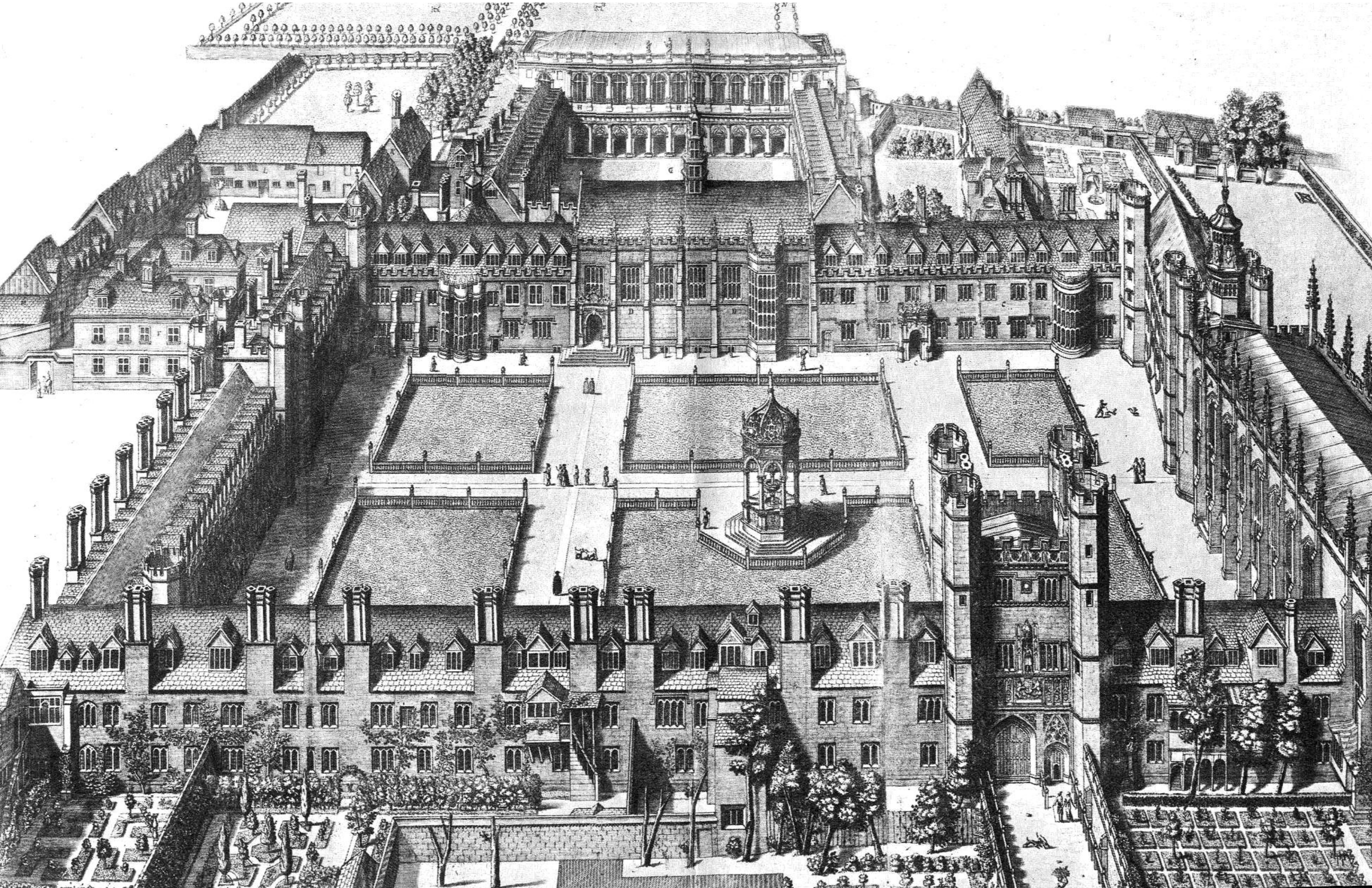
CHALCOGENIDE GLASSES: TRANSFORMATION AND CHANGE

Stephen Elliott
Department of Chemistry &
Trinity College
University of Cambridge

sre1@cam.ac.uk

School on Glass-formers & Glasses: Bangalore (4-20 January 2010)

Trinity College, Cambridge: Loggan (1690)



LECTURE 1: Chalcogenides

- What are they?
- Why are they interesting?
- Rigidity percolation
- Photoinduced (*c*-*c*, *a*-*c*, *a*-*a*) transformations
- Some applications

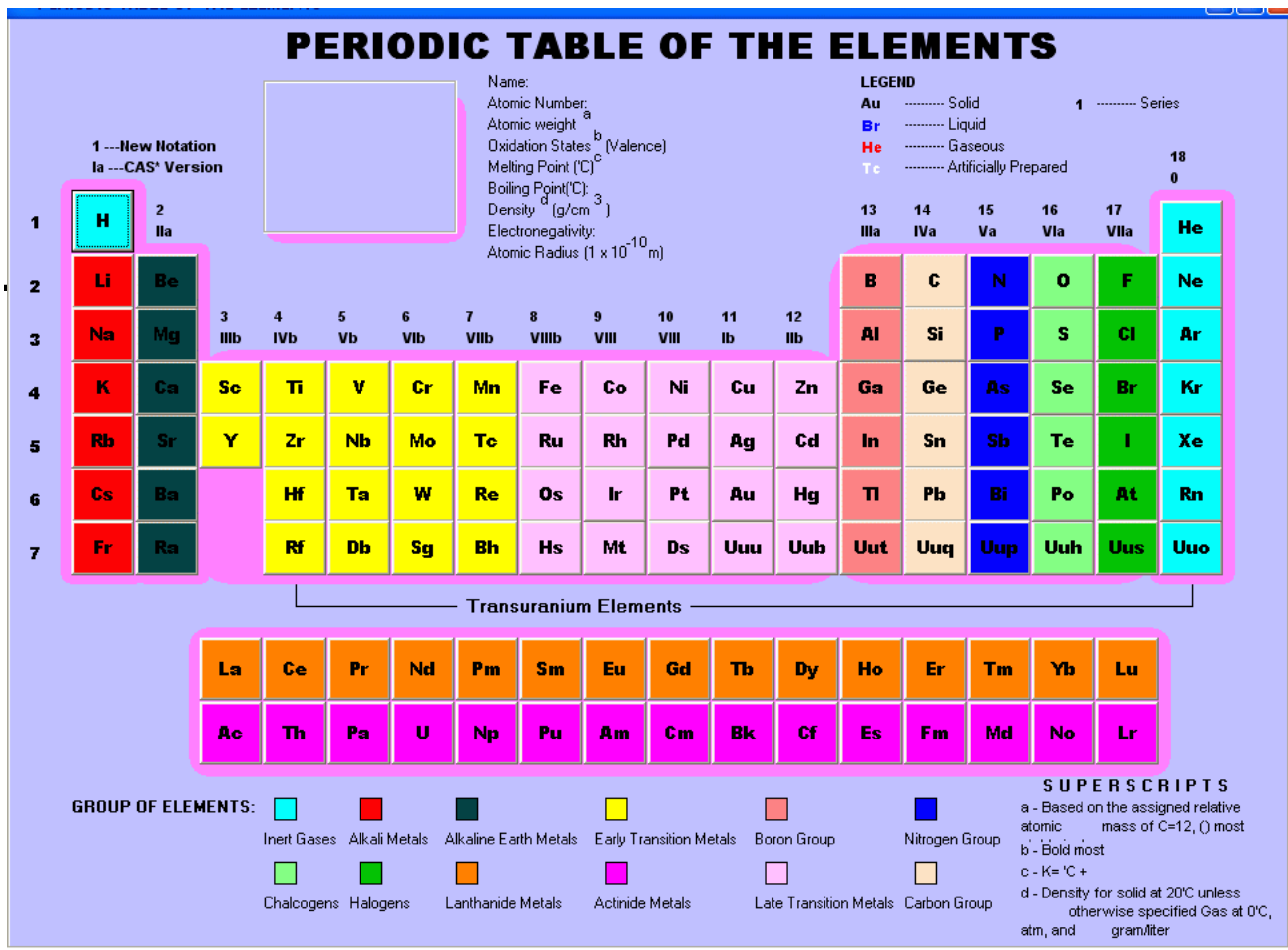
Chalcogenide Glasses

- Chalcogen – Gp. VI element: {O}, **S, Se, Te,** {Po}

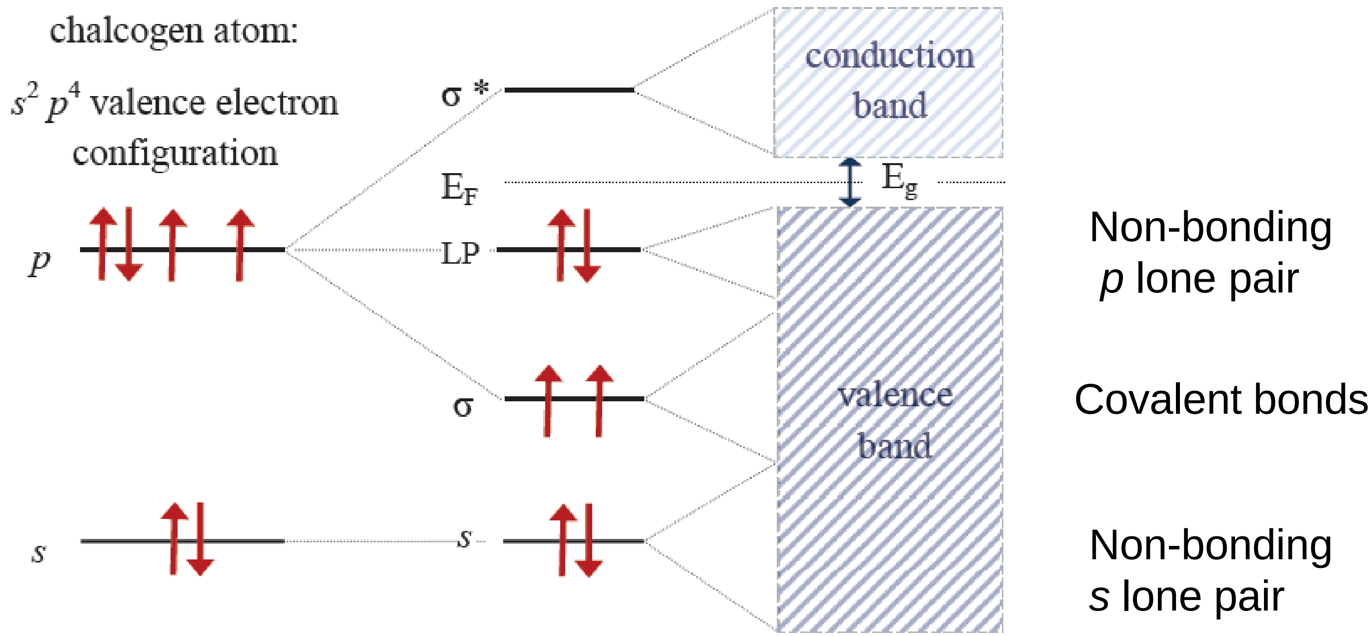
- Chalcogen*ide* –
  alloy of chalcogen
  & Gps. III,IV,V,VII…

- eg As_2S_3, $GeSe_2$,
  $Ge_2Sb_2Te_5$ etc

- glass-forming over
  wide composition
  ranges



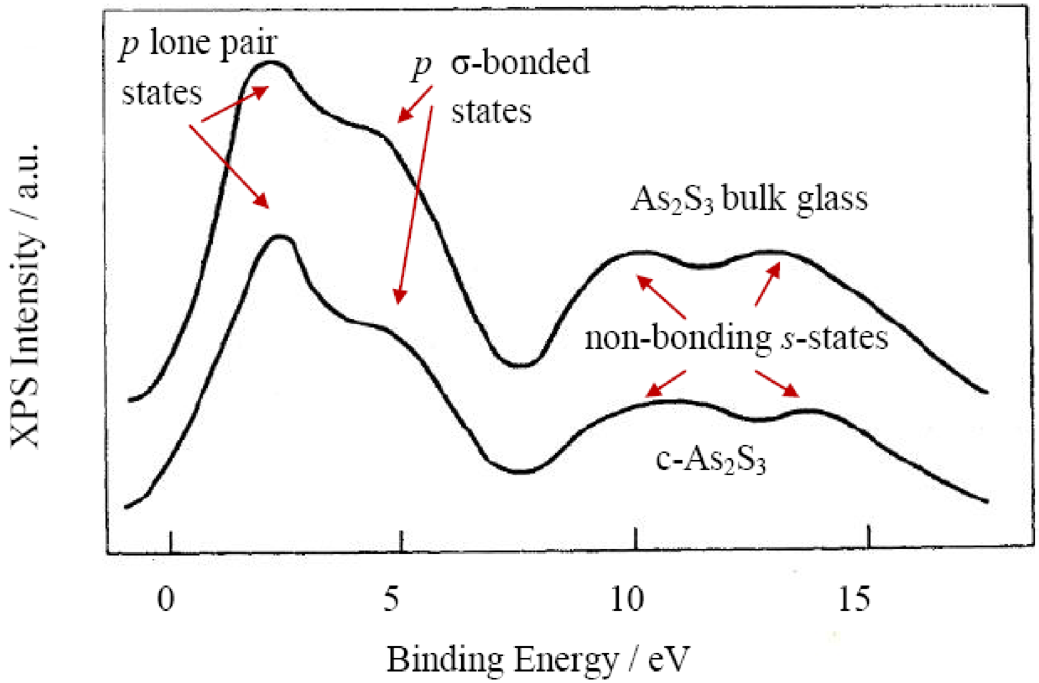
Chalcogens: Electronic structure



Atomic coordination is generally **2**-fold: 2 *p*-σ bonds

- although 3-fold coordination is also possible using *dative* bonding involving *p*-π lone-pair states

Chalcogenide Glasses: Electronic Structure



Photoemission of valence band

Bishop & Shevchik 1975

NB 1) Electronic structure of binary, etc, *chalcogenide* glasses is very similar to that of pure *chalcogens*

2) Electronic structure of *glasses* is very similar to *crystals*

Atomic Coordination of Chalcogenide Glasses
‘8-N Rule’

- Chalcogens ({O}, S, Se) = 2
  (Te) = 2 (3)
- Pnictogens (P, As, Sb) = 3
- ‘Tetragens’ (Si, Ge) = 4
- Halogens (Cl, Br, I) = 1

Phillips-Thorpe Constraint Theory

- Assume glass structure is a *continuous network* satisfying CNs, r_i, of constituent elements, i :

  - average CN = $\langle r \rangle$

- Stretching constraints: $\langle r \rangle/2$
- Bending constraints: $2\langle r \rangle - 3$
- Total no. of constraints, $N_c = \{5\langle r \rangle/2\} – 3$
  - if equals dimensionality, $N_d = 3$

- i.e. $\langle r_{cr} \rangle = 12/5 = 2.4$ 'optimal' CN

Liquid/Glass Anomalies at <*r*>=2.4

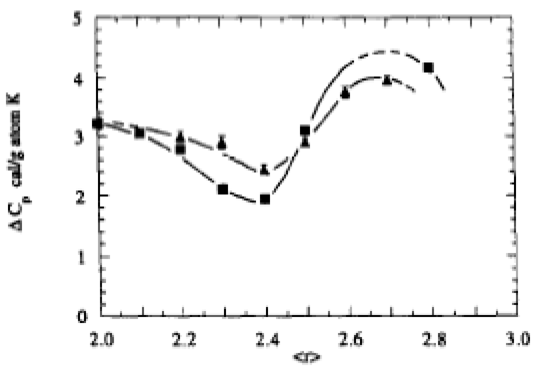


Fig. 10. ΔC_p versus $\langle r \rangle$ for binary Ge–Se and ternary Ge–Sb–Se systems. The ΔC_p values for the binary and the ternary are represented by ■ and ▲, respectively. The curves are drawn as a guide to the eye. The maximum measured error is 1.8%.

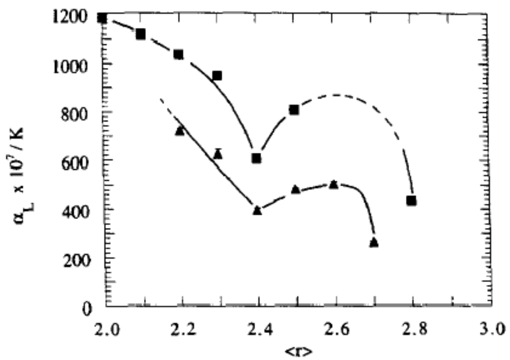
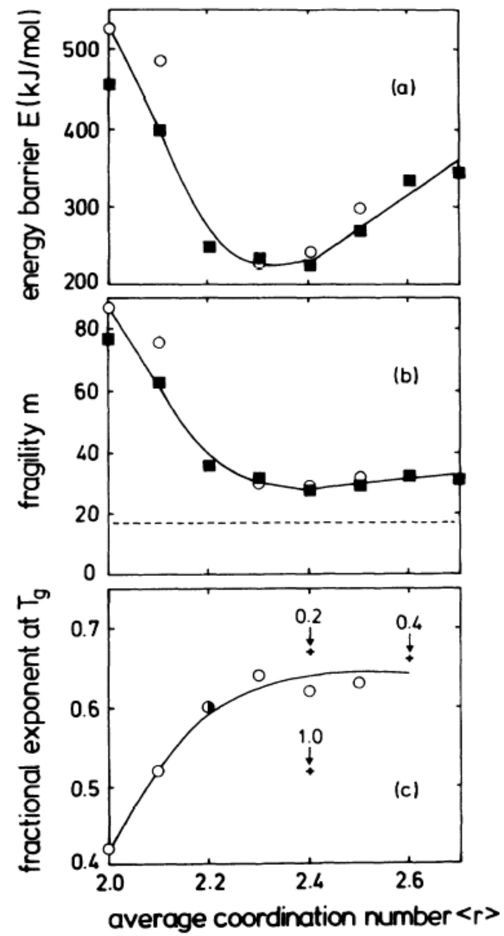


Fig. 4. Liquid state thermal expansion coefficient, α_L, versus $\langle r \rangle$ for the binary Ge–Se and ternary Ge–Sb–Se systems. The α_L values for the binary and the ternary are represented by ■ and ▲, respectively. The curves are drawn as a guide to the eye. The maximum measured error is 3.5%.



Varshneya et al 1991

Boehmer & Angell 1994

Modulated DSC

- Sinusoidal modulation of linear heating rate

- Jump in ‘reversing heat flow’:

  position → T_g; jump height → ΔC_p

- ‘non-reversing’ (NR) heat flow peak:

  → non-equilibrium properties (e.g. ageing)

  peak area → ΔH_{nr}

Relation between mDSC & Rigidity

1. ‘*Elastically flexible, floppy*’: <r> ~ 2

- Narrow temperature width of NR peak

- ΔH_{nr} ages with time as stretched exponential

Relation between mDSC & Rigidity

2. ‘*Elastically rigid, stress-free*’: <*r*> ~2.4

- $\Delta H_{\mathrm{nr}} \sim 0$

- Little ageing

Relation between mDSC & Rigidity

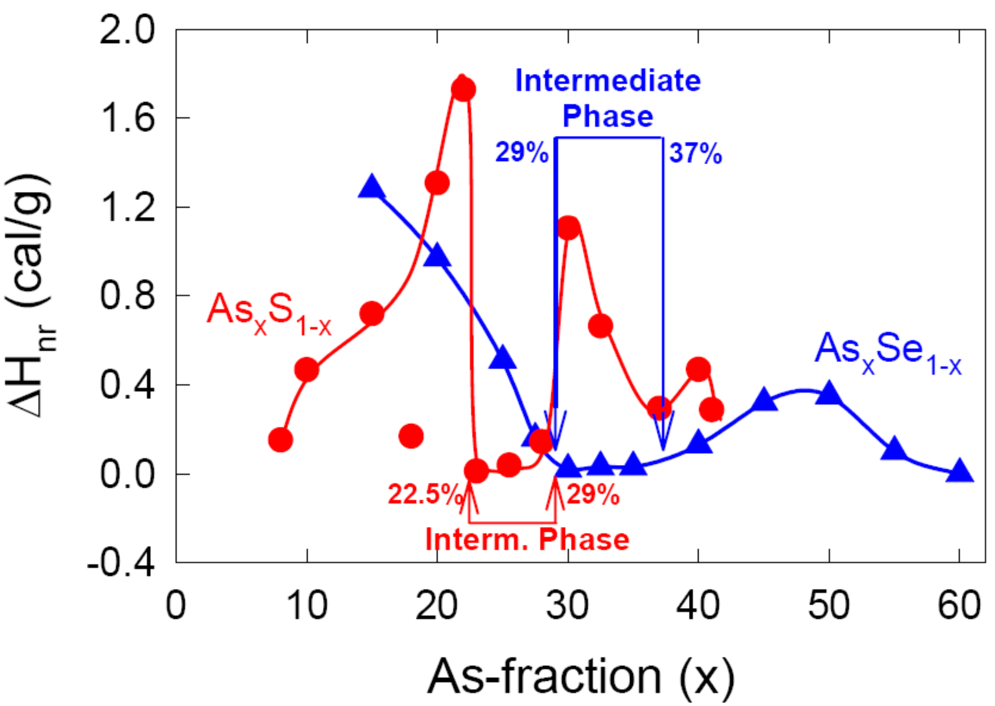
3. ‘*Elastically rigid, stressed*’: $\langle r \rangle \sim 3$

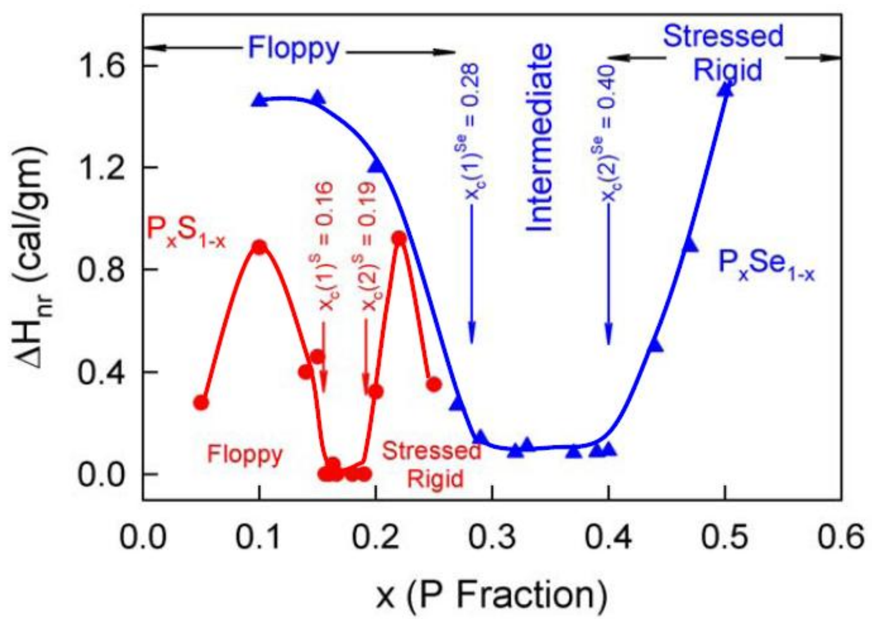
- Broad, asymmetric NR peak with temperature
- ΔH_{nr} ages with time

‘Intermediate’ (‘Boolchand’) Phase

Sulphide glasses

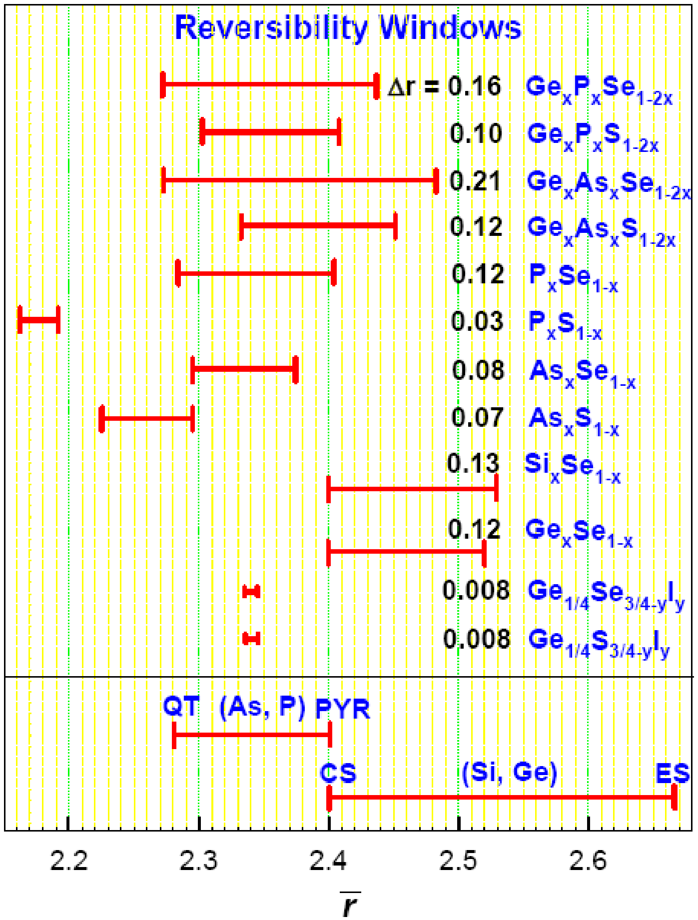
‘Reversibility window’ in compositional dependence of non-reversing heat flow





Boolchand et al 2009

Universality of ‘Reversibility Windows’?



Boolchand et al 2009

Reversibility windows do NOT all occur at <*r*> ~ 2.4

- indicative of nanoscale phase separation?

- or a failure of the model?
  (need to modify constraints)

Does the ‘intermediate ‘phase exist?

Arsenic Chalcogenides

- For stoichiometry: As_2S_3 ,
- $<r> = \{2x3 + 3x2\}/5 = 2.4 = <r_{cr}>$

- → good glass former

- For stoichiometry: As_4S_4,

  $<r> = \{4x3 + 4x2\}/8 = 2.5 > <r_{cr}>$

  → $N_c = 3.25 > N_d=3$

  - ‘overconstrained’ ***if*** in network structure

  → poor glass former (or another reason..)

Chalcogenide Structures: Networks or Molecular Aggregates?

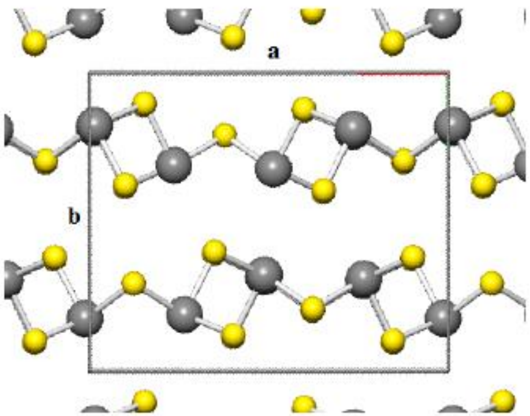
- The low values of atomic coordination of chalcogens (2) and pnictogens (3) mean that glass structures can be either: 2-3D networks or
  0D molecular clusters (VdW-bonded)

- E.g. structure of stoichiometric As_2S_3 consists of network of corner-shared AsS_3 pyramidal units
- But how are As atoms distributed in *As-rich* glasses – (non)randomly - in network/molecule?

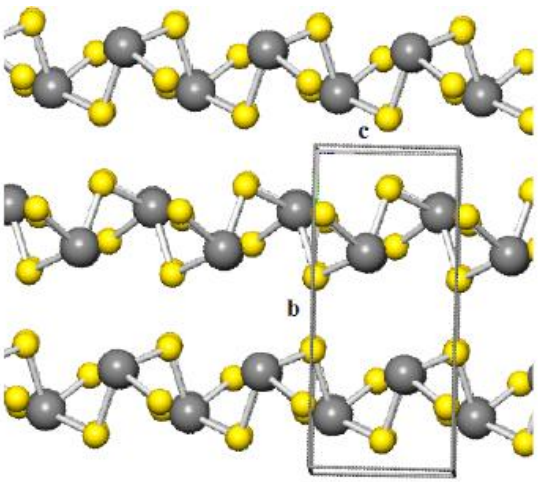
- For possibilities, refer to *crystals* – e.g. As-S

c-As_2S_3: orpiment

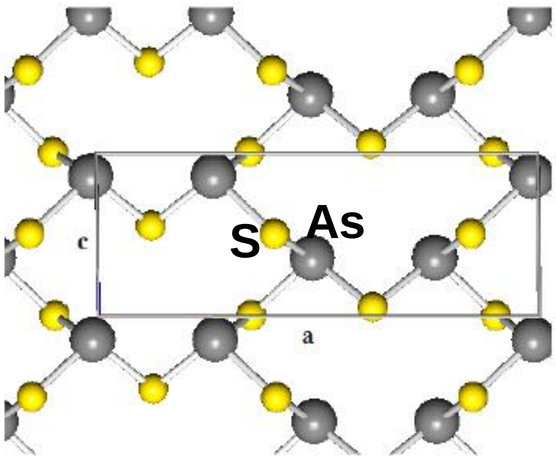
2D layer structure



c-axis



a-axis



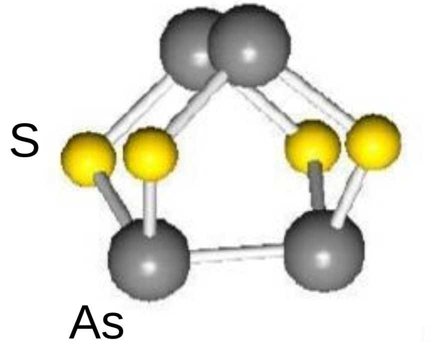
b-axis

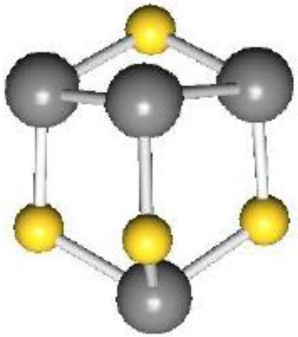
As-rich Molecular As-S Species

- Molecules are approximately *spherical*

  -real-life atomic model for hard-sphere systems

c-As_4S_4



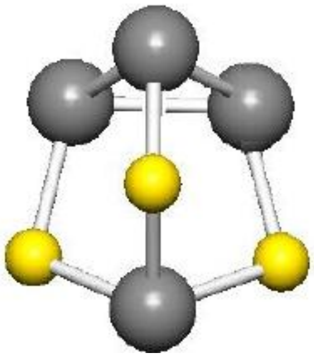


α,β- realgar

(α,β different packings)

pararealgar

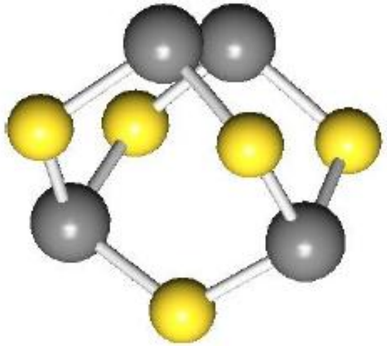
c-As_4S_3



‘= para-realgar – S’

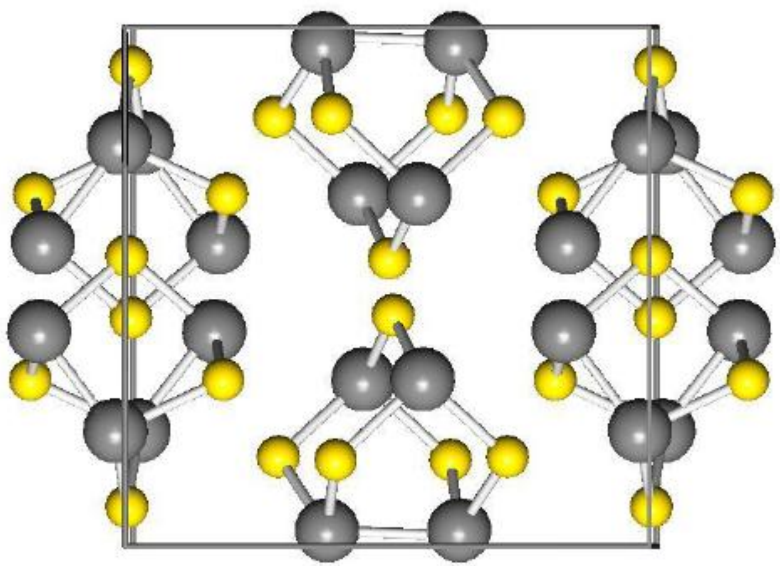
α,β-dimorphite

c-As_4S_5: uzonite



‘= α,β-realgar + S’

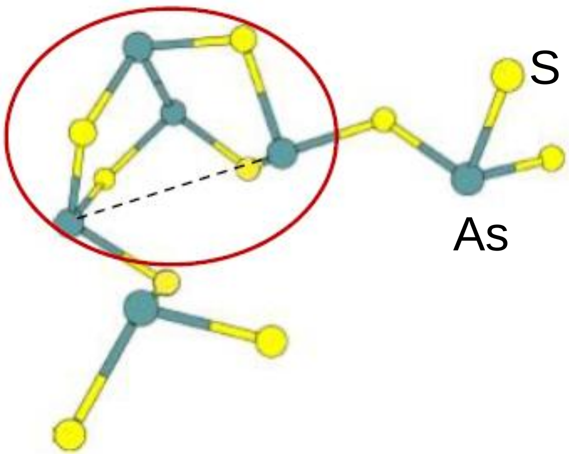
c-As_8S_9: alacranite



As_4S_4 As_4S_5 As_4S_4

Realgar-like molecular fragment in network structure

- *Ab initio* molecular-dynamics model of As_2S_3



Ideally, expect stoichiometric glass to be chemically *ordered*

Does chemical disorder - (oriented) homopolar bond) -promote quasimolecular formation?

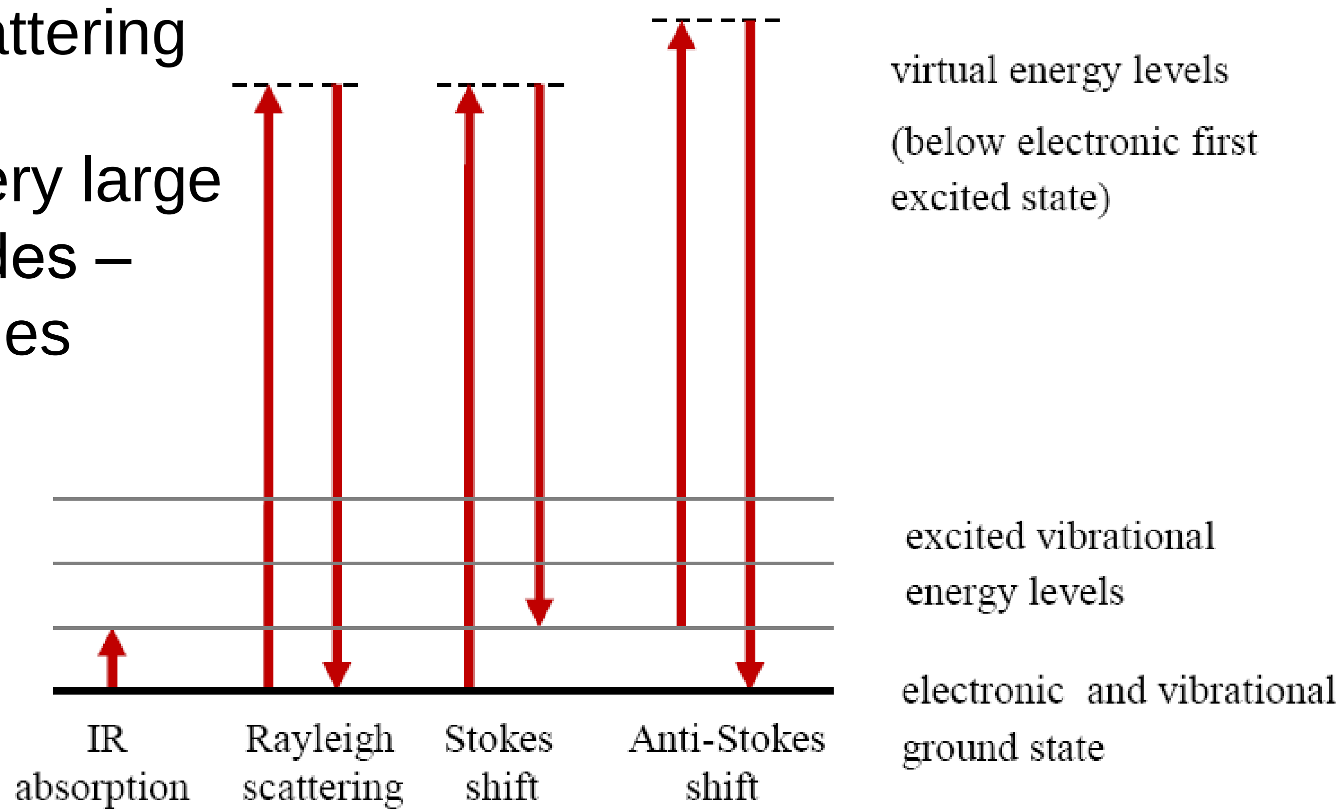
S. Simdyankin, S.R.E……., Phys. Rev. **B69**, 144202 (2004).

How to Detect Molecular Entities?

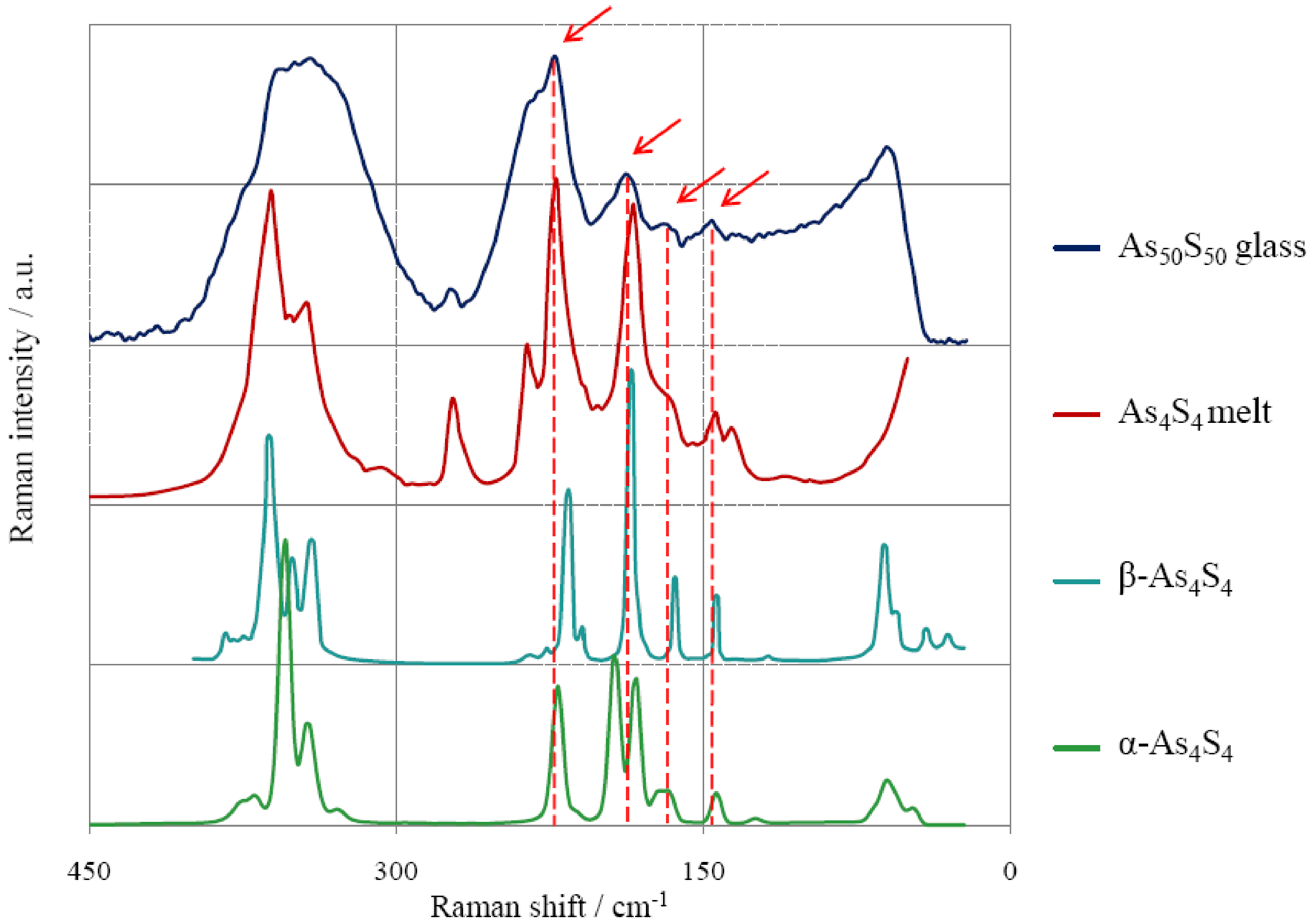
- Raman Scattering from vibrational modes

Inelastic light scattering

Cross-section is very large for ‘molecular’ modes – e.g. breathing modes



Raman Spectra of AsS



Glass Formation of AsS

- As_4S_4 (para-) realgar-like molecules, etc, are near-*spherical*

- Van der Waals interactions between molecules are spherically symmetrical

  → low-viscosity molecular melts

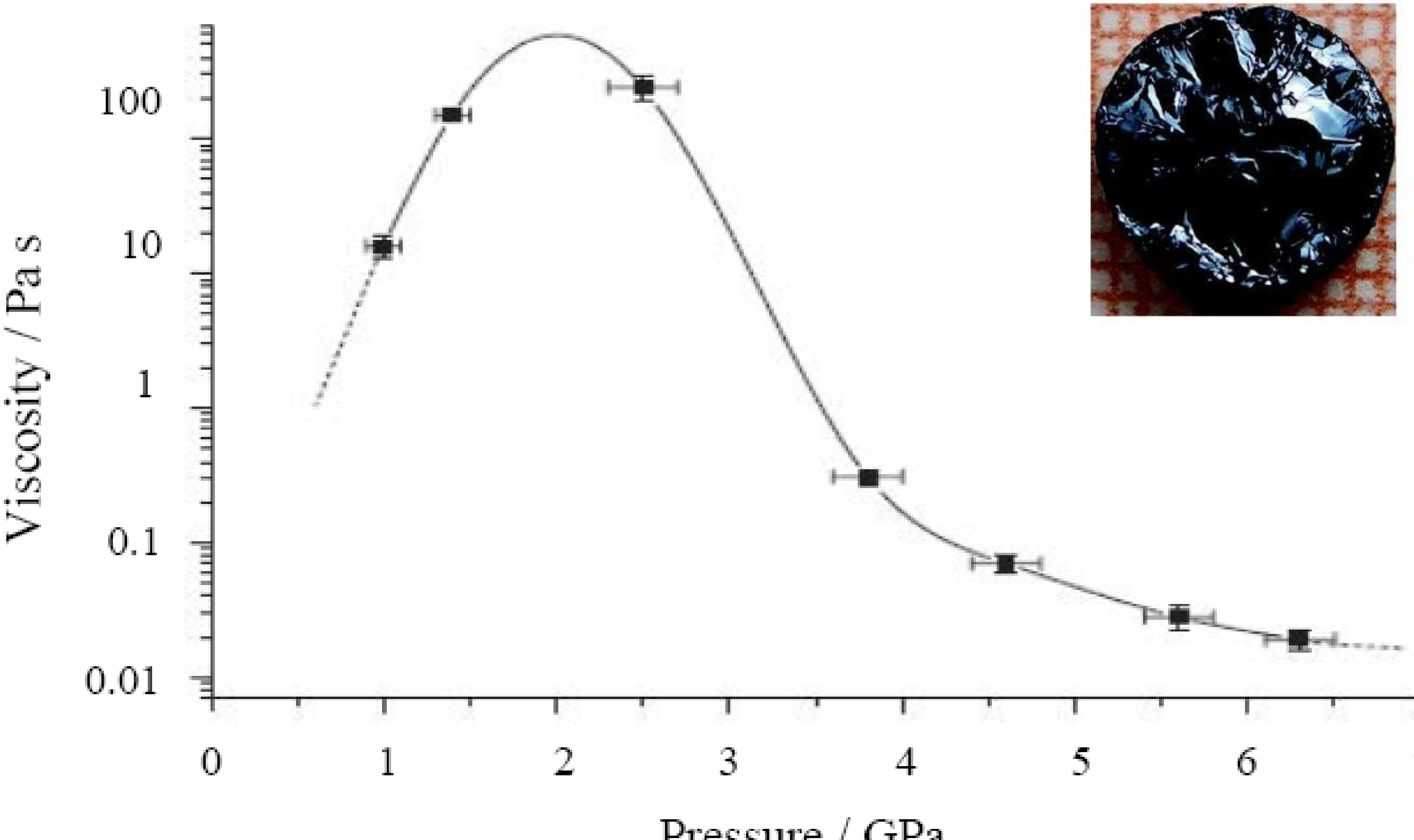
→ bad glass-formation ability (ambient pressure)

(limit normally 43% As)

(c.f. rare-gas/ Lennard-Jones systems)

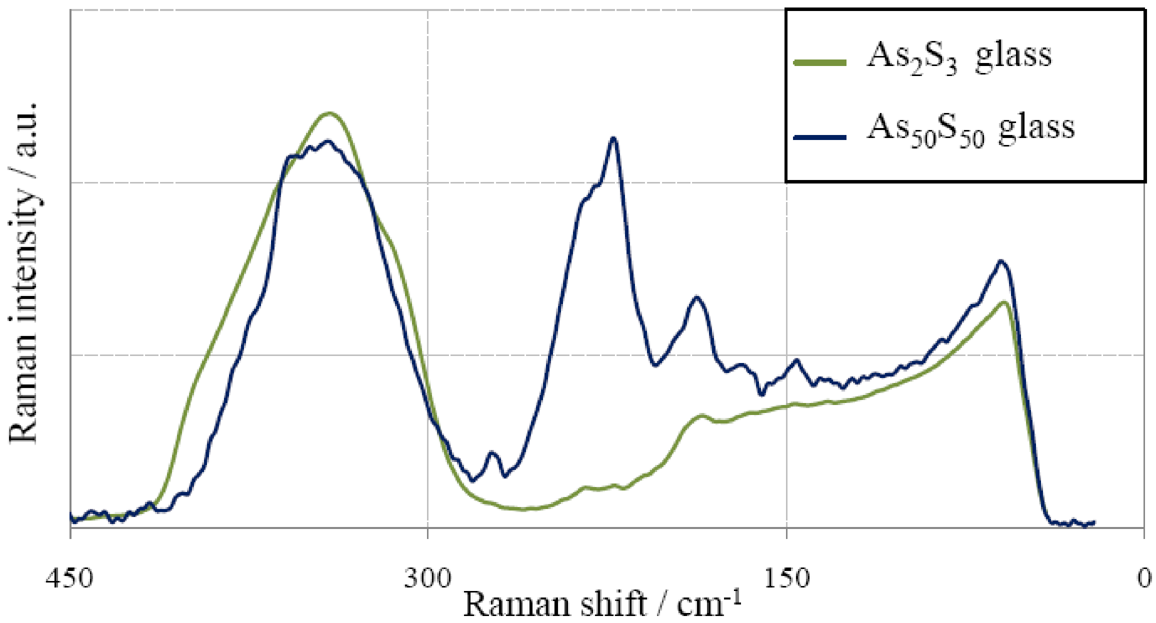
Glass Formation of AsS

High-pressure quenching (Brazhkin et al 2009)



2 GPa quench

Molecular vs. Network As-S Glasses

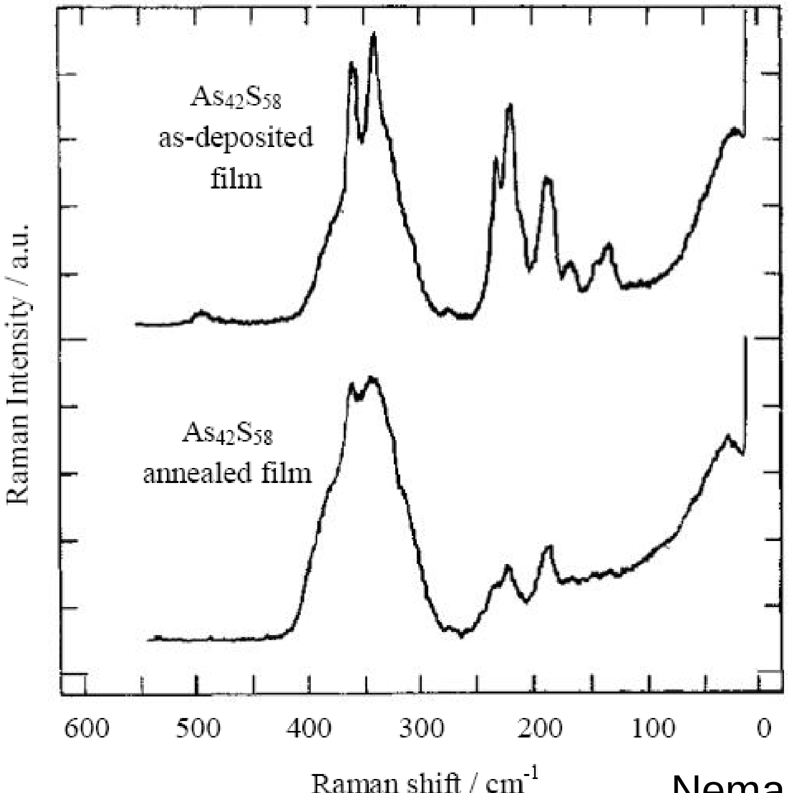


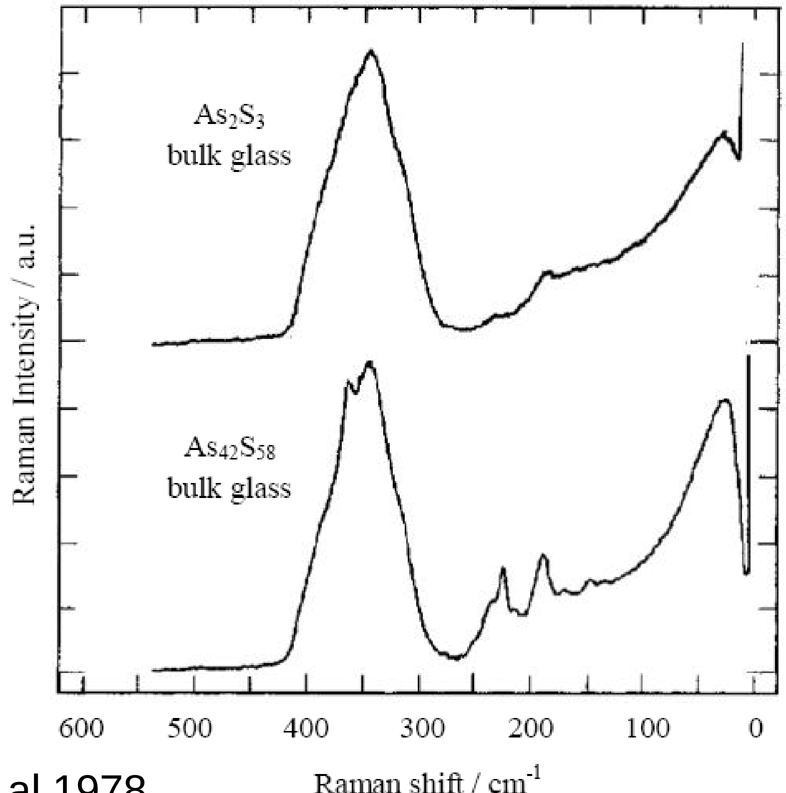
As-S_3 pyramid stretch modes

Molecular modes

Molecular character of *a*-As-S films

Molecular species are stable in precursor vapour



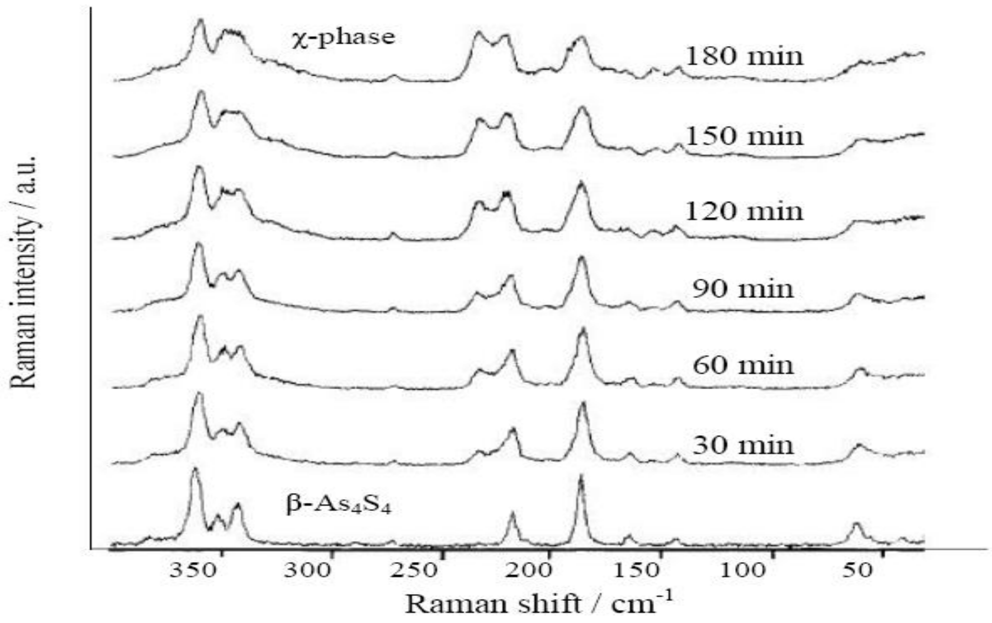


Nemanich et al 1978

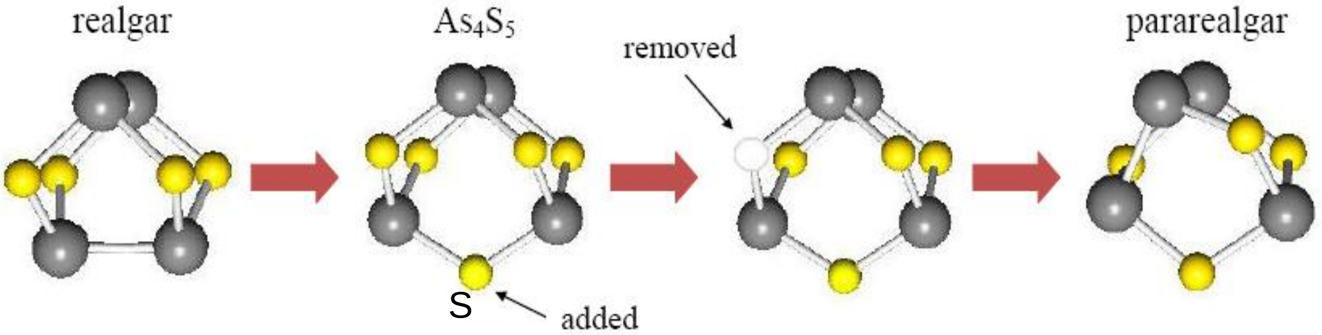
Nb Thermal annealing destroys molecular character → 'network' glass

Photoinduced *c-c* transformations: β-realgar → pararealgar

Bonazzi et al 1996



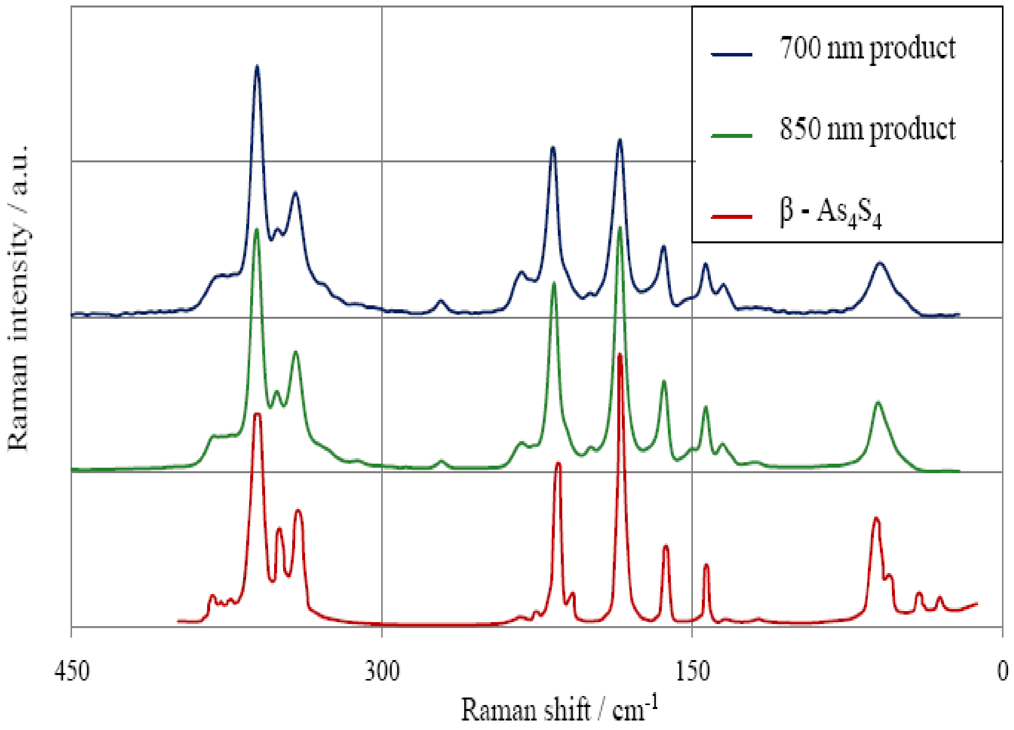
X-phase is intermediate, involving As_4S_5

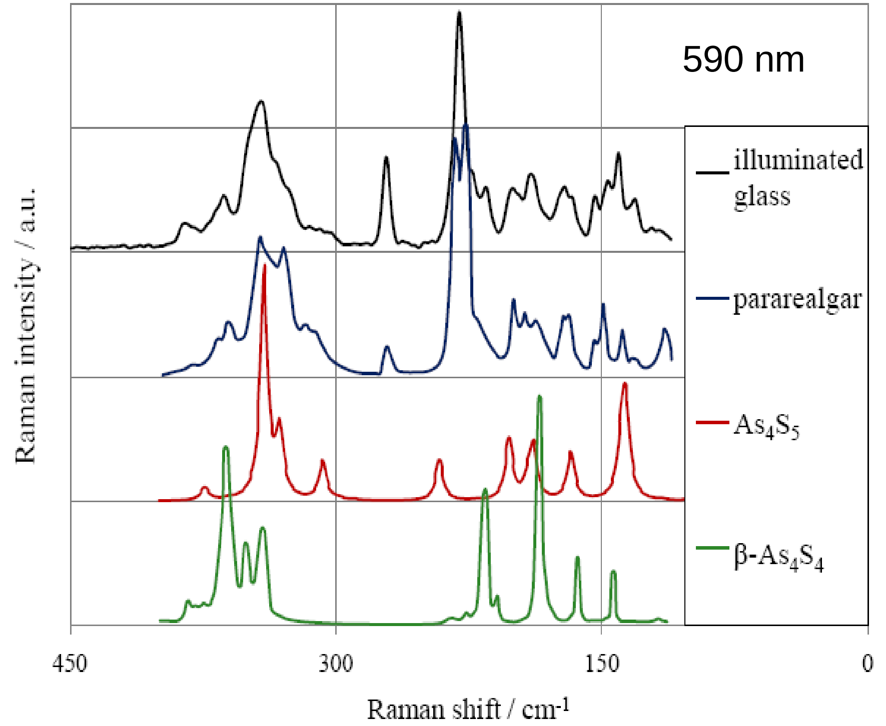


Photocrystallization of As_4S_4 glass

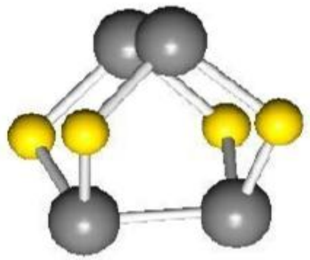
VdW 'bond-breaking → molecular reorientation

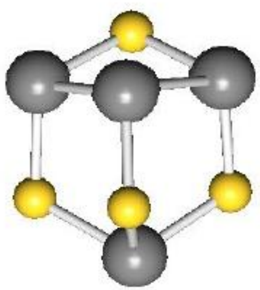
Bond-breaking→ molecular reforming





α,β-realgar

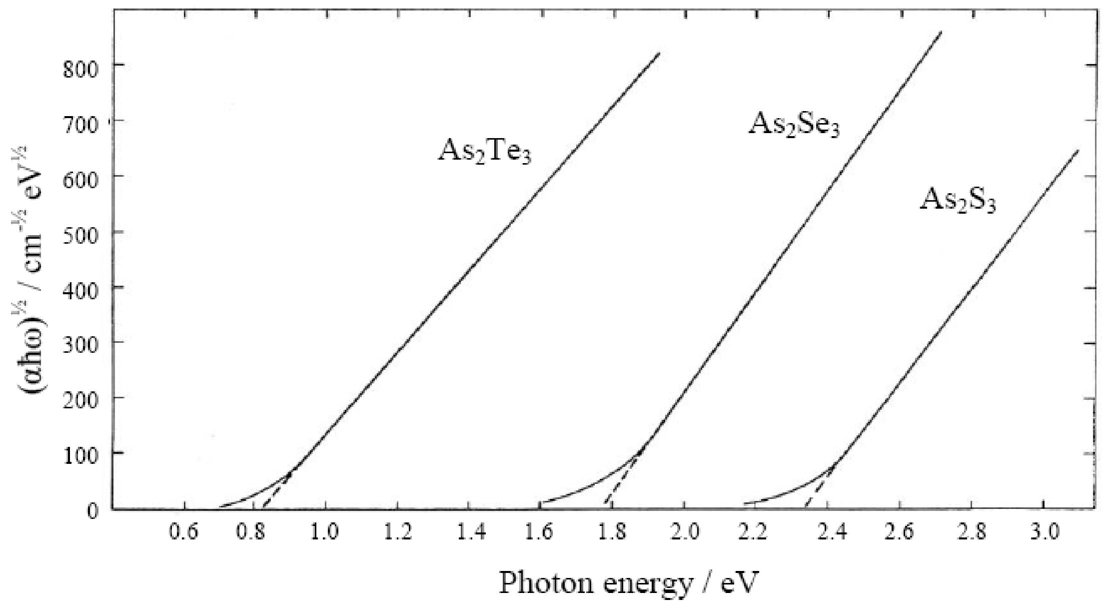




para-realgar

Chalcogenide Glasses: Semiconductors

Optical Absorption



Mott & Davis 1979

Bandgaps range from <1eV to >3eV:

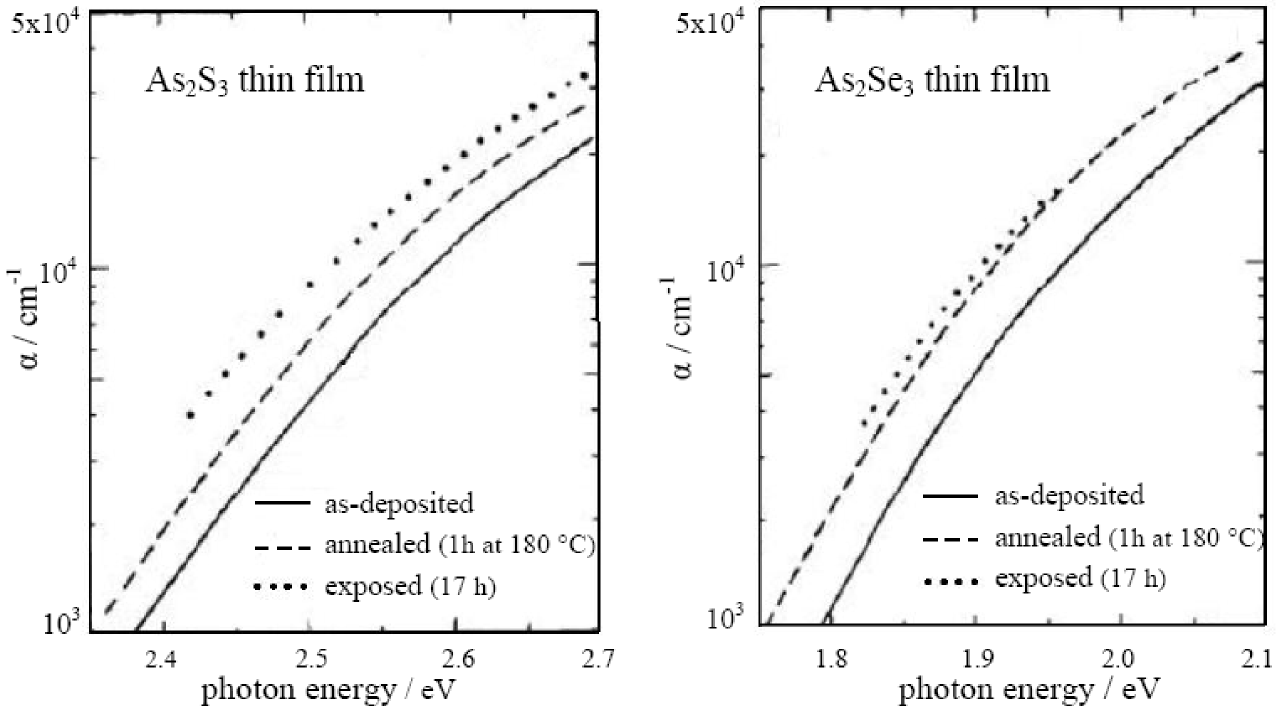
Te < Se < S << O

Photoinduced *a-a* Phenomena in Chalcogenide Glasses

- Bandgap-illumination changes can be:
  - metastable or transient
  - reversible or irreversible
  - scalar or vectoral

  - structural
  - optical ($\Delta\alpha$, Δn)
  - chemical (etching rate)…..

Amorphous-amorphous photoinduced changes



DeNeufville et al 1973

Photodarkening – redshift of optical absorption edge

Irreversible change from as-deposited state
- then *reversible* change from annealed state to new *'photo-state'*

Photoinduced Changes

- To paraphrase the Heineken beer advert:

‘Light can reach parts of the energy landscape no other stimulus can reach’

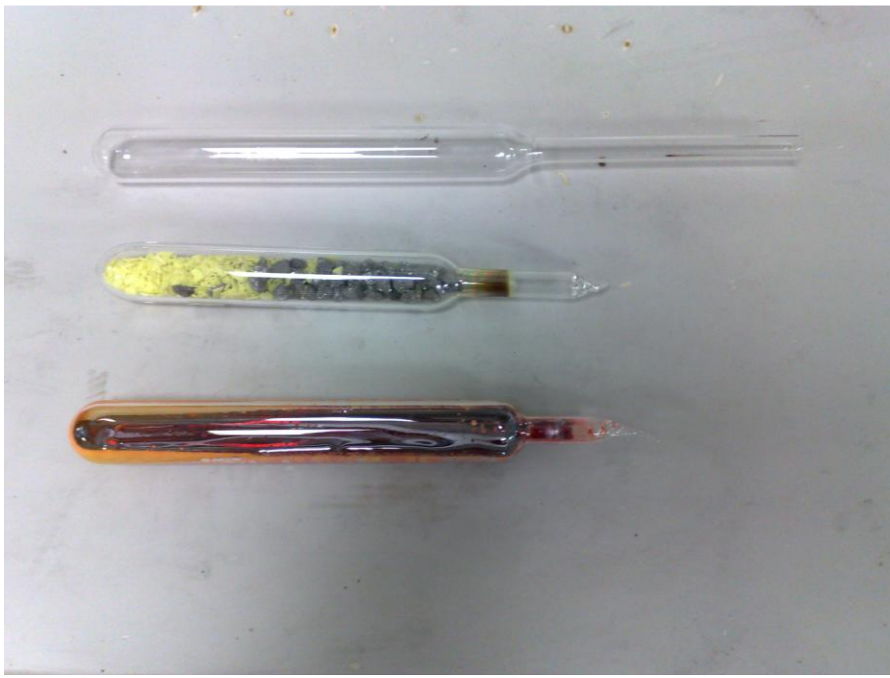
Photoinduced Optical Changes

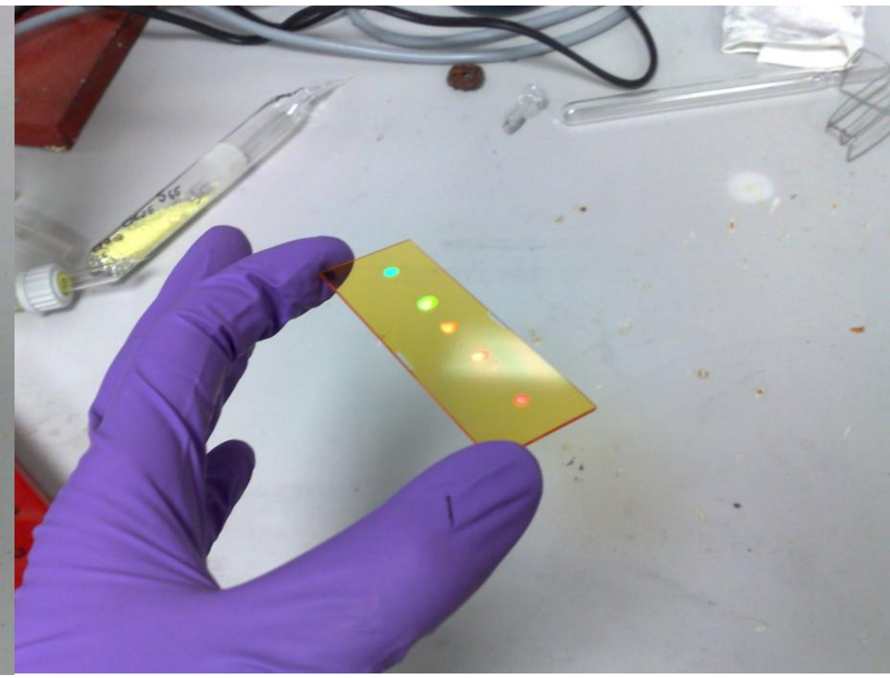
- Refractive-index changes of $\Delta n \sim 0.1$ can be produced by bandgap illumination –
- ‘direct’ laser writing (no post-processing)

  → ‘buried’ optical waveguides

- Or photoinduced changes in chemical-etching rate can produce ‘ridge’ optical waveguides

As_2S_3 Glass & Film



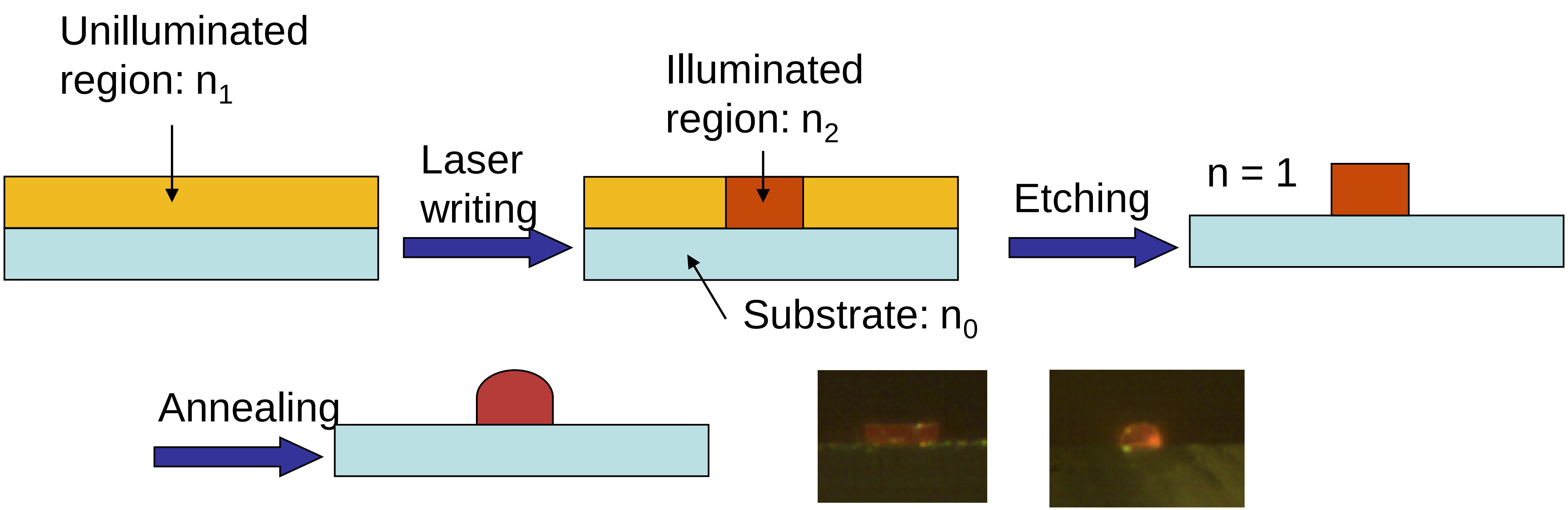


As + S → g-As_2S_3

a-As_2S_3 film with directly written Bragg gratings

Sensor on a chip

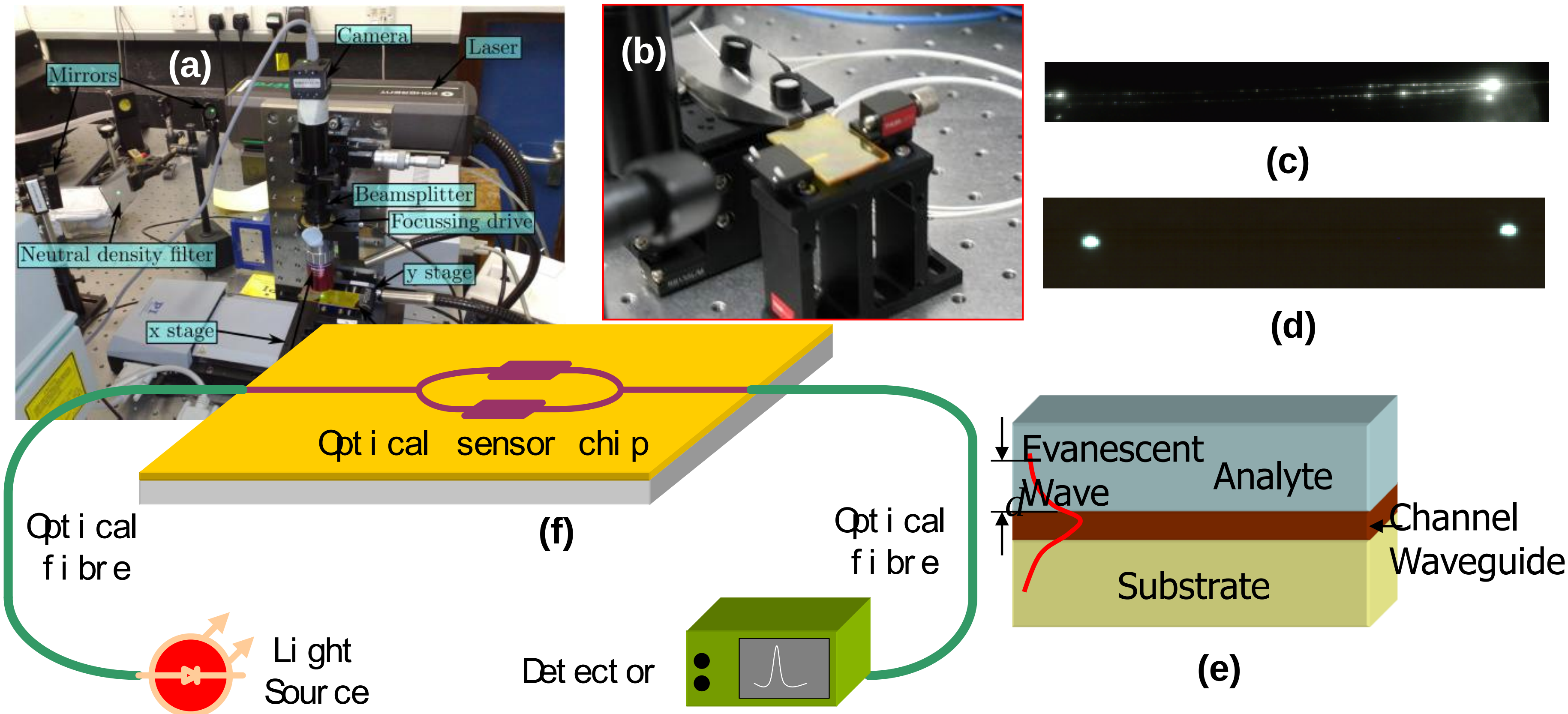
- Chalcogenide glass (ChG) offers **excellent transparency from visible to middle infrared**
- Enhance the **refractive-index difference (Δn)** by **selective etching**
- Smooth the waveguide surface by **thermal annealing**



- Before etching: Δn≈0.05; optical loss 7dB/cm
- After etch + annealing: Δn ≈1.5; optical loss down to **0.1dB/cm**

➡ **Achieved low transmission loss for straight and bent waveguides, *inc 24 cm serpentine waveguide***

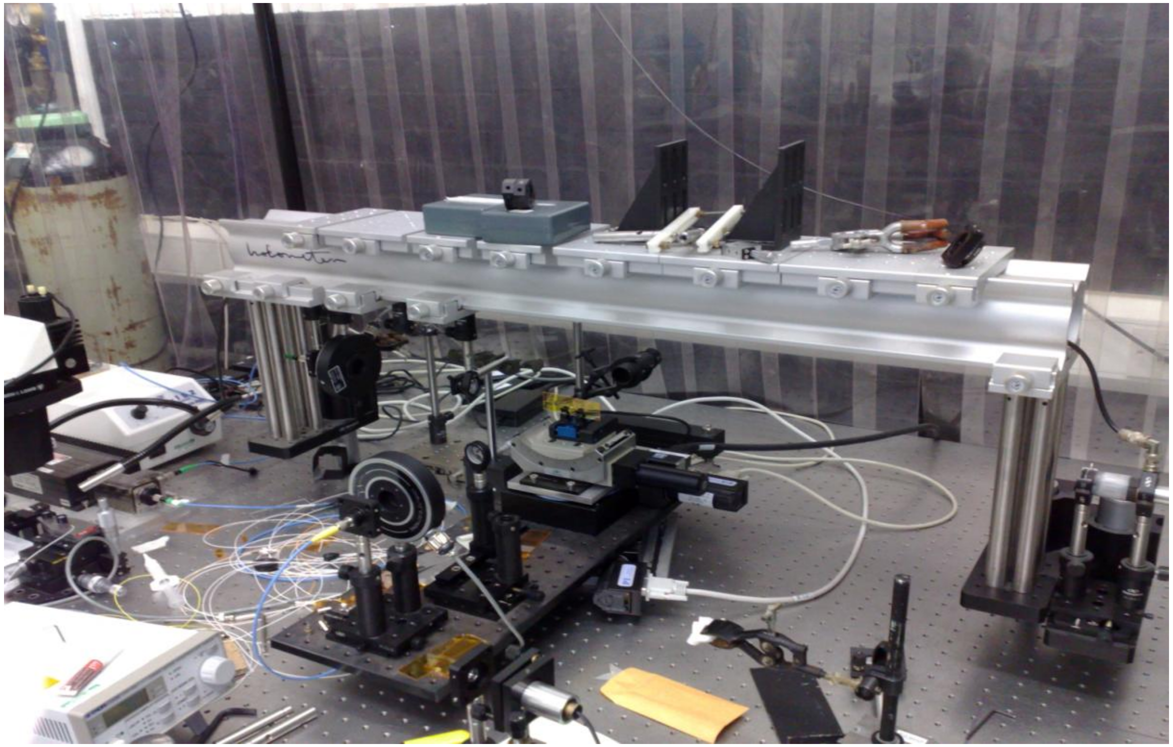
Sensor on a chip



- Low-loss planar optical waveguide devices can be made in the lab
- Sensor on a chip can be implemented by using evanescent-wave sensing, surface-plasmon resonance sensors, etc.

(a) Waveguide writing ; (b) laser coupling via optical fibre; (c) Top view of our waveguide interferometer; (d) Output at our Y splitter; (e) Evanescent-wave sensing; (f) Sensor on a chip system

‘Holometer’



1. Write Bragg grating (parallel-line pattern)

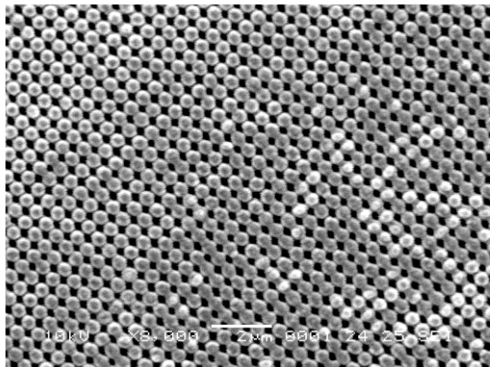
2. Rotate sample by 90^{o}

3. Write 2^{nd} Bragg grating

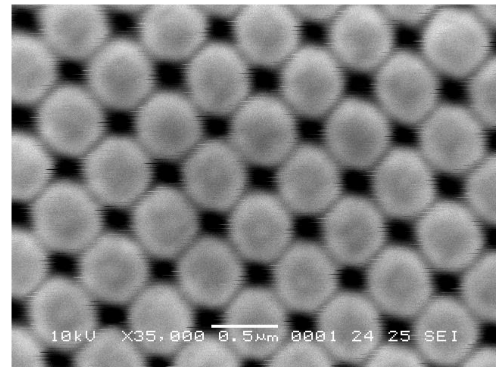
4. Develop ‘checker-board’ image using etchant (diisopentylamine in dimethyl sulfoxide)

5. Sputter Au film to make SERS substrate

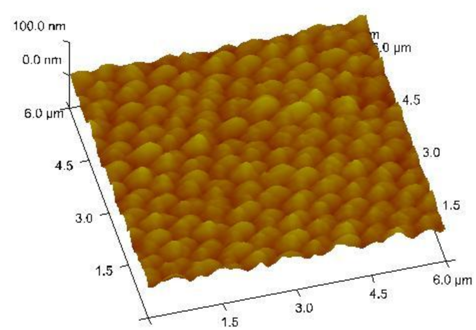
Surface-enhanced Raman scattering (SERS) substrates using chalcogenide glasses (ChG)



(a)



(b)

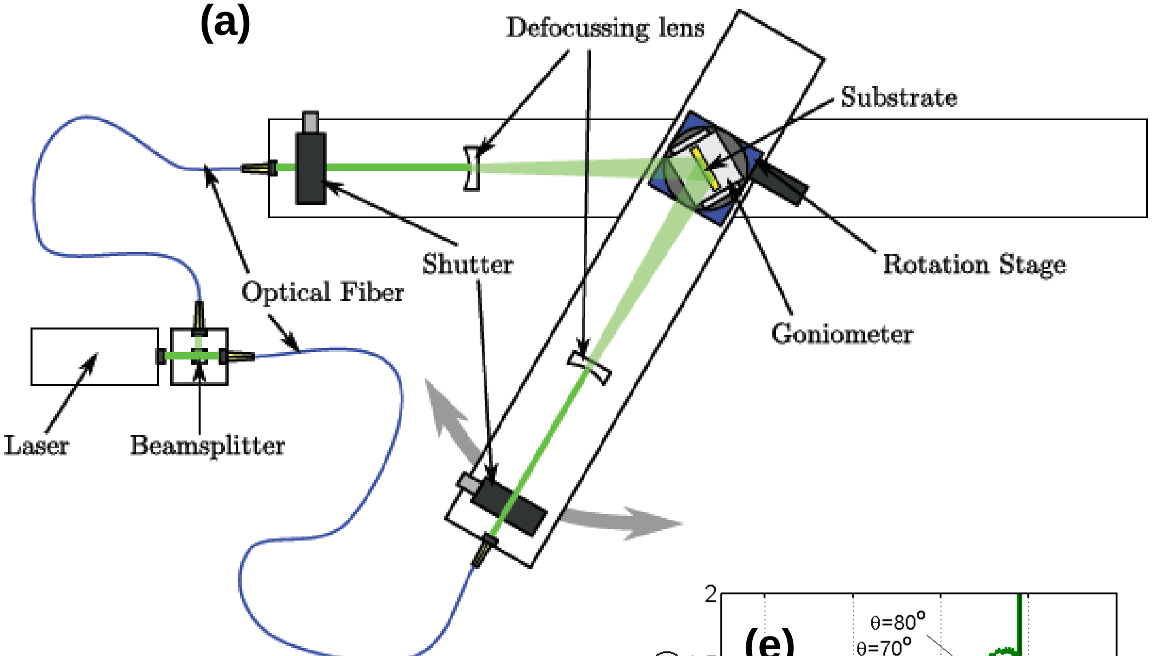


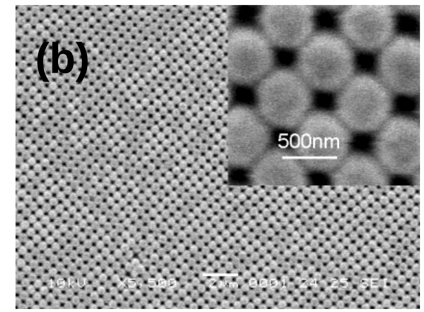
(c)

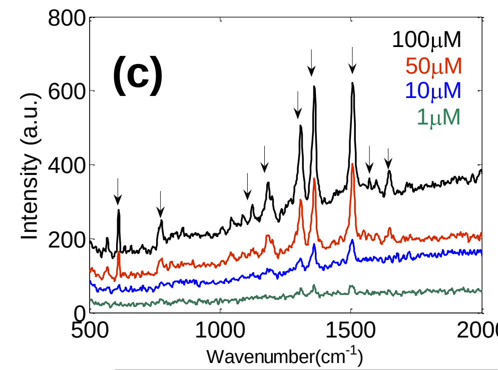
Su, Rowlands, SRE, *Opt. Lett.* **34** 1645 (2009)

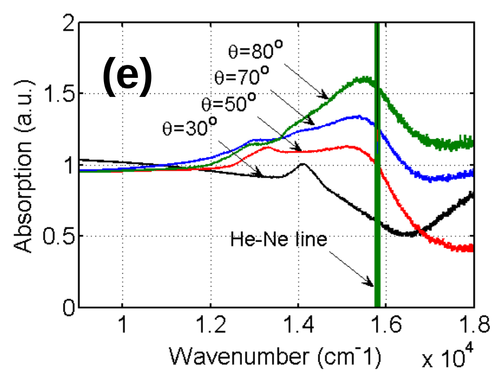
(a) and (b) are SEM images of an SERS substrate in ChG at different magnifications; (c) is the AFM image of the same SERS substrate.

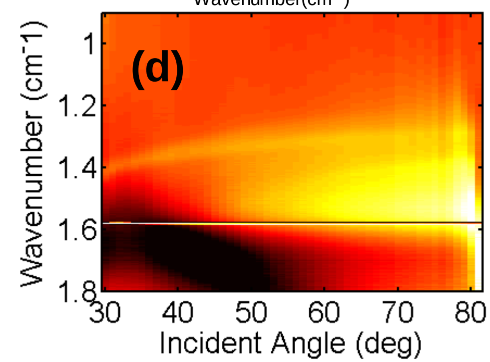
Chalcogenide-resist SERS sensor









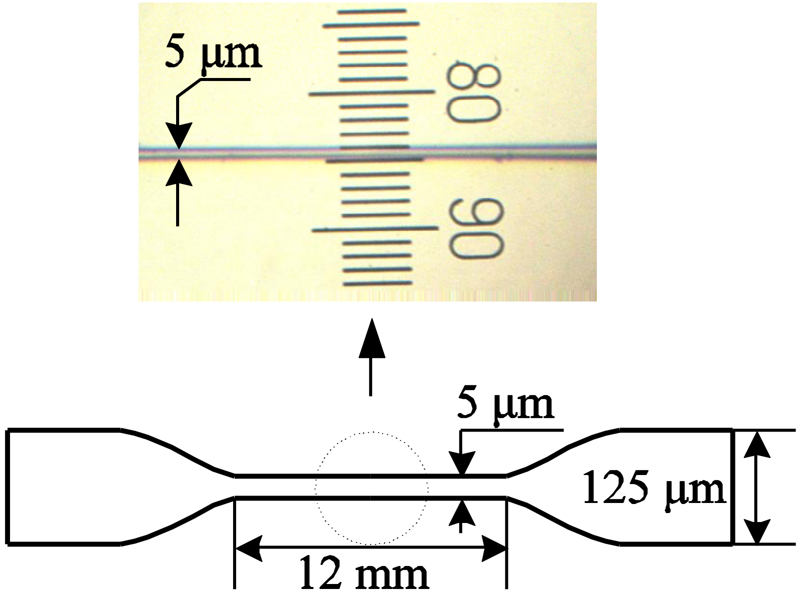


- Experiment shows that strong surface-plasmon resonances can be effectively excited on our SERS substrates at very large (grazing) angles of incidence

(a) Two-beam interference system; (b) SERS substrate; (c) SERS spectra of R6G; (d) Angle-resolved absorption spectra; (e) Cuts on map (d)

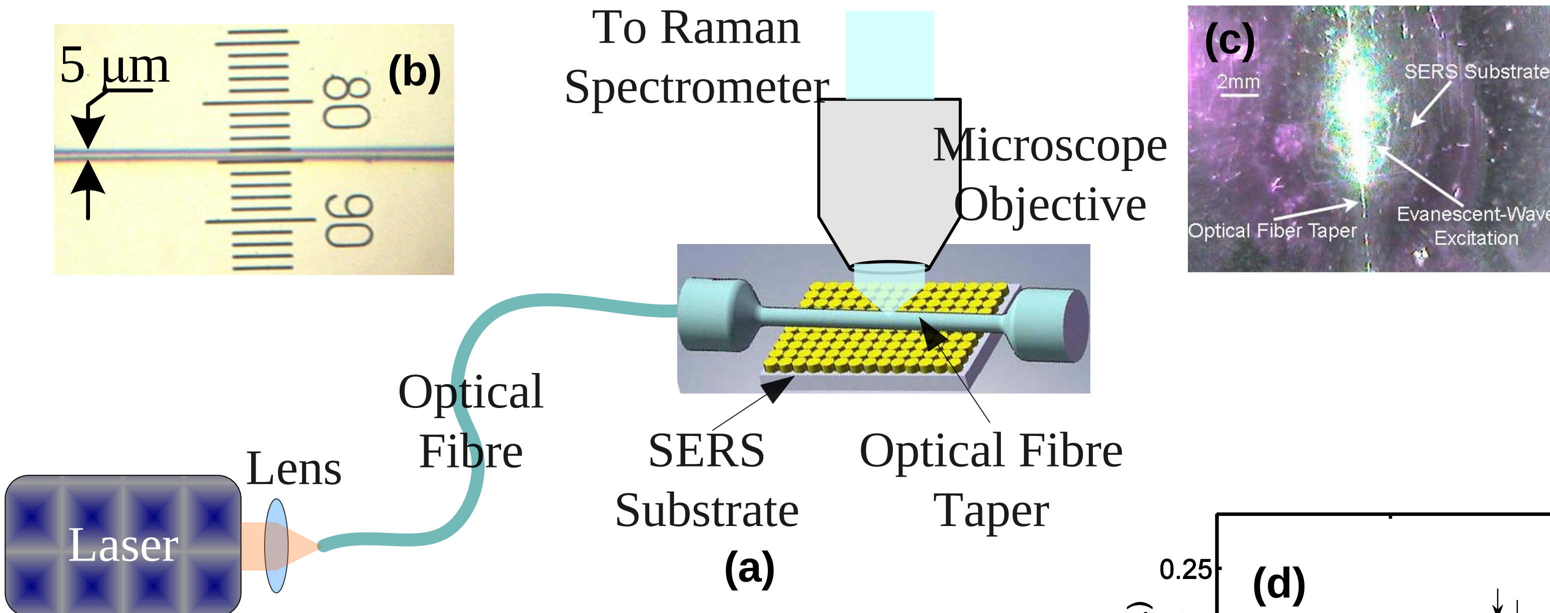
Evanescently excited Raman spectra

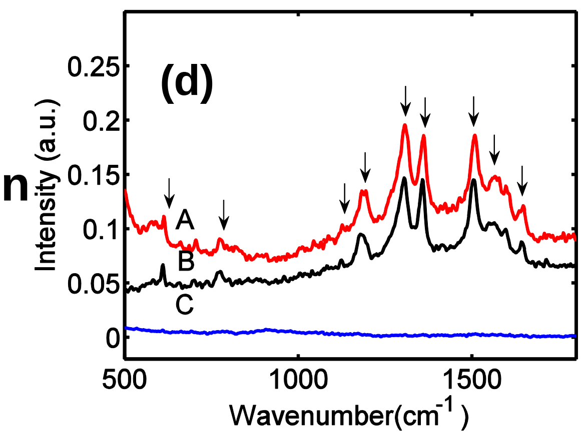
Evanescent sensing element



- A thin (5μm) and long (12mm) fibre taper was fabricated from a silica fibre
- Evanescent light field is greatly enhanced along taper

Evanescent-wave SERS sensor





•Advantages: low cost, robustness, **long interaction length** and good sensitivity.

• Suggested new SERS configurations:

- •Planar integrated SERS chips
- •Novel optical-fiber-based SERS sensors

(a) Configuration; (b) An optical-fibre taper; (c) Experimental photo; (d)Experimental results with R6G: A, Evanescent SERS; B, Conventional SERS; C, Control experiment (Su, Lee, SRE, Opt. Lett., **34**, 2685 (2009)

CONCLUSIONS

- Chalcogenides exhibit a wide range of:

- Atomic structures
- Physical & chemical behaviour: *‘photo-states’*
- Applications

- Next Lecture: ‘Unstable’ glasses & optical computer memories

Acknowledgements

- Miss Sandra Samulski
- Mr Christopher Rowlands
- Dr Lei Su

- UK Home Office
- Oppenheimer Trust
- UK Ministry of Defence