Effect of Glass Formation-Thin Films

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Glass – ancient transmission medium

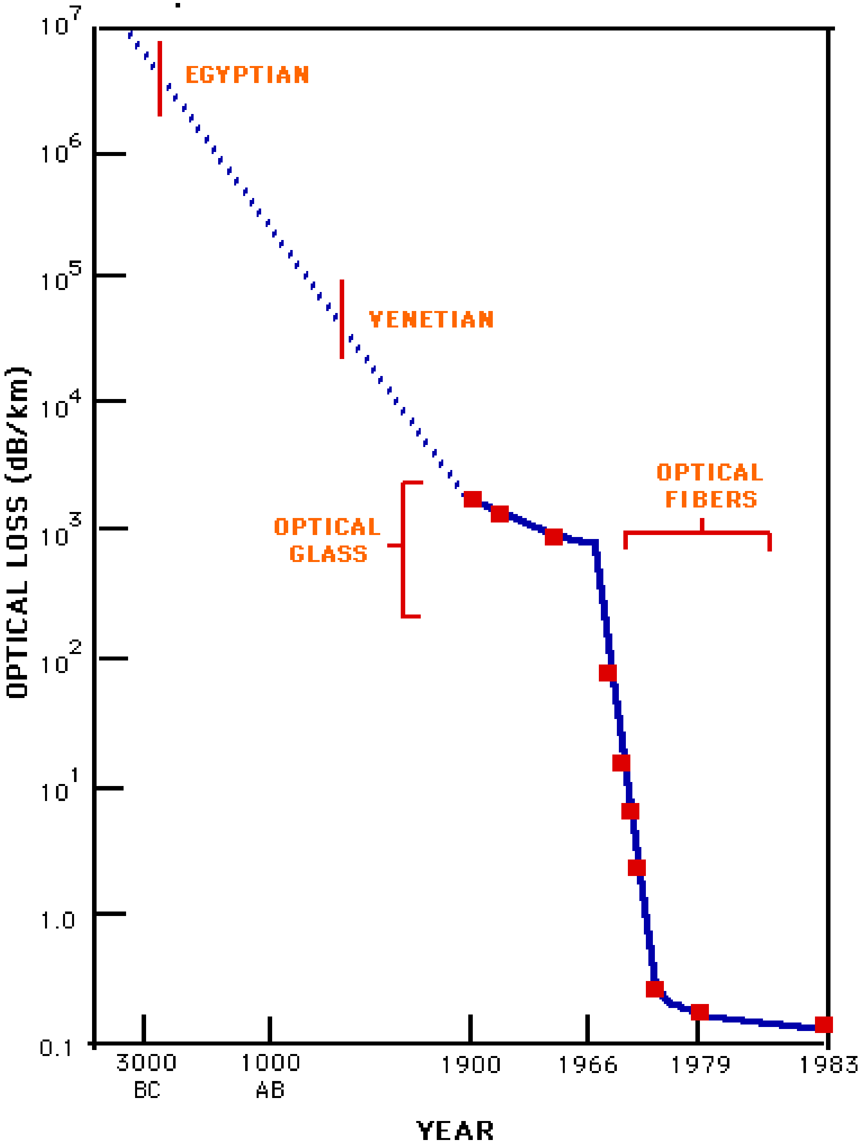

Photo courtesy of the Optoelectronics Research Centre (ORC) at the University of Southampton, UK

…..beauty can have function too!

http://people.deas.harvard.edu/~jones/cscie129/nu_lectures/lecture10/images/fo_abs.html

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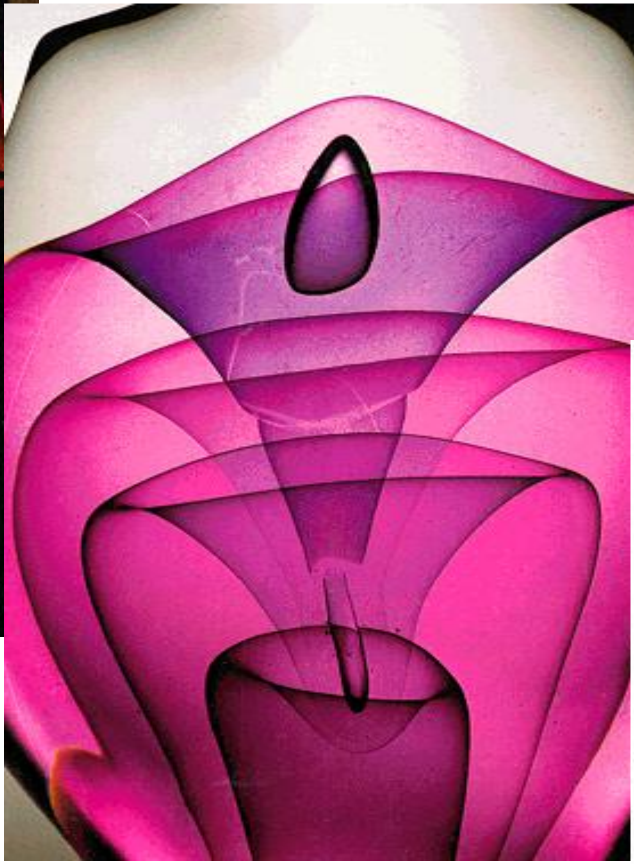
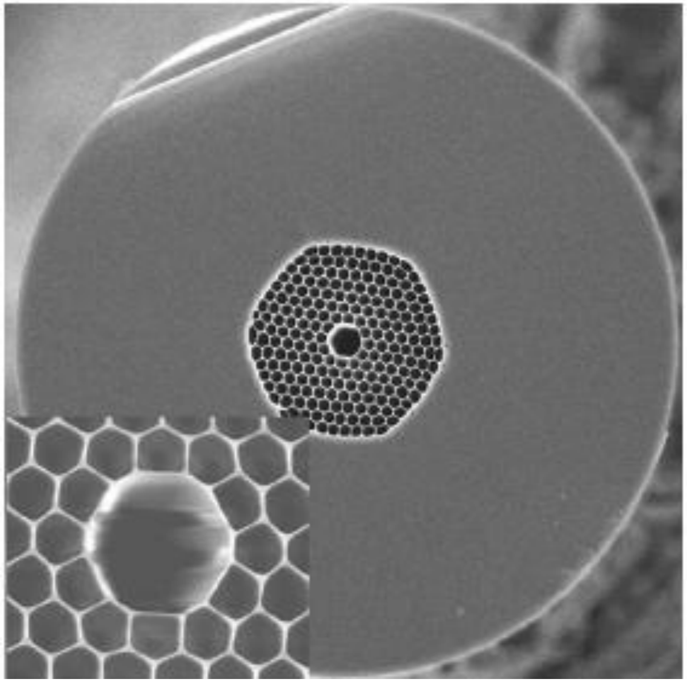
Its not just what its made of…



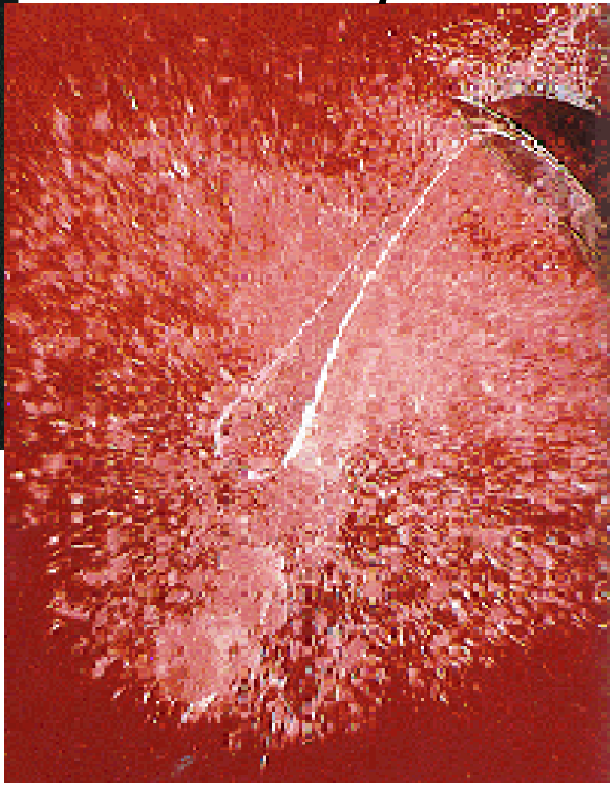
Photos courtesy of National Geographic (left) and the Optoelectronics Research Centre (ORC) at the University of Southampton, UK (below)



…***its the secret of the manufacturing technology that makes the final part unique and functional ….***

Processing history dictates properties

Formation-induced attributes dictate the form, performance and lifetime on a resulting glass part. Here, residual stress frozen into a Prince Rupert's drop during its formation (which appears as birefringence under crossed polarizers) ultimately limits the drop's mechanical stability and life.

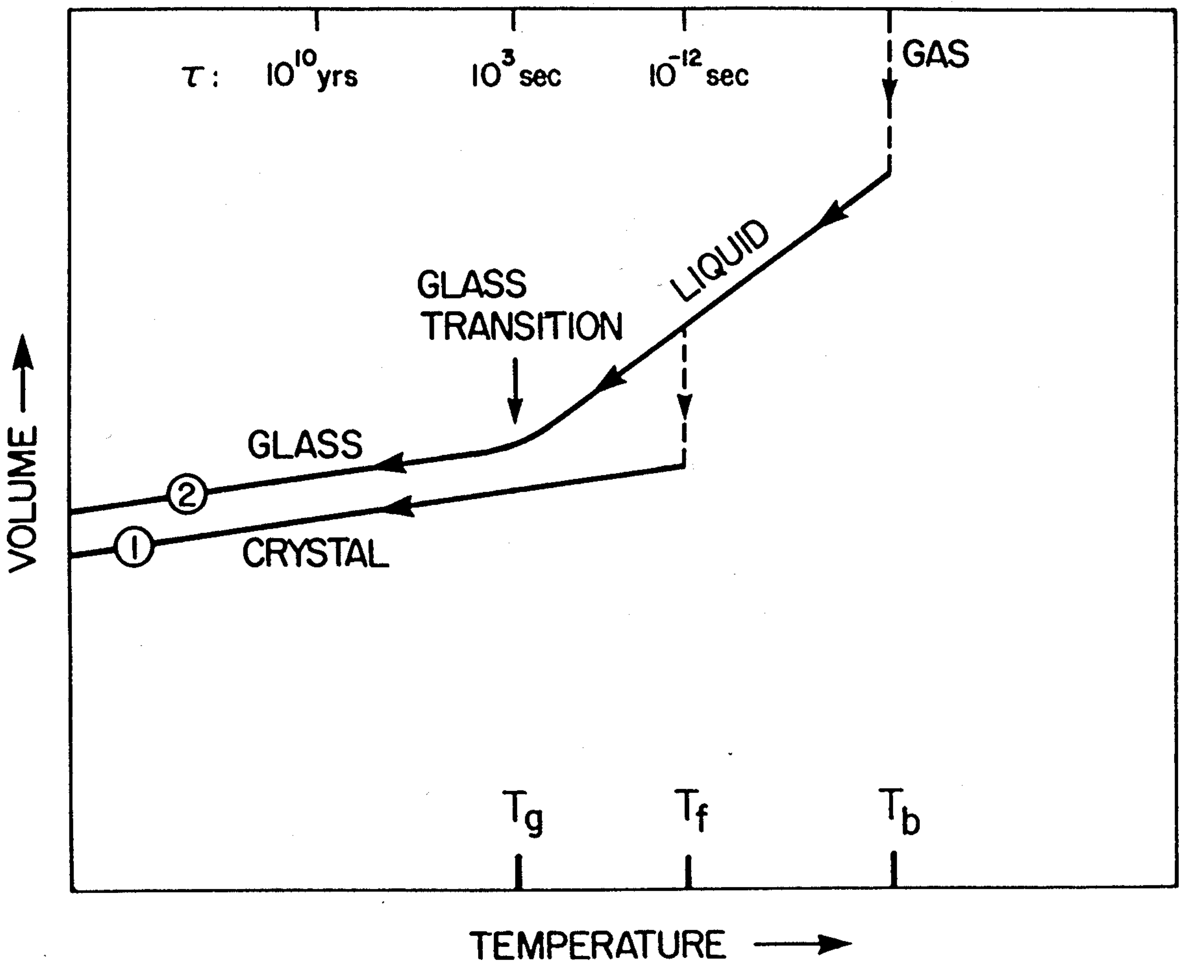


Photos courtesy of National Geographic

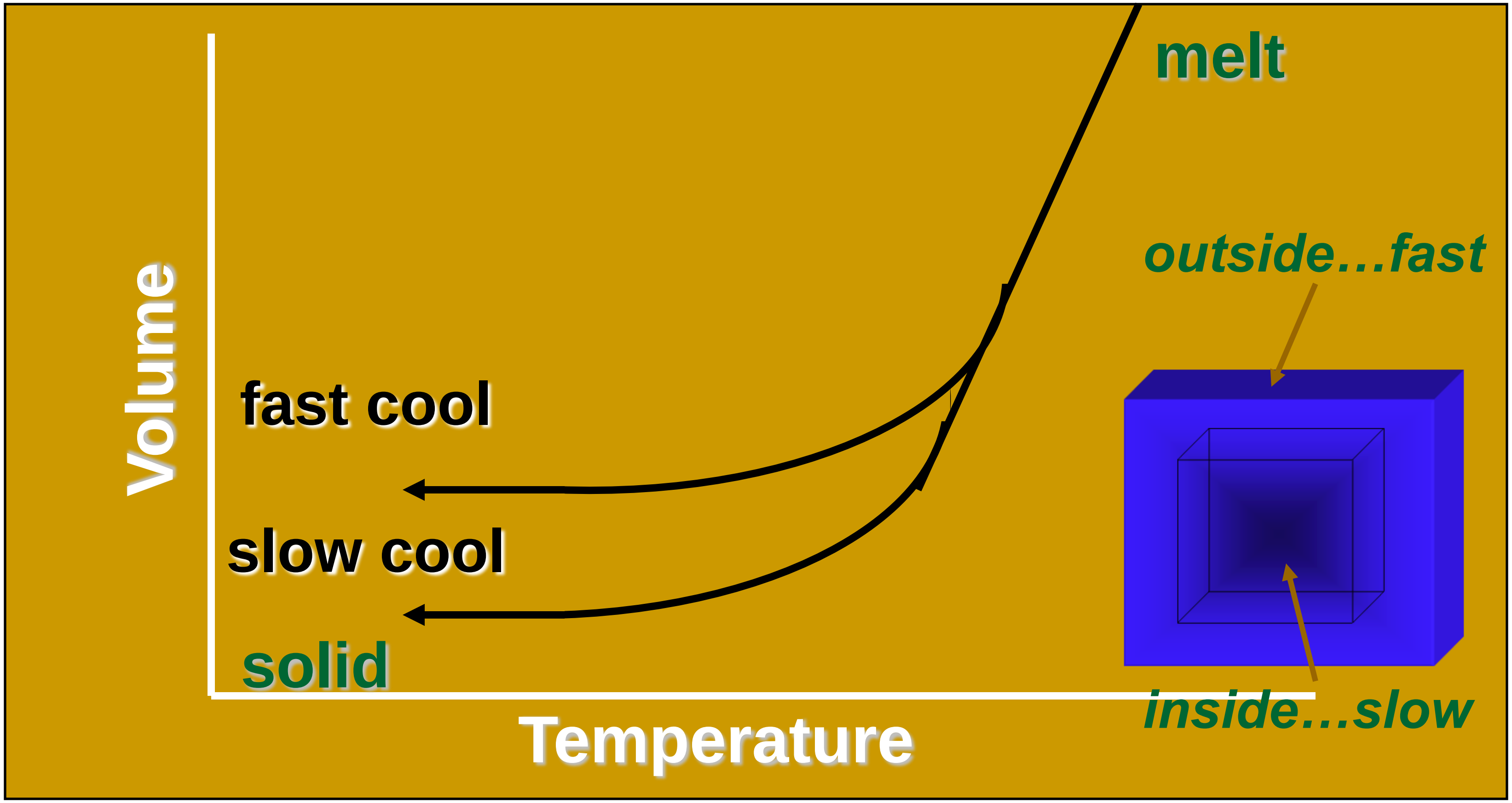
Outline

- Formation of glassy films – the basics
  - Vapor deposition
    - CVD
    - PLD
  - Thermal Evaporation
  - RF Sputtering
  - Others: e^- beam deposition, ion beam assist, sol gel
- Amorphous versus non-crystalline films
- Effect of processing parameters
- Defects and damage
- Characterization tools
- Bulk/film variations

Volume versus Temperature Plot

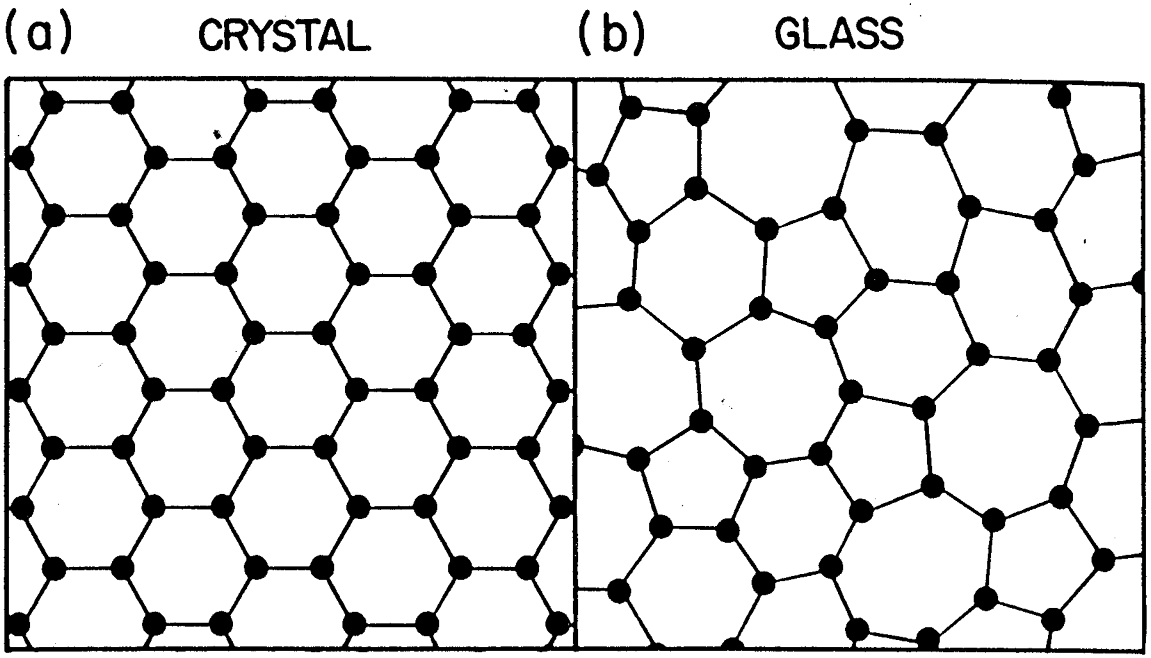


Viscosity Temperature curve

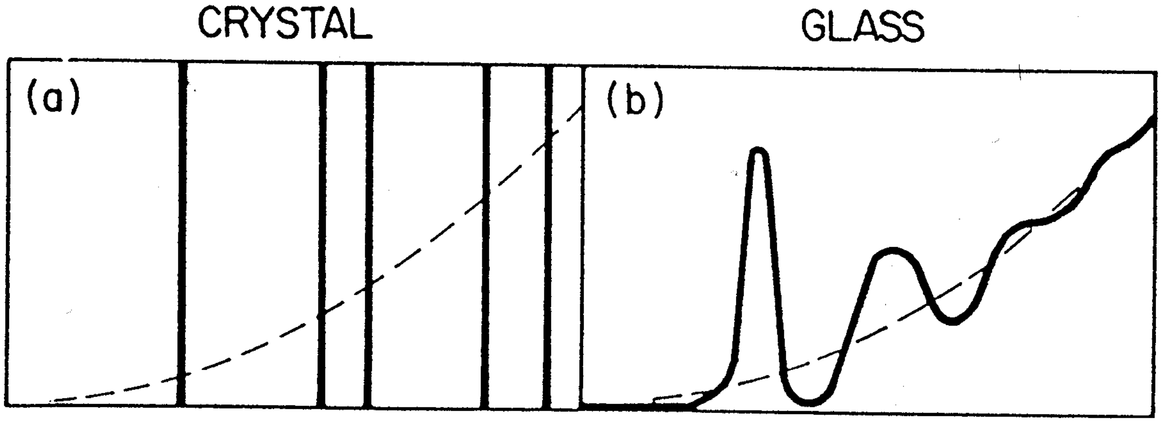


Difference in cooling rates--> stress outside (compression), inside (tension)

Schematic Sketches of the Atomic Arrangements in Solids



Schematic of the Radial Distribution Functions



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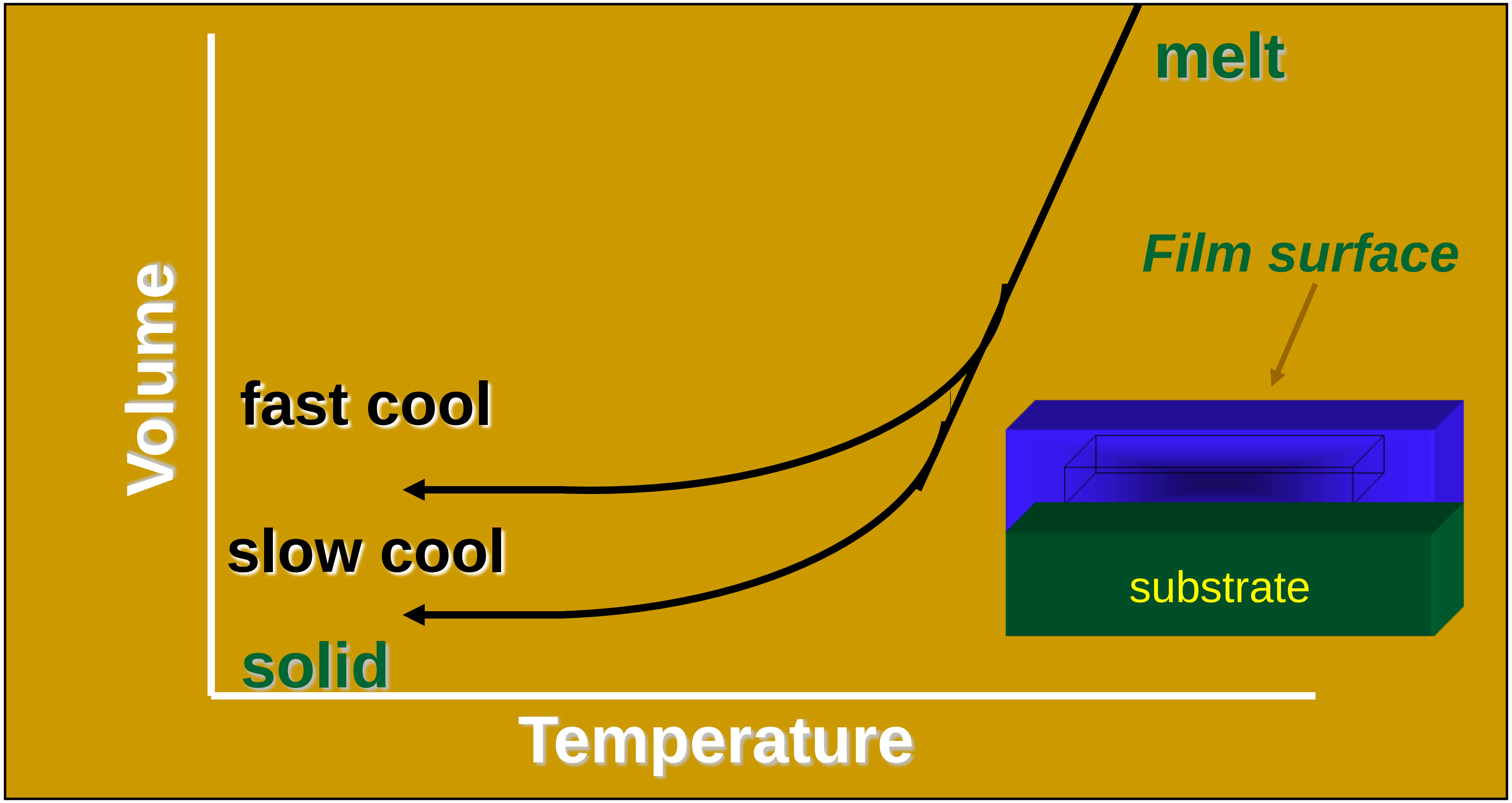
Viscosity-Temperature curve – film deposition



Difference in cooling rates leads to

- ***stress, anisotropy (Δn, Δρ, ΔTg, Δbonding), relaxation rates***

Bulk optical glass manufacturing process

- Batching
- Melting
- Refining
- Stirring
- Forming
- Annealing
- Relaxation to equilibrium

Thin film glass manufacturing process

- Target processing
- Deposition (means of energy deposition influences residual “stored energy”)
- Annealing
- Relaxation to equilibrium

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Type of deposition influences structure

- Heating rate analogy
- Higher energy process creates glass structure “further” from equilibrium
- Glass film structure is “further” from that of parent bulk glass
- Stability of film structure over time influenced by distance from equilibrium

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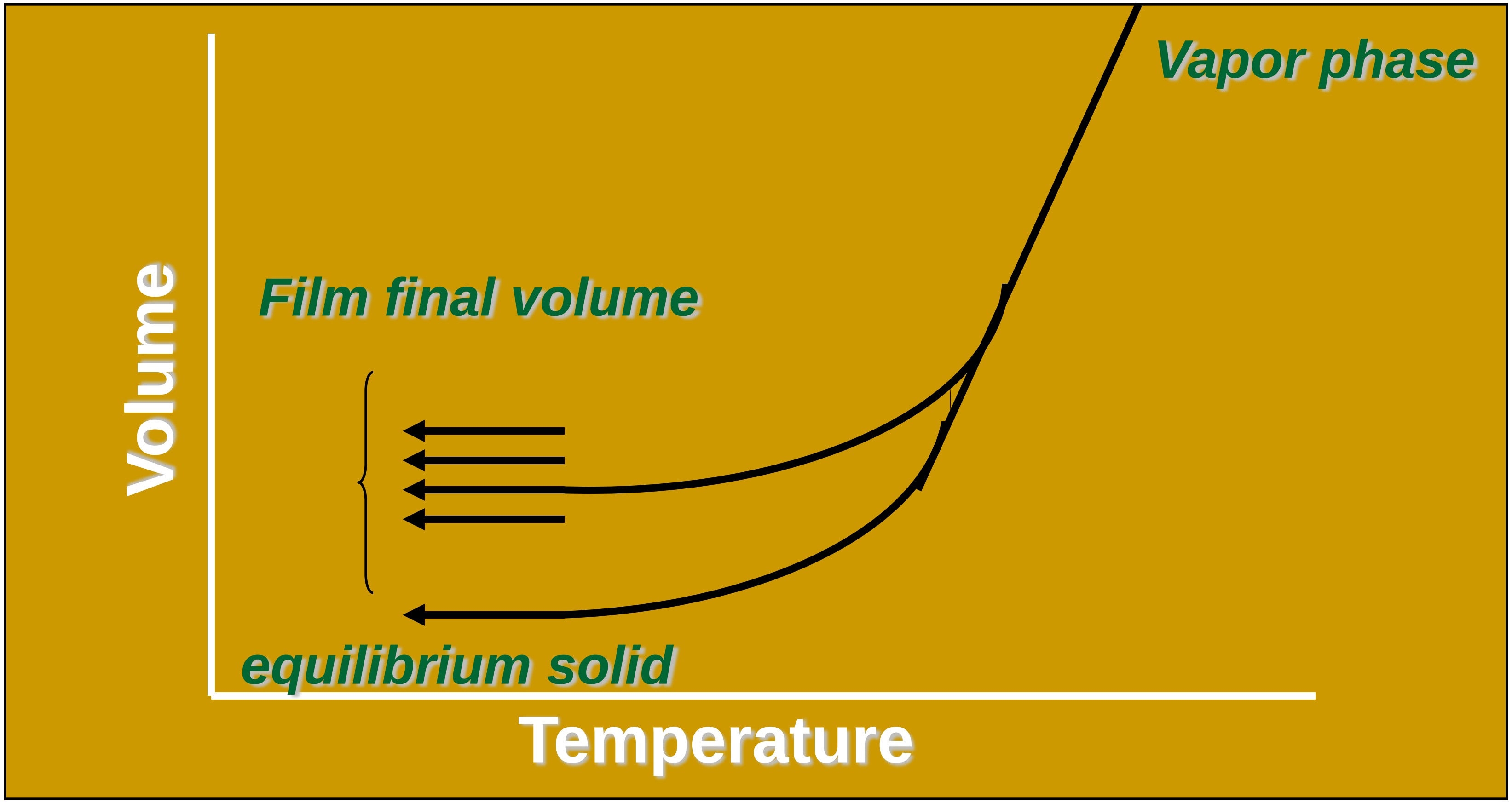
Deposition rate ~ condensation rate



Final film volume dictates film properties and stability

Films – key issues

- Maintaining compositional similarity
  - Bulk-film properties vary when thermal history varies
  - Compositional variation (from the vapor or plasma phase)
    - Vapor phase > variation than plasma
    - Preferential target removal
      - variation in vapor pressures
    - Preferential film condensation
      - Molecular units present in vapor or plasma may be “fragments of structural units” OR “clusters of structural units”
  - Structural variation
    - Results from composition and condensation rate differences

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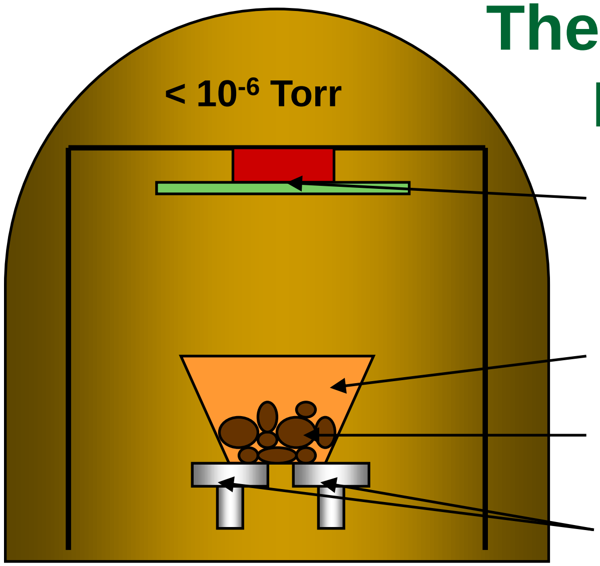
Film Deposition Techniques

Thermal Evaporation



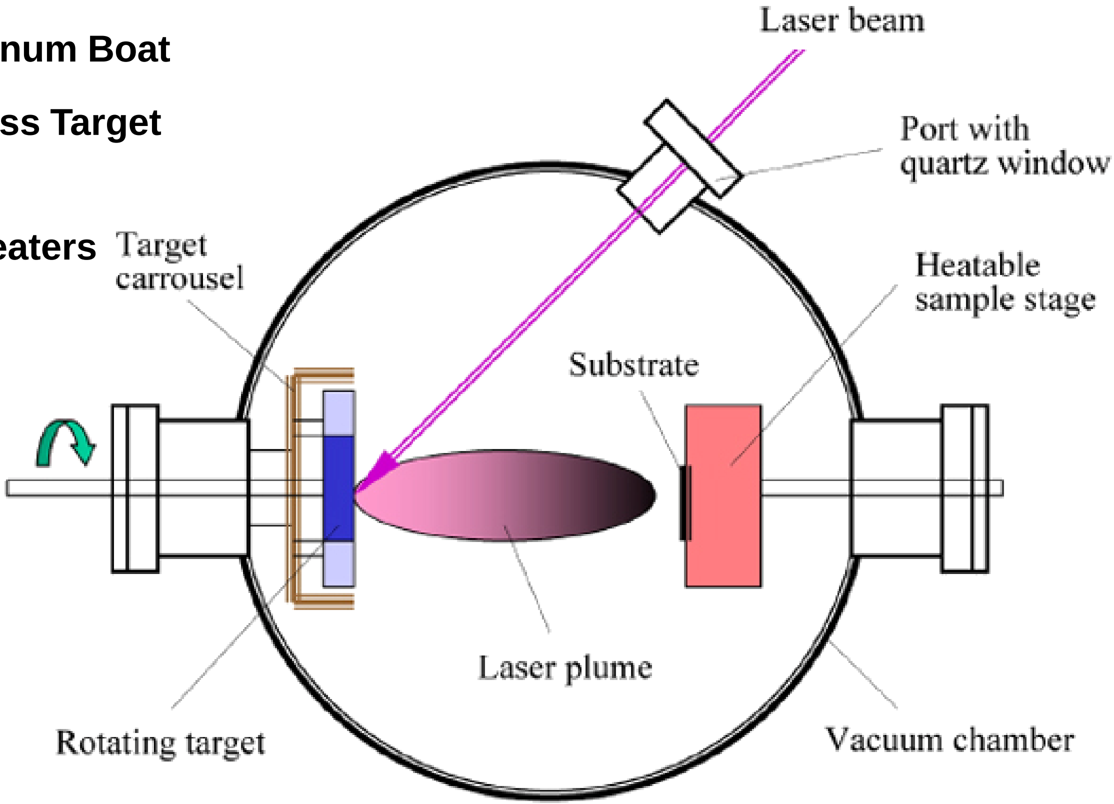
Substrate (Glass/Si)

Molybdenum Boat

Bulk Glass Target

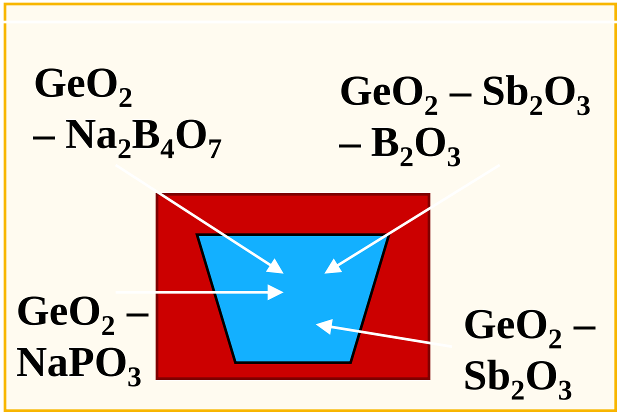
Target heaters

Pulsed Laser Deposition



Targets for deposition

- **Bulk glass can be utilized as starting "parent" glass**



$GeO_2 - Na_2B_4O_7$

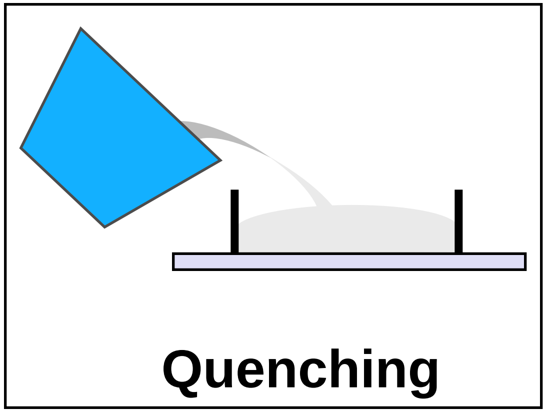
$GeO_2 - Sb_2O_3 - B_2O_3$

$GeO_2 - NaPO_3$

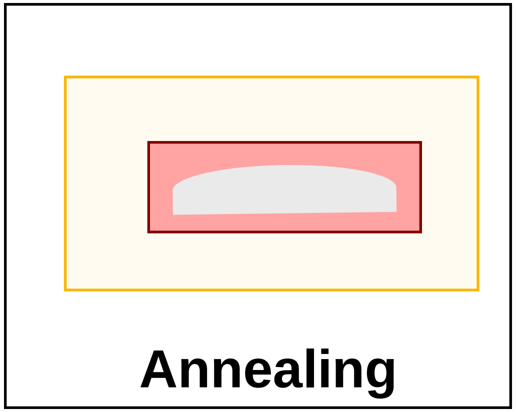
$GeO_2 - Sb_2O_3$

Melting

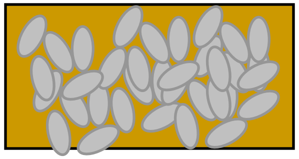
t=30min



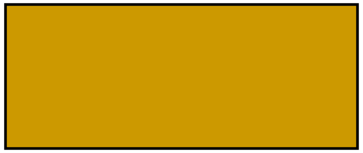
Quenching



Annealing



Crush to form pieces of target glass



Polished bulk piece of glass

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Film Deposition Techniques - Targets

- **Single component targets**
  - Good chance at maintaining stoichiometry
  - Deposition environment (Ar, O_2, air) influences
- **Bi-component targets**
  - Some variation may result due to variation in constituent properties (Tm, vapor pressure, etc)
  - Stabilty versus crystallization depends on similarity
- **Multi-component targets**
  - Selectivity of deposition rate can result in non-uniform film
  - Preferential deposition rates can lead to graded properties
    - Near-substrate properties ≠ top of film properties ≠ bulk glass properties
  - Target fabrication technique is crucial
    - Uniformity in target composition yields higher probability of uniform film → structure and properties

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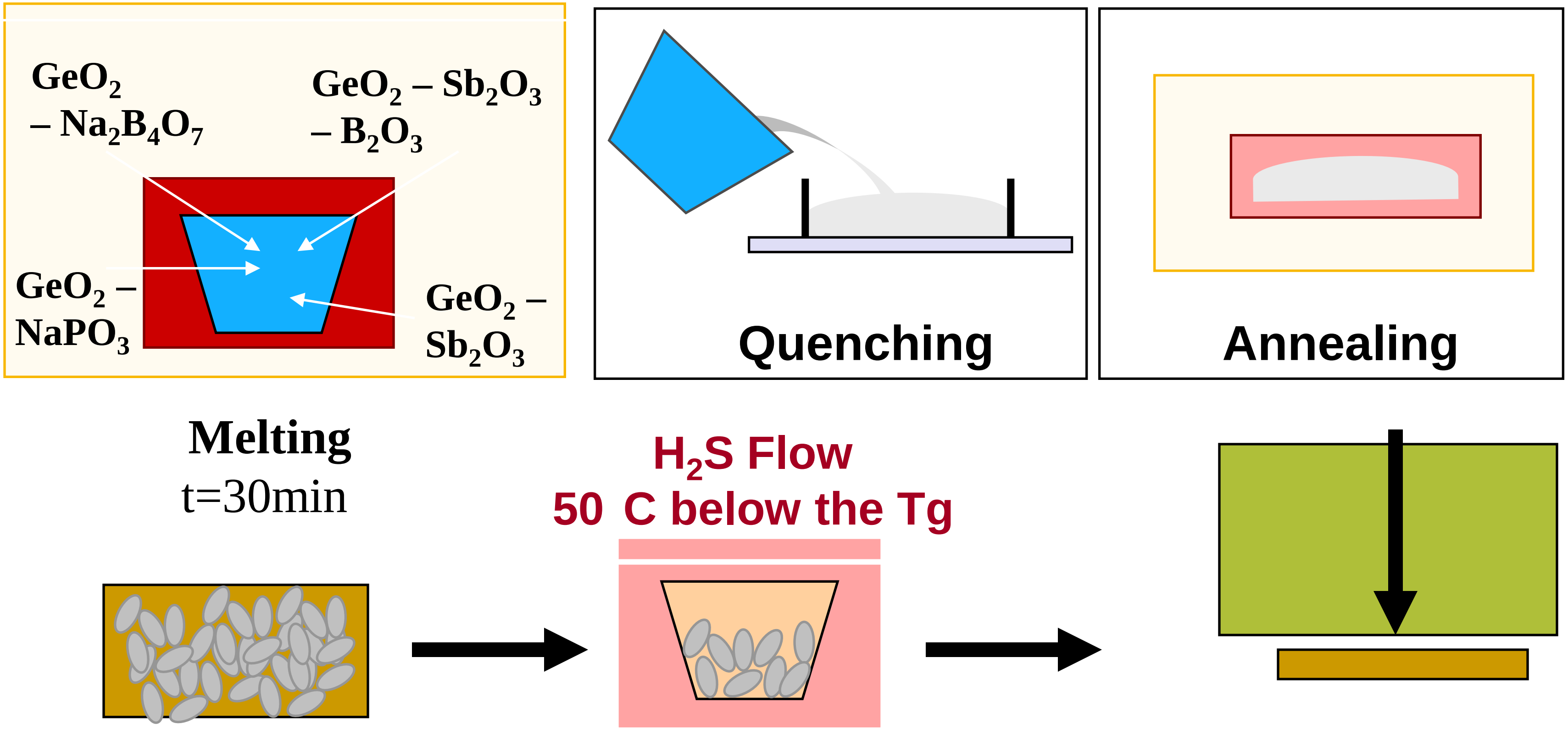
Target fabrication

- Multi-component glass: oxide/oxy-sulfide



$GeO_2 - Na_2B_4O_7$

$GeO_2 - Sb_2O_3 - B_2O_3$

$GeO_2 - NaPO_3$

$GeO_2 - Sb_2O_3$

Melting
t=30min

Quenching

Annealing

H_2S Flow
50 C below the Tg

Pulverize to form a powder

Sulfination

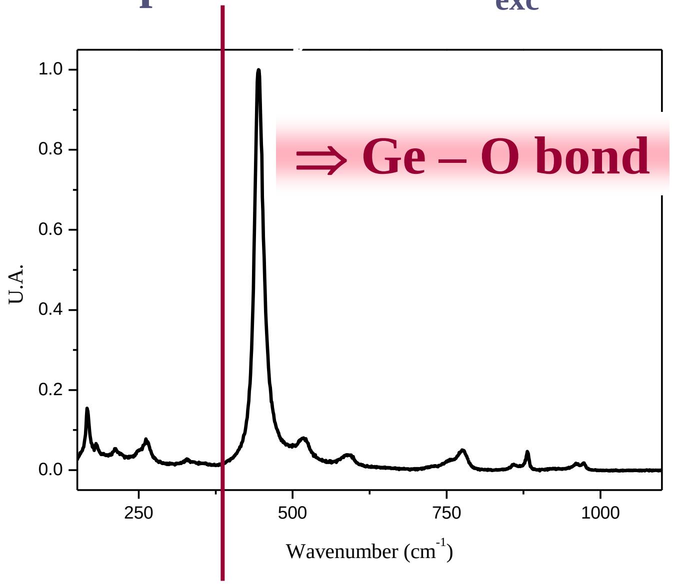
Press to form pellet target

Sulfination process (*crystalline* GeO_2)

H_2S

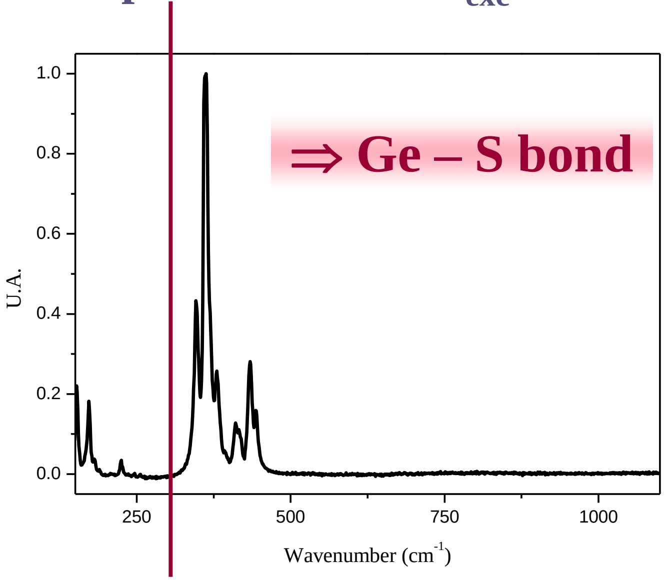
24 hours / 550 C

◆ **Raman spectrum** λ_{exc} = 632 nm



⇒ Ge – O bond

◆ **Raman spectrum** λ_{exc} = 632 nm



⇒ Ge – S bond

⇒ Confirmation of substitution of oxygen by sulfur

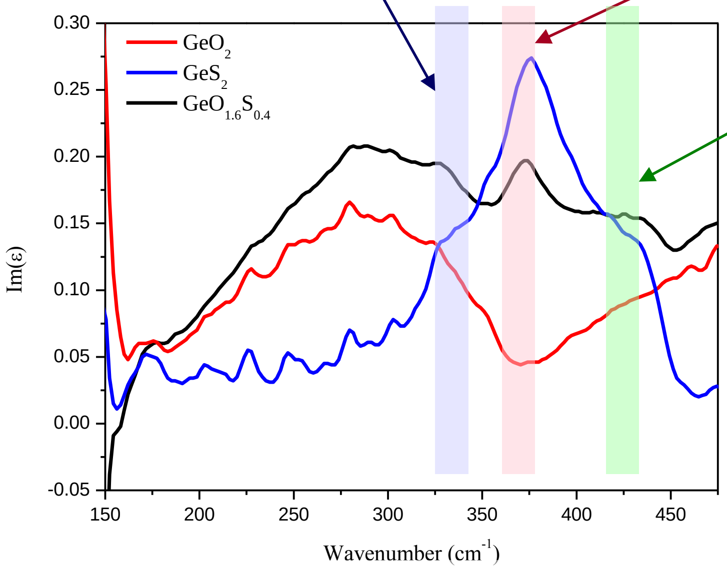
Confirmation of mixed oxysulfide

- ♦ IR Spectra

IR Forbidden mode of $[GeS_4]$

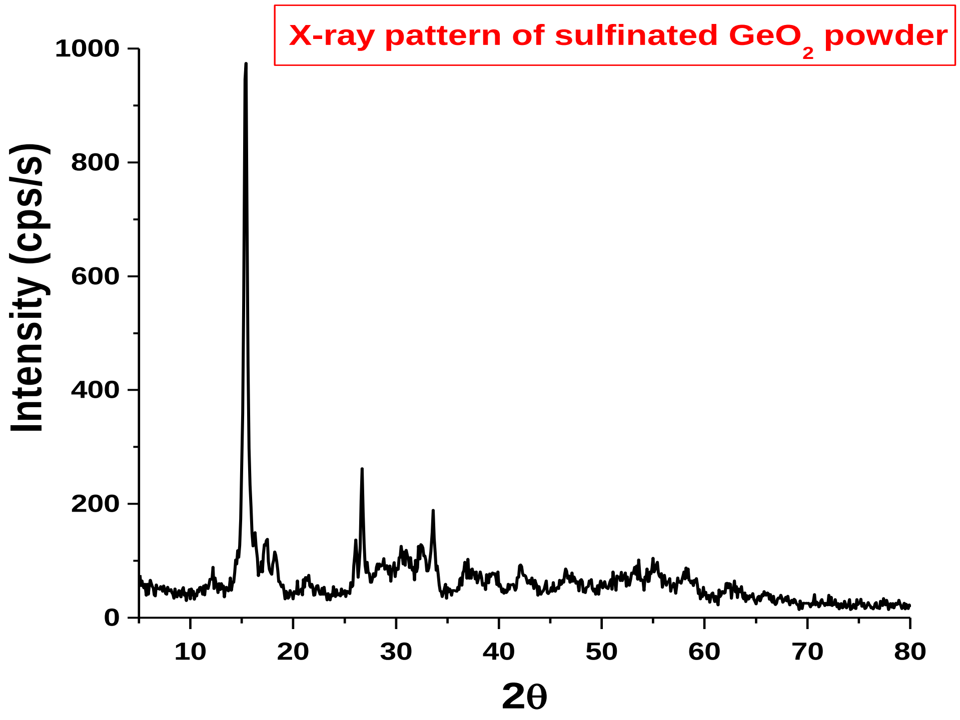
Asymmetrical stretch Ge – S – Ge in $[GeS_4]$

Asymmetric stretching $S_3Ge – GeS_3$



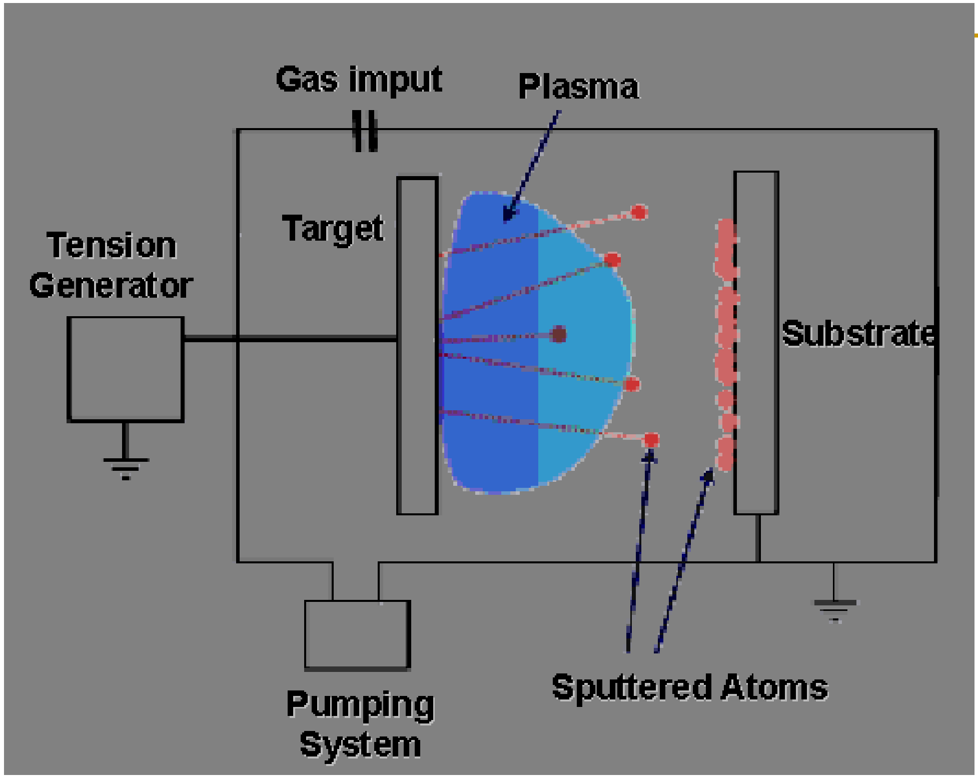
IR absorption peaks for $GeO_{1.6}S_{0.4}$ ⇒ Presence of Ge – S vibrations

Compositional tailoring of target



Composition	Sulfur percent
GeO_2	0
$GeO_{1.42}S_{0.58}$	29
GeOS	50
$GeO_{0.42}S_{1.58}$	79
GeS_2	100

Physical Vapor Deposition (aka RF sputtering)

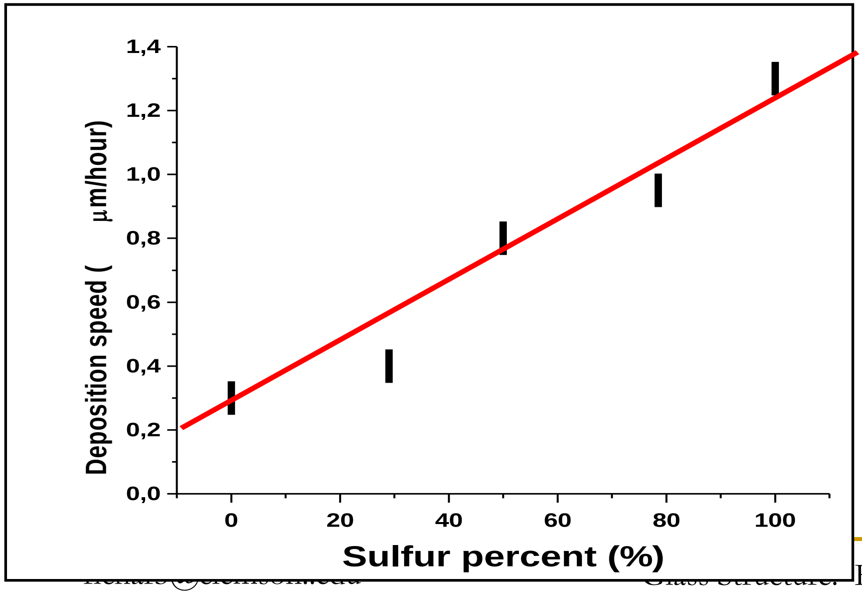


Argon pressure of 10^{-2} mbar

Power applied of 15 mW

Homogeneous thin films obtained

High deposition speeds can be attained

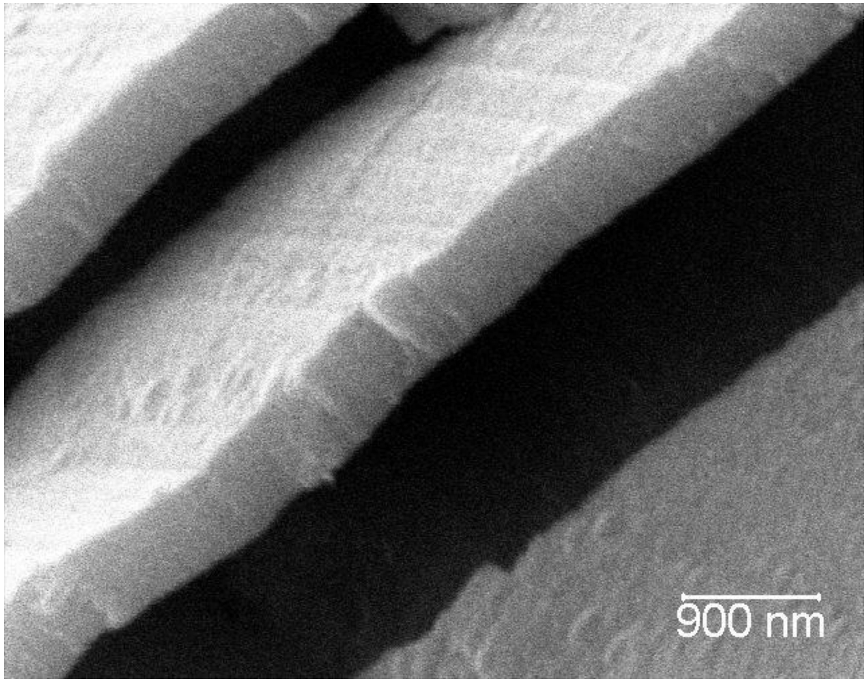


Deposition speed of the material is correlated to O/S ratio of the target

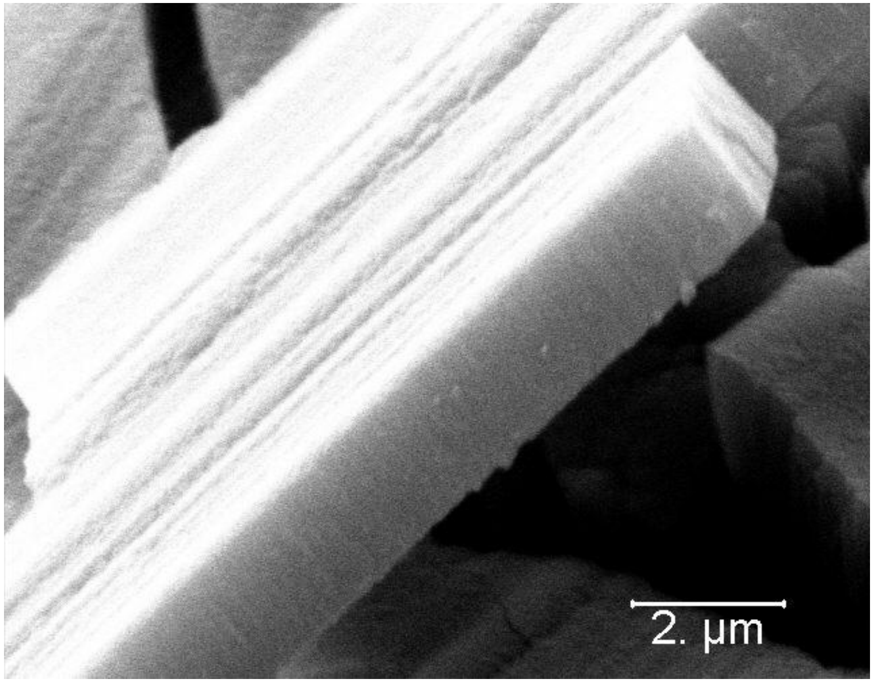
No apparent selectivity of constituents in film

Film thickness can be controlled

Oxide and oxy-sulfide films: morphology



SEM image of GeO_2 thin film



SEM image of $GeO_{1.42}S_{0.58}$ thin film

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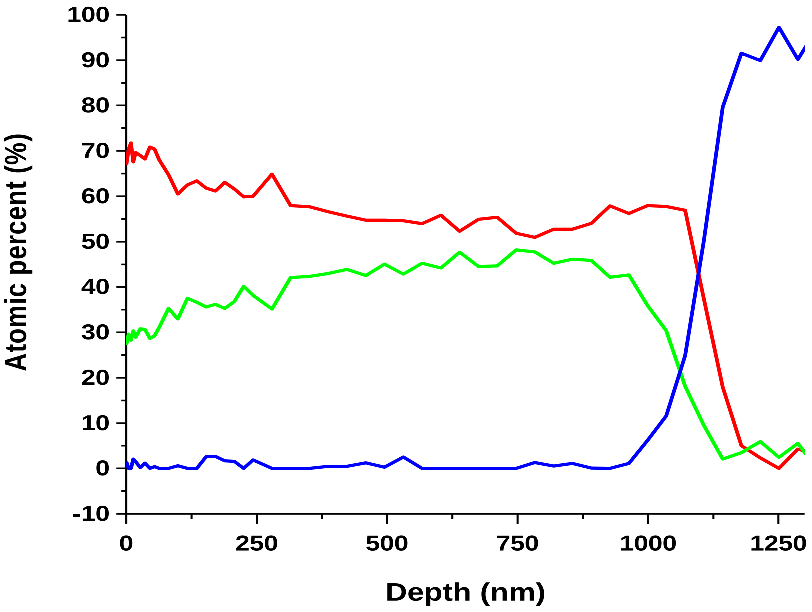
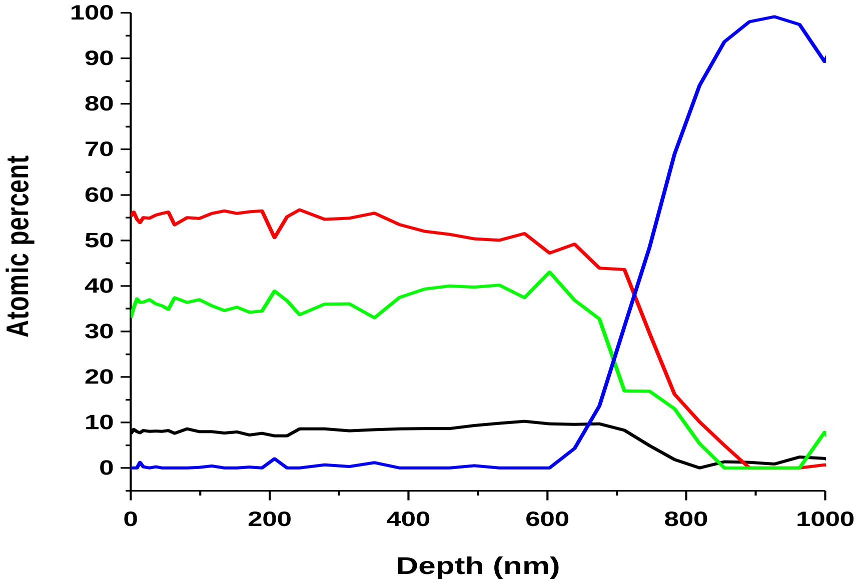
Auger data: compositional variation

Auger spectroscopy measurements

- Films deposited on Al foil



GeO_2



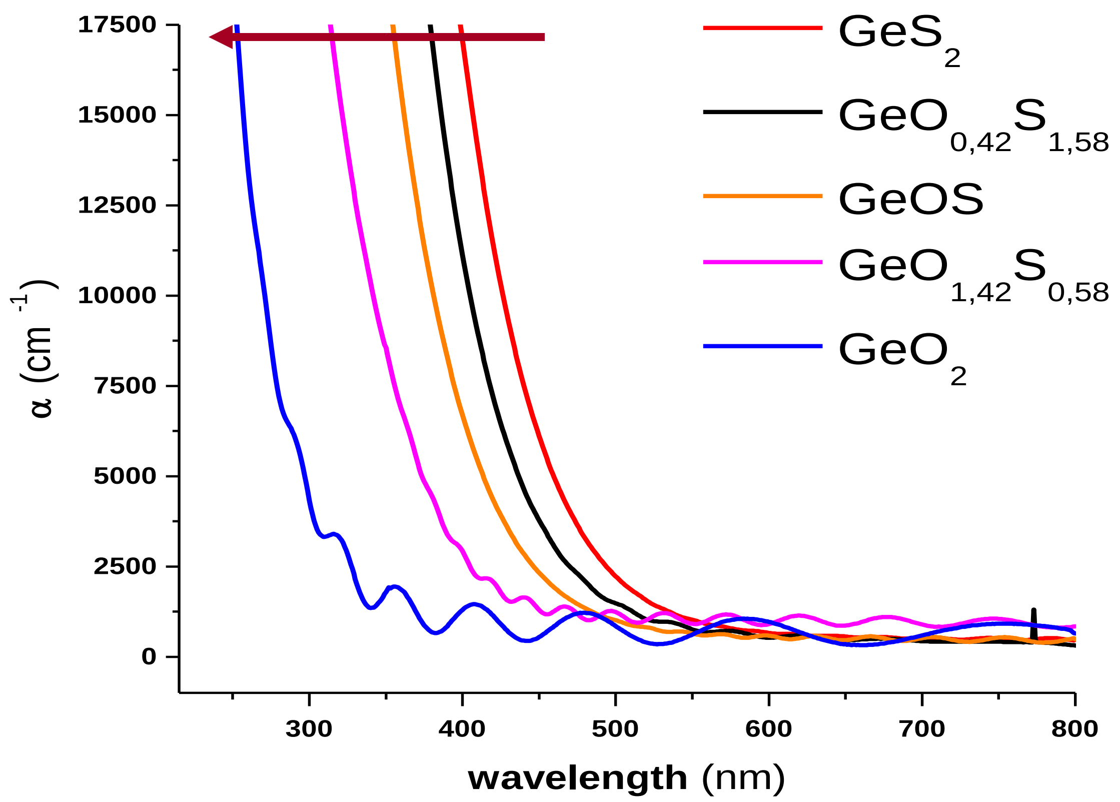
$GeO_{1.42}S_{0.58}$

🟦 **Aluminum** 🟩 **Germanium**

⬛ **Sulfur** 🟥 **Oxygen**

Homogeneity from the surface to the depth of the films

Enhancement of optical and physical properties example: oxysulfide thin films

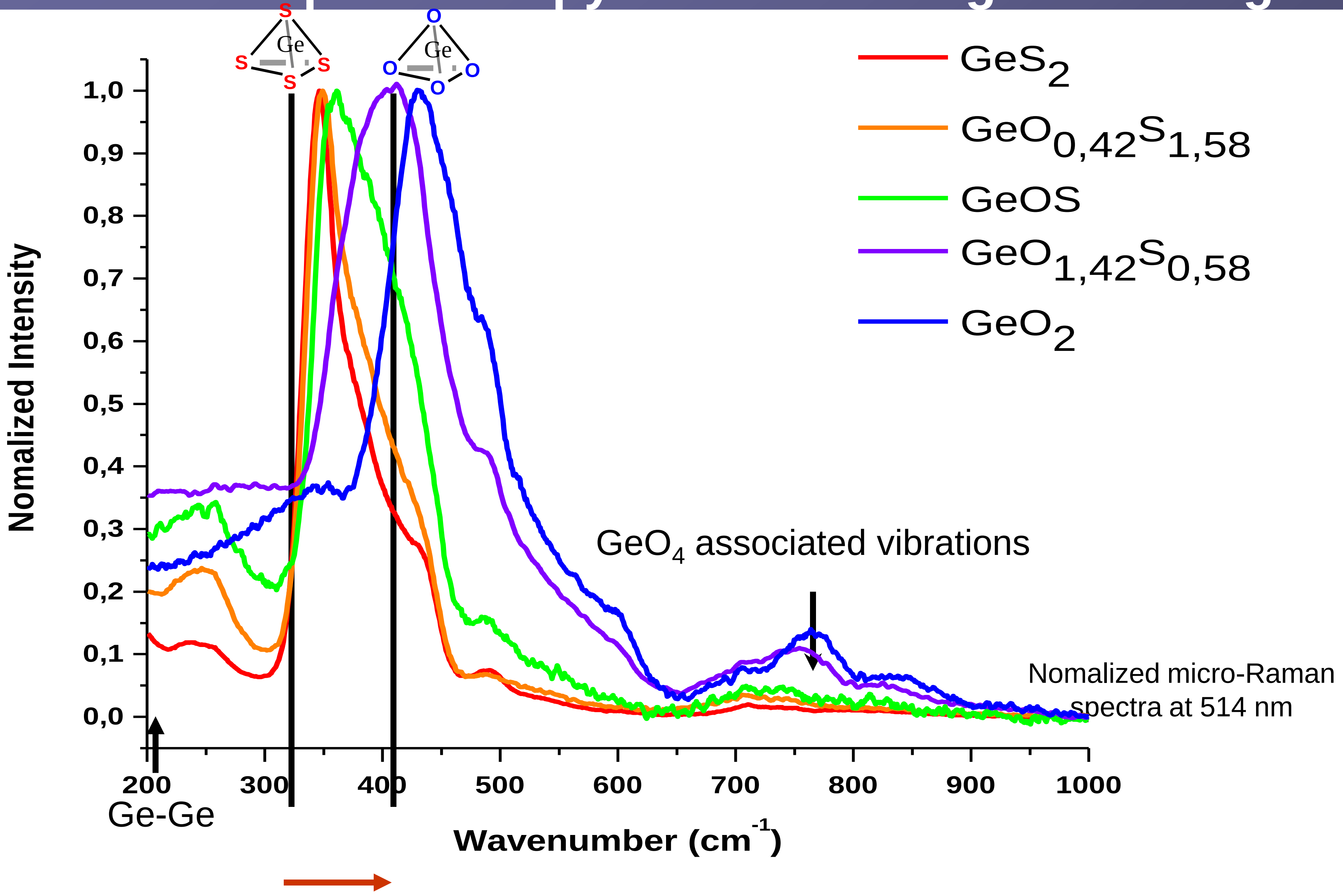


Absorption spectra

Blue-shift with decreasing sulfur content (UV and multiphonon); increased T_g, thermal stability and mechanical integrity of resulting film material

“Germanium Oxysulfide Thin Film Glasses for Optics,” C. Maurel, et al., submitted Mat. Res. Bull. (2007)

Micro-Raman spectroscopy: structural origin of changes



GeO$_4$ associated vibrations

Nomalized micro-Raman spectra at 514 nm

Ge-Ge

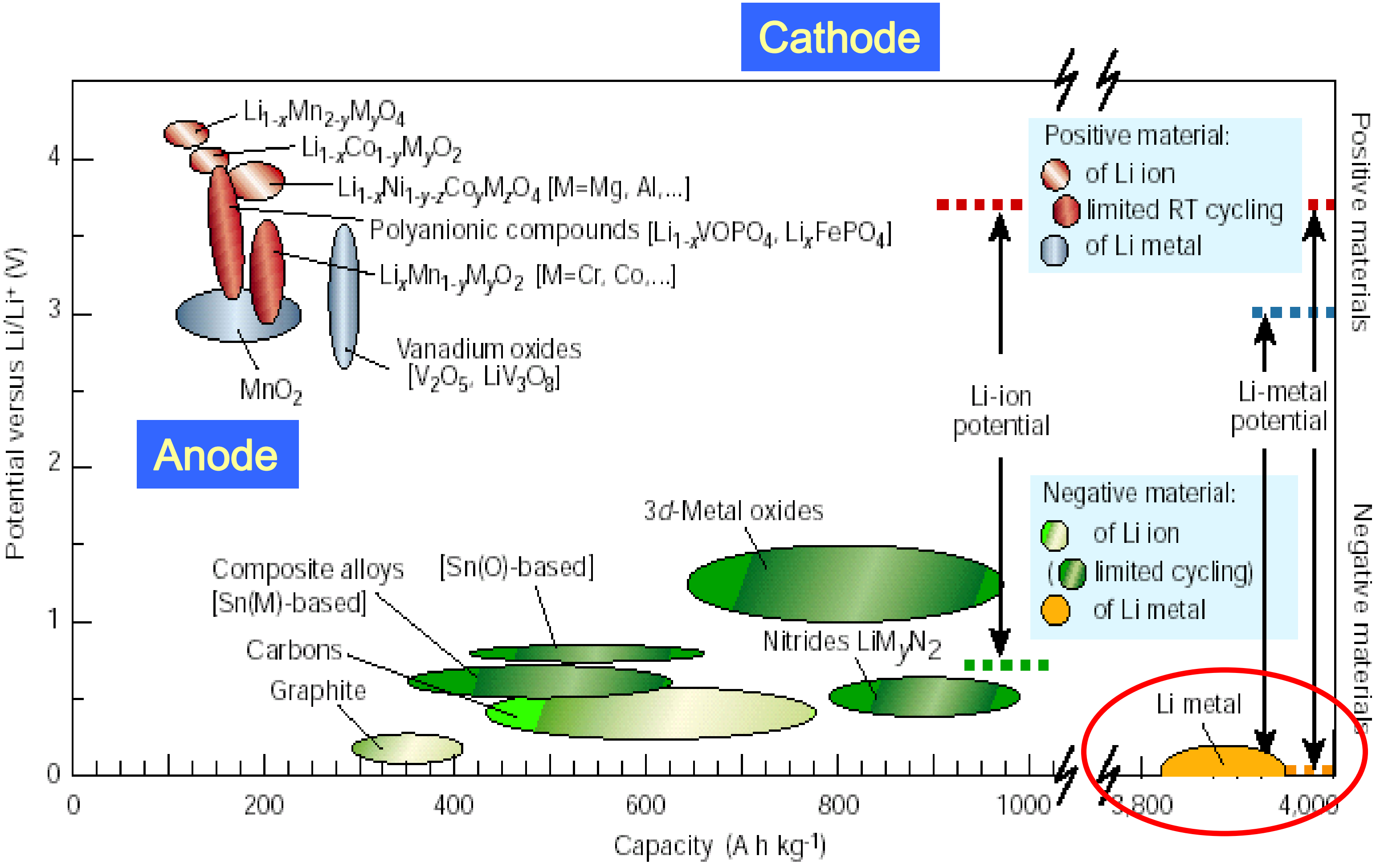
Vibration of tetrahedral unit peak shifts with sulfide to oxide ratio

Y. Kim, J. Saienga, S. W. Martin, J. Non-Cryst Solids, 351 (2005), 1973-1979

Other applications driving film processing technology:
Portable Energy Sources are Critical Technologies




Anode and Cathode Combinations Determine the Energy Density



J.M. Tarascon, M. Armand, Nature, 414, 15 (2001) 359

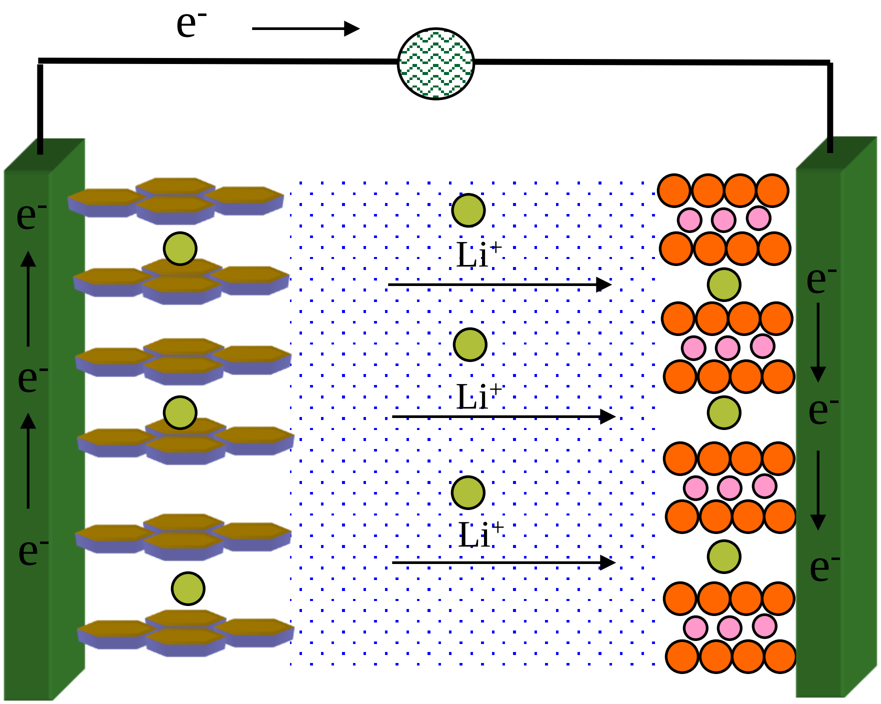
Li-ion Batteries

C_6 is a common anode material for Li-ion batteries

The maximum capacity of graphite (LiC_6): 372 mAh/g 1339 C/g

Good cycle-life

But, low capacity for new portable devices



Li_xC_6 $\quad$ Li^+ conducting electrolyte $\quad$ $Li_{1-x}CoO_2$

Anode: $Li_xC_6 \longrightarrow xLi^+ + xe^- + C_6$

Cathode: $Li_{1-x}CoO_2 + xLi^+ + xe^- \longrightarrow LiCoO_2$

Polymer Li$^+$- ion Conducting Electrolytes

- Li ion conducting polymer electrolytes
  - *Advantages*
  - Polypropylene oxide + $LiClO_4$ (Salt + polymer electrolyte)
  - High Li$^+$ ion conductivity
  - Excellent thin film properties
  - Enable multitude of “form factors” for use

  - *Disadvantages*
  - Chemically unstable
  - Degrades with time
  - Soft
  - Cannot be used high energy anodes such as Li

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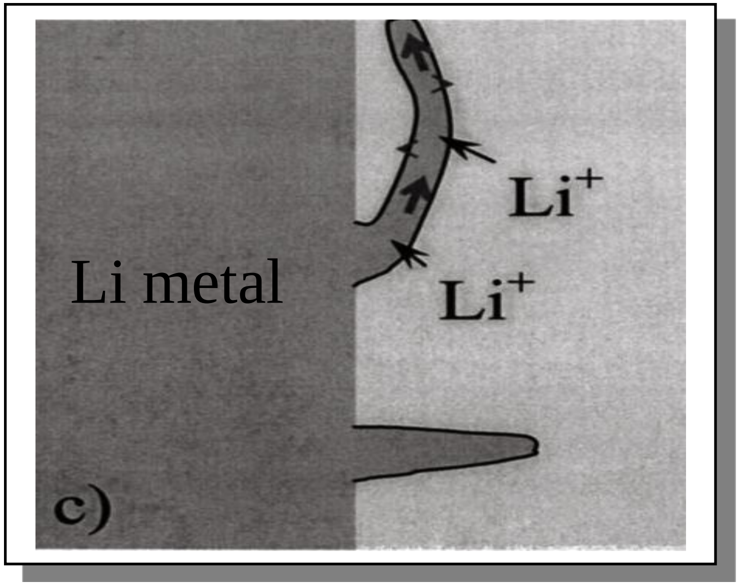
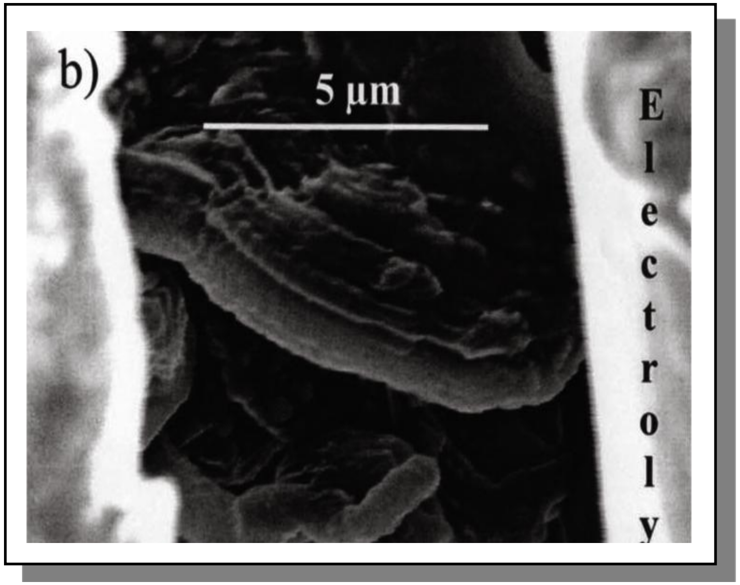
Lithium Dendrite Formation in Li ion Batteries with polymer electrolyte membranes





Non-epitaxial deposition of lithium after each cycle leads to the growth of uneven “fingers” or dendrites

Internal connection results which short circuits the battery

M. Dolle et al. Electrochemical and Solid-State Letters, 5(12) (2002)A286

Li^+ - ion Conducting Glasses (FIC) as Alternative Electrolytes

- ***Advantages***
- Inorganic chemistry can be more chemically stable
  - No reaction with high activity anodes
- Stronger bonding (ionic) gives higher mechanical strength
  - No Li penetration from dendrites
- Chemically bonded anion ($Si\text{-}O^-$, $Ge\text{-}S^-$) is immobile
  - Unit transference number for Li^+
  - Higher Li^+ ion conductivity
- Smaller temperature dependence of the conductivity
  - Polymers are used above Tg in liquid state
  - Glasses are used below Tg in solid state

Li^+- ion Conducting Glasses as Alternative Electrolytes

- ***Disadvantages***
- Solid structure does not accommodate volume changes
- Anode and cathode shrink and swell during discharge
- Anode and cathode swell and shrink during recharge cycle
- Volume changes promote debonding between electrode and electrolyte
- Debonding creates open circuit and reduces battery performance

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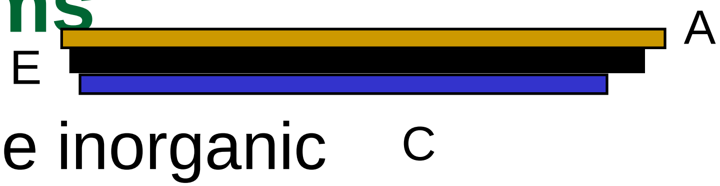
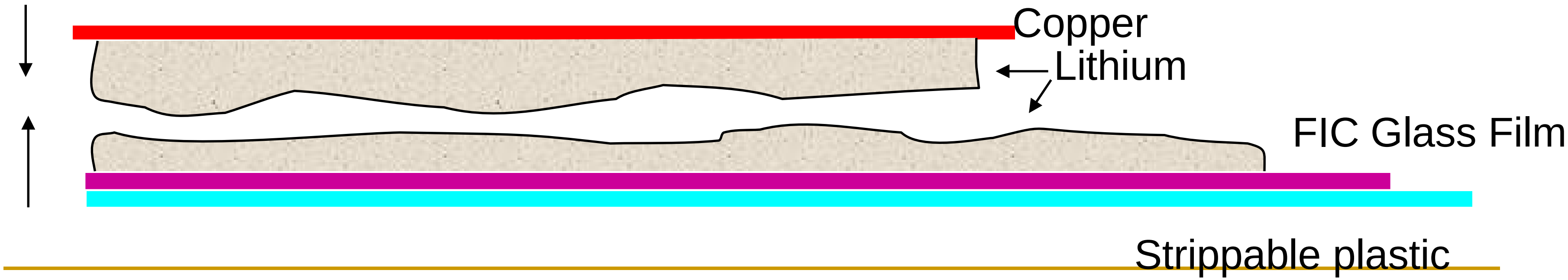
Thio-Oxynitride FIC Thin Films



- Combine electrochemically durable inorganic electrolyte with flexible and volume accommodating polymer electrolyte
  - Thin strong Li$^+$ ion conducting film will block dendrite growth
  - Polymer electrolyte will allow required volume changes in the battery
- Oxide chemistry to enable atmospheric stability for ease of handling
- Sulfide chemistry to enable fast Li$^+$ ion conduction and transport across thin film electrolyte
- Nitride chemistry to enable electrochemical stability in contact with metallic Lithium

Thio-Oxynitride FIC Thin Films

- ***Solution***
  - Back Lithium metal anode with copper current collector on back side
  - Coat Lithium metal anode with inorganic glass FIC electrolyte on front side
  - Sandwich the two layers together to create new stable anode
  - Copper protects backside and collects electrons
  - Inorganic glass protects front side – carries Li^+ ions to polymer electrolyte
  - Strippable polymer film is removed when battery is manufactured
  - Thin glass film
    - Limits dendrites, hard inorganic glass
    - Protects polymer electrolyte from reactive Lithium



Thio-Oxynitride FIC Thin Films

- Problems with existing glasses
  - Glass compositions that are stable in contact with metallic Li are not conductive enough to Li^+ ions
    - Oxide Glasses
    - $Li_2O + P_2O_5$
  - Glasses that have high enough Li^+ ion conductivities are not stable enough in contact with Li
    - Chalcogenide Glasses
    - $Li_2S + GeS_2$
- Solutions
  - Can oxy-sulfide mixtures be both conductive enough and stable enough?

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Thio-Oxynitride FIC Thin Films

- Bates at Oak Ridge also found that nitrogen added to oxide glasses makes them stable in contact with Li
  - Li_3PO_4 + N (RF reactive sputtering) produces $Li_{3.3}PO_{3.9}N_{0.17}$
  - Good stability with Li
  - But poor conductivity 10^{-6} $(\Omega cm)^{-1}$ at RT
- Sulfides can be sputtered in Ar and have excellent conductivities, but poor stabilities
- Will Thio-Oxynitride thin films combine properties of all three components?

Thio-Oxynitride RF sputtered thin films

- Objectives of the ISU project
  - Build RF magnetron reactive materials sputtering system capable of sputtering chalcogenide targets
  - Test with Li_3PO_4 in Ar and N
    - Characterize Li_3PO_4 and LiPON
  - Sputter Chalcogenide Targets, Li_4GeS_4
    - Sputter in Ar and N
    - Oxygen as a ubiquitous contaminate used to advantage
    - Characterize structure, properties, conductivities
    - Improved atmospheric stability?
    - Improved stability with Li metal?
    - Improved conductivity?

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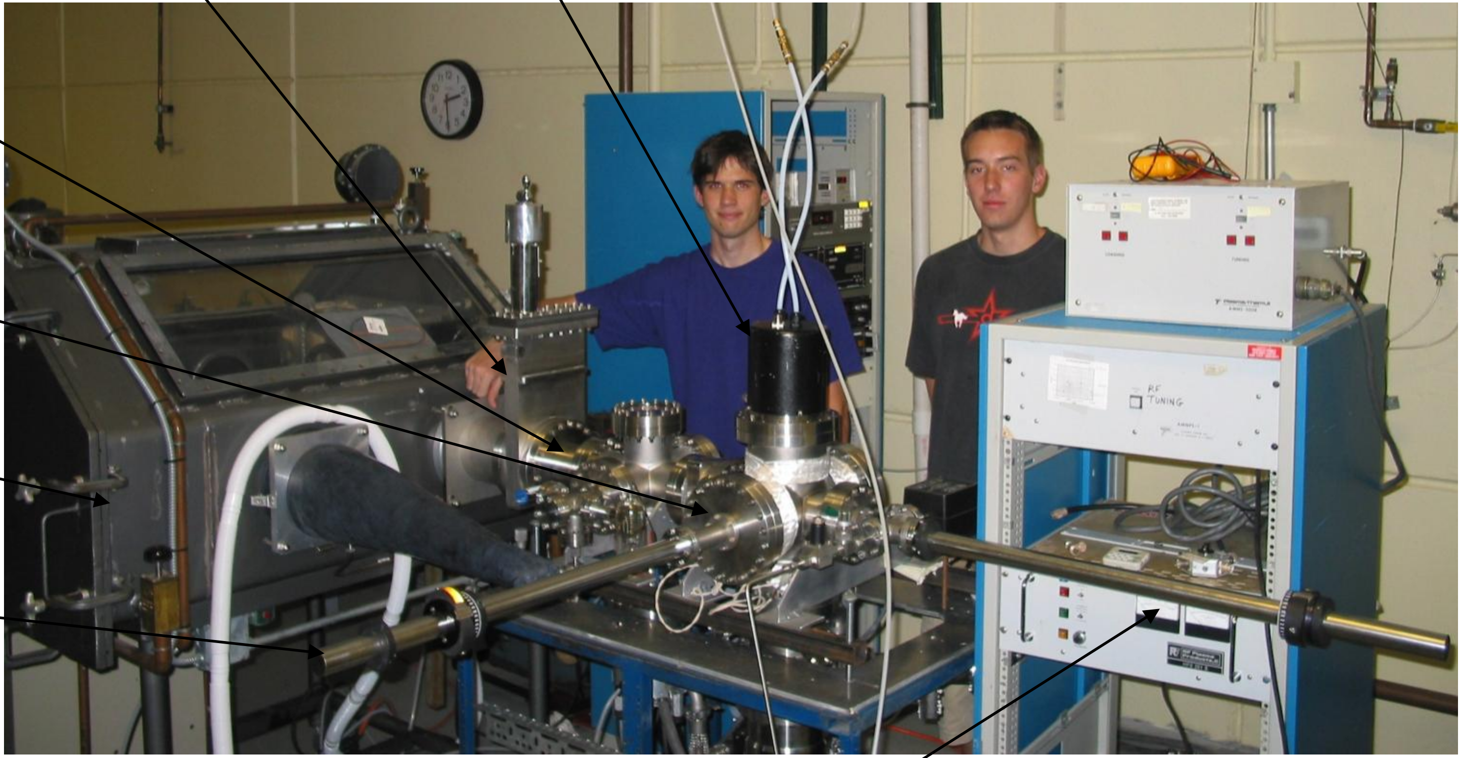
Thionitride Thin Films – ISU effort

- 2004-2005
- Construction of RF magnetron sputtering system
  - Attached to a N_2 filled glove box
  - Tested and debugged sputtering system, glove box, and vacuum system
- Purchased commercial Li_3PO_4 target
  - Sputtered Li_3PO_4 target in Ar – No N incorporation
  - Sputtered LI_3PO_4 target in N_2 – N incorporation
    - ~ the same amount of N reported in literature
    - ~ the same atomic ratios of Li, P, and O
  - Achieved ~ 1μm/hr deposition rate
  - Controllable sputtering gases, power, time, and pressure
  - Connected to glove box so targets and deposited films can be handled without contamination

Reactive Materials RF Sputtering System



Load lock chamber

Sputtering Head

Sputtering anti-chamber

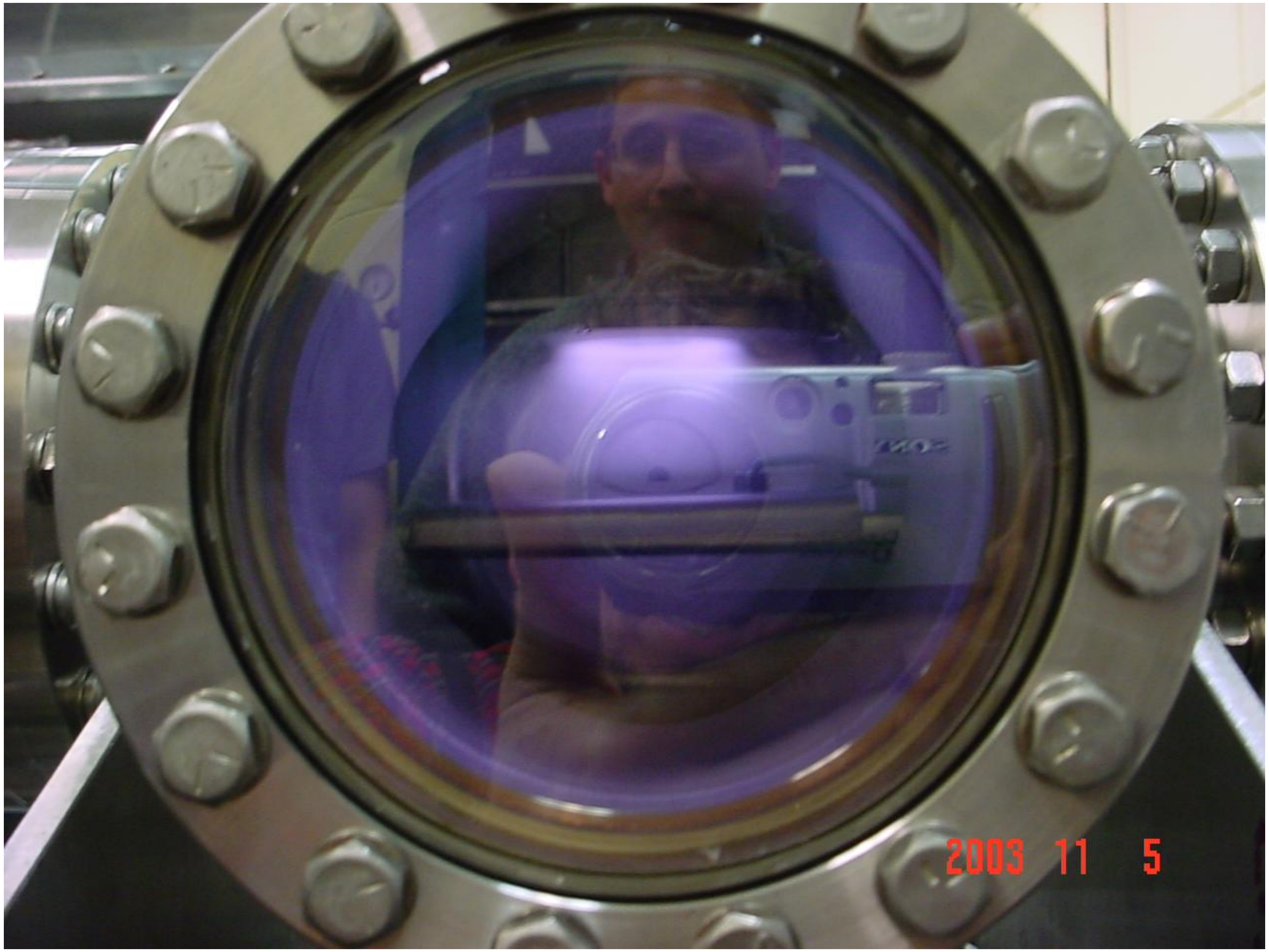
Sputtering Chamber

Glove box

x load lock arm

y load lock arm

Li_4GeS_4 plasma in N_2 at ~ 20 mTorr



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Li_4GeS_4 Target Preparation

- Commercial source for Li_2S – Lorad, Alfa, Cerac
- $Ge + 2S \rightarrow GeS_2$ – Sealed SiO_2 tube, 800 °C for 8 hours with rotation @ 5-8 rpm
- $2Li_2S + GeS_2 \rightarrow Li_4GeS_4$, 900°C for 2 hours
  - Vitreous carbon crucibles
  - Slowing cooling to ensure crystallization of the melt
  - Milling of the powder to ~ 5-25 microns
- Dry pressing to a 1/8” x 2” pellet
- Sintering 700, 720, 740, 800 °C, 2 – 6 hours

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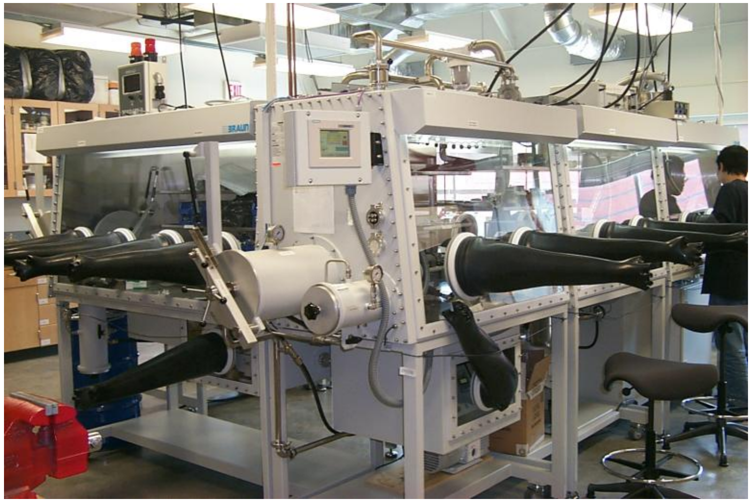
Sample preparation facilities at ISU



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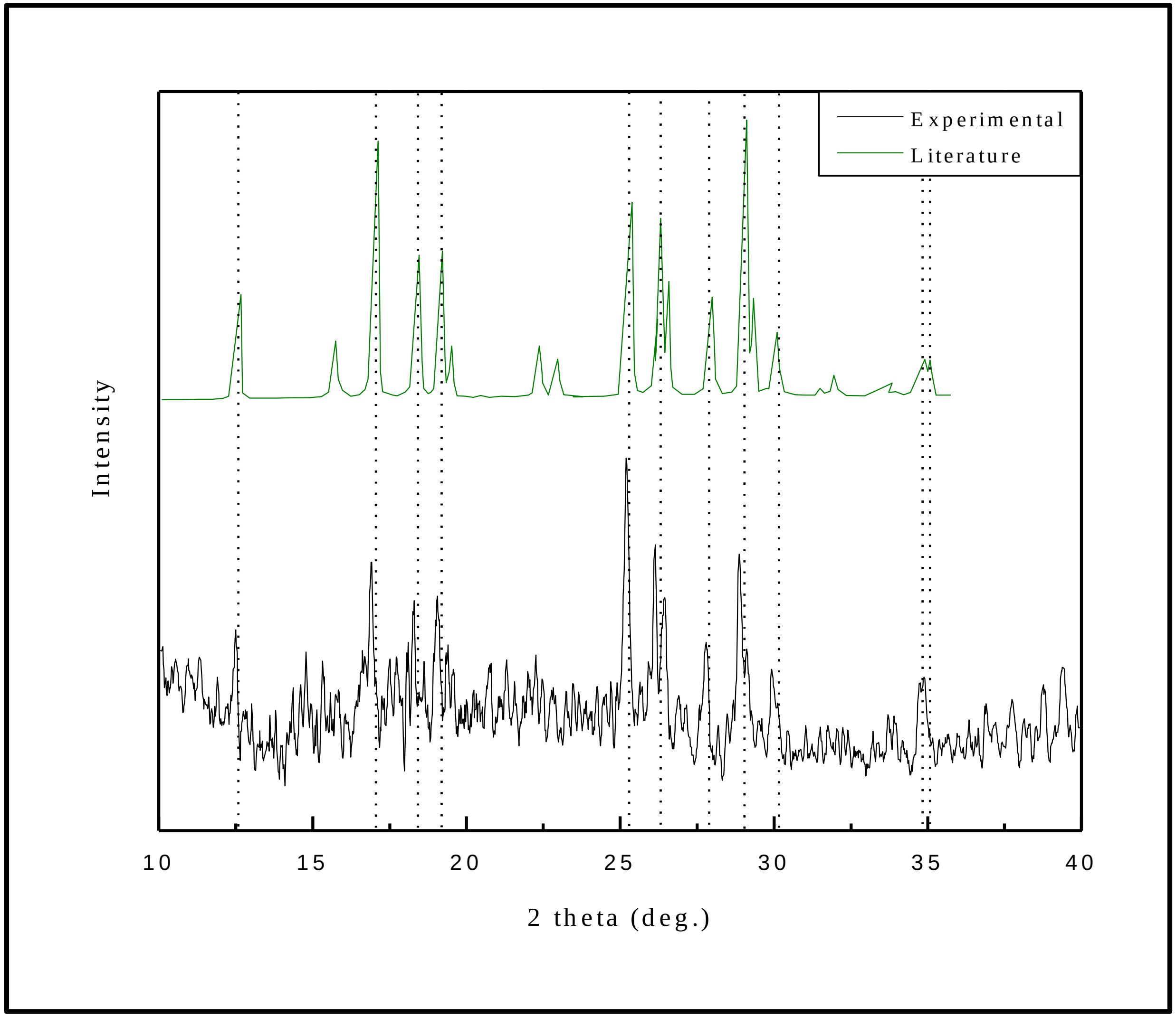
Li_4GeS_4 Target Characterization - XRD



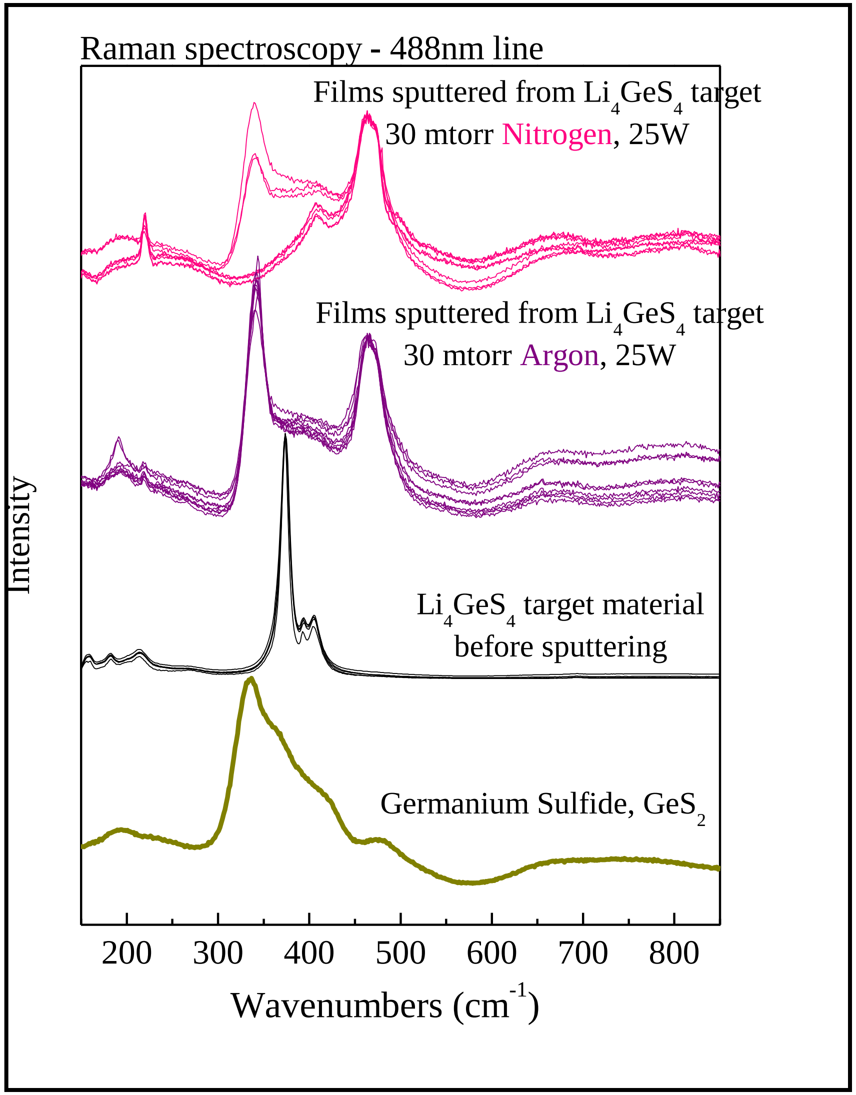
Li_4GeS_4 Target Characterization

- Effects of Sintering Time and Temperatures
  - Green bulk density 1.91 g/ml
  - Theoretical density 2.25 g/ml

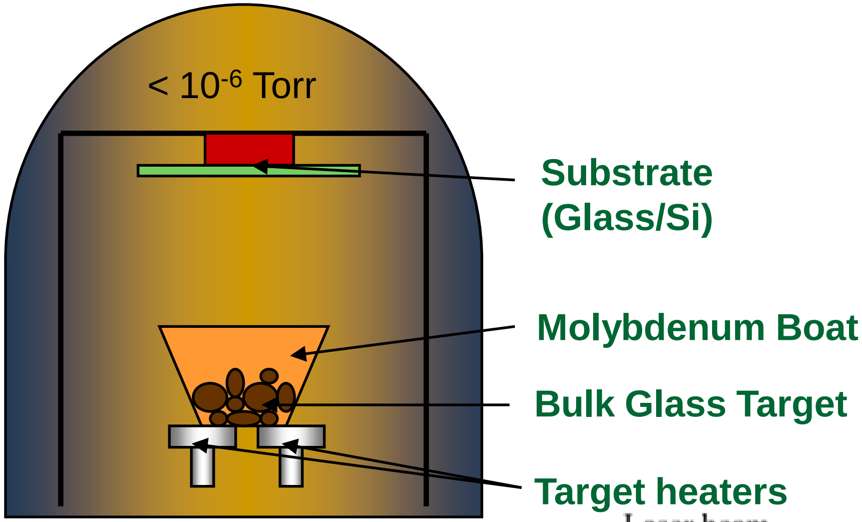
Time	Temp (C)	Apparent Density (g/ml)
2 hrs	730	2.052
	740	2.173
	750	2.203
4 hrs	740	2.147
	750	2.399

Sputtering of Li_4GeS_4 thin films

- Raman Spectra
- Li_4GeS_4 shows sharp lines from GeS_4^{4-} tetrahedra
- Sputtered films in N_2 and Ar are very similar
- Shows evidence of bridging sulfur units
- Under modified with Li
- GeS_2 is more easily sputtered than Li_2S

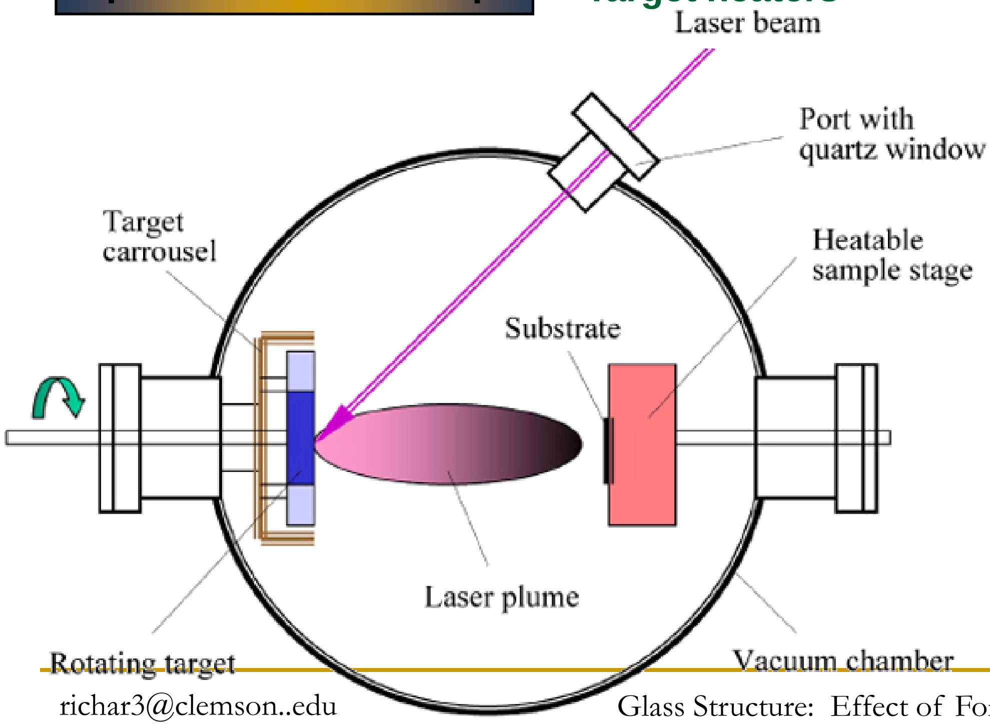


Film Deposition Techniques



Thermal Evaporation

Deposition parameters:
112 Evap-Sputter Station (PVD Systems Inc)
Thermostat stage held to 25 C
Base pressure: 2.0×10^{-7} Torr
Deposition rate: ~2 nm/s



Pulsed Laser Deposition

Laser parameters:
Mode-locked Nd:YVO_4 laser
Frequency tripled – 355 nm
Repetition rate: 28 MHz
Pulse width: 12 ps
Peak intensity: ~10^{10} W/cm^2

Deposition parameters:
Target-Substrate distance: 160 mm
Base pressure: 5.0×10^{-7} Torr
Ablated using 2.5 cm spiral pattern

Characterization tools - films

- Composition and thickness – ***SEM w/EDS***
- Refractive Index, thickness and extinction coefficient - ***Ellipsometry***
- Refractive Index change (Δn) -
  - Stress birefringence measurements (magnitude and sign of stress)
  - Induced refractive index change
- Thermal properties (μTMA, thermal conductivity) - ***Micro-thermal analysis***
- Bonding and local structure/structural changes - ***Micro-Raman and Waveguide Raman Spectroscopy (WRS)***
- Composition/stoichiometry, thickness, density - ***Rutherford Backscattering Spectroscopy (RBS)***

Lecture 23
Ends here

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