

Lehigh University Center for Optical Technologies

Fundamental Origin of Novel Photoinduced Optical Effects in Chalcogenide Glasses*

Faculty: H. Jain (PI), Grad Student: K. Antoine

Collaborators: M. Vlcek (U. Pardubice, Czech), D. A. Drabold (Ohio U.), S. R. Elliott (U. Cambridge, U.K.)

The photosensitivity of As-Se chalcogenide glasses is significantly altered by the presence of oxygen.

1. OBJECTIVE

- (a) Establish how the electronic structure of chalcogenide glass is affected by the stimulus of bandgap light.
(b) Obtain optimum composition for maximizing a specific photoinduced effect.

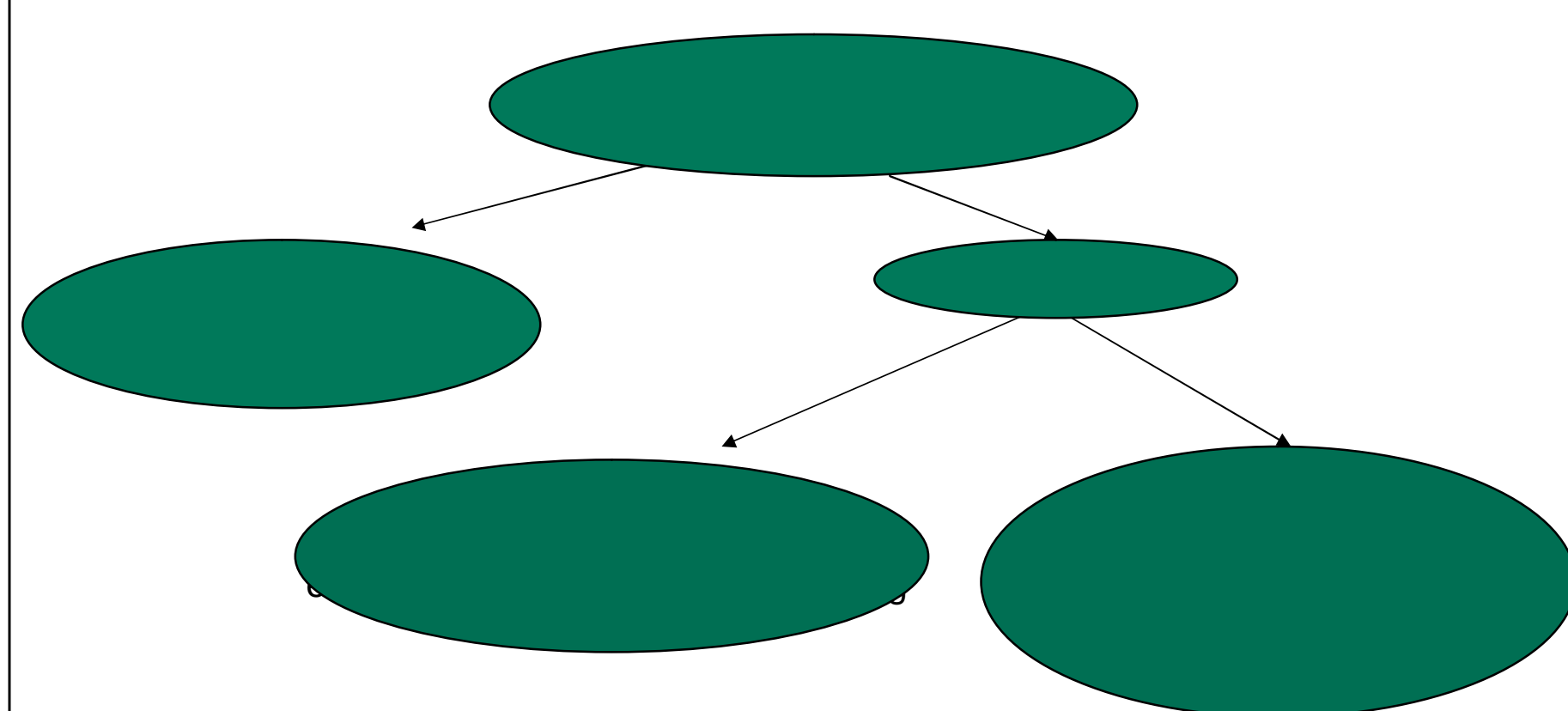
2. INTRODUCTION

Chalcogenide Glasses:

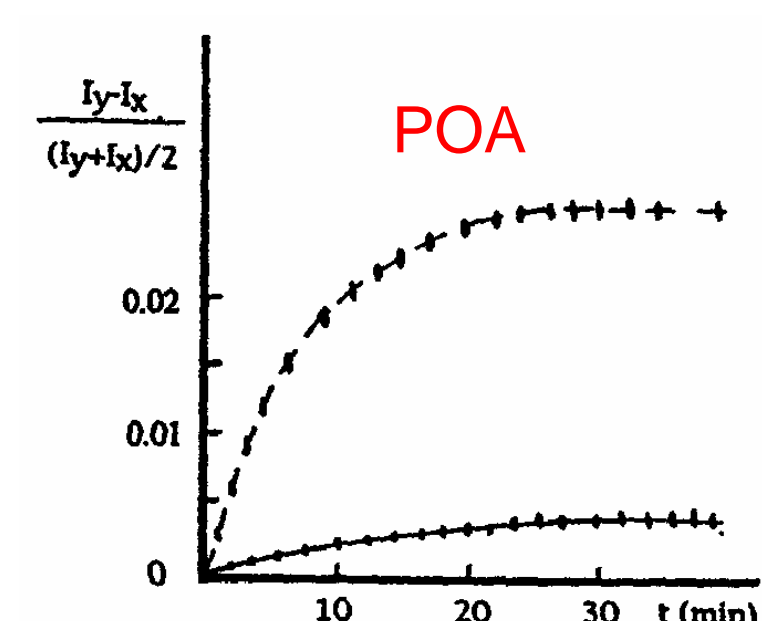
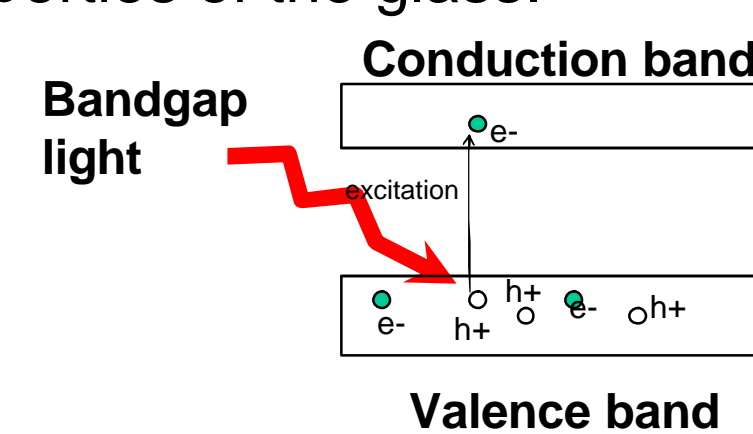
Compounds of S, Se and Te. Most common examples are Se or the Selenides and sulfides of As, Ge and Sb.

These glasses have many optical applications because of their high refractive index (~ 1.75 – 2.5), high nonlinearity and uncommon photosensitivity. Exposure to bandgap light produces a variety of phenomena that is useful in photonics, for example :

- photodarkening, photorefraction, photomelting, photoplasticity, photodissolution, photoexpansion
- photoinduced optical anisotropy (POA), etc.



Absorption of photons creates electron-hole pairs. In turn, the field of such pairs may modify the electronic structure and hence optical properties of the glass.

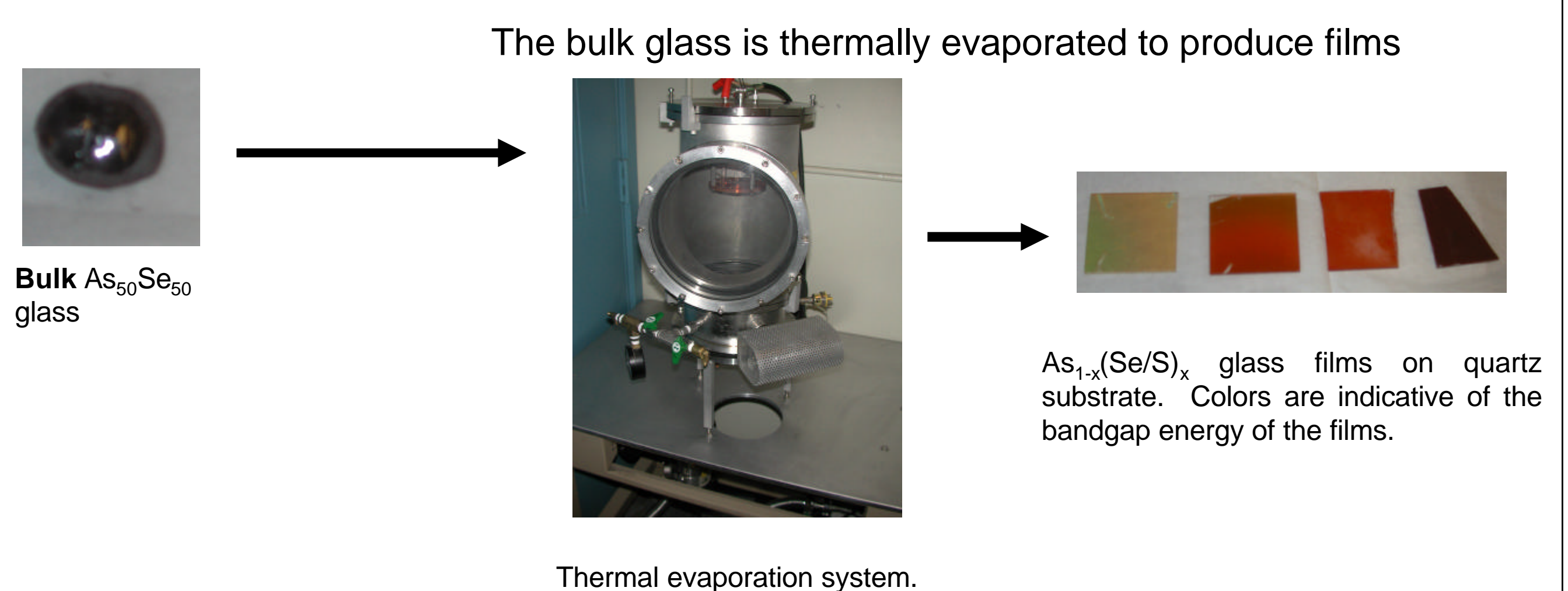
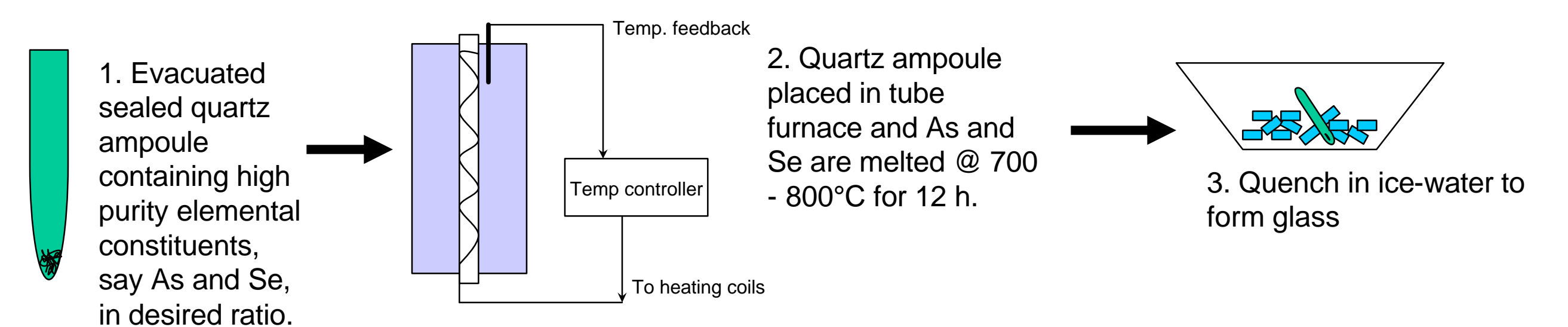


Basis of next generation DVDs

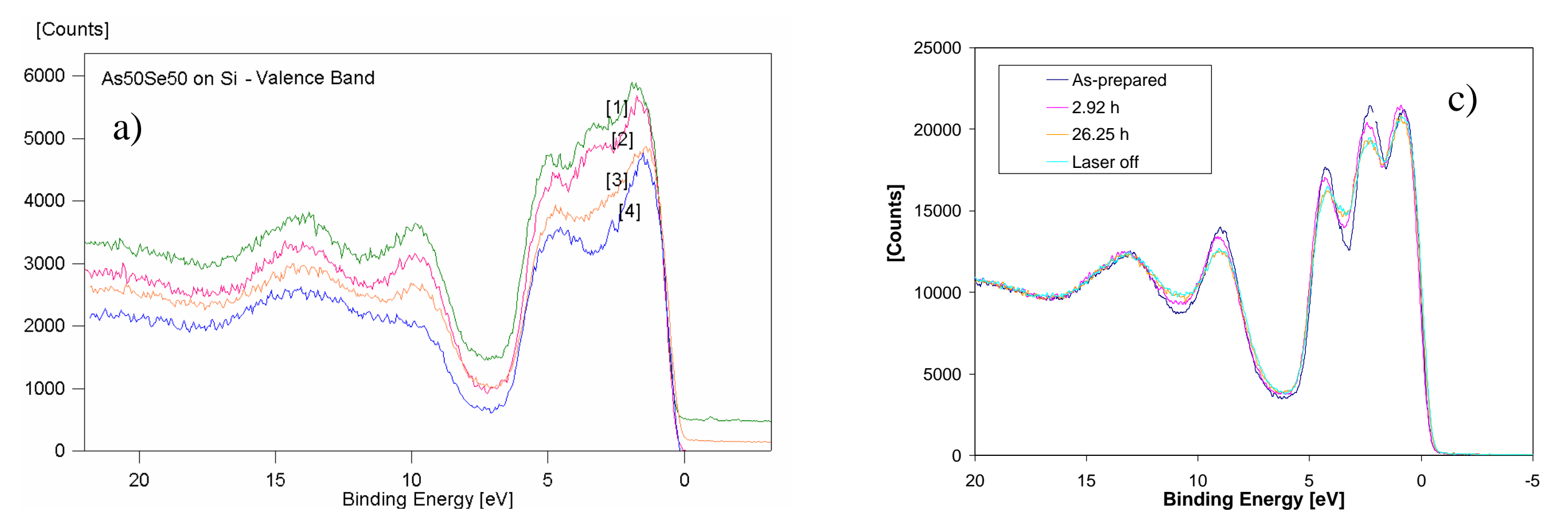


Photoinduced effects in the **optical properties** of this class of materials are mainly due to the changes in their electronic structure!

3. GLASS SYNTHESIS



5. RESULTS

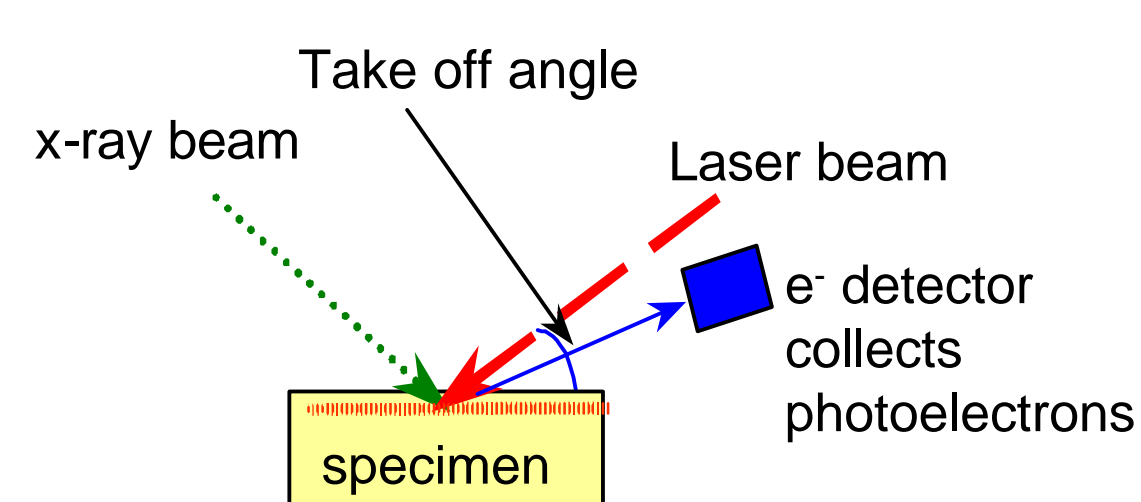


- a) Comparison of valence band spectra of unirradiated/oxygen-free $As_{50}Se_{50}$ (1) with samples that were (2) laser irradiated in vacuum for ~12 h and unexposed to air, (3) unirradiated but exposed to air and (4) irradiated in air for ~12 h and exposed to air. These spectra show the evolution of *permanent changes* with bandgap laser irradiation, and their enhancement by oxygen.
- b) Reversible changes observed on bulk $As_{50}Se_{50}$ fractured in situ. The bandgap light was the stimulus for change from (1) to (2). The valence band reverted to its original state when the light was shut off (3).
- c) Valence band spectra of the oxygen-free As_4Se_3 film showing both the permanent and transient changes in electronic structure. Results showed systematic changes in density of states with increasing exposure. Some of the changes were recovered when the light was turned off.

4. UNRAVELLING THE MYSTERY USING XPS

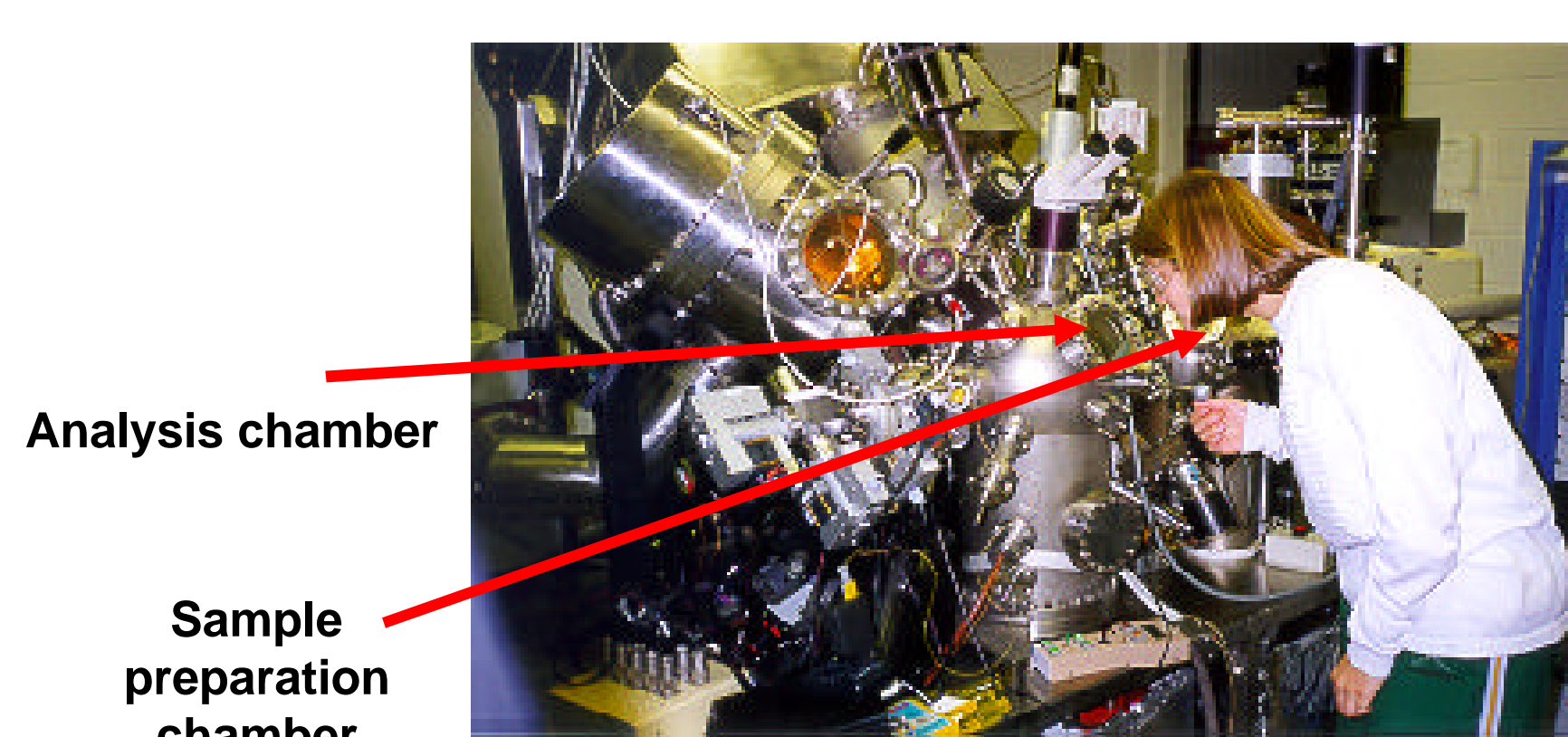
X-ray photoelectron spectroscopy (XPS) gives quantitative information on (i) the elemental composition of a surface, (ii) the local "chemical environment" of the atoms comprising the surface and (iii) the valence band structure that determines the optical response. From this information one can infer identity of:

- the elemental electrons that contribute to the different types of effects observed
- the formal oxidation states from the observed chemical shifts



Angle-resolved spectra allow us to characterize the photoinduced changes as a function of depth. These measurements are especially useful in understanding the influence of adsorbed and absorbed oxygen on photoinduced phenomena.

The Scienta ESCA-300 has a sample preparation chamber for depositing oxygen-free films.



The first observation of transient effects by high-resolution XPS on oxygen-free samples under *in situ* laser irradiation. Samples: (i) *in situ* prepared film, or (ii) the fractured surface of bulk glass.

6. CONCLUSIONS

1. Permanent changes are observed in the density of states of As-Se glass when the glass is irradiated.
2. These effects are even more pronounced when the glass is irradiated in the presence of oxygen.
3. Reversible changes are observable in the density of states, which are relatively less prominent than the permanent changes.