ion detection based on (1-X)Sb\(_{12}\)Ge\(_{28}\)Se\(_{60}\) - XCu glassy thin films.

Elaboration of the (Sb-Ge-Se)/(Cu) material

Thin films produced by r.f. sputtering of a composite target

(Sb$_{12}$Ge$_{28}$Se$_{60}$)  copper

<table>
<thead>
<tr>
<th>Target</th>
<th>Chemical composition of thin films</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(Sb$<em>{11.3}$Ge$</em>{30.4}$Se$<em>{58.3}$)$</em>{40}$(Cu)$_{60}$</td>
</tr>
<tr>
<td>2</td>
<td>(Sb$<em>{11}$Ge$</em>{29}$Se$<em>{60}$)$</em>{50}$(Cu)$_{50}$</td>
</tr>
</tbody>
</table>

S.E.M cross sectional view of a thin film

Film thickness varies from 0.4 to 1 µm depending on sputtering conditions and sputtering time.
Electrode response

The material with $x = 0.6$ gives the best electrode performance.

Mixed solution method with constant $a_{interfering ion}$ concentration.

<table>
<thead>
<tr>
<th>Interfering Ion</th>
<th>log $K_{Cu^{2+}/j}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K^+$</td>
<td>-5.1</td>
</tr>
<tr>
<td>$Na^+$</td>
<td>-5.3</td>
</tr>
<tr>
<td>$Ca^{2+}$</td>
<td>-5.1</td>
</tr>
<tr>
<td>$Ni^{2+}$</td>
<td>-4.1</td>
</tr>
<tr>
<td>$Cd^{2+}$</td>
<td>-4.1</td>
</tr>
<tr>
<td>$Pb^{2+}$</td>
<td>-2.5</td>
</tr>
<tr>
<td>$Mn^{2+}$</td>
<td>-3.4</td>
</tr>
</tbody>
</table>

Influence of pH on electrode response

![Graph showing $E (mV)$ vs $ECS$ for different pH values]
Diffusion under $\vec{E}$: chemical energy storage

Superionic Conductive Glasses

Conductivity 100-1000 times larger than that of their oxide counterpart

$\varepsilon_r > 10$ (Weak electrolyte theory)

$\sigma_{Ag^+} \sim 10^{-2}$ Scm$^{-1}$

$\sigma_{Li^+} \sim 10^{-3}$ Scm$^{-1}$

Application: all solid state batteries based on solid electrolytes

Rocking-chair Li-ion batteries for various portable equipments

- Safety: prevent from igniting and leaking (liquid combustible organic solvent)
- Miniaturisation
At the beginning: Li batteries

- our first works (1983) Li/LiI-Li$_2$S-GeS$_2$(g)/V$_2$O$_5$
- Eveready (USA)(90's) Li/ sulfide (oxysulfide) (g)/various cathodic materials

Now Li-ion batteries (mainly japanese teams)

- Minami-Tatsumisago group (Osaka)
  In/Li$_2$S-P$_2$S$_5$glass-ceramics/LiCoO$_2$ (Chem.Letters 2002)
- Takada et al (NIMS-Tsukuba)
  C/LiI-Li$_2$S-P$_2$S$_5$ (g)//Li$_3$PO$_3$-Li$_2$S-SiS$_2$(g)/ LiCoO$_2$ (SSI 2003)
**Li (or Li-ion) microbattery**

Reduction of power supply of electronics devices

- **Active power sources:**
  implantable medical devices, remote sensors, miniature transmitters, smart cards

- **Standby power sources:**
  CMOS-SRAM memory devices (few mWh.cm$^{-2}$ are required to back up a CMOS memory chip)

Thin-films lithium battery developed at ORNL

Levasseur group Bordeaux Fr; Industrialization HEF Group (SVF Gazette du Vide 2 march 2003)
Photodissolution (« photodoping »)

Illumination of a chalcogenide film in contact with silver

-> rapid penetration of the metal into the semiconductor (Kostyshin (1966))

Typical features:
- large amount of Ag can be dissolved 30-40 at%, and even 57% in GeS$_3$
- rate of dissolution depends on chalcogenide composition (excess in chalcogen)

**Mechanism**

1. **ionization of Ag**
   (semiconductor → presence of holes or electrons)
   \[
   \text{Ag} + h^+ \rightarrow \text{Ag}^+
   \]
   \[
   \text{Ag} \rightarrow \text{Ag}^+ + e^-
   \]

2. **reduction of chalcogenide**
   \[
   2\text{Ag} + \text{Se} \rightarrow \text{Ag}_2\text{Se} \quad \Delta G_{298}^\circ \approx -25 \text{ kJ/mol}
   \]
   \[
   4\text{Ag} + 2\text{As}_2\text{Se}_3 \rightarrow 2\text{Ag}_2\text{Se} + \text{As}_4\text{Se}_4 \quad \Delta G_{298}^\circ \approx -12 \text{ kJ/mol}
   \]

**Photon-enhanced solid state reaction**

Application of photodissolution

- Very sharp edges between doped and undoped regions
- Local creation of pairs « electron-hole » + small diffusion length of free carriers
  - Hardly any lateral diffusion
- Solubility of doped region in alkaline solvents much reduced
  - Local change in chemical composition

photoresists $\longrightarrow$ etched gratings
Photomigration - Photodeposition

Phenomenon observed in highly doped chalcogenide: Ag-Ge-S(e), Ag-As-S(e). For example in \((\text{Ge}_{0.3}\text{S}_{0.7})_{100-\times}\text{Ag}_{\times}\) films when \(\times > 0.45\)

Illumination

lower silver content (\(\times < 0.45\))

increase in Ag density in the illuminated part

higher silver content (\(\text{Ag}_{45}\text{As}_{15}\text{S}_{40}\))

precipitation of Ag

Small clusters or crystals 10nm in diameter and 1nm in thickness

Reversible process

Annealing \(\rightarrow\) dissolution of the Ag clusters

T. Kawaguchi et al JNCS 212 (1997) 1666
Mechanism of photomigration—photodeposition

**Point of view of physicist**

Illumination

creation of pair « electron-hole »

\[ \text{Ag}^+ + e^- \rightarrow \text{Ag} \]

\( h^+ \) moves away from illuminated spot

**Point of view of chemist**

Photodecomposition = decomposition of an oversaturated Ag solid solution

Under illumination the metastable system approaches equilibrium with excess Ag segregation.

Annealing at higher temperature allows Ag to dissolve again in the solid solution
Application of photomigration-phodeposition

- Increased reflectivity for Ag rich region
- Photoexpansion

Gratings/ microlenses

Optical memories

Au addition → increase in the photosensitivity of photodeposition by two orders of magnitude (Au clusters = nucleation centers for Ag)

Photocrystallisation (phase change)

Exist in chalcogenide with or without ion

Ge-Sb-Te (GST-Ge$_2$Sb$_2$Te$_5$)

Ag-In-Sb-Te (AIST)

Ordered state

crystalline AgSbTe$_2$ + amorphous In-Sb

Disordered state

amorphous AgSbTe$_2$ + amorphous In-Sb

Critical cooling rate
3.4 K/ns

Different reflectivity for amorphous and crystalline AgSbTe$_2$
Application of photocristallisation

Rewritable optical disk memory
Phase change:
Write/Erase phenomena

Laser-induced annealing/melting

Pulse structure
Ge-edge data (Ge$_2$Sb$_2$Te$_5$)

The transition between the crystalline and amorphous states can be viewed as an umbrella-switch of Ge atoms from a octahedral to tetrahedral symmetry position within the Te fcc sublattice.

Very big change in EXAFS and XANES

Real disc structure

Fig. 6. Cross-sectional TEM observation of the basic 4-layer phase-change optical disk.

UV resin
Reflection layer (heat sink)
Protection layer ZnS-SiO$_2$
Active layer (GST, AIST)
Protection layer ZnS-SiO$_2$
Polycarbonate disc

T. Ohta, JOAM 2001
WHY PHOTOSTRUCTURAL CHANGES OCCUR ONLY IN AMORPHOUS CHALCOGENIDES?

• Excitation of lone-pair electrons is a trigger of the structural change - presence of LP-electrons is crucial - group VI elements (chalcogens);
• Localization of photo-excited carriers and hence disorder is important - amorphous;
• Low coordination number is beneficial since it makes the structure floppy.

Amorphous chalcogenides are the only materials that satisfy all these requirements.
**Diffusion under \( \vec{E} \) and \( h\nu \): PMC memories**

« Programmable Metallization Cell Memory Devices »

- **bias** → accumulation of silver metal creating a conductive link (« on » state) - Ag is oxidised at the anode and reduced at the cathode
- Reversing the bias breaks down the silver and restore the initial resistive state (« off » state)

**Anode:** Ag or Ag-containing material

**Solid electrolyte:** Ag photodissolution in GeS(Se)y

**Cathode:** inert metal (Cr, Ni..)

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Ionic conductive chalcogenide glasses

Glasses exist in large composition domains

**Evolution of conductivity with composition**

- Non-Arrhenius behaviour ($\log \sigma \propto 1/T$)

**Ag (Na)-based chalcogenide glasses**

- $\text{Ag}_2\text{S} - \text{GeS}_2$
- $\text{Ag}_2\text{S} - \text{GeS} - \text{GeS}_2$
- $\text{Ag}_2\text{Se} - \text{GeSe}_2$
- $\text{Ag}_2\text{S} - \text{As}_2\text{S}_3$
- $\text{Na}_2\text{S} - \text{GeS}_2$

**Ag (Na) content varying from 0.01 - 30 at%**

*References:
M. Kawasaki, Kawamura J, Y. Nakamura and M. Aniya; SSI 123 (1999) 259
M.A. Urena, A.A Piarristeguy, M. Fontana and B. Arcondo; SSI 176 (2005) 505
3 different behaviours

- **Na$_2$S–GeS$_2$**: Change in the transport regime at about 1 at % in sodium (electronic to ionic ?)

- **Ag$_2$S–GeS–GeS$_2$ and Ag-based glasses**: Change in the transport regime at about 5-8 at % in silver

- **Ag-based glasses**: Large increase of 4-5 orders of magnitude in the conductivity at about 5-8 at % in silver
Ag$_2$S-GeS-GeS$_2$ and Ag-based glasses
Structural studies (microscopic, nanoscopic scale)

FE-SEM (Field Effect - Scanning Electron Microscopy)

Chemical inhomogeneities

EFM (Electric Force Microscopy) Surface potential imaging and surface electric modification

Electrical inhomogeneities
FE-SEM (LEO-982)

Ag$_2$S-GeS-GeS$_2$

No phase separation

Log (Conductivity Scm$^{-1}$)

$t_\sigma = 1.93$
Ag-based glasses showing a large increase (4-5 orders of magnitude) in the conductivity at about 5-8 at % in silver
The change in the conductivity regime occurs when the Ag-rich phase starts connecting.
Ag$_2$S - GeS$_2$

Glasses are phase separated

Ag-rich phase

Ag-poor phase

The change in the conductivity regime occurs when the Ag-rich phase starts connecting
Comparison FE-SEM / EFM (Ag2S-GeS2 glasses)

- Weak conductivity domain: Ag-poor phase connected
- High conductivity domain: Ag-rich phase connected

5%Ag

Clear areas (Ag-rich phase)
d~0,3µm

15%Ag

Dark areas (Ag-poor phase)
d~0,8-0,9µm

EFM -3V

Dark areas (Ag-rich phase)

EFM -3V

Clear areas (Ag poor phase)
(Ge$_{25}$Se$_{75}$)Ag:10%

Electrons retrodiffusés

Clear areas (Ag-rich phase in a Ag-poor matrix)

Dark areas in a clear matrix but a weaker contrast!
(Ge_{25}Se_{75})Ag:15% 

Electrons retrodiffusés

d~1µm

EFM

-3V

+4V

Topo

Z: 1.0 a.u.
X: 1.0 a.u.

Z: 156.0 nm
X: 5.0 µm
(Ge$_{25}$Se$_{75}$)Ag:25%
Variation of conductivity (298 K) with Ag content (at %) in Ag$_2$S - GeS$_2$ and Ag$_2$S - As$_2$S$_3$ glasses

The glasses are phase separated

The jump in the conductivity occurs when the phase previously embedded in the connecting phase becomes the connecting one

percolation threshold with the Ag-poor phase (Ag-rich phase) being responsible for the conductivity at low silver (high silver) content

At low Ag content, power law dependence: $\sigma = Cx^{t_\sigma}$

Nature of the charge carriers (electrons to ions)?

EMF $\leftarrow\rightarrow$ Tracer diffusion coefficient
Ag$_2$S - As$_2$S$_3$ glasses

Conductivity

$\sigma = C_\sigma x^{t_\sigma}$

$t_D = t_\sigma - 1$

low silver content: conductivity mainly ionic

high silver content: conductivity purely ionic $t_\sigma > 0.99$

(same conclusions for: Ag$_2$S-GeS$_2$ and Ag$_2$S-GeS-GeS$_2$)


Non-Arrhenius behaviour \((\log \sigma \propto 1/T)\) in glasses and more generally in super-ionic conductors
Arrhenius plots of $\sigma$ for different « superionic » glasses (temperatures below $T_g$)
Arrhenius plots of $\sigma$ for different « superionic » Crystallised phases

- Ag$_7$GeSe$_5$I
- Ag$_7$GeSe$_5$I Abdel
- Ag$_8$GeSe$_6$
- Ag$_7$PSe$_6$
- Ag$_8$SnSe$_6$
- Ag$_8$SiSe$_6$
- Li$_{0.5}$La$_{0.5}$TiO$_3$
- Nab''Al$_2$O$_3$
- Ag$_7$GeS$_5$I
- a-Agl
- RbAg$_4$I$_5$
- BiMeVOx$_x$
- SnCl$_2$
- CaF$_2$
- SrF$_2$
- BaF$_2$
Because of super-Arrhenius behaviour below Tg in glasses one can think that it exists a « Mobile ion » glass transition

Such a transition cannot be observed easily because its weakness. (To date it has only been reported by Hahashi and Ojuni – AgPO3-AgI glass at ~80K).

It is also possible to imagine a « mobile ion Tg » for superionic crystalline compounds with disorder in the mobile ion sub-lattice (for temperature higher than this hypothetical temperature ions move in a quasi-liquid sub-lattice)

For temperature greater than that of « mobile ion Tg » cooperative cation motions  → super-Arrhenius behaviour
Scaled Arrhenius plots of $\sigma$ for different “superionic” Glass and Crystalline compounds

In the absence of experimental data one can tentatively take for "mobile ion $T_g$" the temperature where the conductivity is about $10^{-9}$ S cm$^{-1}$, allowing a scaling of the variation of the conductivity

$$\log \sigma \propto T (\sigma = 10^{-9}) / T$$

Work done with Austen Angell
ASU - Tempe
STOP pour le moment