Lecture 5, Part 2: Novel functionalities of chalcogenide glasses

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Novel functionalities of chalcogenide glasses

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Thanks to ....
G. Chen, A. Ganjoo, K. Antoine, I. Biaggio
Lehigh University

National Science Foundation
International Materials Institute for New Functionality in Glass
Outline

- Introduction
- Photosensitivity
- Structure of ChG
- Speed of photosensitivity
- Examples of New Functionalities
What are Chalcogenide Glasses?


- transmission in the infrared
- high refractive index (~ 1.75 – 3)
- sensitive to bandgap light (1 – 3 eV), e-beam, x-rays
- photosensitive (photodarkening & photoexpansion)

Compounds of S, Se and Te e.g. elemental Se, Ge-Se, As-Se, As-S, Sb-Te,…

<table>
<thead>
<tr>
<th>Compounds</th>
<th>T&lt;sub&gt;g&lt;/sub&gt; (°C)</th>
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<tbody>
<tr>
<td>Silicates</td>
<td>~ 700</td>
</tr>
<tr>
<td>As-Se</td>
<td>~ 150</td>
</tr>
<tr>
<td>As-Se</td>
<td>~ 150</td>
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</tbody>
</table>
Recent new functionalities: **CD-RW and DVD-RW:** Phase-change memory

Laser power controls the switching between amorphous and crystalline states.

- High power → amorphous
- Medium power → crystalline
Recent new functionalities: FIR Night vision system on BWM 7 series

IR imaging
http://www.seniimg.co.za/index.php?ArticleId=2621784
Micro/Nano Lithography


Etchless Lithography

Optically written honeycomb structure with \(~1 \ \mu\text{m}\) radius

Outline

✓ Introduction
✓ Photosensitivity
✓ **Structure of ChG**
✓ Speed of photosensitivity
✓ Examples of New Functionalities
Crystal structure of $\text{As}_2\text{Se}_3$

Two-dimensional layer structure

Covalent bonding:
- 8-N rule
- Se: 2-fold
- As: 3-fold
- Each As bonds to Se
- Each Se bonds to As
Layered structure

Covalent bonding:
S: 2-fold
As: 3-fold
Each As bonds to S
Each S bonds to As

Crystalline structure of $\text{As}_2\text{S}_3$
3D Four fold coordinated

Covalent bonding:
Se: 2-fold
Ge: 4-fold
Each Ge bonds to Se
Each Se bonds to Ge
First Principles MD simulation of $\text{a-As}_2\text{Se}_3$ structure

- Se atom
- As atom

Chemical disorder:
- As-As and Se-Se
Coordination defects:
- Se$_3^+$, Se$_1^-$, As$_4^+$, As$_2^-$
Valence alternation pairs (VAP):
- $2 \text{Se}_2^0 \rightarrow \text{Se}_3^+ + \text{Se}_1^-$

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<th>Chemical disorder</th>
<th>Coordination defects</th>
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<tbody>
<tr>
<td>As</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Se</td>
<td>High</td>
<td>High</td>
</tr>
</tbody>
</table>

Li and Drabold (2001)
Wide composition range

As based films expand and photodarken

Ge-based films contract and photo bleach

Potential new applications:
Creating micro and nano-sized optical components (lenses, gratings etc.)
Convex and concave structures can be developed by light on changing the composition

What happens at the atomic scale? Can we see similar features at an atomic scale??

Temporary reversible effects

**photodarkening**

Change in absorptivity with time for a-As$_2$Se$_3$ films, $\Delta \alpha$, after illumination at 50 K (solid line) and 300 K (dashed line). Ar laser ON and OFF for 20 s each at 50 K; and 10/20 s at 300 K. (Ganjoo et al.)
**Photostructuring of ChG: Why ChG?**

Based on group VI elements (S, Se, Te) as one of the major components. e.g. Se, sulfides or selenides of Ge, Sb or As, etc.

**Materials that may show photosensitivity have:**
- Low average coordination number
- Low steric hindrance or large internal volume
- Strong localization of light generated e-h pair: tight binding, lack of periodicity / disorder → Concentration of recombination energy in a small volume and change in valence of atoms before recombination.

Chalcogenide glasses are best suited for producing photosensitive phenomena by the near and above-bandgap-light illumination.

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**Diagram:**
- **Conduction band**
- **Valence band**
- **Bandgap light**
- **Excitation**
- **Recombination**
Consequence of photostructuring
What does it do?

Miracles…

- volume: integrated optics devices
- amorphization/ devitrification: CD-RW, DVD-RW
- mechanical properties - plasticity
- viscosity - athermal melting
- optical properties - darkening, birefringence
- electrical properties - conductivity, dielectric constant
- chemical properties - etching, dissolution
Optical field-induced mass transport

Salimia et al., (2000)

- A gaussian polarized Ar laser (514.5 nm) beam of circular x-section created an anisotropic crater on the surface of an a-As₂S₃ film.
- Circularly polarized light makes a dip with circular pile up.
Photoinduced Changes

Ability to recover
- Permanent
- Reversible

Effect of light polarization
- Scalar
- Vector

- Metastable
- Temporary

Permanent: can't be recovered w/o remaking the glass
Metastable: recovered on heating to ~Tg
Temporary: recovered on removing the light
Scalar: don’t depend upon the polarization of the light
Vector: depend upon the polarization of the light

Temporary + Vector = Smart
Outline

- Introduction
- Photosensitivity
- Structure of ChG
- Speed of photosensitivity
- Examples of New Functionalities
XPS with *in situ* laser irradiation

- Monochromatic x-rays → photoelectrons
- Electrons emitted with kinetic energies related to their binding energies
- Density of states
- Shift in peaks shows the change in the bonding character of the atoms

Scienta ESCA 300
Distribution of coordination configurations for Se in $a$-As$_2$Se$_3$

Laser irrad.

Se-[2(Se/As)]

Se-[3(Se/As)]

Se-(Se)

Laser reduces coordination defects around Se permanently ⇒ Optical annealing
X-ray absorption fine structure (XAFS)

X-rays of varying photon energies excite the electrons in a central atom (absorbed=> absorption edge)
Resulting photoelectrons have a low kinetic energy and are backscattered by the atoms surrounding the emitting atom. Probability of backscattering depends on the energy of the photoelectrons.
The net result is a series of oscillations on the high photon energy side of the absorption edge.

What can we obtain from EXAFS?
✓ Local structure around a specific element.
✓ Average inter atomic distance (R)
✓ Mean square relative displacement (MSRD)
✓ average coordination number (CN)

EXAFS spectrum of Se K-edge

Honorary Symposium Recognizing the Life Long Contributions of Professor Cornelius T. Moynihan
Structure and Properties of Non-Oxide Glasses
Experimental details

a-As$_2$S$_3$ films; a-GeSe$_2$ films

In-situ EXAFS at NSLS, BNL

For a-As$_2$S$_3$ films: beamline X19A; As (11.867 keV) and S (2.472 keV) K-edges
  (Different spots, different scans)

For a-GeSe$_2$ films: beamline X18B; Ge (11.103 keV) and Se(12.658 keV) K-edges
  (Same spot; one scan)

Data collected in fluorescence mode before (As prepared: AP), during (ON) and after laser illumination (OFF) states of the sample

Illumination sources

For a-As$_2$S$_3$ films: Ar$^+$ laser (488 nm; 50 mW/cm$^2$)

For a-GeSe$_2$ films: Semiconductor laser (633 nm; 50 mW/cm$^2$)
In-situ experimental setup at X19A beamline

X-rays

Si (111) monochromator

Huber slit

I₀ ion chamber

Laser

Fluorescence detector

(PIPS, 13 element Ge detector, Lytle detector)

Sample

Reference sample

Iₜ ion chamber

Iₗ ion chamber

NSLS X18B beamline hutch

Honorary Symposium Recognizing the Life Long Contributions of Professor Cornelius T. Moynihan Structure and Properties of Non-Oxide Glasses
In situ EXAFS

Synchrotron x-rays: linearly polarized

Looking for laser-induced polarization-dependent changes.
(a): X-ray absorption spectrum of an a-As$_{40}$Se$_{60}$ film beyond As and Se K-edges.

(b) and (c): The EXAFS oscillations derived from (a).
Structural changes around As atoms

Sample: as-prepared As$_{40}$Se$_{60}$ film

AP: as-prepared
ON: laser is on
OFF: laser is off

VP: laser has vertical polarization.
HP: laser has horizontal polarization
X-rays’ polarization is horizontal.
Structural changes around Se atoms

Sample: as-prepared As$_{40}$Se$_{60}$ film

AP: as-prepared
ON: laser is on
OFF: laser is off

VP: laser has vertical polarization.
HP: laser has horizontal polarization
X-rays’ polarization is horizontal.
1. **Photo-chemical reaction**

Microscopic heterogeneity in AP films

\[ \text{Se–Se} + \text{As–As} \xrightarrow{\text{Light}} 2\text{As–Se} \]

\[ \text{R}_{\text{As-As}} > \text{R}_{\text{As-Se}} > \text{R}_{\text{Se-Se}} \implies \uparrow \text{R}_{\text{Se-NN}} \text{ and } \downarrow \text{R}_{\text{As-NN}} \]

However, experiments: \( \uparrow \) in both \( \text{R}_{\text{Se-NN}} \) and \( \text{R}_{\text{As-NN}} \)

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**Mechanisms of Scalar Changes**

**R}_{\text{As-NN}}: small permanent ↑ expansion**

**R}_{\text{Se-NN}}: large permanent ↑ expansion**

**Covalent Radii:**

As: 1.21 Å. Se: 1.17 Å
2. **Strain relief**

Intramolecular bonds in As-rich molecules are highly strained

⇒ breaking of such molecules by light will \( \uparrow R_{\text{As-Se}} \)

⇒ \( \uparrow R_{\text{Se-NN}} \) and \( \uparrow R_{\text{As-NN}} \)

\[ 1 + 2 \Rightarrow \text{large } \uparrow \text{ in } R_{\text{Se-NN}} \text{ & small } \uparrow \text{ in } R_{\text{As-NN}} \]
PRDF around Ge for α-GeSe₂ films

As deposited film
During Illumination
After Illumination

R (Å)

FT (χ(k)xk³) (x10⁻¹) (a.u.)

R (Å)
GeSe₂ EXAFS
a-GeSe₂ films:
Decrease in Geₙₙ and Seₙₙ distances with illumination ⇒ CONTRACTION IN VOLUME

Mechanism of photoinduced changes

AP films: Chemical disorder: Ge-Se, Ge-Ge and Se-Se bonds

1. Photochemical reaction
Ge - Ge + Se - Se ⇒ 2 Ge - Se (similar to effect of annealing)
Ge-Se bonds energetically favored

Bond lengths from covalent radii:
Ge-Ge (2.44 Å) > Ge-Se (2.36 Å) > Se-Se (2.32 Å)
⇒ R₉e-NN should decrease and Rₜe-NN should increase;
but Rₜe-NN is also decreasing

2. Strain relief
Light has similar effect on the NN distance as thermal annealing does
Light relieves highly strained atoms
(mostly strained 2 fold Se atoms bonded both to Ge and Se)
Decrease in Se NN distances - Experimentally observed by in-situ EXAFS
Mechanism of photo-structural change

MD simulation shows Se 4p lone pair (LP) electrons occupy top of the valence band

Li, Drabold, et al. (2003)
**Mechanism of Vectoral Changes**

MD simulation shows Se 4p lone pair (LP) electrons occupy top of the valence band

Li, Drabold, et al. (2003)

AP: As-rich molecules ($\text{As}_4\text{Se}_4$) and Se-rich phase co-exist in AP a-$\text{As}_2\text{Se}_3$ film.

ON: As dangling bonds (from As-As bonds in $\text{As}_4\text{Se}_4$ molecules) react with preferentially excited Se 4p LP’s (orbital $\parallel E_{\text{laser}}$), form anisotropic As-Se.

OFF: Anisotropic As-Se bonds can be detected by polarized X-rays.
Amorphous Semiconductors

Excited electronic carriers

Relaxation

Within ps region, electrons relax to the bottom of conduction band (sometimes forming polarons)

System → Equilibrium mainly through:
Electronic relaxations and lattice relaxations

Carriers recombine radiatively or non-radiatively, and the electronic relaxation terminates

In capture process (trapping and detrapping), lattice distortion may be enhanced

Lattice relaxations may occur in time domain extending from ~ps to infinite times

Energy-relaxation processes in amorphous semiconductors

A: Non-radiative recombination
B: Radiative recombination
C: Capturing process

Ke. Tanaka, JAP (1989)
Photoinduced changes in absorption coefficient

Absorption edge believed to shift in parallel by annealing and illumination (Tanaka et. al., 1981)

Measurements after illumination (Metastable state only)

In-situ measurements at a single wavelength should represent changes at other wavelengths as well?

Tanaka et. al., JNCS (1981)
Speed of reversibility is crucial: In situ vis-NIR spectroscopy

Use of an optical spectrometer (450 – 1000 nm) that allows real time data acquisition in the millisecond range.

Light from probe beam and pump beam are coincident on the film. Probe beam size is smaller than pump beam.
Evolution of photodarkening

The strength of fringes $\Delta I = (I_{\text{max}} - I_{\text{min}})$ i.e. the optical path first decreases and then increases in time $\Rightarrow$ photodarkening and photoexpansion have different kinetics. Be careful when using the classical Swanepoel’s method for data analysis of transmission spectra of thin films.

Tanaka: $a\text{- As}_2\text{S}_3$ indicate that the rate of photovolume expansion (a photostructural change) is greater than that of photodarkening for bandgap illumination.
PD kinetics in the strong absorption region ($\geq 10^4$ cm$^{-1}$)

012506 - Optical transmission spectra of $\alpha$-As$_2$Se$_3$ film
Pump laser $\lambda = 660$ nm
$I_0 = 280$ mW/cm$^2$

Strong absorption region ($\alpha \geq 10^4$ cm$^{-1}$)
Photobleaching in Ge-Se glass

- Ge$_{22}$As$_{23}$Se$_{55}$, 660nm, 146mW/cm$^2$
Evolution of photodarkening

\[ \Delta \alpha = [\alpha - \alpha(t=0)] \left[ 1 - \exp\left(-\frac{t}{\tau}\right)^\beta \right] \]

Initial photodarkening: \( \text{As}_2\text{S}_3: \lambda_{\text{pump}} = 488 \text{ nm}, I_0 = 25 \text{ mW/cm}^2 \)

\( \lambda = 633 \text{ nm} \)

Ganjoo and Jain,
Photodarkening kinetics at various intensities

Plot of $\Delta \alpha(I_0)$ vs. $t$ for $\lambda = 600$ nm. $I_0$ = laser intensity.
Plot of $\tau$ vs. $I_0$

012506 - $a$-As$_2$Se$_3$ under in situ illumination
Pump laser $\lambda = 660$ nm

Stretched exponential:

$$\Delta \alpha = [\alpha_\infty - \alpha(t=0)][1-\exp(-t/\tau)^\beta]$$
Fast optical changes

Decay of the transient part of photoinduced changes in transmission with time after pulsed laser illumination (1.1 mJ/cm²)

Fast photo-effects by transient grating method

- Two nearly equal intensity laser pulses made to cross within the sample at an angle.
- Interference of two “writing pulses” within the sample writes a transient grating (by inducing a change in the refractive index).
- The grating spacing varies with angle between the writing beams.
- The refractive index grating is read by diffracting a probe beam off the grating at the Bragg condition.
- The diffracted probe light is collected by a high speed photomultiplier.
- As grating disappears, the time dependence of the probe intensity reflects the decay of the change in refractive index and thus the carrier kinetics.
Advantages of transient grating technique

$$\Lambda \propto \frac{1}{\theta}$$

High signal/noise ratio

Can control the grating spacing (e.g. 0.675, 1.1 and 1.65 μm presently) by changing the angle between the two beams

Helpful in understanding the meaning of the time constants
Ultra fast photoinduced changes from 20 ps pulse

Transient Grating, Four-Wave Mixing method: diffracted intensity

The photo-response to pulsed illumination is composed of a fast ~80 ps component followed by nanosecond component. The “ultra fast” component shows almost third-order power dependence indicating third-order nonlinear effect in As50Se50.
Grating spacing: 1.65 μm

Amplitude (a.u.)

-5.0x10^{-4} -1.0x10^{-4} 0.0 1.0x10^{-4} 2.0x10^{-4} 3.0x10^{-4} 4.0x10^{-4} 5.0x10^{-4} 5.0x10^{-3} 1.0x10^{-3} 2.0x10^{-3} 3.0x10^{-3} 4.0x10^{-3} 5.0x10^{-3}

time (μs)

-0.2 0.0 0.2 0.4 0.6 0.8 1.0

-5.0x10^{-4} -1.0x10^{-4} 0.0 1.0x10^{-4} 2.0x10^{-4} 3.0x10^{-4} 4.0x10^{-4} 5.0x10^{-4} 5.0x10^{-3} 1.0x10^{-3} 2.0x10^{-3} 3.0x10^{-3} 4.0x10^{-3} 5.0x10^{-3}

time (μs)

Center for Optical Technologies

Grating spacing: 1.65 μm

Δn ~1.21x10^{-4}

-0.2 0.0 0.2 0.4 0.6 0.8 1.0

-5.0x10^{-4} -1.0x10^{-4} 0.0 1.0x10^{-4} 2.0x10^{-4} 3.0x10^{-4} 4.0x10^{-4} 5.0x10^{-4} 5.0x10^{-3} 1.0x10^{-3} 2.0x10^{-3} 3.0x10^{-3} 4.0x10^{-3} 5.0x10^{-3}

time (μs)

-0.2 0.0 0.2 0.4 0.6 0.8 1.0

-5.0x10^{-4} -1.0x10^{-4} 0.0 1.0x10^{-4} 2.0x10^{-4} 3.0x10^{-4} 4.0x10^{-4} 5.0x10^{-4} 5.0x10^{-3} 1.0x10^{-3} 2.0x10^{-3} 3.0x10^{-3} 4.0x10^{-3} 5.0x10^{-3}

time (μs)

Center for Optical Technologies

Δn ~1.21x10^{-4}

-0.2 0.0 0.2 0.4 0.6 0.8 1.0

-5.0x10^{-4} -1.0x10^{-4} 0.0 1.0x10^{-4} 2.0x10^{-4} 3.0x10^{-4} 4.0x10^{-4} 5.0x10^{-4} 5.0x10^{-3} 1.0x10^{-3} 2.0x10^{-3} 3.0x10^{-3} 4.0x10^{-3} 5.0x10^{-3}

time (μs)

Center for Optical Technologies

Δn ~1.21x10^{-4}

-0.2 0.0 0.2 0.4 0.6 0.8 1.0

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time (μs)

Center for Optical Technologies

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time (μs)

Center for Optical Technologies

Δn ~1.21x10^{-4}

-0.2 0.0 0.2 0.4 0.6 0.8 1.0

-5.0x10^{-4} -1.0x10^{-4} 0.0 1.0x10^{-4} 2.0x10^{-4} 3.0x10^{-4} 4.0x10^{-4} 5.0x10^{-4} 5.0x10^{-3} 1.0x10^{-3} 2.0x10^{-3} 3.0x10^{-3} 4.0x10^{-3} 5.0x10^{-3}

time (μs)

Center for Optical Technologies
Relaxation time varies as square of grating spacing and nearly independent on the power density of the pump (in the range studied).