

# Lehigh University Center for Optical Technologies

## Unexpected Contraction of Partially Crystallized Chalcogenide Films on Photo-amorphization

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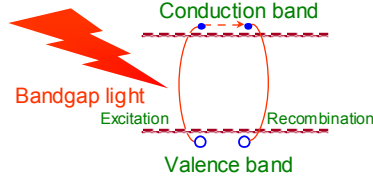
### Background

#### Chalcogenide glasses (ChGs)

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.

- Highly transparent in the Infrared region ( $\lambda \sim 1-12 \mu\text{m}$ ): IR optical devices
- High  $\chi^{(3)}$  optical nonlinearity ( $\sim 10^3$  times higher than  $\text{a-SiO}_2$ ): Ultrafast all optical switching for fiber communications
- Semiconducting: Photocopying (Xerox) machines, digital x-ray imaging
- ...
- **Photosensitive**

#### Fundamentals of Photosensitivity in ChGs



High probability of non-radiative electron-hole recombination process  
 $\Rightarrow$  Changes in material properties:  
 volume, refractive index, viscosity, conductivity, etching rate ...  
 Structural origin of the photosensitivity is not fully understood.  
 e.g. controversy on the origin of photoexpansion in As-Se(S) glasses.

#### Motivation

Model of photoexpansion in As-Se glasses (e.g.  $\text{a-As}_2\text{Se}(\text{S})_3$ ):

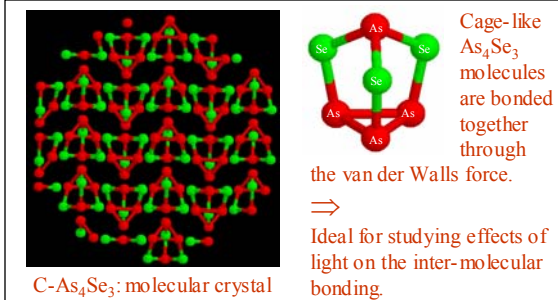


Slip motion (S) and Coulombic expansion (E) among layered structures  $\Rightarrow$  Photoexpansion due to van der Waals interaction.  
 Shimakawa et al, 1998

Lack of experimental proof. Also it cannot explain photocontraction in  $\text{As}_4\text{GeSe}_5$   
 $\Rightarrow$  Require experiments to verify and/or improve this model.

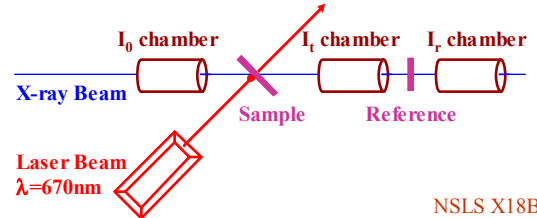
### Experiments and Results

#### Material Selection

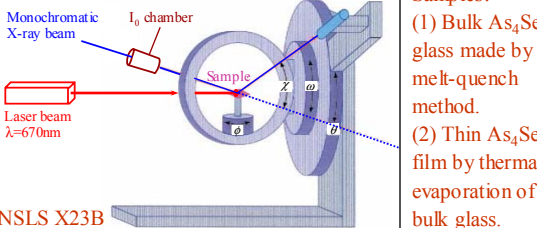


#### Experimental Methods

Extended X-ray Absorption Fine Structure (EXAFS) setup

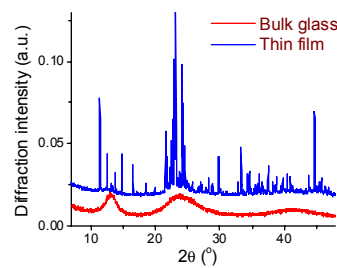


X-ray Diffraction (XRD) setup

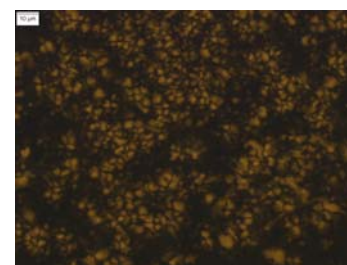


Samples:  
 (1) Bulk  $\text{As}_4\text{Se}_3$  glass made by melt-quench method.  
 (2) Thin  $\text{As}_4\text{Se}_3$  film by thermal evaporation of bulk glass.

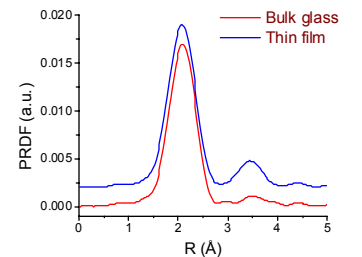
#### Sample Structure



Bulk: amorphous  
 Film:  $\alpha\text{-As}_4\text{Se}_3$  + amorphous phase

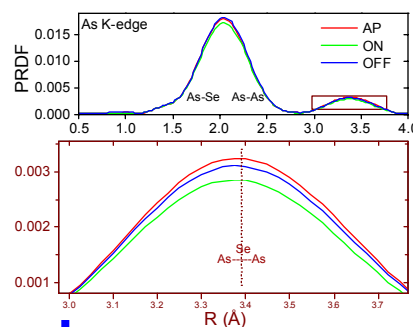


Optical Microscope:  
 Film: crystallites + amorphous phase

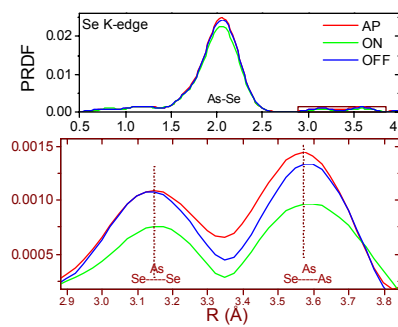


Bulk:  $\text{As}_4\text{Se}_3$  molecules in amorphous matrix  
 Film: Higher fraction of  $\text{As}_4\text{Se}_3$  molecules

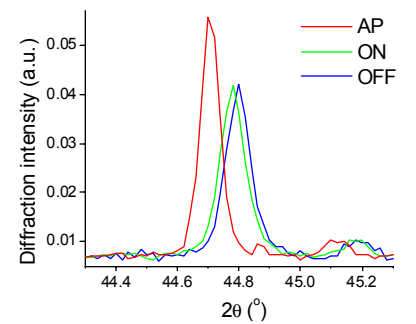
#### Results of in situ Illumination



During illumination  $R_{\text{As-Se-As}} \downarrow$   
 $\Rightarrow$  As atoms are pushed toward the cage center  
 After illumination  $R_{\text{As-Se-As}}$  Partly recovers.



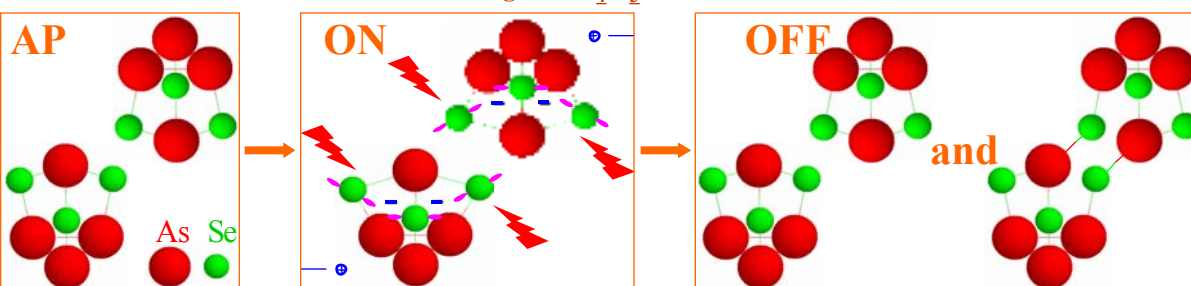
During illumination  $R_{\text{Se-As-Se}} \& R_{\text{Se-As-As}} \downarrow$   
 $\Rightarrow$  Se atoms are pulled away from the cage center  
 Both bond lengths partly recover after illumination.



Permanent compressive stress and transient tensile stress applied on the film by light.  
 $\Delta d/d \sim -0.4\%$ .  
 Sample experiences photo-amorphization and photocontraction.

### Discussion

#### Mechanism of Photo-induced Structural Changes in $\text{As}_4\text{Se}_3$ Films:



AP: Cage-like molecules exist in as-prepared  $\text{As}_4\text{Se}_3$  films  
 ON: Bandgap light excites Se lone pairs (LP) and creates electron-hole pairs. The holes drift away and leave negatively charged  $\text{As}_4\text{Se}_3$  molecules behind, which repel each other. Such repulsive force pushes rigid As toward and flexible Se out of the cage center.  
 OFF: A fraction of the molecules returns to the original state; others cross-link nearby molecules and cause contraction and compressive stresses.

### Conclusion

- For the first time photoinduced contraction has been observed in an As-Se glass films.
- The contraction occurs as 0-D sub-nano molecules cross-link with each other.
- Possible to control the photoinduced volume change by adjusting 0-D-molecule concentration.

### Acknowledgement

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