US-Japan Winter School

Semester Length Glass Courses and Glass Schools

Winter 1-1-2008

Lecture 5, Part 2: Novel functionalities of chalcogenide glasses

Himanshu Jain
Lehigh University

Recommended Citation

Jain, Himanshu, "Lecture 5, Part 2: Novel functionalities of chalcogenide glasses" (2008). *US-Japan Winter School*. 14.
https://preserve.lehigh.edu/imi-tll-courses-usjapanwinterschool/14

Novel functionalities of chalcogenide glasses

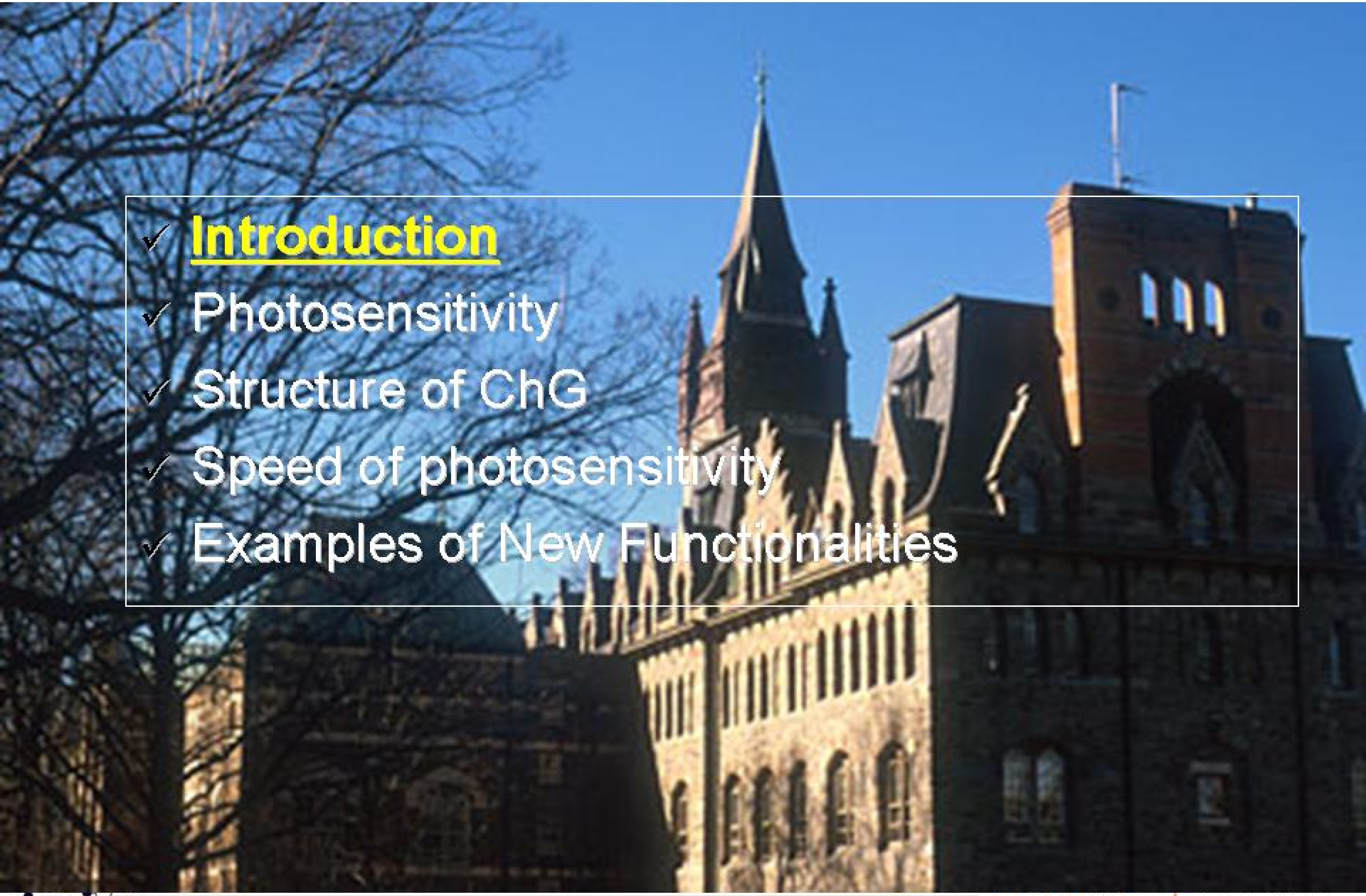
Himanshu Jain
Dept. of Materials Science & Engineering
Lehigh University, Bethlehem, PA 18015

Thanks to ….

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

National Science Foundation
International Materials Institute for New Functionality in Glass

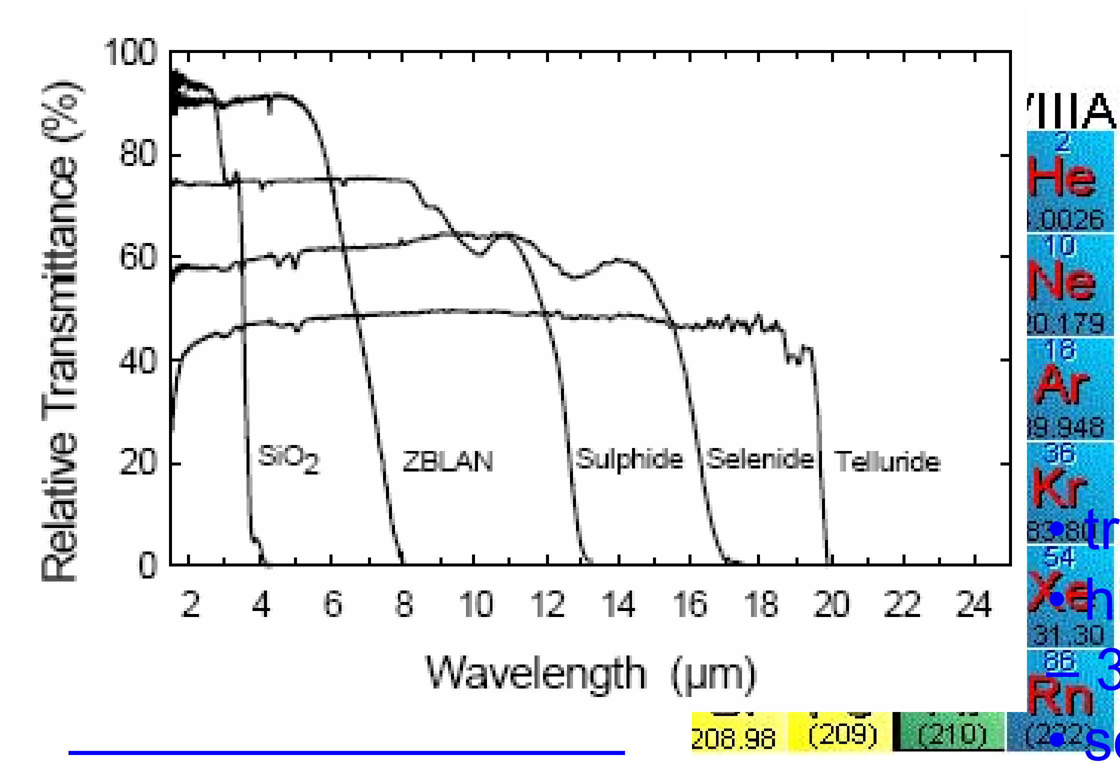
Outline



- ✓ **Introduction**
- ✓ Photosensitivity
- ✓ Structure of ChG
- ✓ Speed of photosensitivity
- ✓ Examples of New Functionalities

What are Chalcogenide Glasses?

After I.D. Aggarwal, J.S. Sanghera, “Development and Applications of Chalcogenide Glass Fibers at NRL”



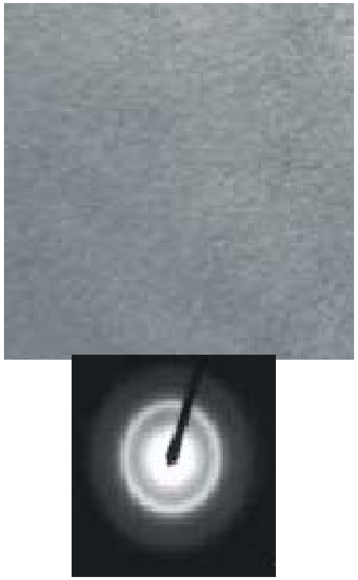
- transmission in the infrared
- high refractive index (~ 1.75 – 3)
- sensitive to bandgap light (1 – 3 eV), e-beam, x-rays
- **photosensitive** (photodarkening & photoexpansion)

	T_g (°C)
Silicates	~ 700
As-Se	~ 150

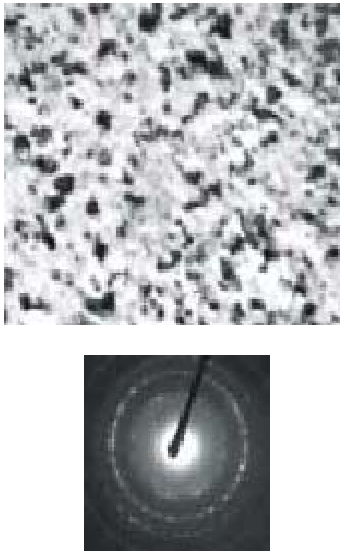
Compounds of S, Se and Te e.g. elemental Se, Ge-Se, As-Se, As-S, Sb-Te,…

Recent new functionalities:
CD-RW and DVD-RW: Phase-change memory

Laser power controls the switching between amorphous and crystalline states.



High power
→ amorphous



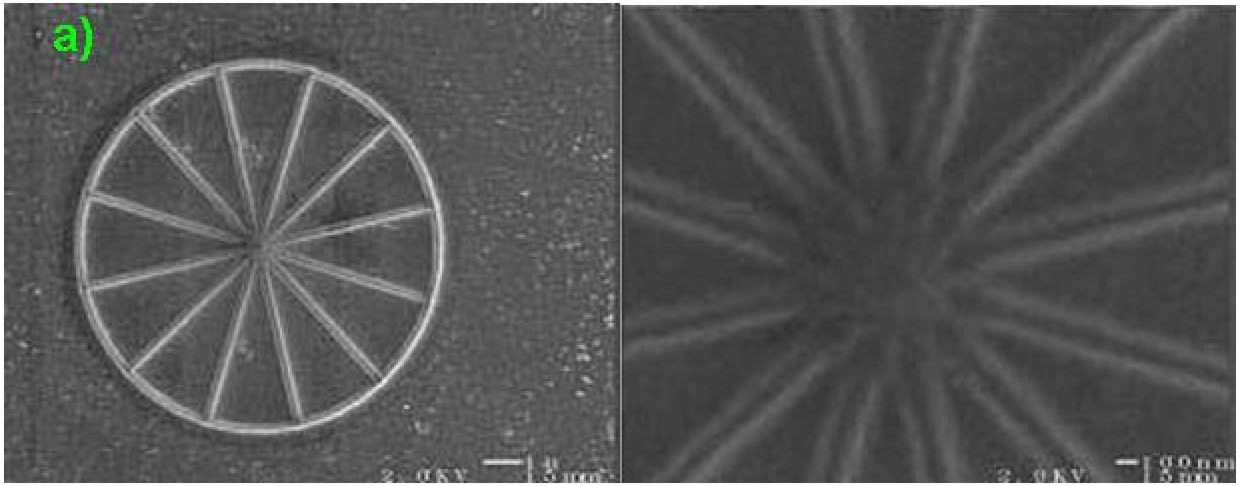
Medium power
→ crystalline

Recent new functionalities:
FIR Night vision system on BWM 7 series

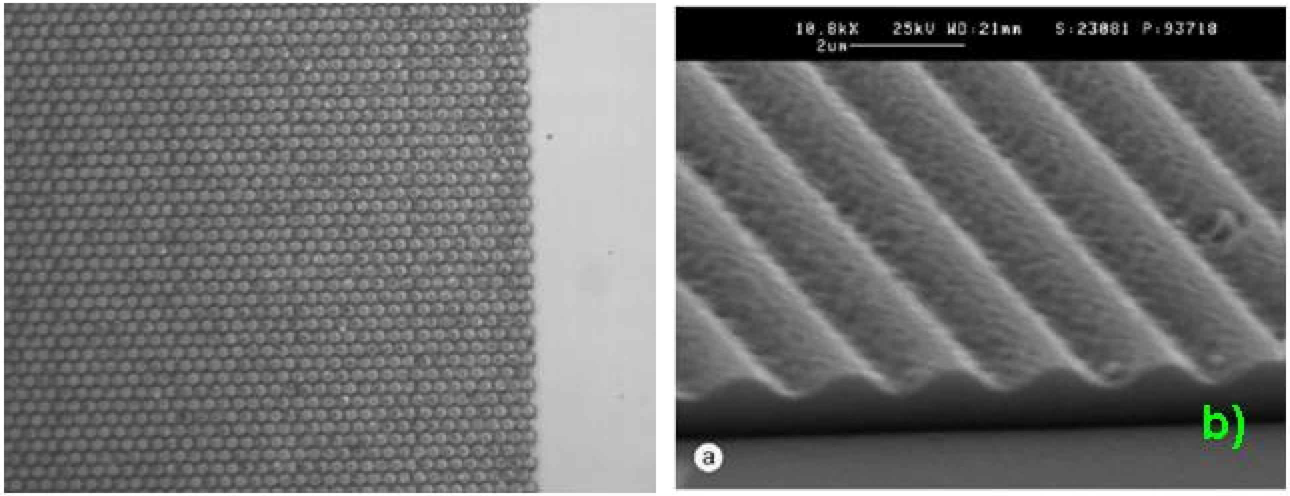
IR imaging

http://www.motoring.co.za/index.php?fArticleId=2621784

Micro/Nano Lithography



J.R. Neilson, A. Kovalskiy, M. Vlček, H. Jain, F.C. Miller, JNCS 353 (2007) 1427–1430.



Etchless Lithography

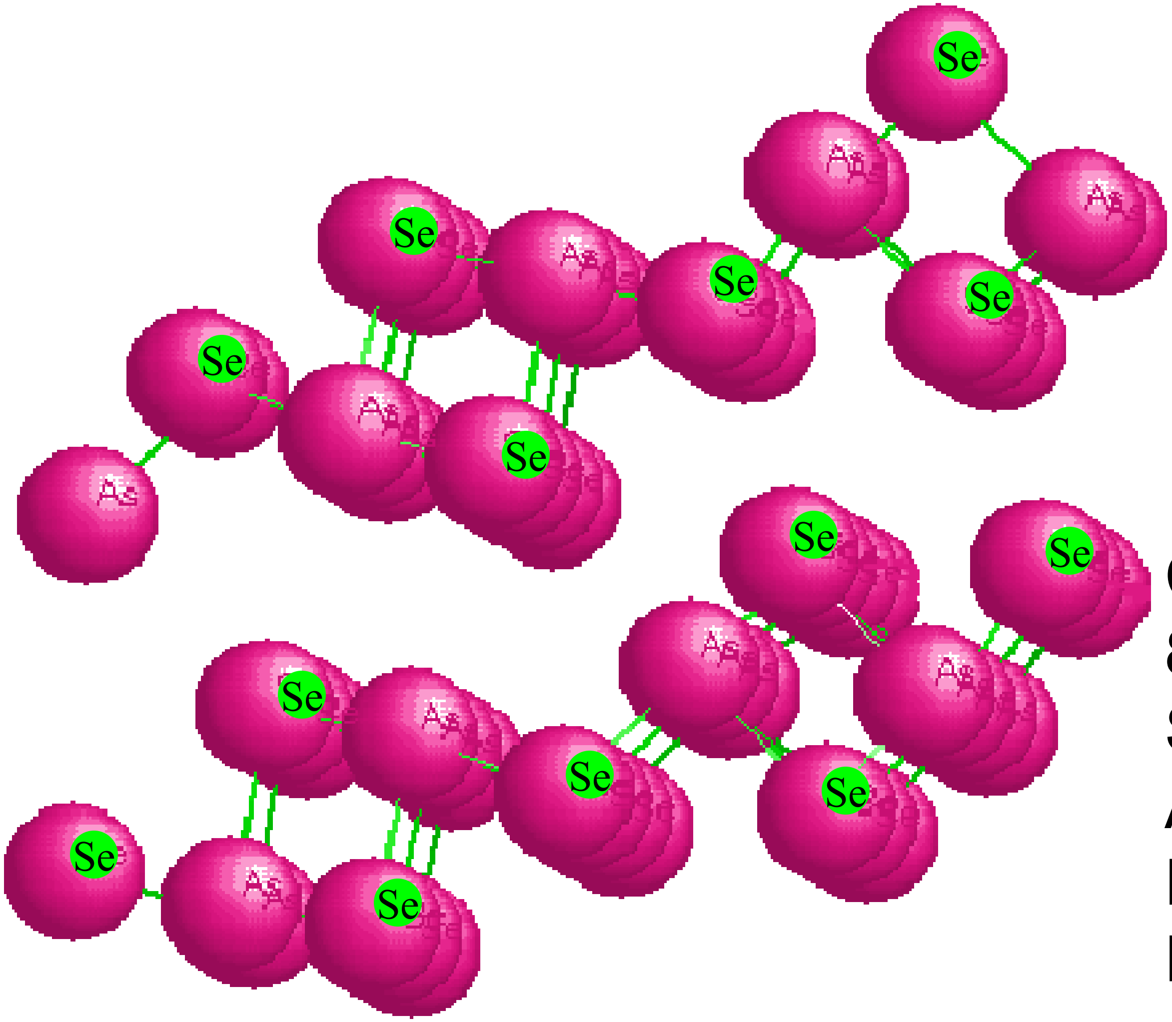
Optically written honeycomb structure with ~1 μm radius

M. Vlček, S. Schroeter, J. Čech, T. Wágner, T. Glaser, J. Non-Cryst. Solids, 326&327 (2003) 515

Outline

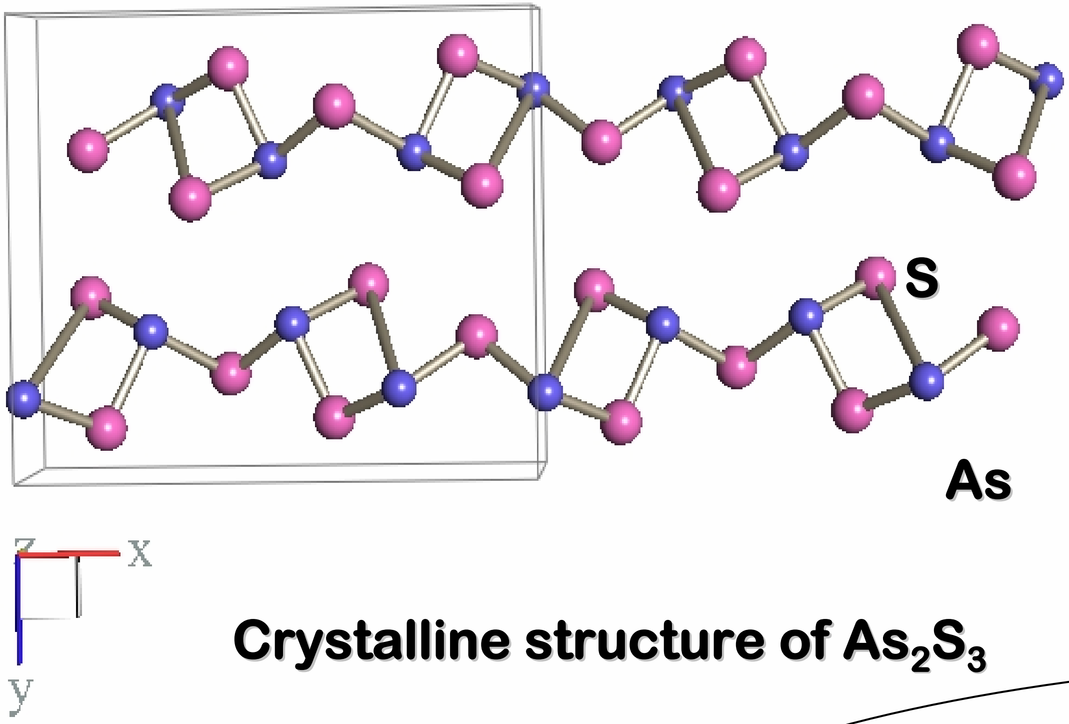
- ✓ Introduction
- ✓ Photosensitivity
- ✓ **Structure of ChG**
- ✓ Speed of photosensitivity
- ✓ Examples of New Functionalities

Crystal structure of As_2Se_3

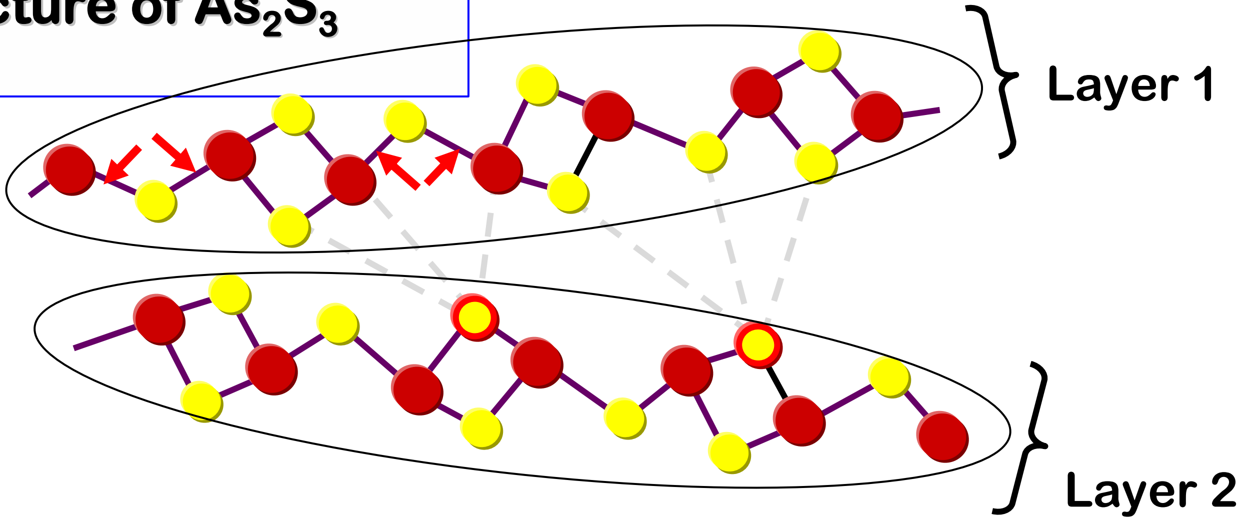


Two-dimensional layer structure

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



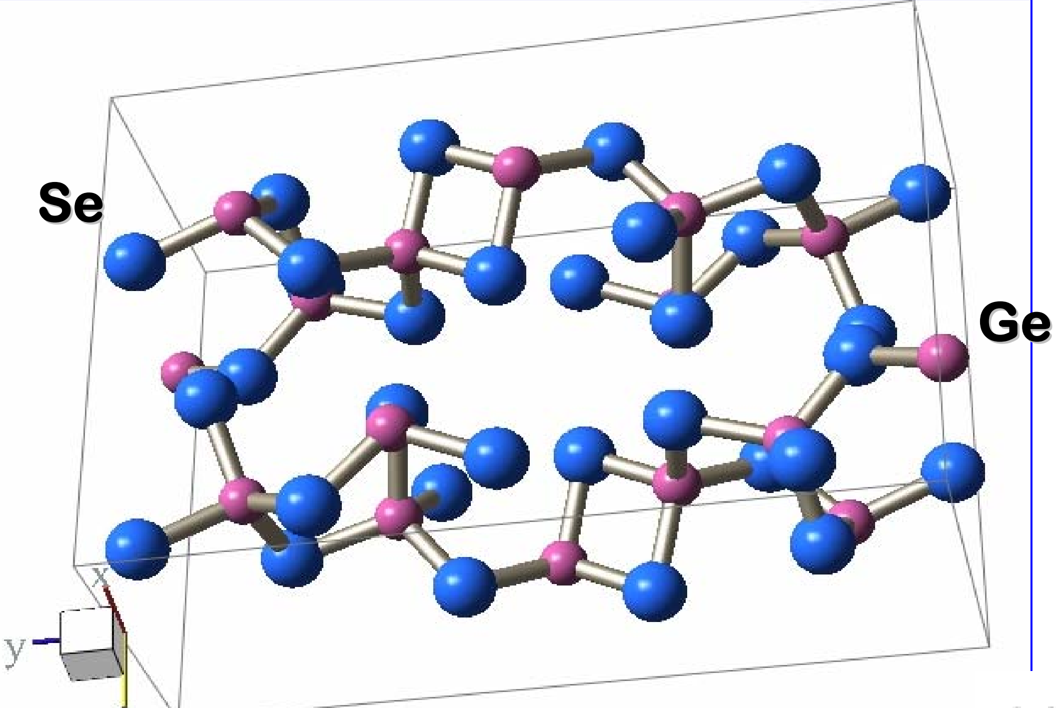
Crystalline structure of As_2S_3



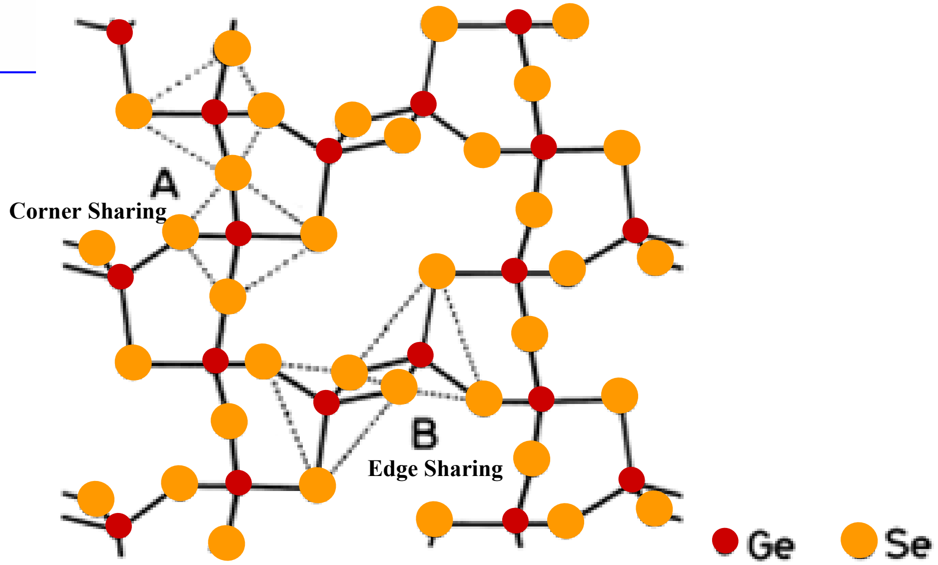
Layered structure

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

● As ● S (Se)



Crystalline structure of $GeSe_2$



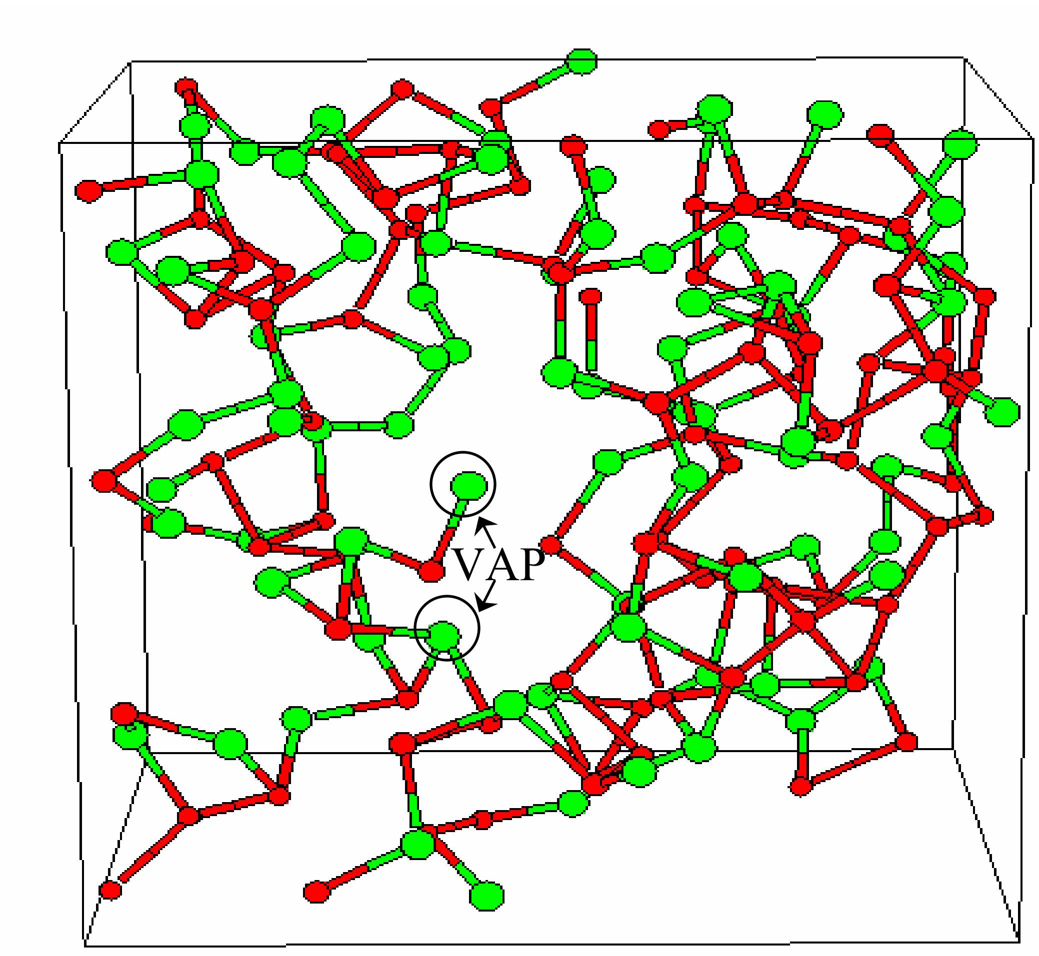
3D Four fold coordinated

Covalent bonding:
Se: 2-fold
Ge: 4-fold
Each Ge bonds to Se
Each Se bonds to Ge

First Principles MD simulation of a-As_2Se_3 structure

🟩 Se atom

🟥 As atom



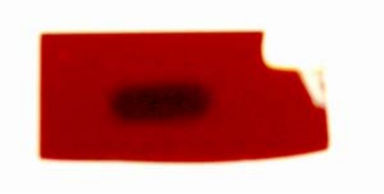
Li and Drabold (2001)

Chemical disorder:
As-As and Se-Se
Coordination defects:
Se_3^+, Se_1^-, As_4^+, As_2^-
Valence alternation pairs (VAP):
$2\ Se_2^0 \rightarrow Se_3^+ + Se_1^-$

	Chemical disorder	Coordination defects
As	**High**	**Low**
Se	**High**	**High**

Wide composition range

As based films expand and photodarken



Ge- based films contract and photo bleach

Potential new applications:

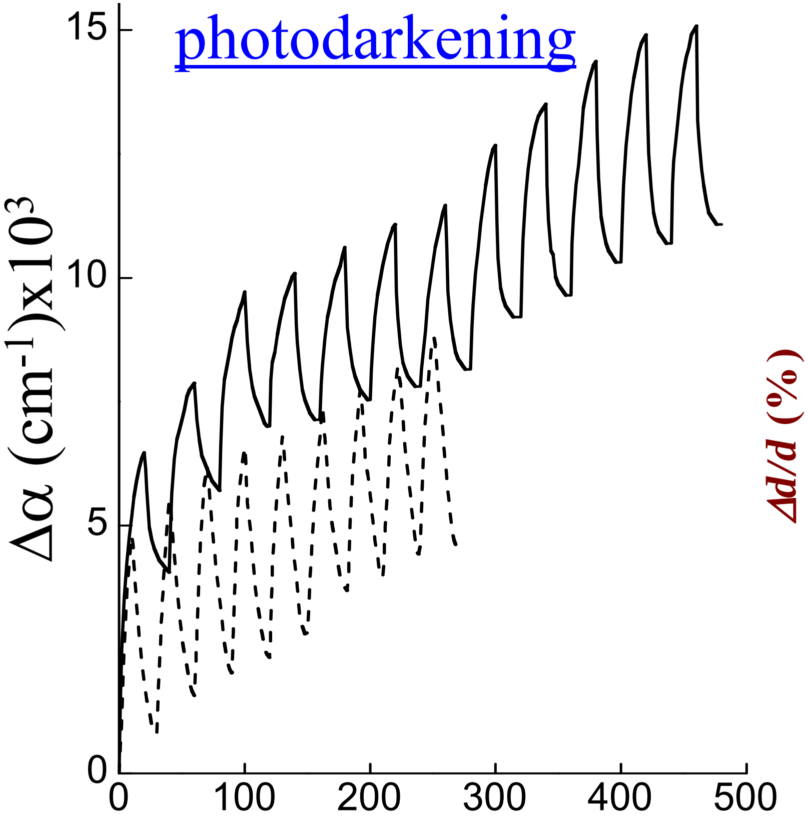
Creating micro and nano-sized optical components (lenses, gratings etc.)

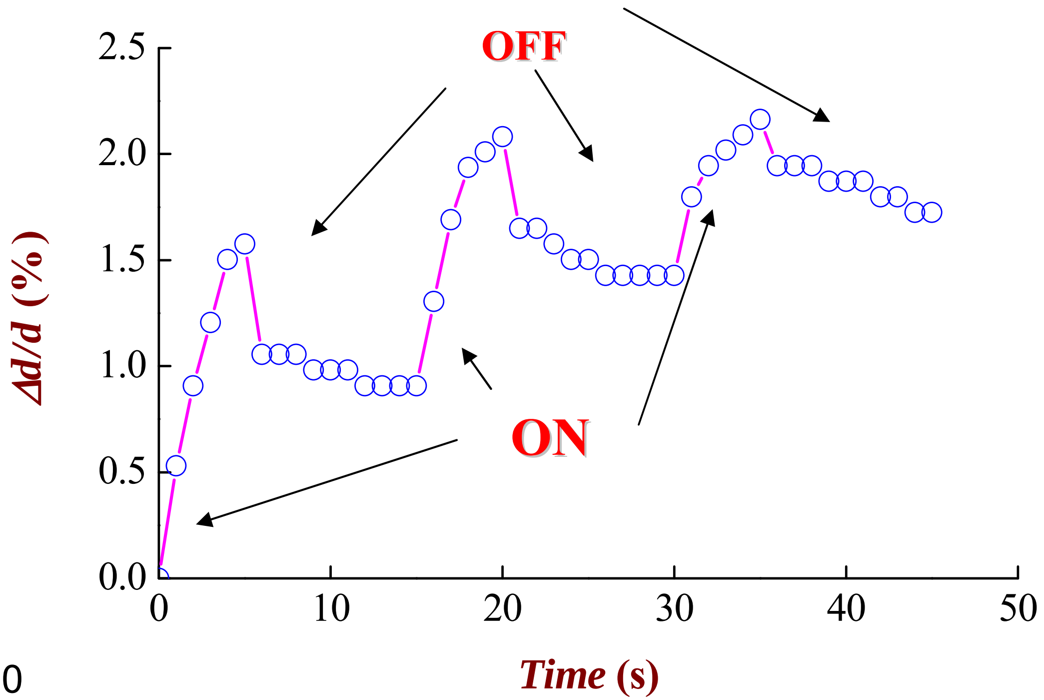
Convex and concave structures can be developed by light on changing the composition

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

*** Kuzukawa, Ganjoo and Shimakawa; J. Non-Cryst. Solids (1998)**

Temporary reversible effects


photodarkening


photoexpansion

Change in absorptivity with time for a-As_2Se_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.

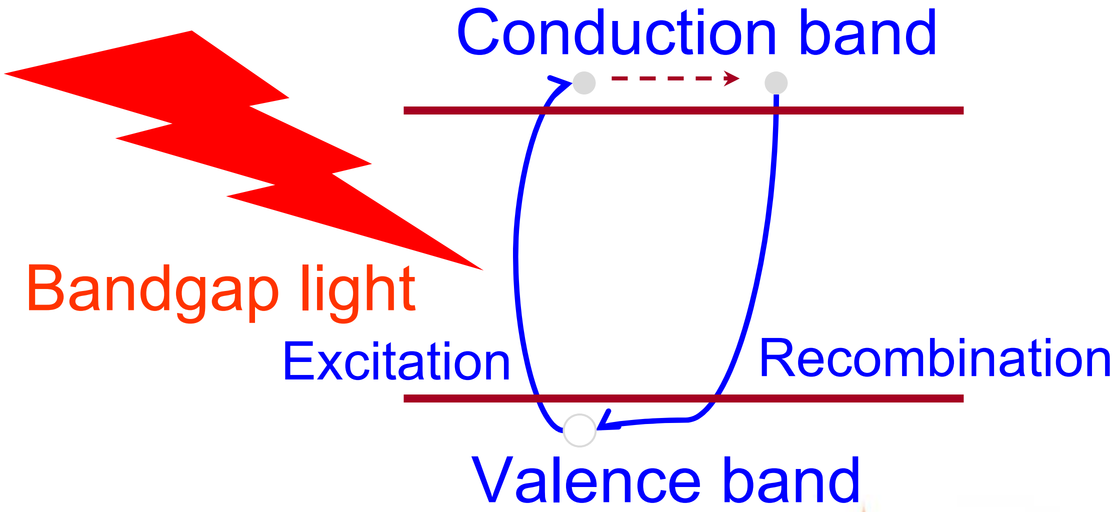
Materials that may show photosensitivity have:

- Low average coordination number
- Low steric hindrance or large internal volume

Also favor glass formation

- 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.



Consequence of photostructuring

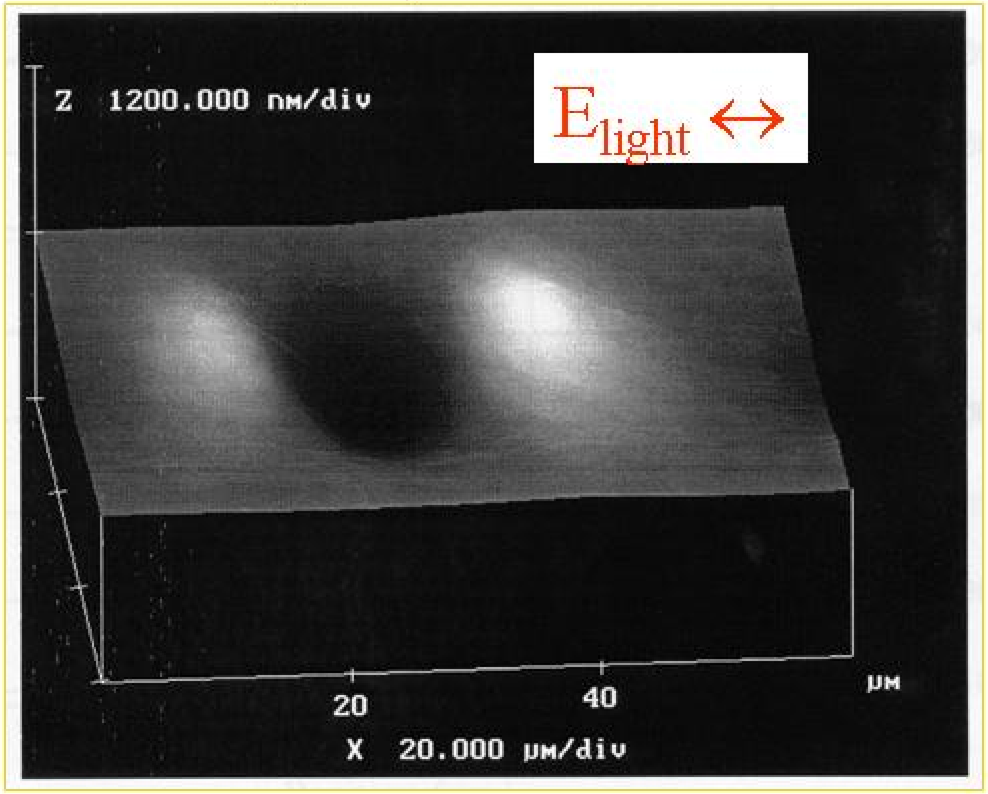
What does it do?

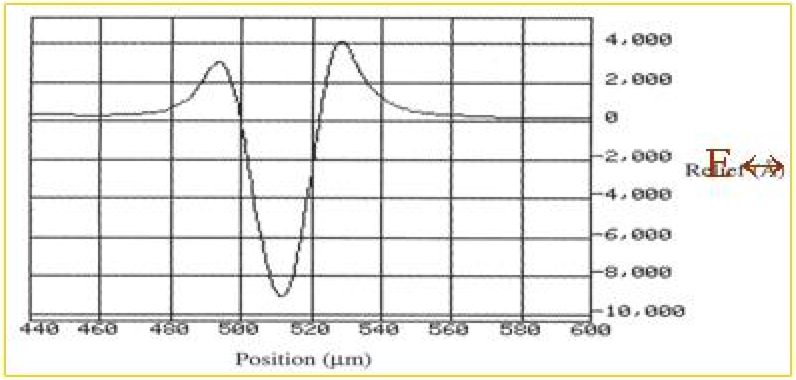
Miracles…

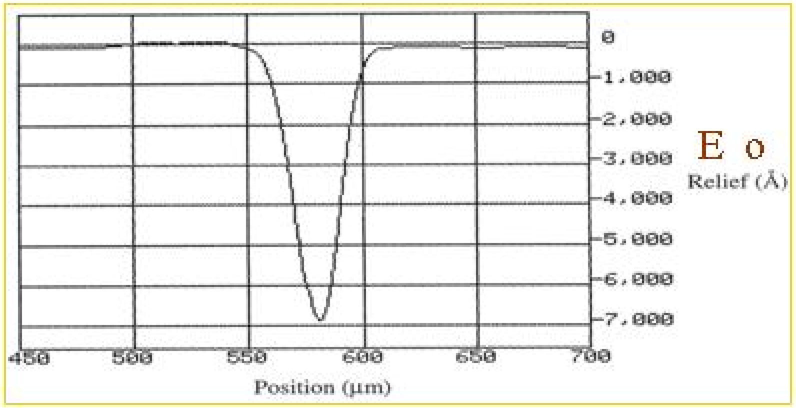
- volume: integrated optics devices
- amorphization/ devitrification: CD-RW, DVD-RW
- mechanical properties - plasticity
- viscosity - athermal melting
- optical properties - darkening, birefringence
- electrical properties - conductivity, dielectric constant
- chemical properties - etching, dissolution

Optical field-induced mass transport

Saliminia et al., (2000)

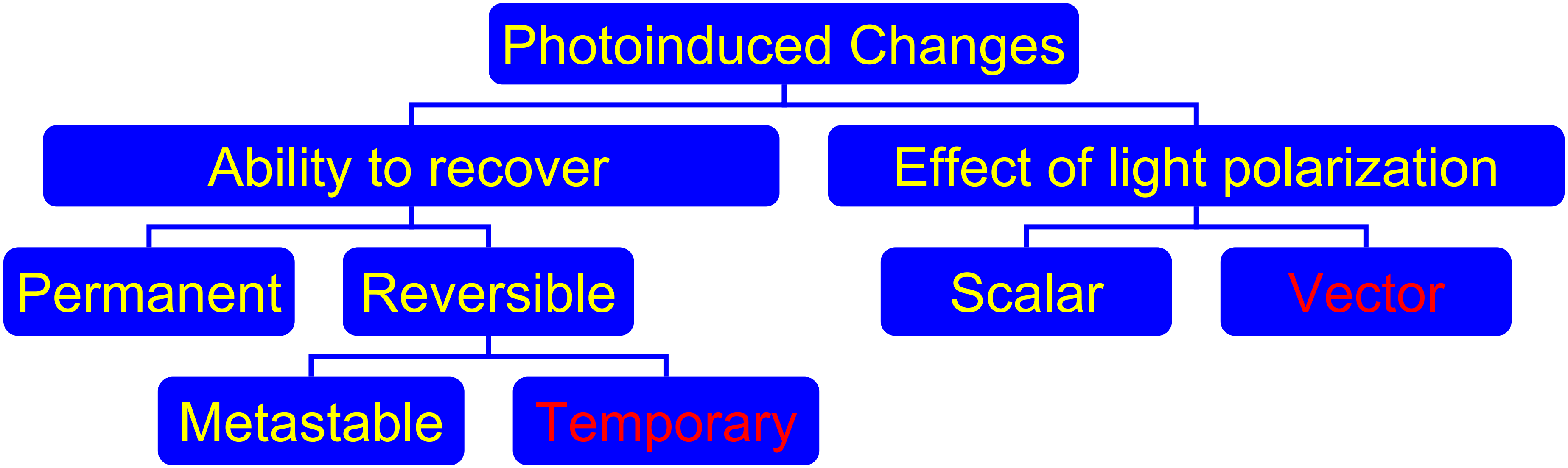






- A gaussian polarized Ar laser (514.5 nm) beam of circular x-section created an anisotropic crater on the surface of an a-As_2S_3 film.
- Circularly polarized light makes a dip with circular pile up.

Classification



Photoinduced Changes

- Ability to recover
  - Permanent
  - Reversible
    - Metastable
    - Temporary
- Effect of light polarization
  - Scalar
  - Vector

Permanent: can't be recovered w/o remaking the glass

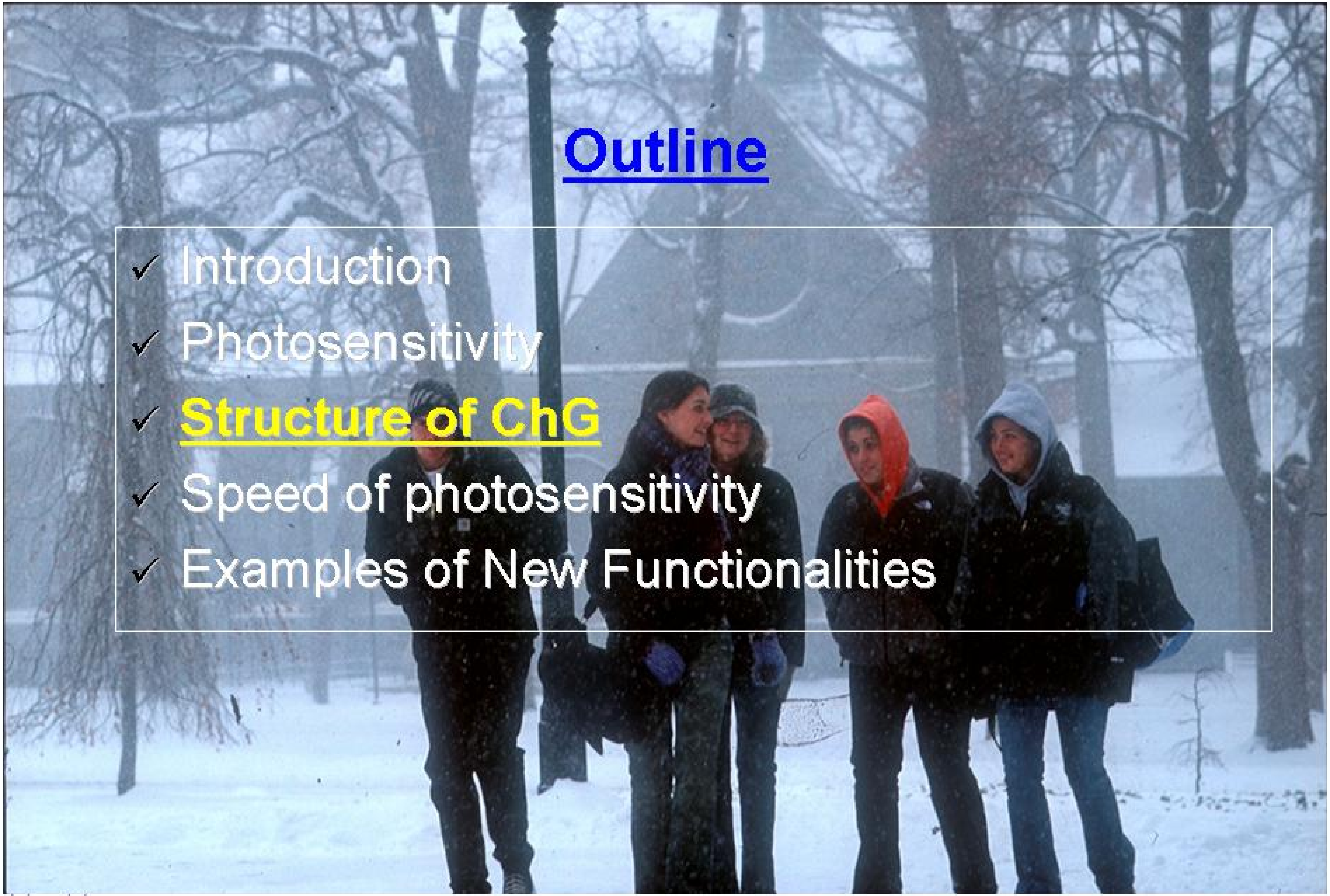
Metastable: recovered on heating to ~Tg

Temporary: recovered on removing the light

Scalar: don’t depend upon the polarization of the light

Vector: depend upon the polarization of the light

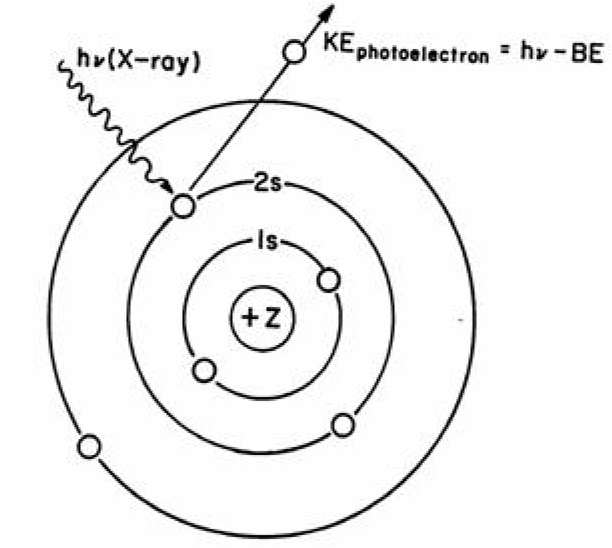
Temporary + Vector = Smart

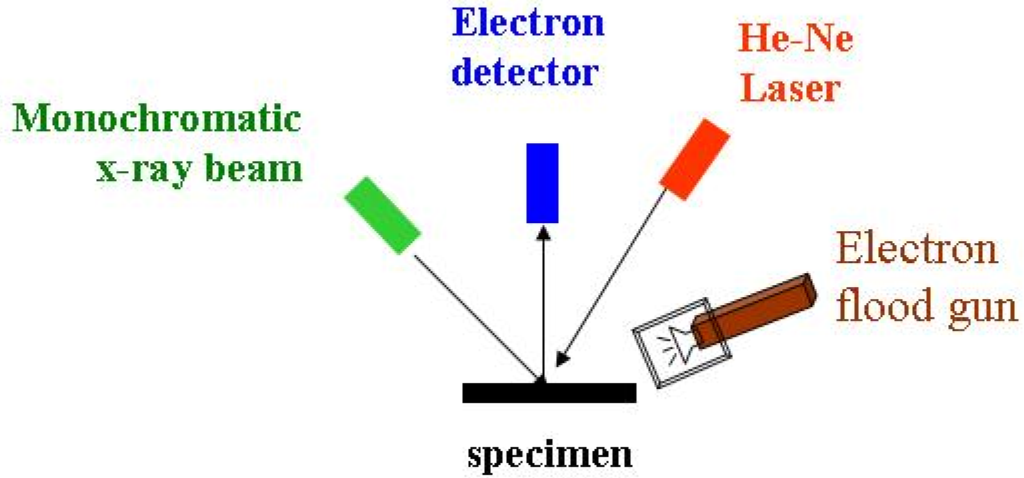


Outline

- ✓ Introduction
- ✓ Photosensitivity
- ✓ **Structure of ChG**
- ✓ Speed of photosensitivity
- ✓ Examples of New Functionalities

XPS with *in situ* laser irradiation




Monochromatic x-ray beam

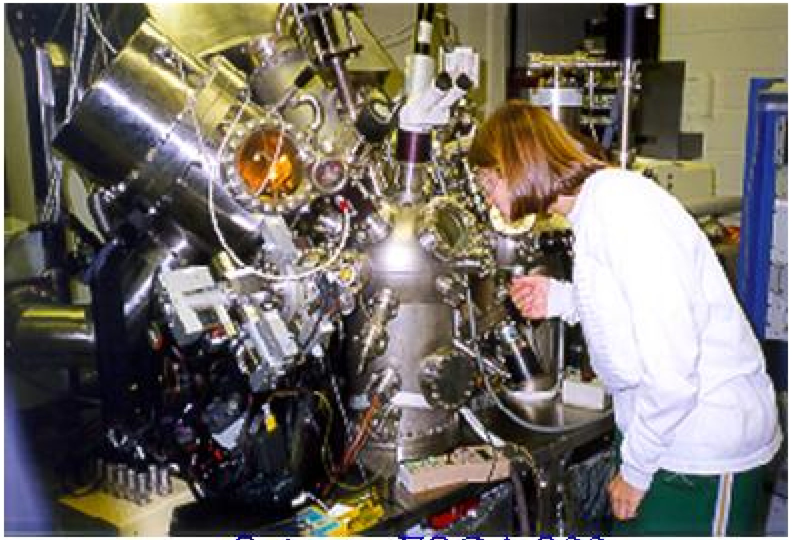
Electron detector

He-Ne Laser

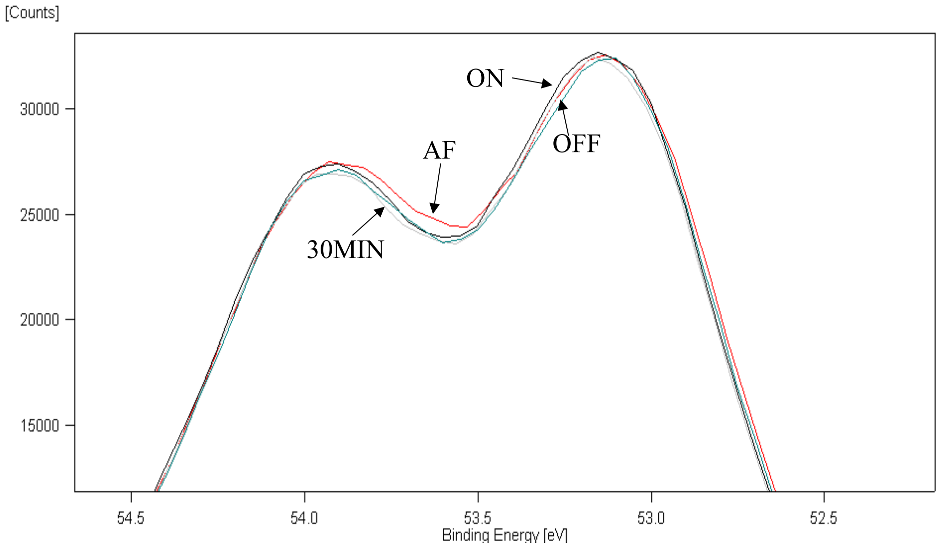
Electron flood gun

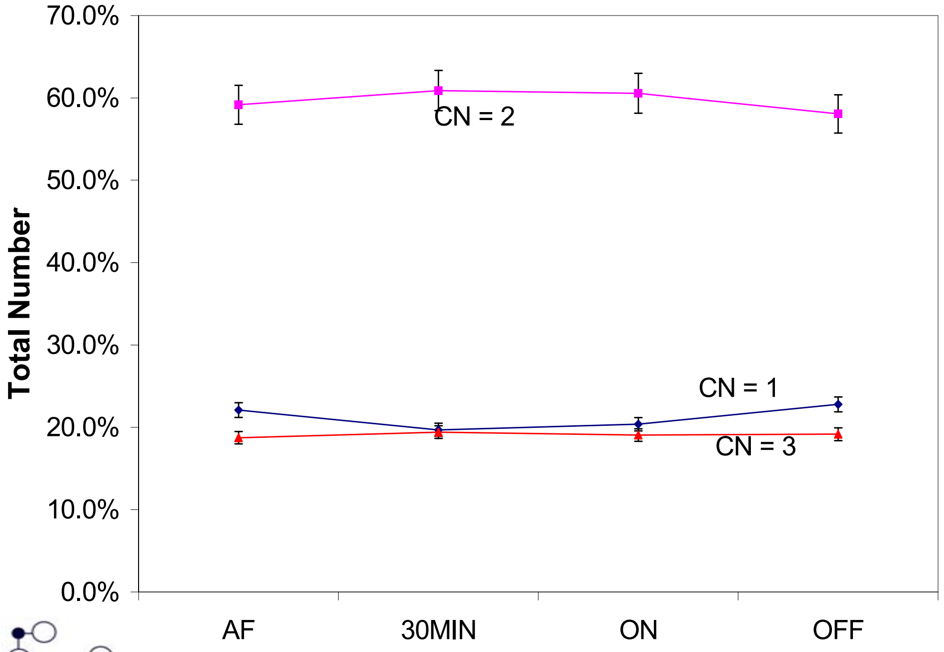
specimen

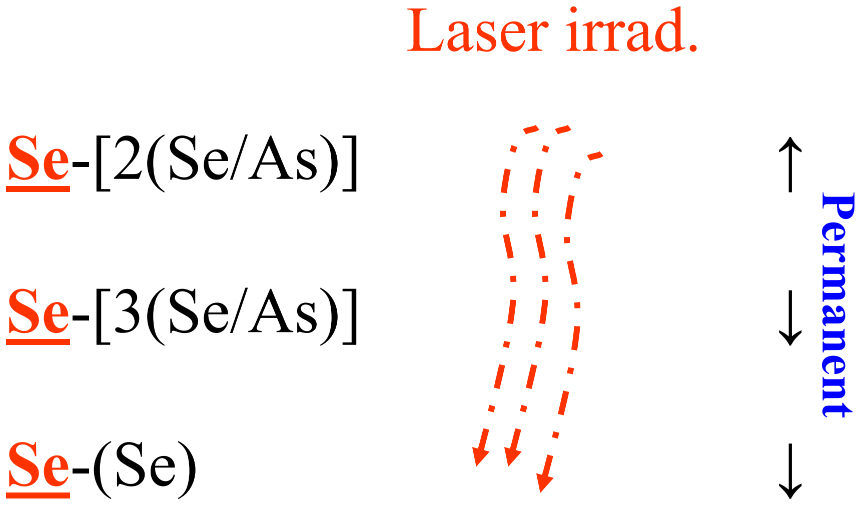
- Monochromatic x-rays => photoelectrons
- Electrons emitted with kinetic energies related to their binding energies
- Density of states
- Shift in peaks shows the change in the bonding character of the atoms


Scienta ESCA 300

Distribution of coordination configurations for Se in a-As_2Se_3







Laser irrad.

Se-[2(Se/As)] ↑

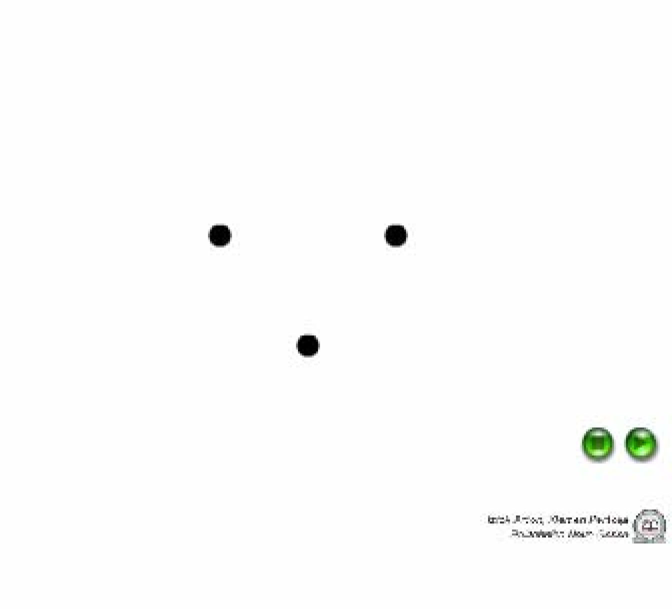
Se-[3(Se/As)] ↓

Se-(Se) ↓

Permanent

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)

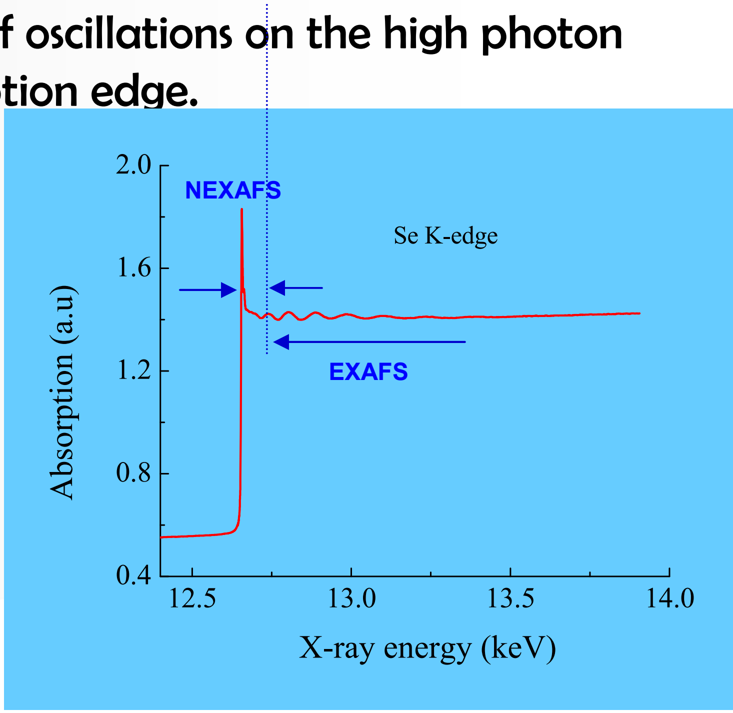
Resulting photoelectrons have a low kinetic energy and are backscattered by the atoms surrounding the emitting atom.

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)



XAFS spectrum of Se K-edge

Experimental details

a-As_2S_3 films; a-$GeSe_2$ films

In-situ EXAFS at NSLS, BNL

For a-As_2S_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)

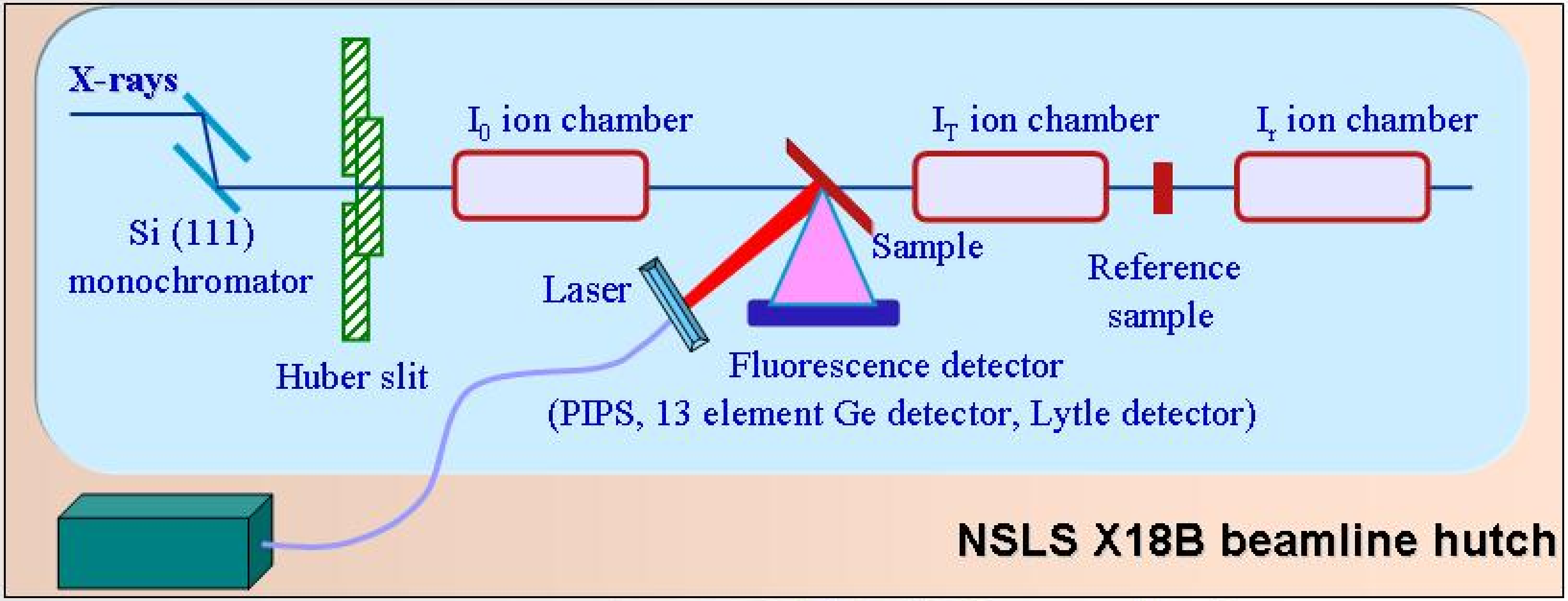
Data collected in fluorescence mode before (As prepared: AP), during (ON) and after laser illumination (OFF) states of the sample

Illumination sources

For a-As_2S_3 films: Ar^+ laser (488 nm; 50 mW/cm^2)

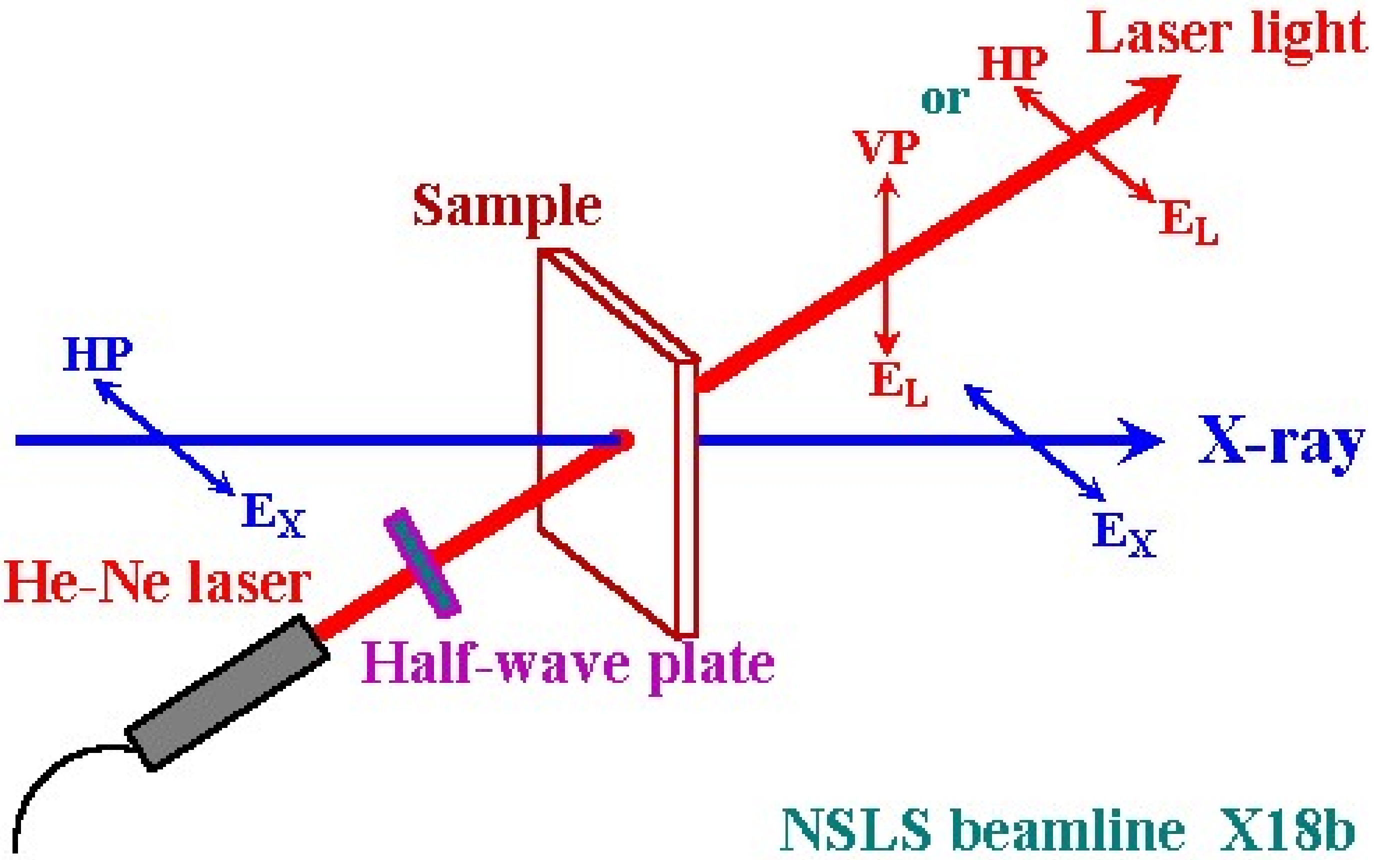
For a-$GeSe_2$ films: Semiconductor laser (633 nm; 50 mW/cm^2)

In-situ experimental setup at X19A beamline



In situ EXAFS

Synchrotron x-rays: linearly polarized

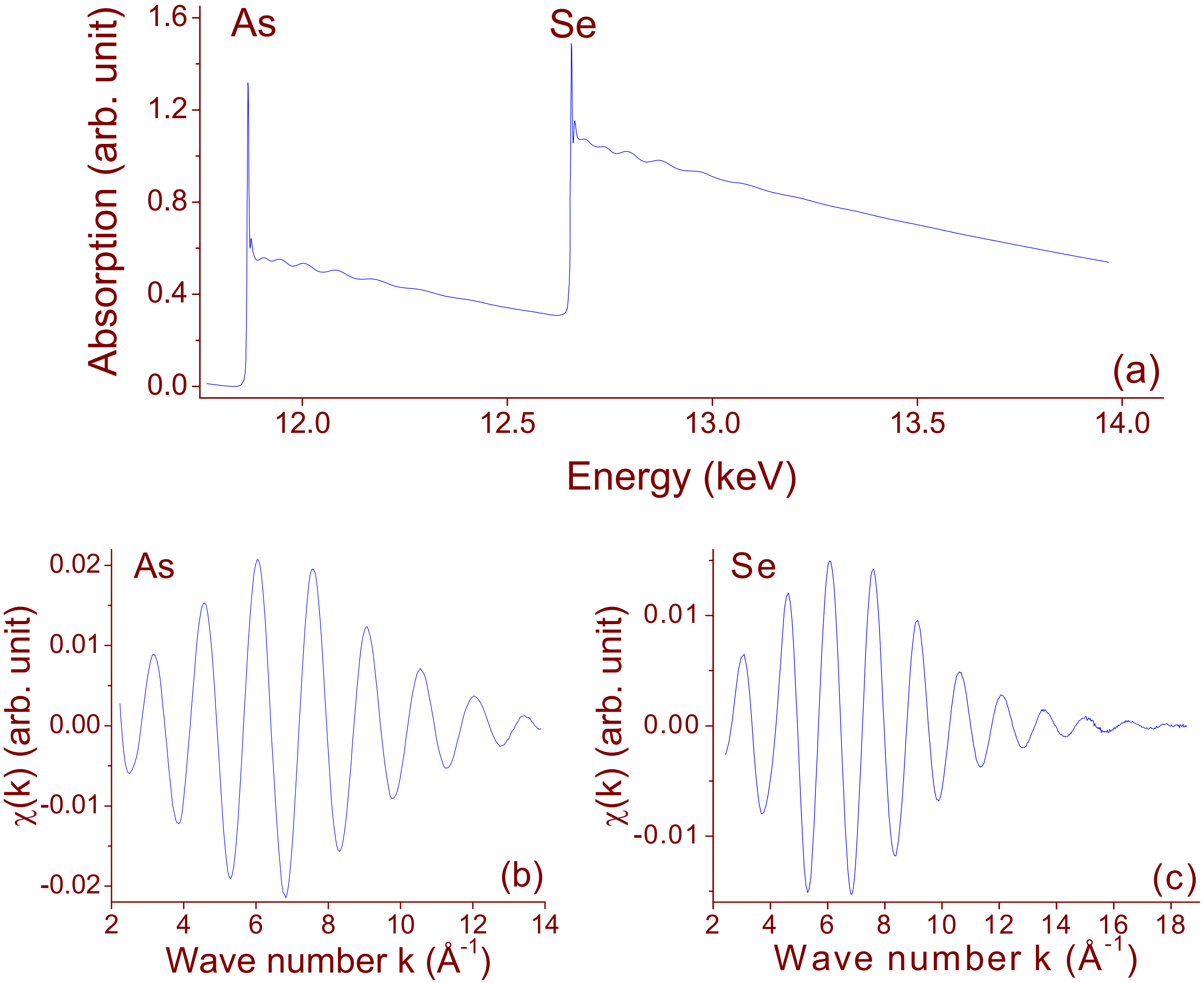


Looking for laser-induced polarization-dependent changes.

EXAFS Spectra

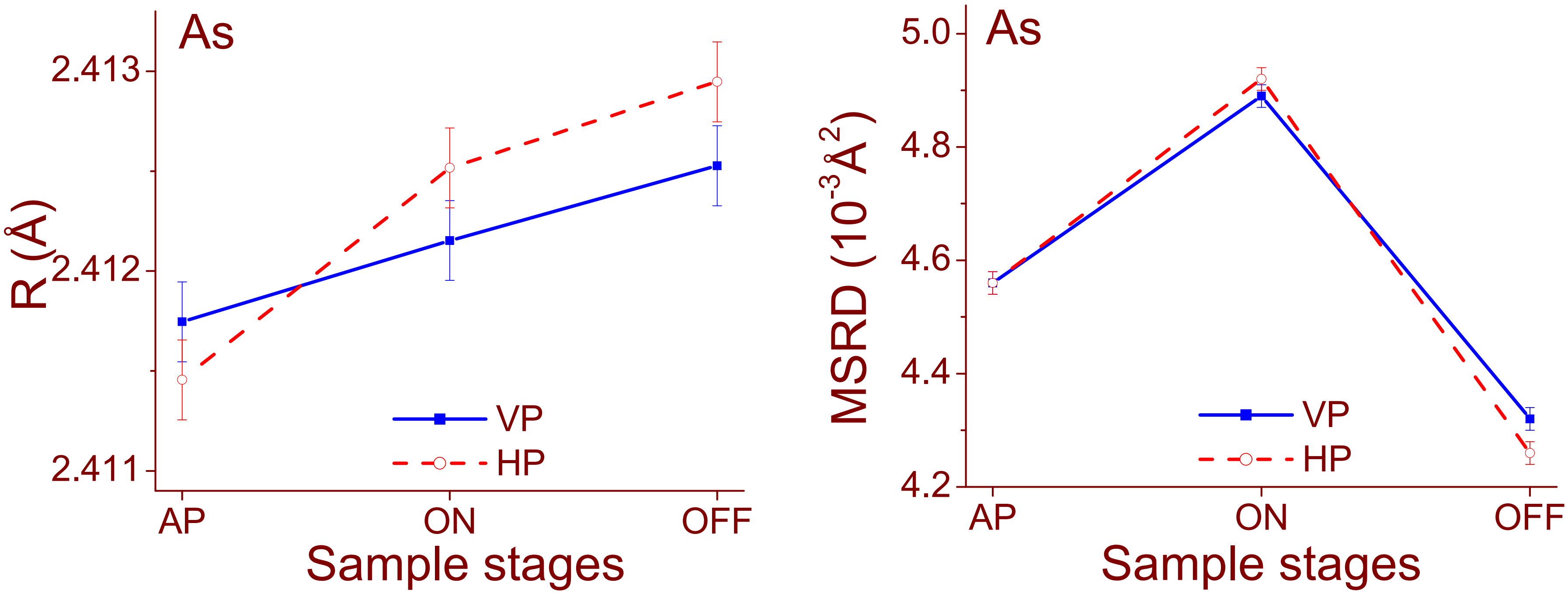
(a): X-ray absorption spectrum of an a-$As_{40}Se_{60}$ film beyond As and Se K-edges.

(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

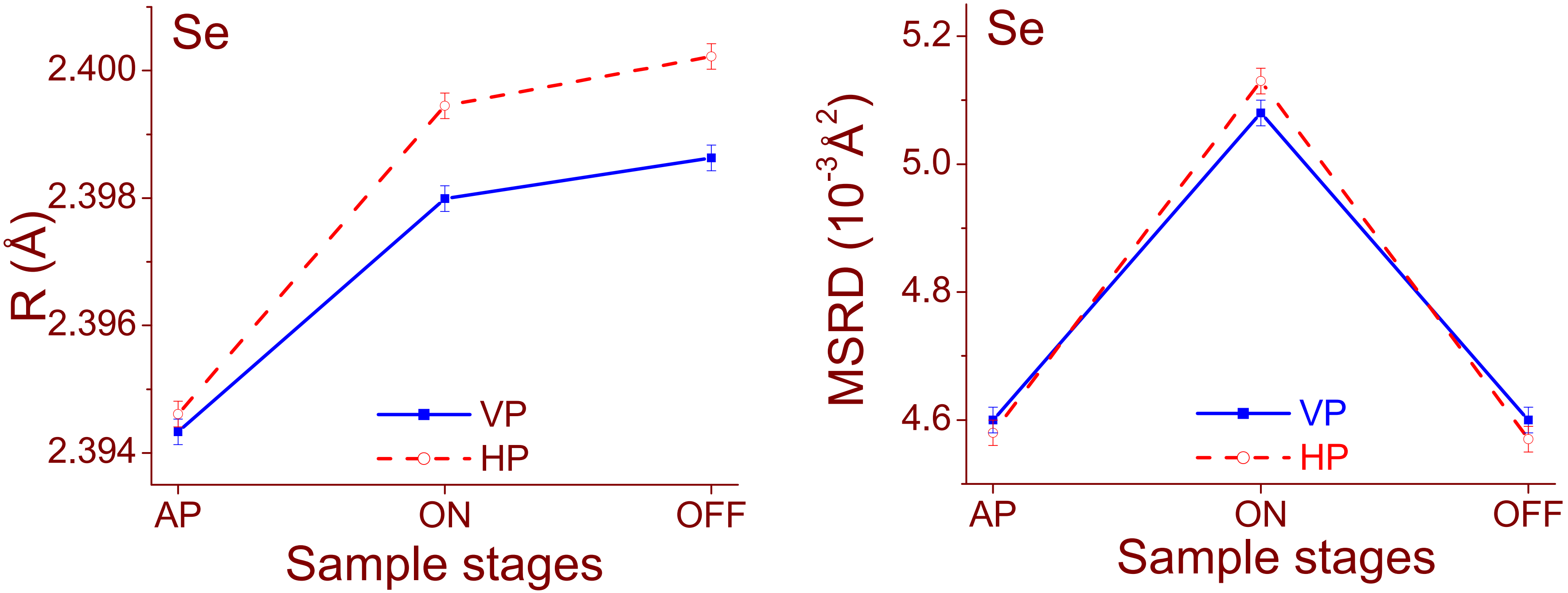
VP: laser has vertical polarization.

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.

Mechanisms of Scalar Changes

$R_{As\text{-}NN}$:
small permanent ↑ expansion

$R_{Se\text{-}NN}$:
large permanent ↑ expansion

1. Photo-chemical reaction

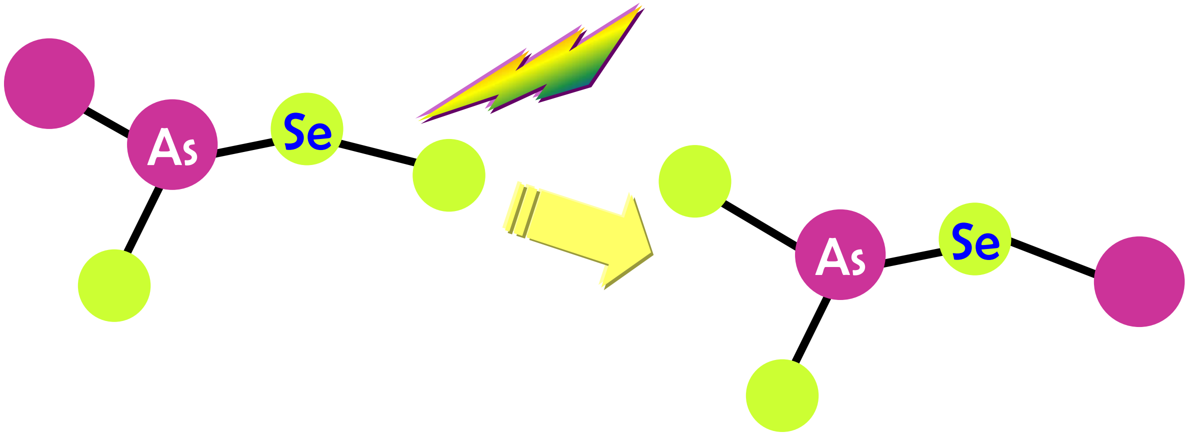
Covalent Radii:
As: 1.21 Å. Se: 1.17 Å

Microscopic heterogeneity in AP films

$\Rightarrow$ Se–Se + As–As $\xrightarrow{\text{Light}}$ 2As–Se

$R_{As\text{-}As} > R_{As\text{-}Se} > R_{Se\text{-}Se} \Rightarrow$ ↑ $R_{Se\text{-}NN}$ **and** ↓ $R_{As\text{-}NN}$

However, experiments: ↑ in both $R_{Se\text{-}NN}$ and $R_{As\text{-}NN}$



2. Strain relief

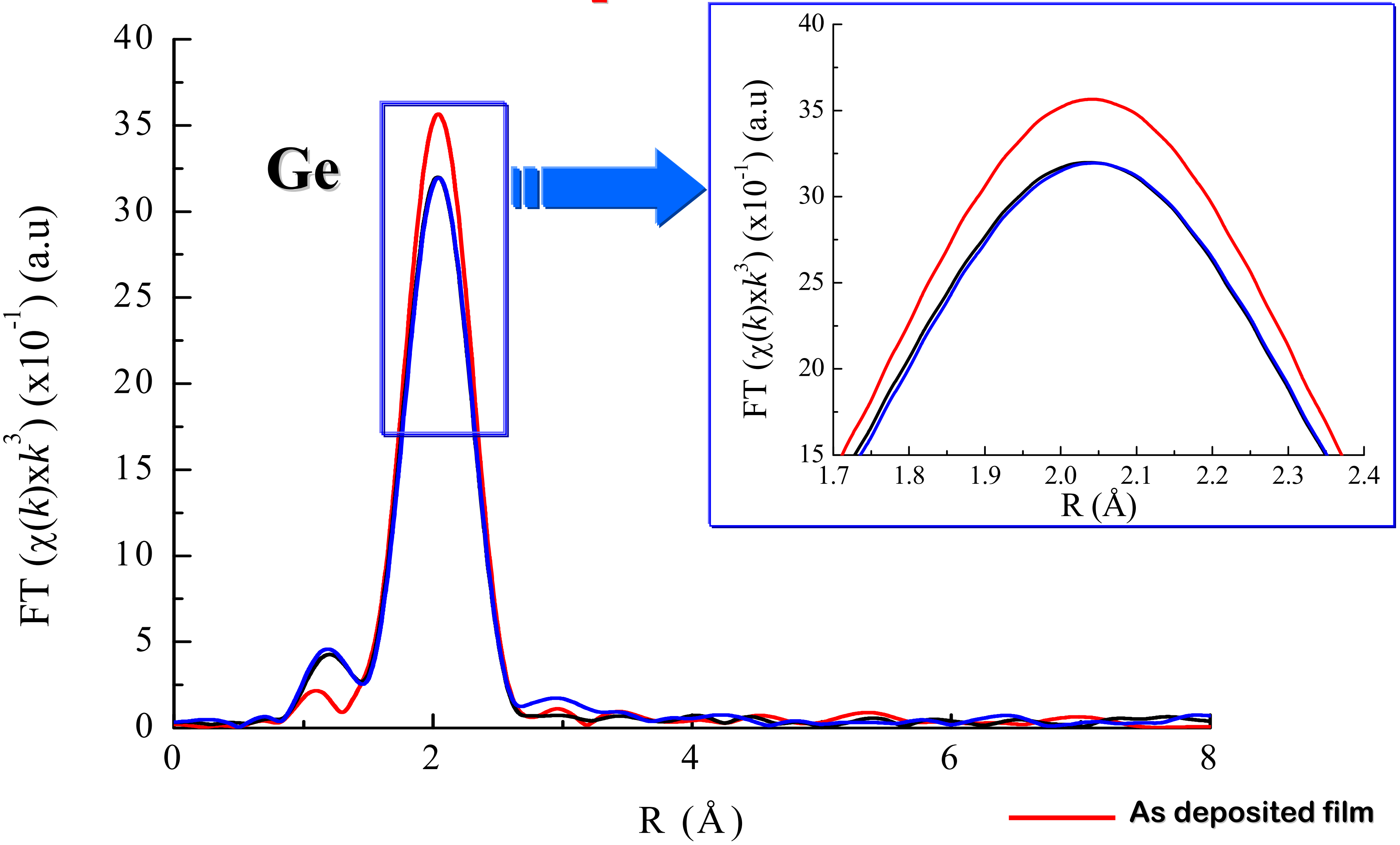
Intramolecular bonds in As-rich molecules are highly strained

$\Rightarrow$ breaking of such molecules by light will ↑ $R_{\text{As-Se}}$

$\Rightarrow$ **↑ $R_{\text{Se-NN}}$ and ↑ $R_{\text{As-NN}}$**

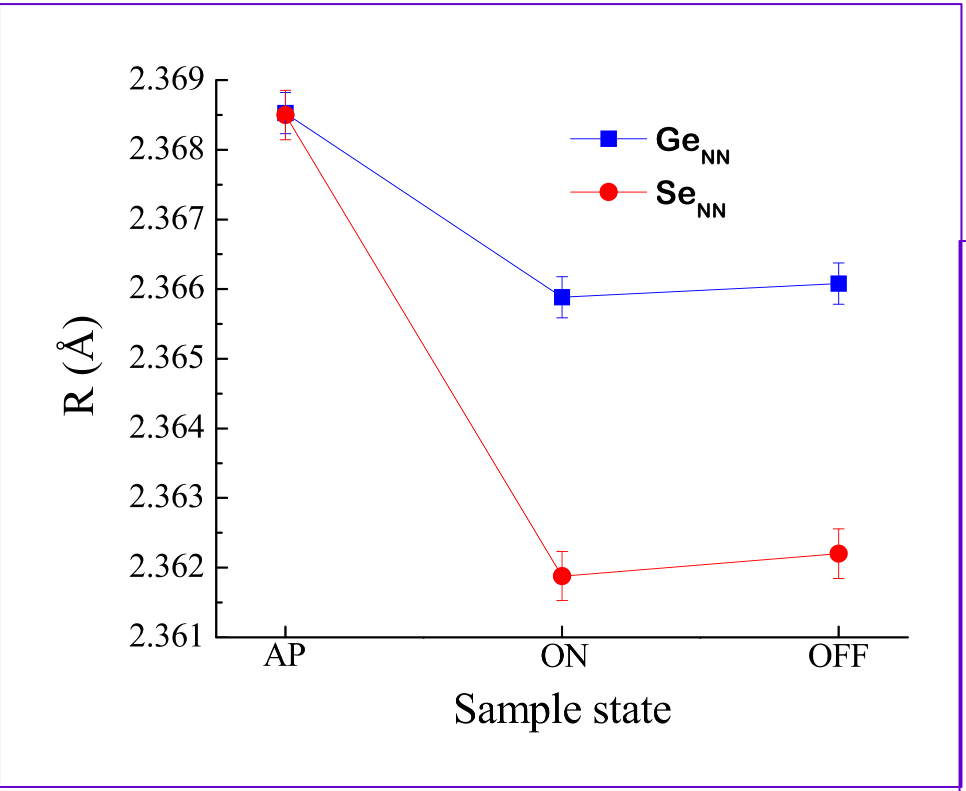
1 + **2** $\Rightarrow$ large ↑ in $R_{\text{Se-NN}}$ & small ↑ in $R_{\text{As-NN}}$

PRDF around Ge for a-GeSe$_2$ films

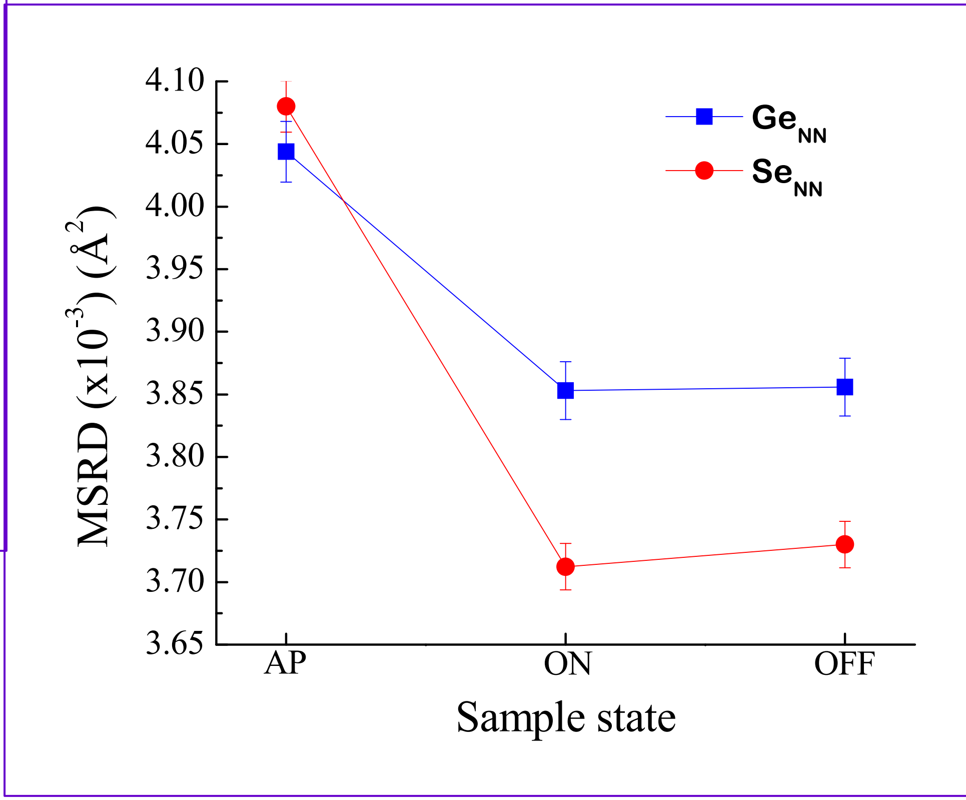


- As deposited film
- During Illumination
- After Illumination

GeSe$_2$ EXAFS



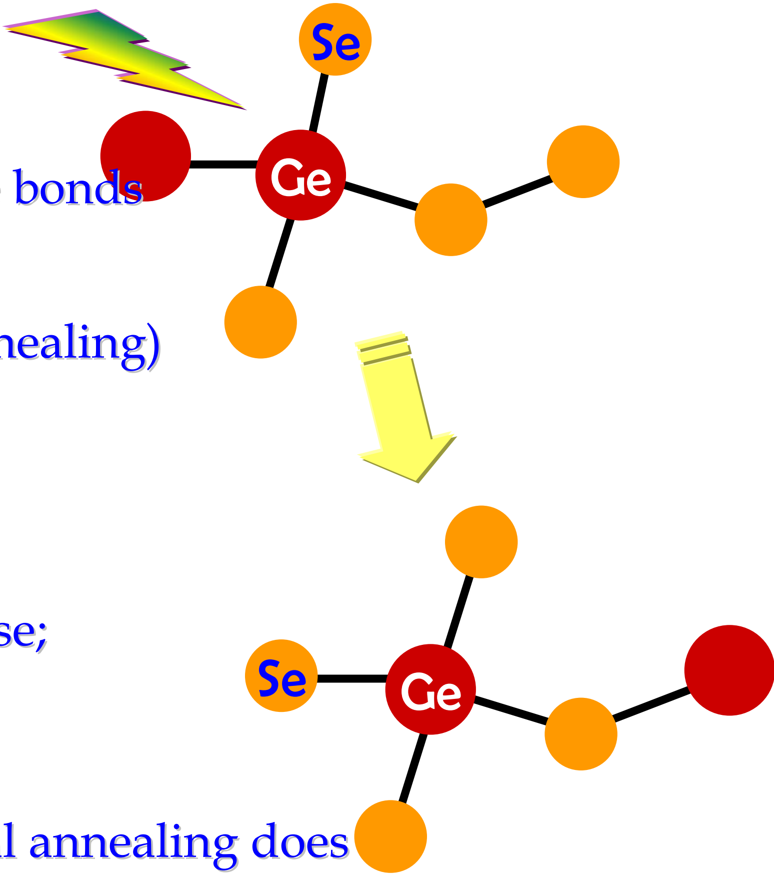
2.369
2.368
2.367
2.366
2.365
2.364
2.363
2.362
2.361
R (Å)
AP
ON
OFF
Sample state
Ge$_{NN}$
Se$_{NN}$



4.10
4.05
4.00
3.95
3.90
3.85
3.80
3.75
3.70
3.65
MSRD (x10^{-3}) (Å^2)
AP
ON
OFF
Sample state
Ge$_{NN}$
Se$_{NN}$

a-GeSe$_2$ films:

Decrease in Ge_{NN} and Se_{NN} 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)

⇒ $R_{Ge\text{-}NN}$ should decrease and $R_{Se\text{-}NN}$ should increase;
but $R_{Se\text{-}NN}$ is also decreasing

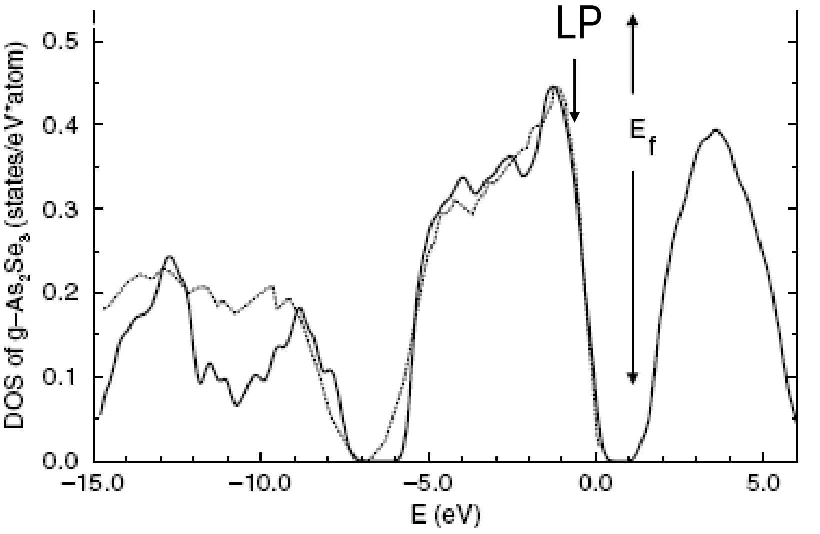
2. Strain relief

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)

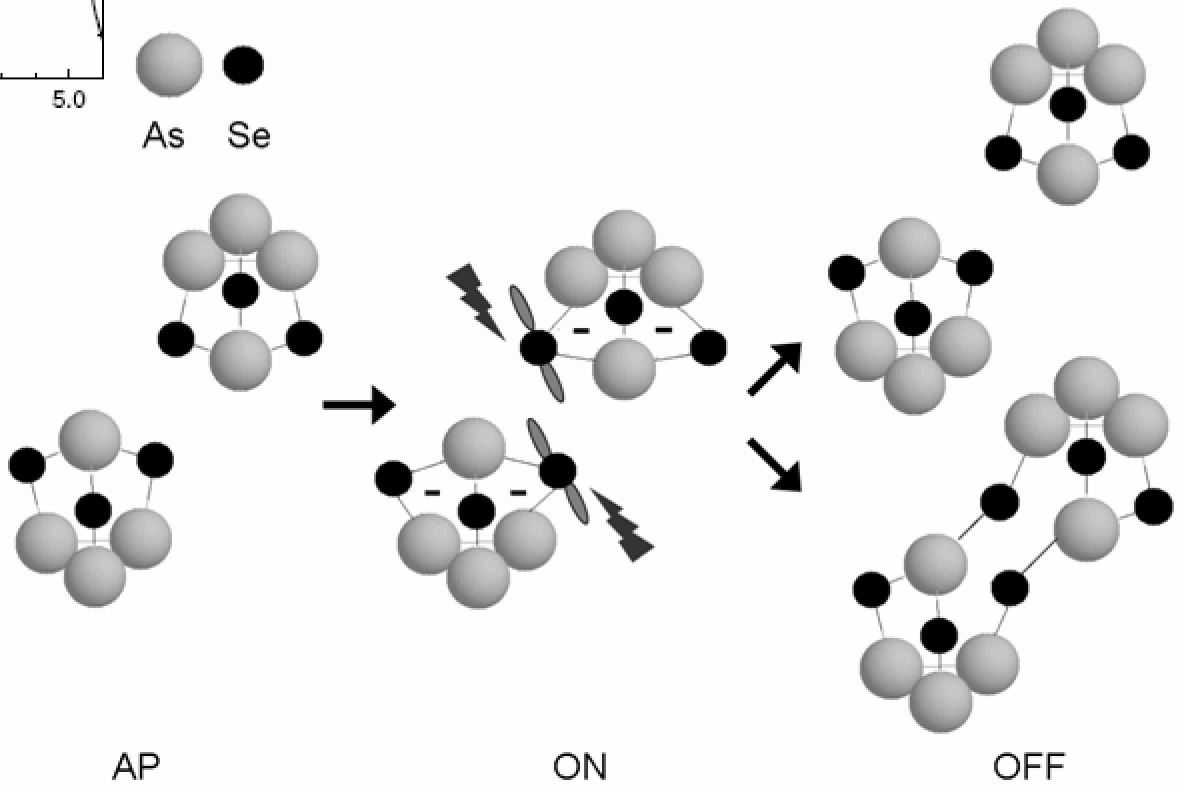
Decrease in Se NN distances - Experimentally observed by *in-situ* EXAFS

Mechanism of photo-structural change

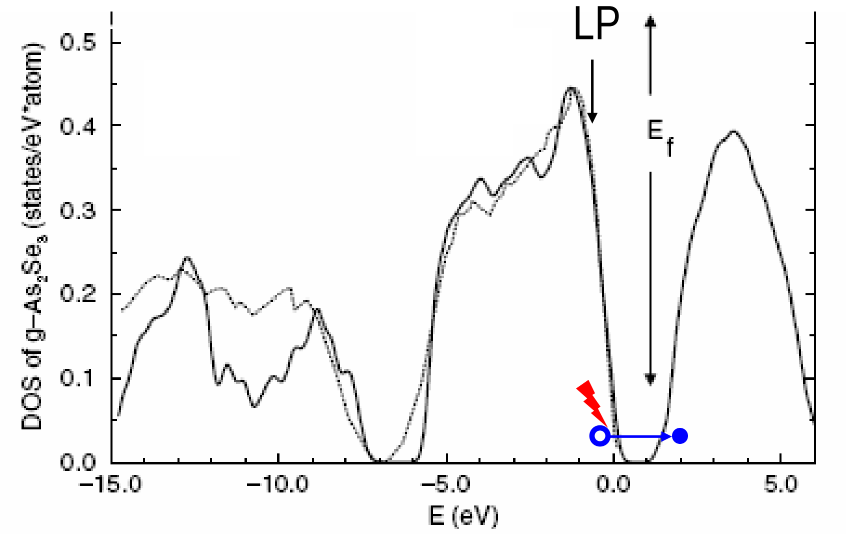


MD simulation shows Se 4p lone pair (LP) electrons occupy top of the valence band

Li, Drabold, et al. (2003)

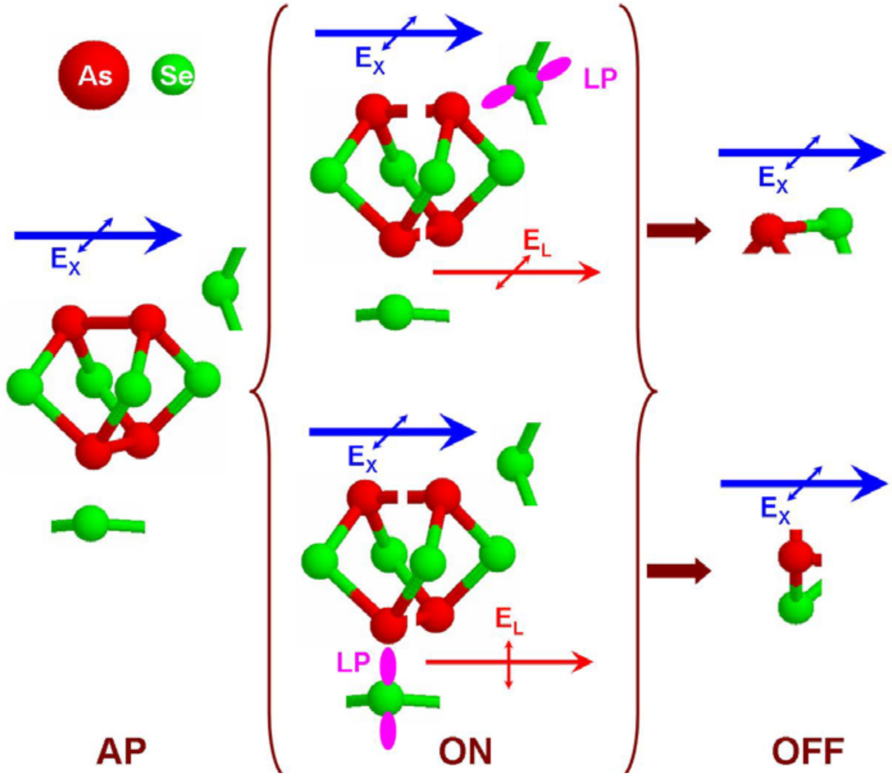


Mechanism of Vectoral Changes



Li, Drabold, et al. (2003)

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



AP: As-rich molecules (As_4Se_4) and Se-rich phase co-exist in AP a-As_2Se_3 film.

ON: As dangling bonds (from As-As bonds in As_4Se_4 molecules) react with preferentially excited Se 4p LP's (orbital // E_{laser}), form anisotropic As-Se.

OFF: Anisotropic As-Se bonds can be detected by <u>polarized</u> X-rays.

Amorphous Semiconductors

Excited electronic carriers

Relaxation

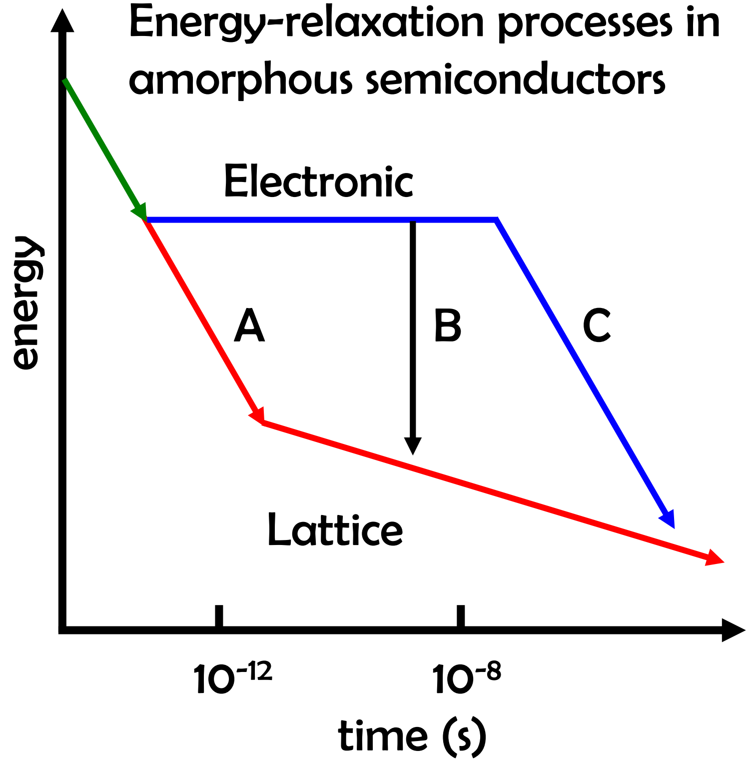
Within ps region, electrons relax to the bottom of conduction band (sometimes forming polarons)

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

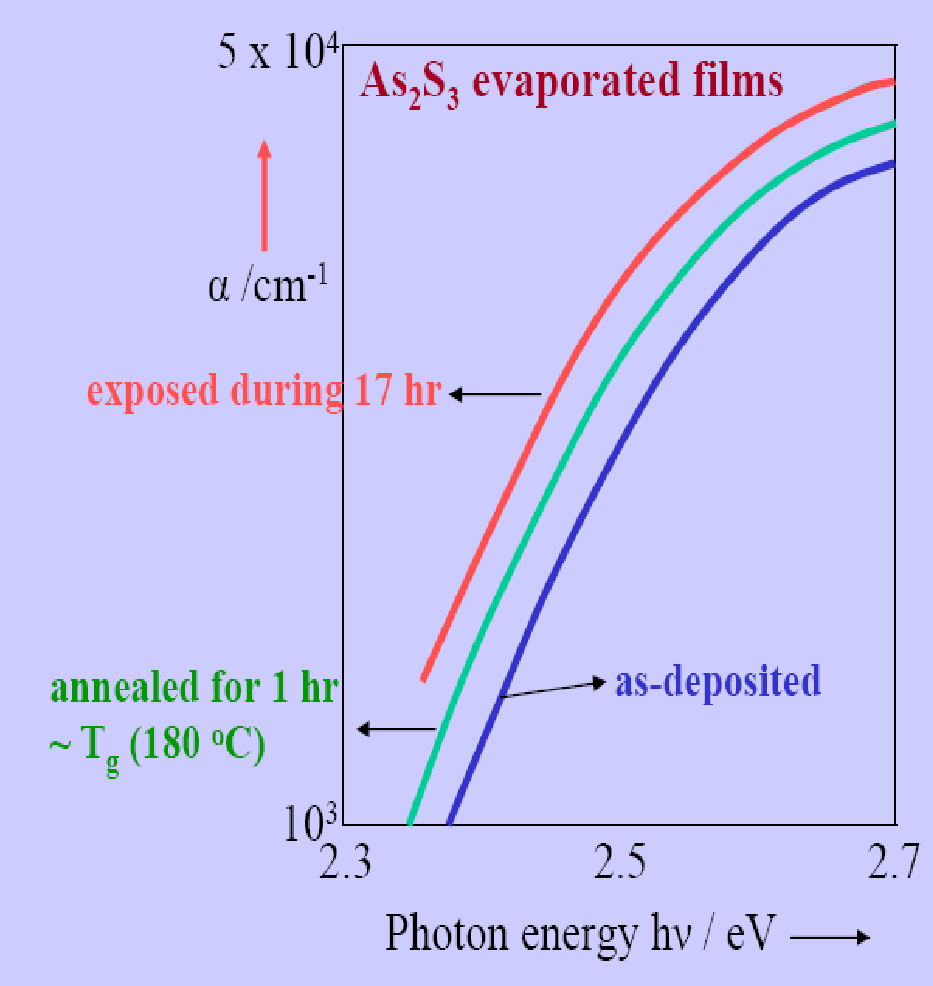
Ke. Tanaka, JAP (1989)

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?

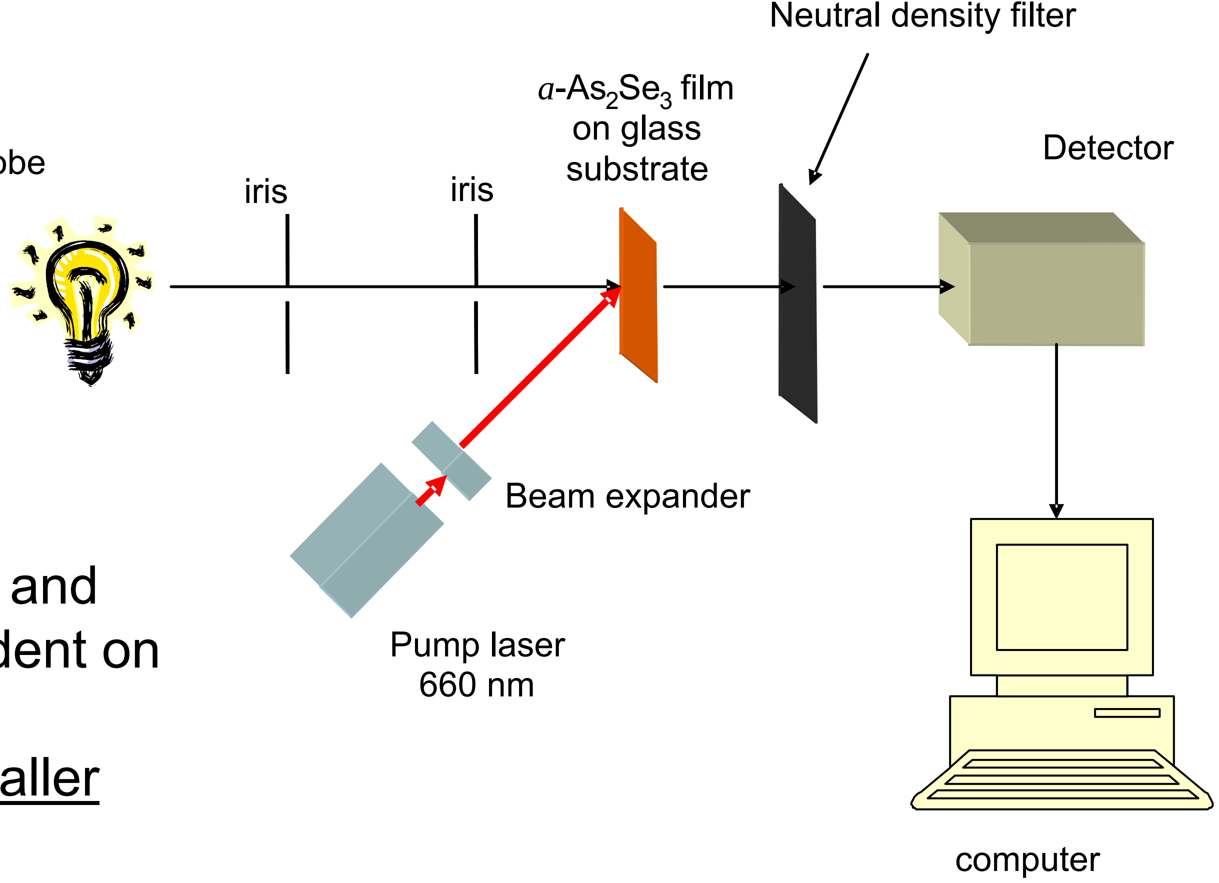


Tanaka et. al., JNCS (1981)

Speed of reversibility is crucial:

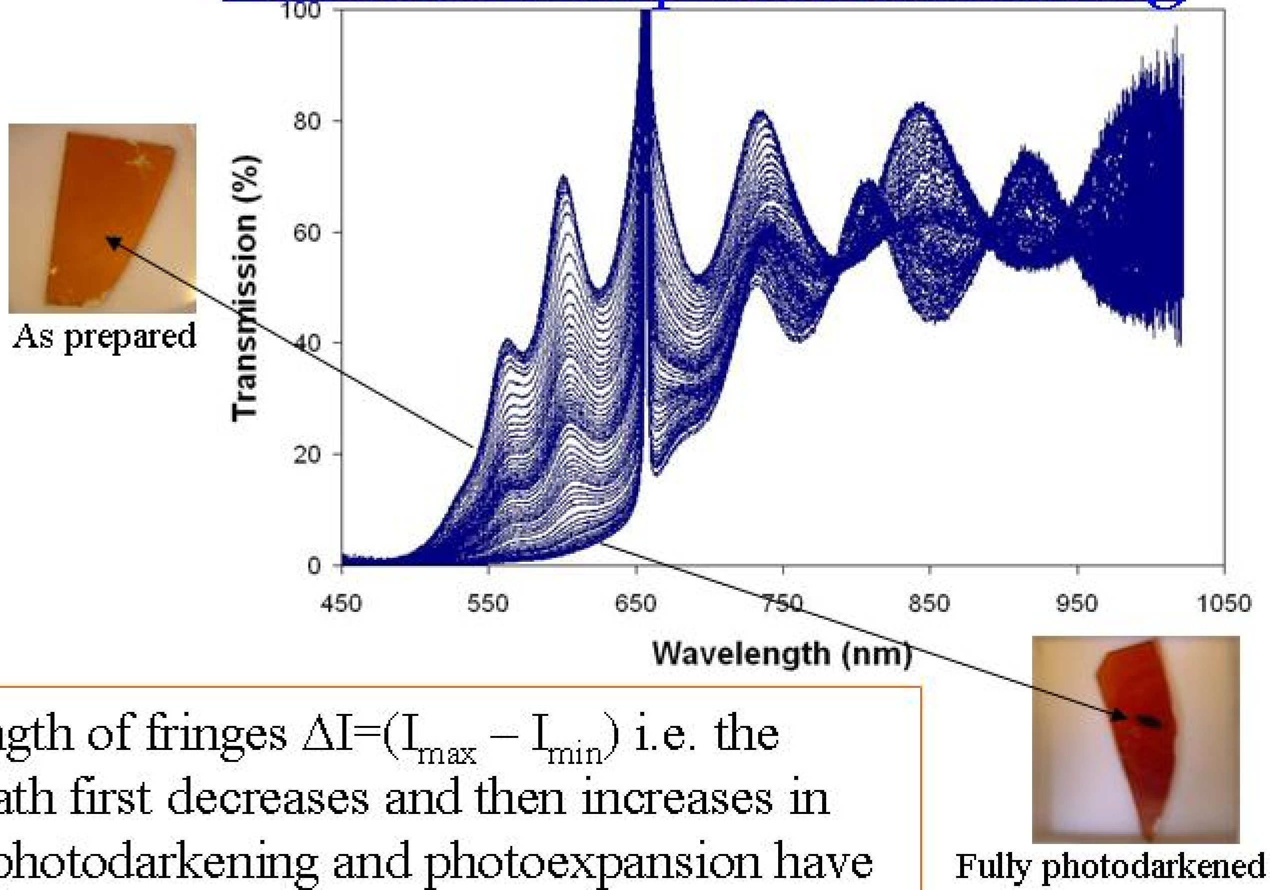
In situ vis-NIR spectroscopy

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 <u>is smaller</u> than pump beam

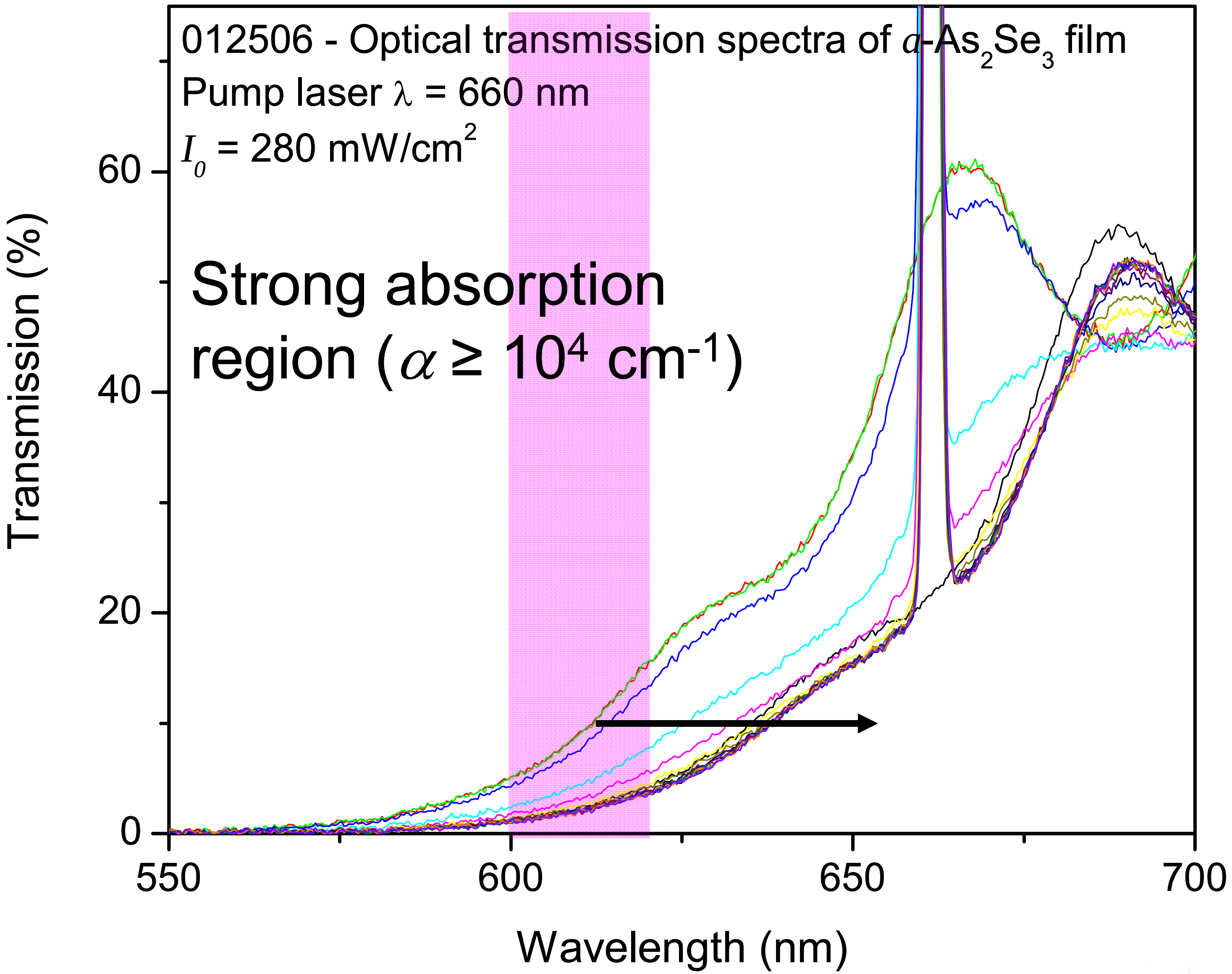
Evolution of photodarkening



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

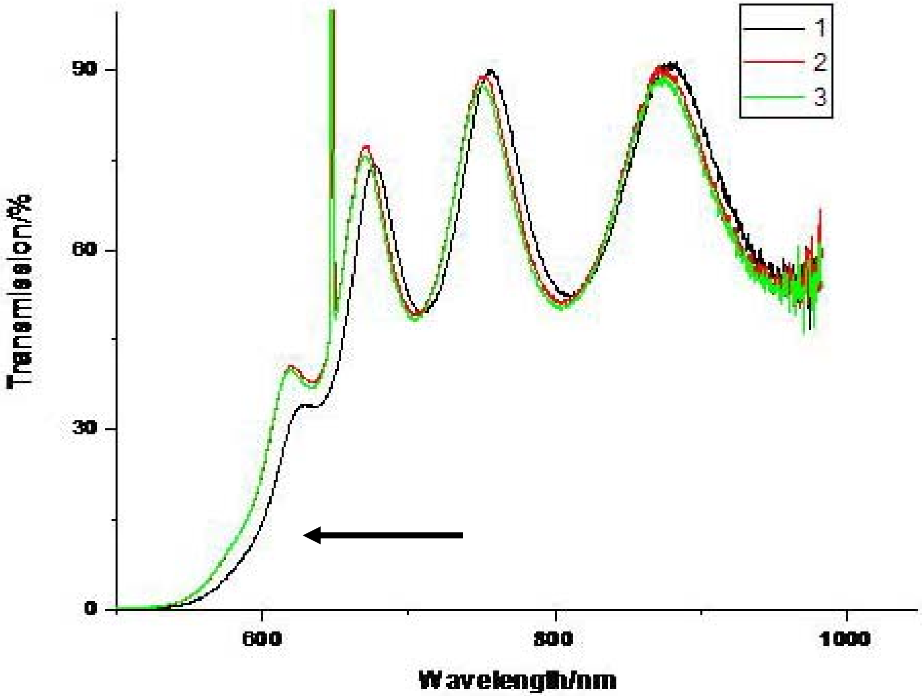
Tanaka: a- As_2S_3 indicate that the rate of photovolume expansion (a photostructural change) is greater than that of photodarkening for bandgap illumination.

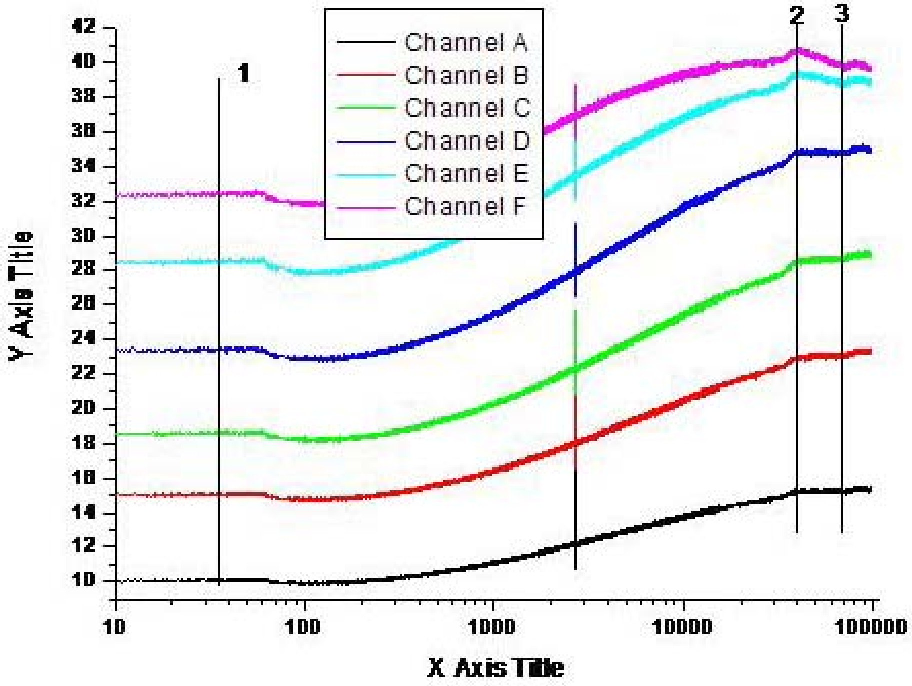
PD kinetics in the strong absorption region (≥ 10^4 cm^{-1})



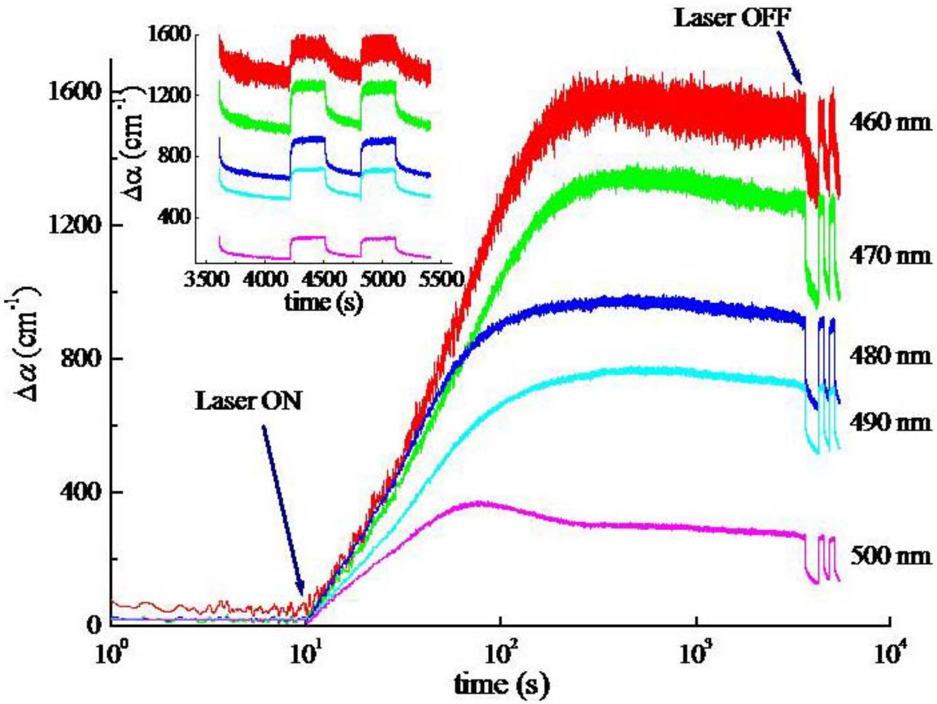
Photobleaching in Ge-Se glass

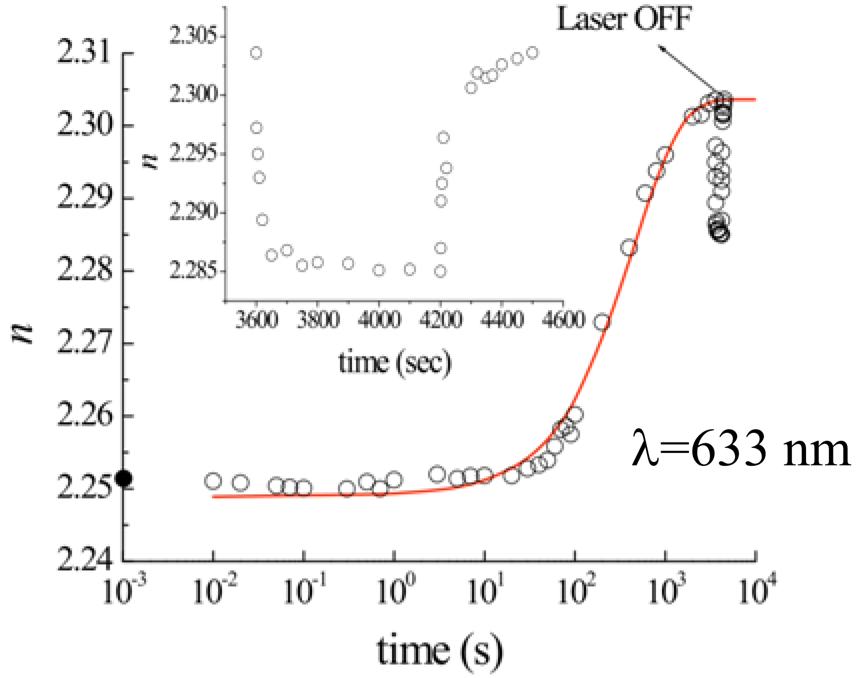
. Ge22As23Se55, 660nm, 146mW/cm^2





Evolution of photodarkening





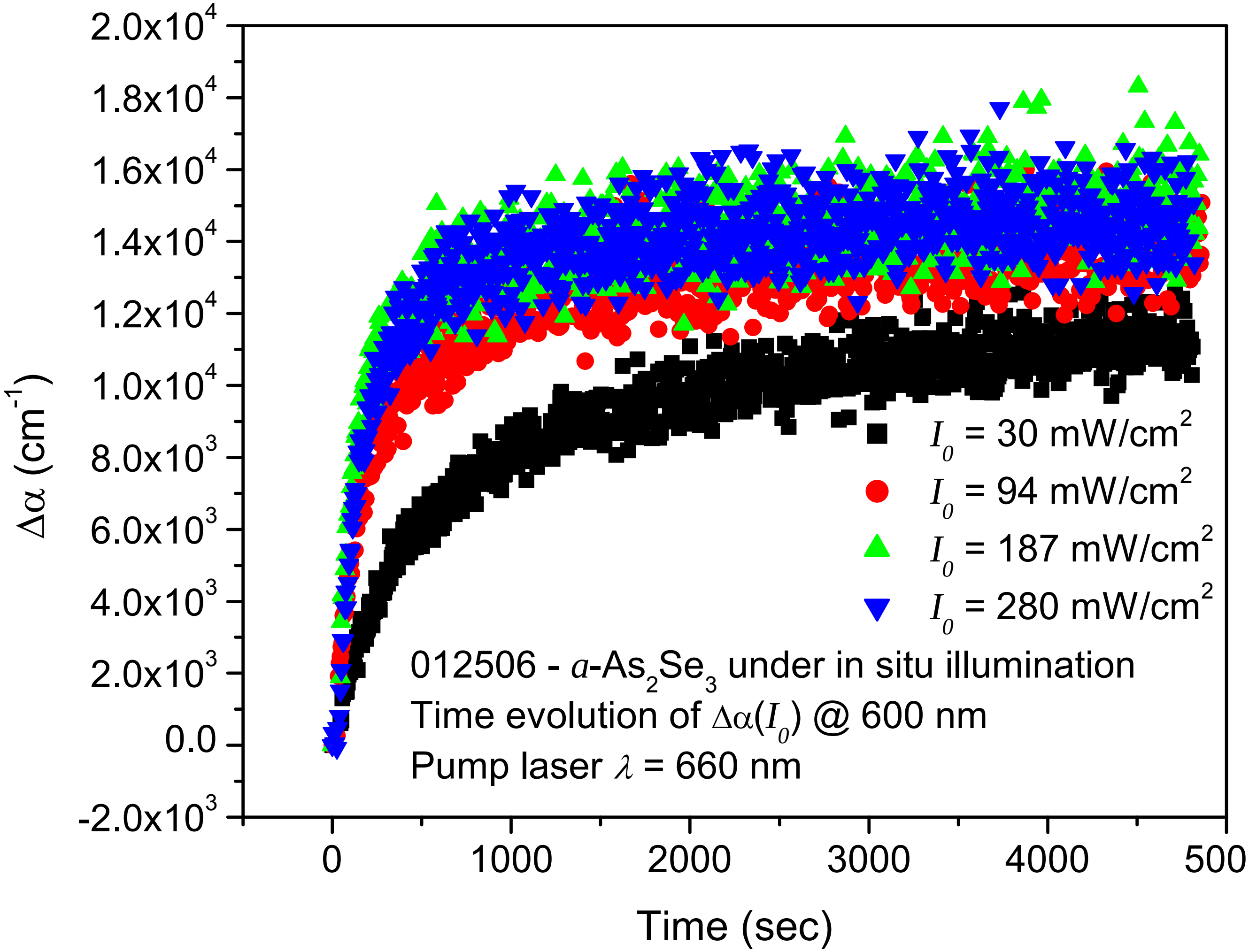
Initial photodarkening: $\underline{As_2S_3}$:λ_{pump}=488 nm, I_0=25mW/cm^2

$$\Delta\alpha = [\alpha - \alpha(t=0)][1 - \exp(-t/\tau)^{\beta}]$$

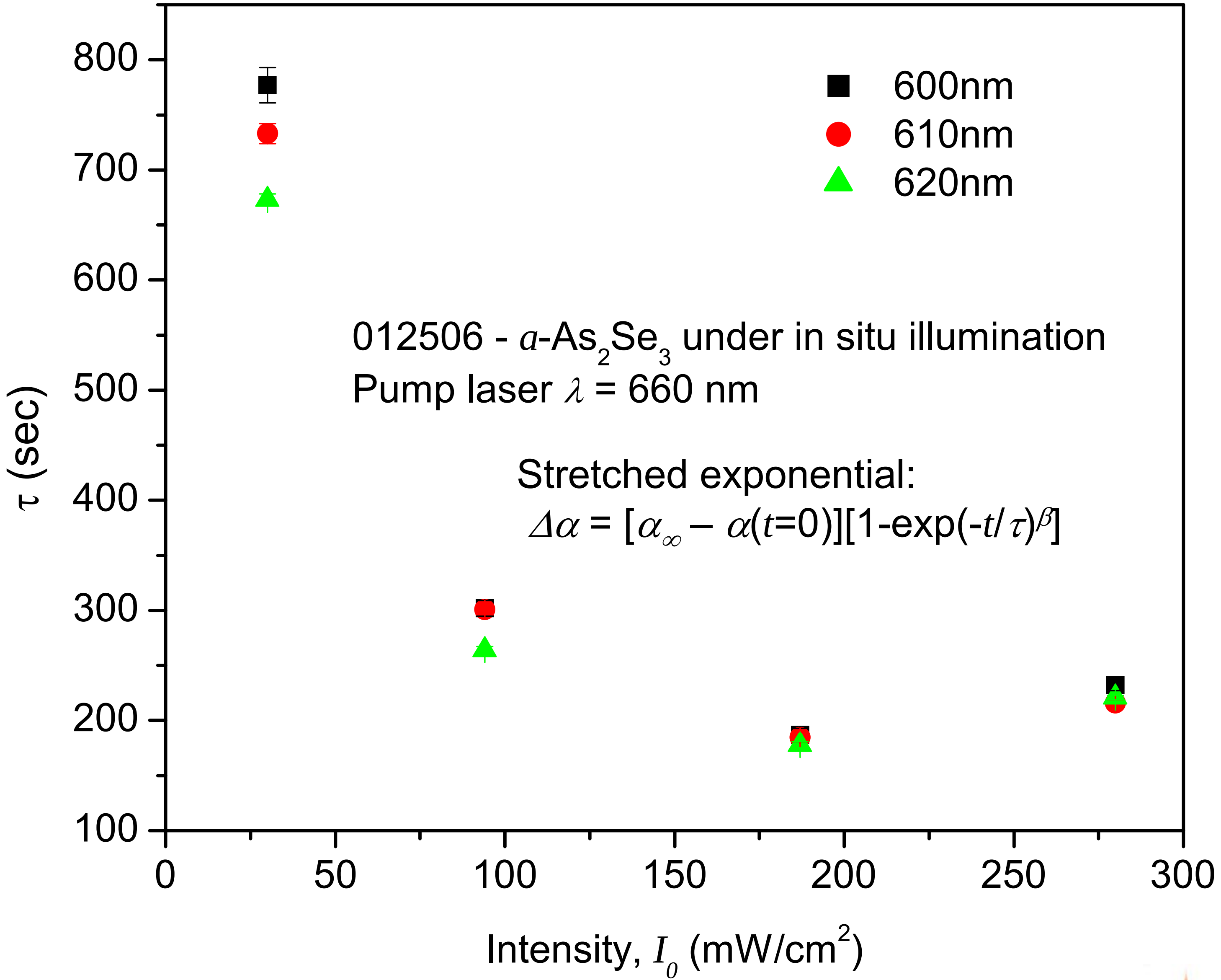
Ganjoo and Jain,
Phys. Rev. B **74**, 024201 (2006)

Photodarkening kinetics at various intensities

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



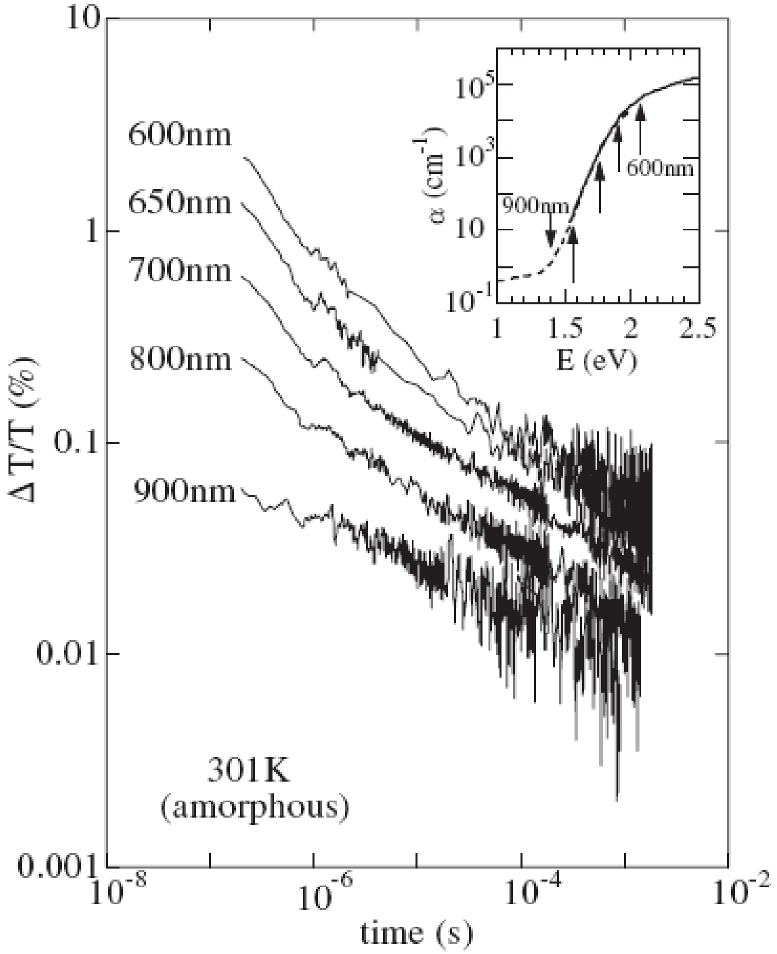
Plot of τ vs. I_0



012506 - *a*-As_2Se_3 under in situ illumination
Pump laser λ = 660 nm

Stretched exponential:
$\Delta\alpha = [\alpha_\infty - \alpha(t=0)][1-\exp(-t/\tau)^\beta]$

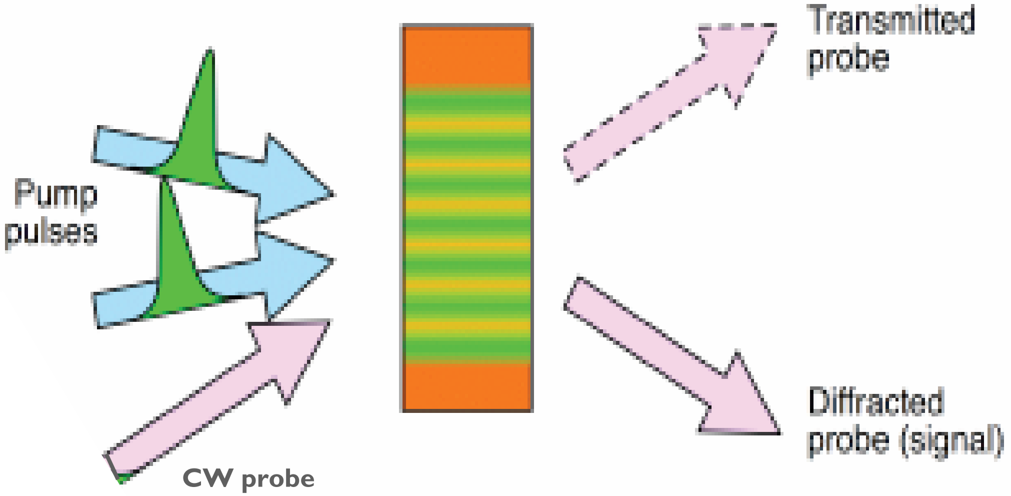
Fast optical changes



Decay of the transient part of photoinduced changes in transmission with time after pulsed laser illumination (1.1 mJ/cm^2)

Sakaguchi and Tamura, Journal of Physics: Condensed Matter (2006)

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.

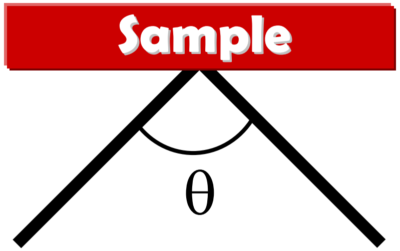
- ➢The refractive index grating is read by diffracting a probe beam off the grating at the Bragg condition

- ➢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

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



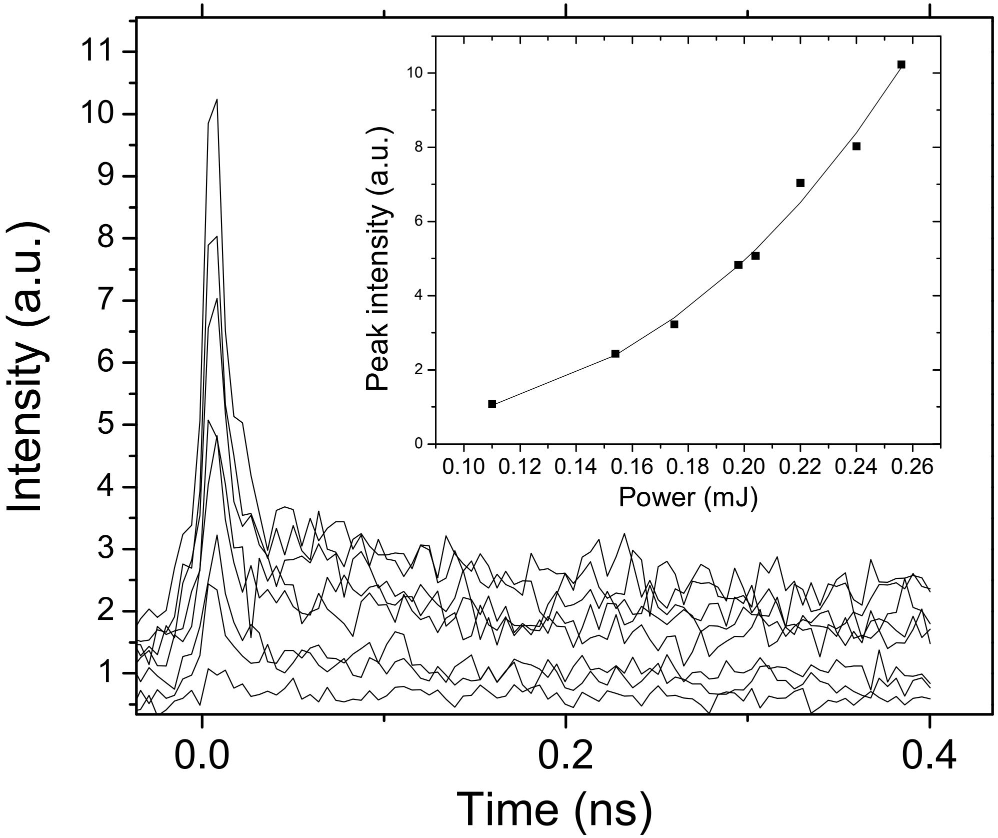
High signal/noise ratio

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

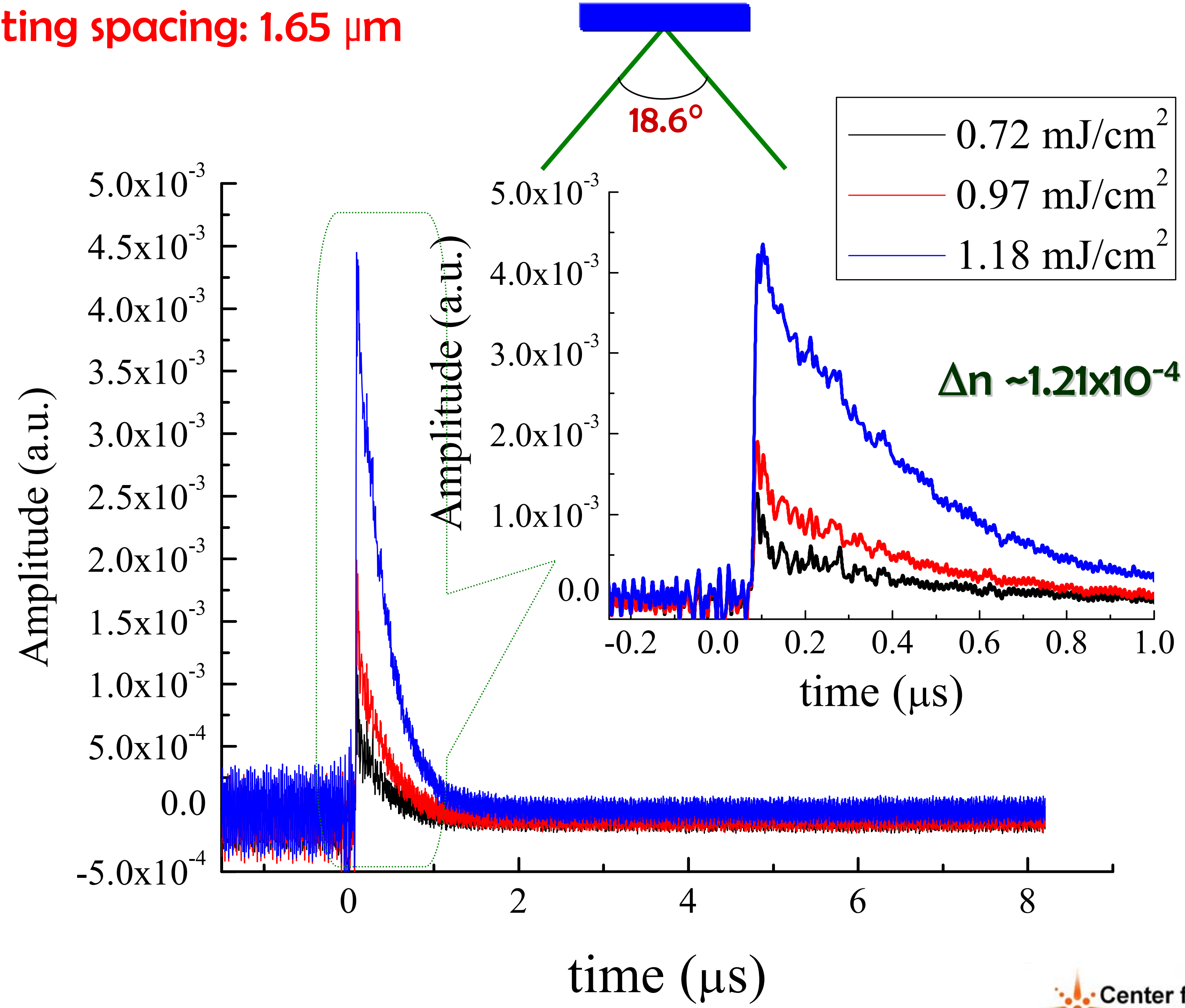
Ultra fast photoinduced changes from 20 ps pulse

Transient Grating, Four-Wave Mixing method: diffracted intensity



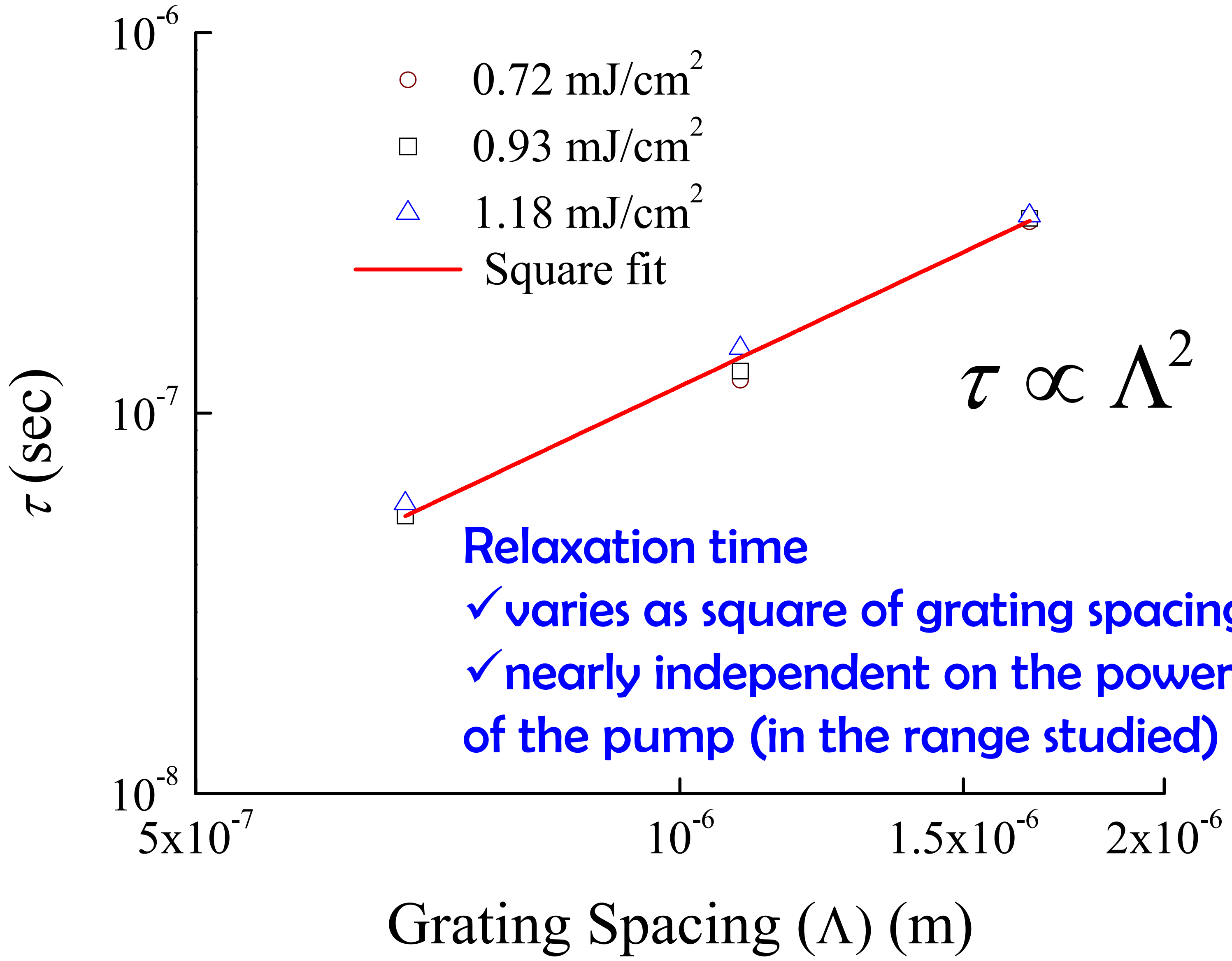
The photo-response to pulsed illumination is composed of a fast ~80 ps component followed by nanosecond component. The "ultra fast" component shows almost third-order power dependence indicating third-order nonlinear effect in As50Se50.

Grating spacing: 1.65 μm



$\Delta n \sim 1.21 \times 10^{-4}$

Center for Optical Technologies



$$\tau \propto \Lambda^2$$

Relaxation time

✓varies as square of grating spacing

✓nearly independent on the power density of the pump (in the range studied)