Photo-induced effects

- ✓ Phenomena
- ✓ Proposed mechanisms

Milestones of photo-induced effects in glasses

- ✓ The E' center in silica (Weeks, 1956[1])
- ✓ Radiation compaction in silica (Primak and Kampwirth in 60's[2])
- ✓ Photo-induced refractive-index increase in Ge-doped silica (Hill et al, 1978[3])
  - ➢ FBG, FBR
- ✓ Effects induced by pulsed lasers with fs or ns durations (Hirao et al, late 90's[4])
  - ➢ micro-machining and drilling
- ✓ Photo-doping of Ag into sulfide glasses (Kostyshin et al, 1966[5])
  - ➢ Potential in photolithography
- ✓ Photo-structural changes in $As_2(S, Se)_3$ films (Berkes et al, 1971[6])
- ✓ Opto-thermal structural changes btw c- and a- states (Ovshinsky et al, 1971[7])
  - ➢ RW-CD and RW-DVD

1. Weeks, J. Appl. Phys. 27 (1956) 1376.
2. Primak and Kampwirth, J. Appl. Phys. 39 (1968) 5651.
3. Hill et al, Appl. Phys. Lett. 32 (1978) 647.
4. Hirao et al, *Active Glass Devices (Springer, 2001).*
5. Kostyshin et al, Sov. Phys. Solid State, 8 (1966) 451.
6. Berkes et al, J. Appl. Phys. 42 (1971) 4908.
7. Feinleib et al., Appl. Phys. Lett. 18 (1971) 254.

Stimulus and response

An energy flow in photoinduced phenomena with typical features

light →	*excitation* →	*structural change* →	*property modification*
cw/pulse	electronic	chemical/ionic reaction	density (volume/shape)
photon energy	electro-thermal	atomic change	thermal/mechanical
irradiance	thermal	normal bonding	optical
polarization	plasma	defective	electrical
focusing		sputtering/explosion	chemical
temperature			surface property

K. Tanaka, Ceramist 10 (2007) 34.

Why is the field of photoinduced changes in ChGs **complicated**?

- Various phenomena:
  Photodarkening/bleaching; photoexpansion/contraction; transient, metastable, permanent; vectoral (anisotropic), scalar;
- Various proposed mechanisms:
  Probably more mechanisms proposed than phenomena
- Various compositions:
  Elementary (S, Se, Te), binary (Ge/As-Ch), ternary (Ge-As-Ch, etc), and more
- Various sample states/conditions:
  Bulk from melt-quench, evaporated/sputtered films; Obliquely or normally deposited films;
  as-deposited, annealed (air, N_2, vacuum)
- Various lasers used:
  Sub band-gap, band-gap & super band-gap lasers: they may cause quite different photoinduced phenomena
- Various laser states/conditions:
  Different polarizations; intensity dependence
- Various environments:
  Ambient, N_2, vacuum; pressure dependence; temperature dependence
- Various processes:
  Electronic , atomic processes; thermal or athermal processes (no good tools to judge)
- No sufficient structural evidence:
  Especially no sound structure evidence for photoinuced reversible change
- Conflict literatures:
  Conflict experimental results, conflict opinions; to obtain unbiased opinions, go back to the ORIGINAL papers.

Slide provided by Donghui Zhao

Observed phenomena 1

The photo-darkening effect: the shifts of the optical absorption edge towards longer wavelengths. The effect appears when ChG (As_2S_3, As_2Se_3 or others) is illuminated by light of energy above the band gap of the material.
The photo-bleaching effect: the reverse effect of photo-darkening. It happens when the sample is heated under T_g or illuminated with light of energy below the band gap.
The photo-plastic effect: a reversible photo-induced transition from brittle to ductile state. The effect was explained in terms of the viscous flow of glasses under band gap illumination.
The photo-induced fluidity effect: the flow of a chalcogenide glass under illumination with sub-band gap light.
The photo-induced ductility effect: related to fiber elongation under the action of light, and reflecting the presence of the combined action of illumination and application of an external stress.
The optomechanical effect: demonstrated by the displacement of a cantilever with a chalcogenide film under the action of light. This displacement is the result of internal stress relaxation or generation caused by increase or decrease in its plasticity.
The polarization-dependent photoplastic effect: linearly polarized band-gap light produces hardness anisotropy of the surface of $As_{50}Se_{50}$ films. The light induced decrease or increase of the plasticity of the glass depends on the polarization state of the incident light.
The light-stimulated interdiffusion effect: the interdiffusion of the layers in multilayer structures based on chalcogenides (i.e. a-Se/As_2S_3) under the influence of light. An effective intermixing of components in a few nanometers of distance is produced and a volume increase is observed.

Popescu, J. Optoelectron. Adv, Mater. 7 (2005) 2189.

Observed phenomena 2

The photo-expansion effect: the increase of the volume of chalcogenide glasses under illumination. Sometimes a giant expansion effect is observed. In some films a photo-contraction effect is also observed.
The self-organization effect: presence of the so-called intermediary phase between the floppy phase and the rigid phase The intermediate phase exists in a narrow compositional interval in several binary glasses (e. g. As_xSe_{1-x} or Ge_xSe_{1-x}) for x~0.20-0.22. This phase is suggested to consist of networks that are optimally constrained and self-organized.
The athermal photo-induced transformation effect: discovered in AsSe molecular films. Two mechanisms were suggested; photon-induced intra-molecular bond breaking which leads to a continuous random network, and inter-molecular bond-breaking resulting in an orientation-disordered molecular glass.
Photo-induced amorphisation effect : not a thermal origin but an electronic one. The driving force of amorphisation is the presence of a small amount of amorphous phase and of strains.
The laser-induced suppression of photo-crystallization: in amorphous selenium films, the action of two laser beams, whose photon energies are different in the optical band gap, makes crystallization much slower than the case of only a laser beam. A decisive role of the polarizations of the two laser beams has been demonstrated. The suppression of the crystallization rate is observed only for the polarizations of the two light sources to be parallel with each other.

Popescu, J. Optoelectron. Adv, Mater. 7 (2005) 2189.

Observed phenomena 3

The photo-induced softening and hardening effect: observed in Ge-As-S films subjected to ultraviolet irradiation. Amorphous chalcogenides are soft semiconductors due to the two-fold coordinated chalcogen atoms, which are susceptible to exhibit electro-atomic responses, and they behaves as a flexible electron-lattice coupling system.

The photo-amplified oxidation effect: in ambient conditions the photo-oxidation is triggered during exposure to light. The composition 35Ge65S is the most sensitive composition to this process.

The photo-dissolution and photo-doping effects: the former indicates that metal layer deposited on the surface of a chalcogenide film diffuses in under the influence of a light beam. Silver diffuses very easily. The photo-doping effect is related to the diffusion of various atoms at long distances under the action of light.

The photo-polymerization effect: the polymerization of the glass during exposure to light, accompanied by a red shift of the optical absorption edge, is a typically irreversible phenomenon, which was observed both in evaporated arsenic-chalcogen films and simple chalcogenide films.

The anisotropy of the transmittance: the anisotropy of transmission when the chalcogenide is illuminated with linearly polarized light. As_2S_3 glass rotates the polarization plane of a polarized ray before light irradiation (therefore this glass exhibits natural optical activity) and, after irradiation, the rotation angle changes (therefore it exists photo-induced optical activity).

The photo-anisotropy effect and the photo-induced dichroism: in As_2S_3 glass, $\Delta\alpha$ and Δn of 10^2 at $\alpha \sim 10^4$ cm^{-1} and 0.002 at $n \sim 2.6$, respectively.

Popescu, J. Optoelectron. Adv, Mater. 7 (2005) 2189.

Observed phenomena 4

Photo-induced circular birefringence: optical activity and photo-induced circular dichroism that leads to ellipticity, therefore the optical properties of chalcogenides are determined by the spatial dispersion.

The anisotropic opto-mechanical effect: a reversible anisotropic volume change induced by polarized light in a thin film of chalcogenide (e.g. 50As50Se). Contraction occurs along the direction of the electrical field vector and expansion perpendicular to that direction.

The photoinduced scattering of light: the light of energy below the gap exhibits a strong photoinduced scattering. Revealed by the change of the shape of the cross-section of the transmitted laser beam. Before the irradiation the image of the transmitted laser beam on a screen is circular. During irradiation a diffuse halo is formed along the original spot. The image is gradually eroded and finally is stabilized as a nebula covered by spots.

The transmittance oscillation effect: in $GeSe_2$ films deposited on glass substrates, it was found that under the influence of the continuous focused He-Ne laser beam, the transmittance and the reflectance show periodic oscillations in time above a threshold of ~1.6 kW/cm^2. Bistability and hysteresis were also found without placing the sample in an optical resonator.

Anisotropic surface corrugation effect: linearly polarized light can produce an anisotropic surface corrugation in amorphous films of As-S-Ag.

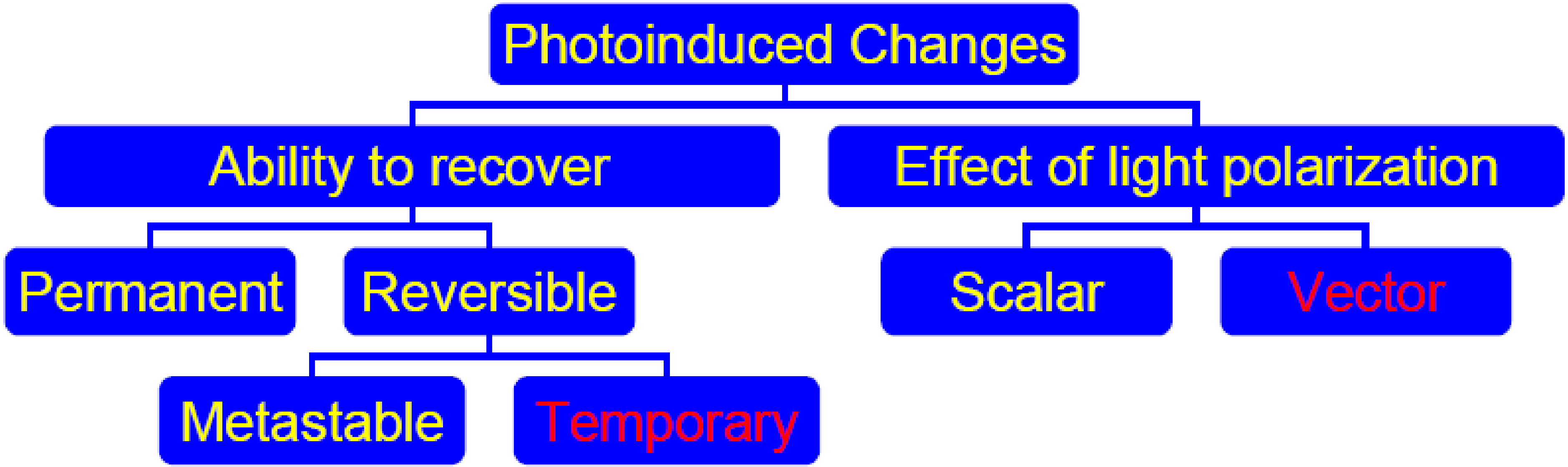
The photo-elastic birefringence effect: the elastically deformed glassy As_2S_3 show photo-elastic birefringence and dichroism. In axially deformed samples unique properties do appear. When the uniaxial compression is released the frozen birefringence is accompanied by isotropic optical modifications, which can be relaxed by illumination or thermal annealing.

Popescu, J. Optoelectron. Adv, Mater. 7 (2005) 2189.
Trunov, J. Optoelectron. Adv. Mater. 7 (2005) 2235.
Kolobov, Photo-Induced Metastability in Amorphous Semiconductors, Wiley, 2003.

Selected photo-induced effects: applications

- ✓ Chemical properties: lithography, selective dissolution
- ✓ Volume expansion: integrated optics, micro-optics
- ✓ Amorphization/devitrification: CD-RW, DVD-RW
- ✓ Plasticity: MEMS actuator
- ✓ Viscosity: athermal melting, memory
- ✓ Darkening, birefringence: memory, optical switching
- ✓ Electrical properties: photoconductor

Photo-induced effects: classification



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

H. Jain, ARL/ARO COT Open House, 2004.

Materials dependence

Comparison of reversible scalar photoinduced changes appearing in some materials at room temperature. X denotes non-existence. Typical data are given for As_2S_3[88], GeS_2 [unpublished], GeO_2[51,114], SiO_2[4,115], and a-Si:H[116,117]. Δn in a-Si:H may be too large.

	E_g [eV]	n	T_g [K]	$\Delta\alpha$	Δn	ΔV [%]
As_2S_3	2.4	2.6	450	PD	+0.02	+0.4
GeS_2	3.3	2.2	750	PD	+0.005	+0.5
GeO_2	5.8	1.6	850	MGA	$+10^{-4}$	+0.5
SiO_2	~9	1.5	1500	MGA	$+10^{-5}$	-10^{-3}
a-Si:H	~1.8	~3.2	x	MGA	-0.05?	$+10^{-3}$

K. Tanaka, Ceramist 10 (2007) 34.

Non-thermal photo-induced phenomena

A classification of non-thermal photoinduced phenomena. $\Delta\alpha$, Δn, ΔV, and $\Delta\eta$ represent changes in optical absorption, refractive index, volume, and viscosity. PSD is for photo-surface deposition, PD for photodarkening, MGA for mid-gap absorption, and PCM for photo-chemical modification.

mode (recovery time)	bulk change	chemical reaction
Irreversible (∞)	crystallization, polymerization, ΔV	oxidation, photodope, PSD
reversible (min)	PD, Δn, ΔV, MGA & ESR	PCM
transitory (ms − s)	$\Delta\alpha$, Δn, ΔV, $\Delta\eta$	

K. Tanaka, Ceramist 10 (2007) 34.

Photoinduced *optical* changes

❑ Permanent changes

$$\Delta\alpha = \Delta\alpha_m\left(1-\exp\left(-\left(\frac{t}{\tau}\right)^{\beta}\right)\right)$$

- ❖ Irreversible photodarkening/photobleaching;
- ❖ (Compressed) exponential kinetics, $\beta \geq 1$;
- ❖ Occurs when irradiation on as-deposited / vacuum annealed films;
- ❖ Photoinduced surface oxidation;
- ❖ Polymerization (unclear); decomposition;
- ❖ Bond switching: homopolar → heteropolar bonds;

❑ Metastable changes

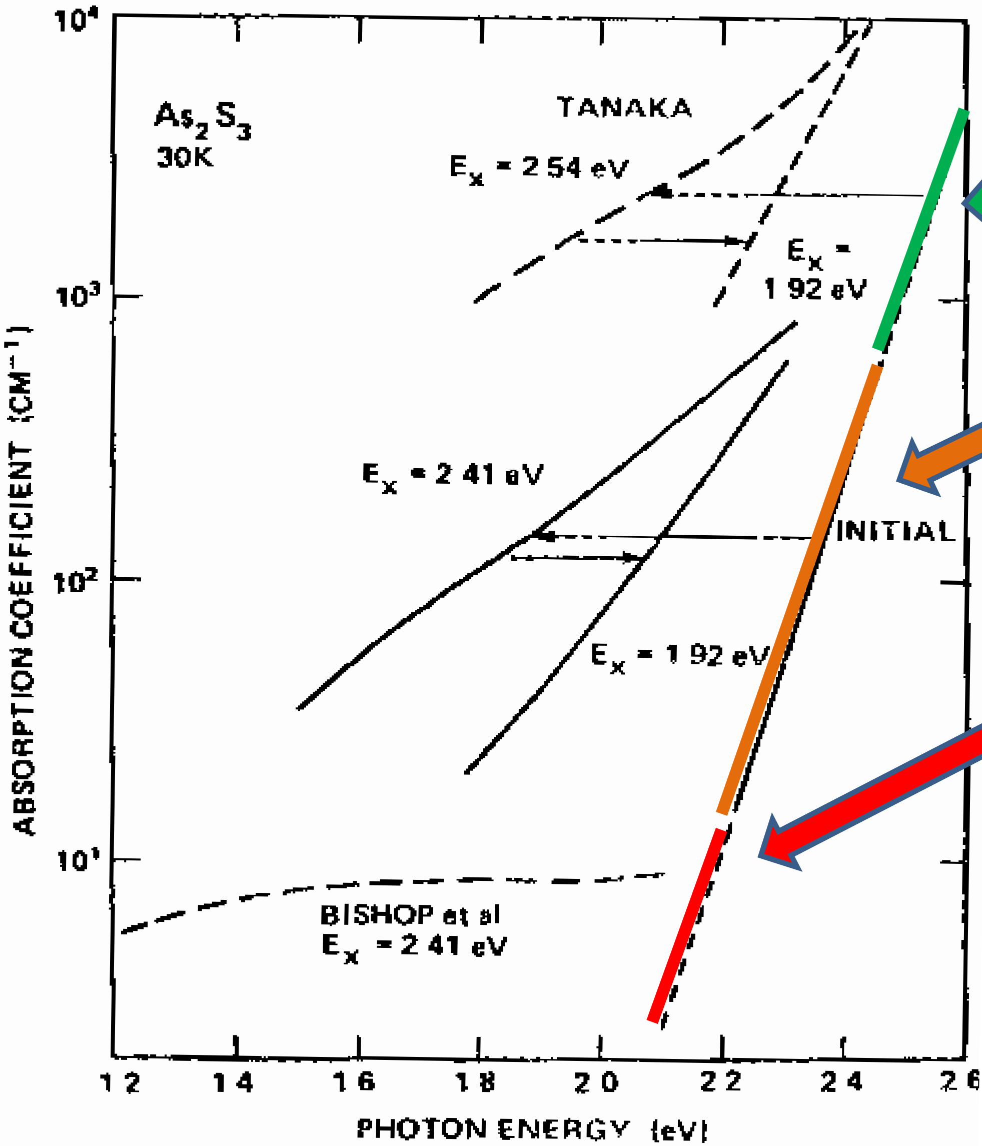
- ❖ Reversible photodarkening, recovered by annealing at ~Tg;
- ❖ Kinetics to examine;
- ❖ Occurs when irradiation on bulk flakes (< 100 μm) and well annealed (air / N_2) films;
- ❖ Structure mechanism is unknown; very few structure evidences.

❑ Transient changes

- ❖ Temporal photodarkening, recovered after removing laser (~hours);
- ❖ Stretched exponential kinetics, $0 < \beta < 1$;
- ❖ Universally exist in chalcogenide glasses and films;
- ❖ Anisotropic: polarization dependent;
- ❖ POA is independent of the metastable change, has constant magnitude & kinetics throughout the photoinduced process;
- ❖ Structural change is not resolved; or presumably electronic process.

Slide provided by D. Zhao

Photoinduced absorption



Shimakawa *et al*, 1995, Adv. Phys.

Optical absorption edge

High-absorption region: determine Eg

Urbach region

Weak absorption region

- **Induced absorption;**
- **Band edge red shift;**
- **Broadening;**
- **Induced mid-gap absorption;**
- **Partially recovered by light with less energy.**

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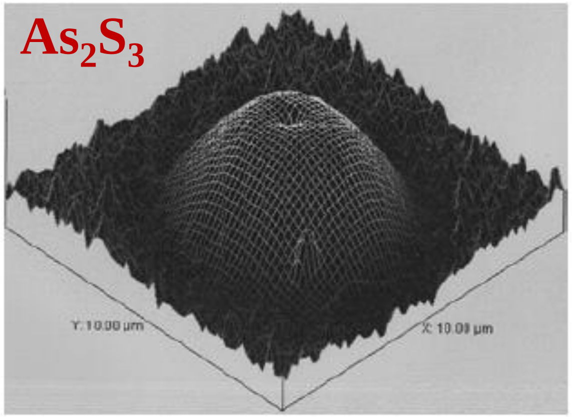
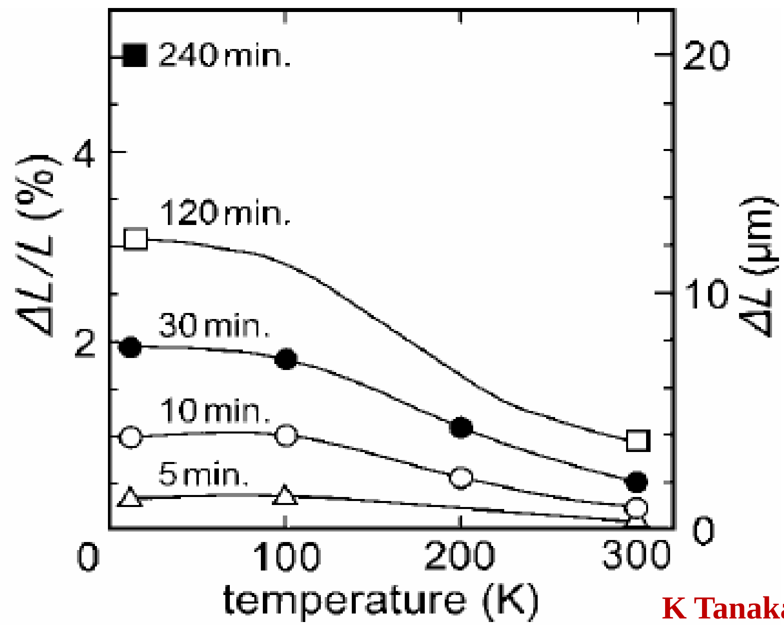
Photoinduced deformations

Photoexpansion





Application: microlens fabrication

Normal photoexpansion: $\Delta V/V \sim 0.4\%$

Giant photoexpansion: $\Delta V/V \sim 5\%$

- **Sub-bandgap light: ~$0.8E_g$**
- **High intensity: $10^3 \sim 10^4$ W/cm^2**

Low T favors photoexpansion.---athermal!

$\Delta V/V$ increases as an exponential function of time: $\Delta V = \Delta V_m [1-\exp(-t/\tau)]$

K Tanaka *et al*, J.Opto.Adv.Mater., 2006

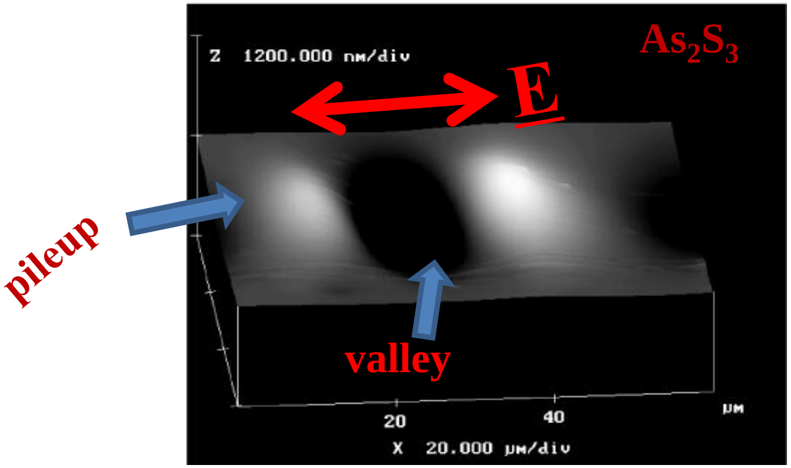
Slide provided by D. Zhao

Photoinduced deformations

Optical field-induced surface relief patterns

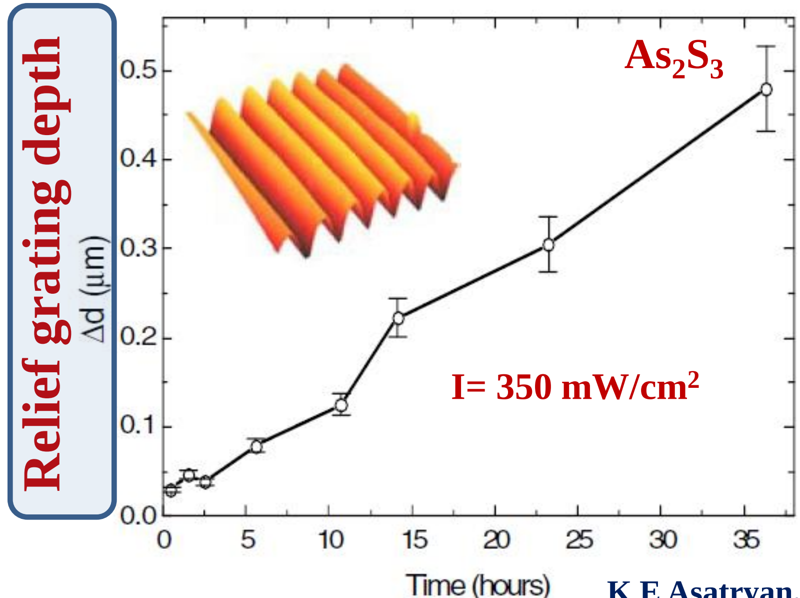
Pump: $\hbar\omega = 2.41$ eV $\approx E_g$

Single plane polarized laser



A Saliminia, Phys.Rev.Lett, 2000

RCP+LCP light interfered



RCP: right circularly polarized

LCP: left circularly polarized

K E Asatryan, Phys.Rev.Lett, 2005

Pileups only along *E* of light

Light intensity not modulated

Only *E* of light modulated spatially: vector holography.

Optical-field drives anisotropic mass-transport; formation of relief gratings is permanent and not be able to anneal out.
→ Photofluidity??

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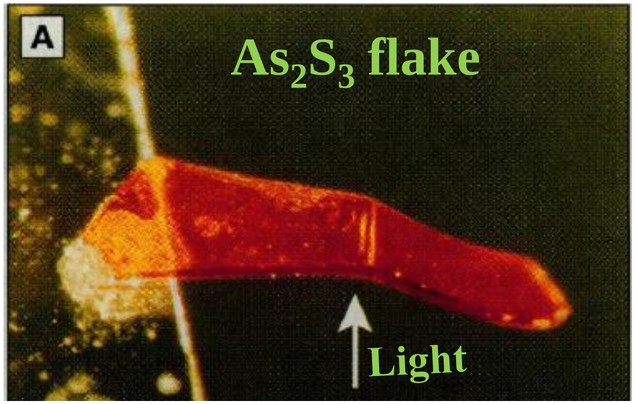
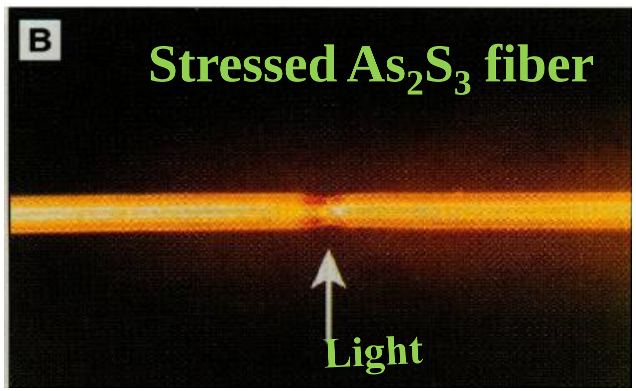
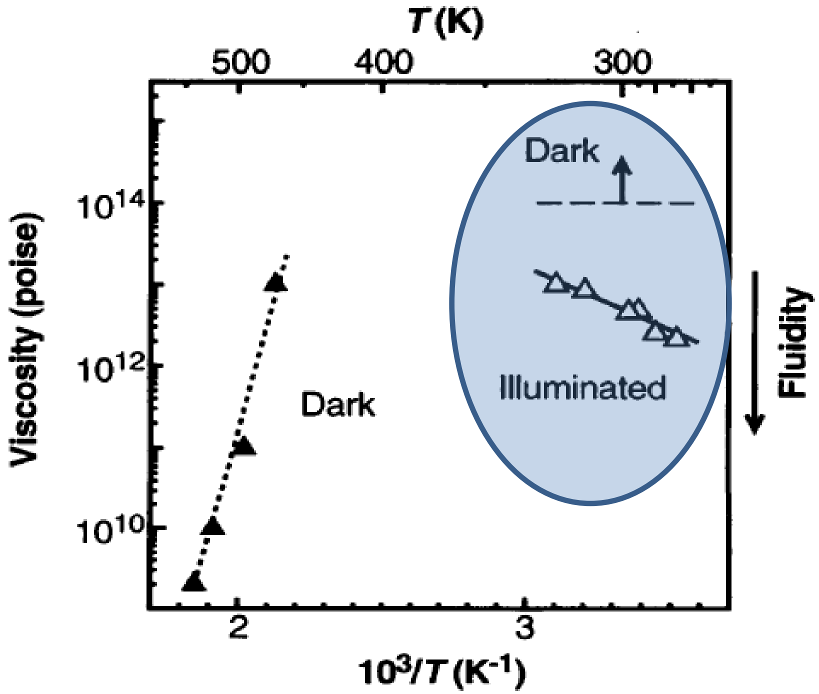
Photofluidity

Pump: ħω = 2 eV < E_g

I= ~10^2 W/cm^2







Under illumination, viscosity η decreases as T decreases!

Athermal process.

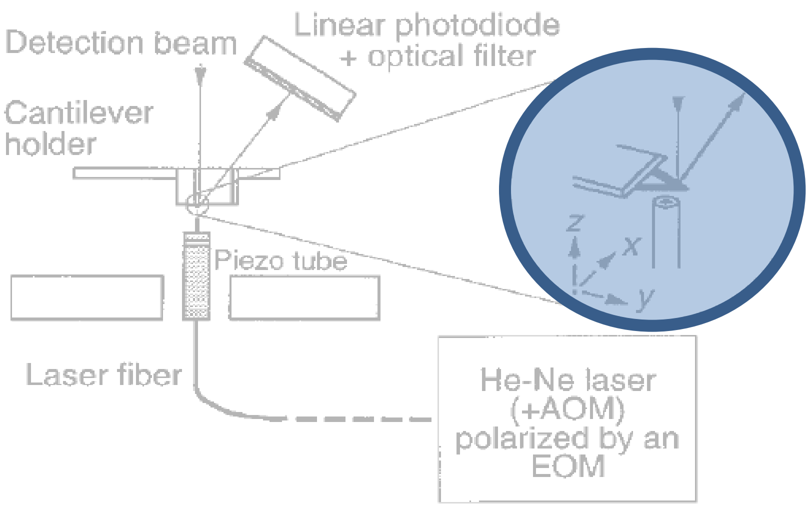
Fluidity is induced via a pure electronic process?

H Hisakuni & K Tanaka, Science, 1995

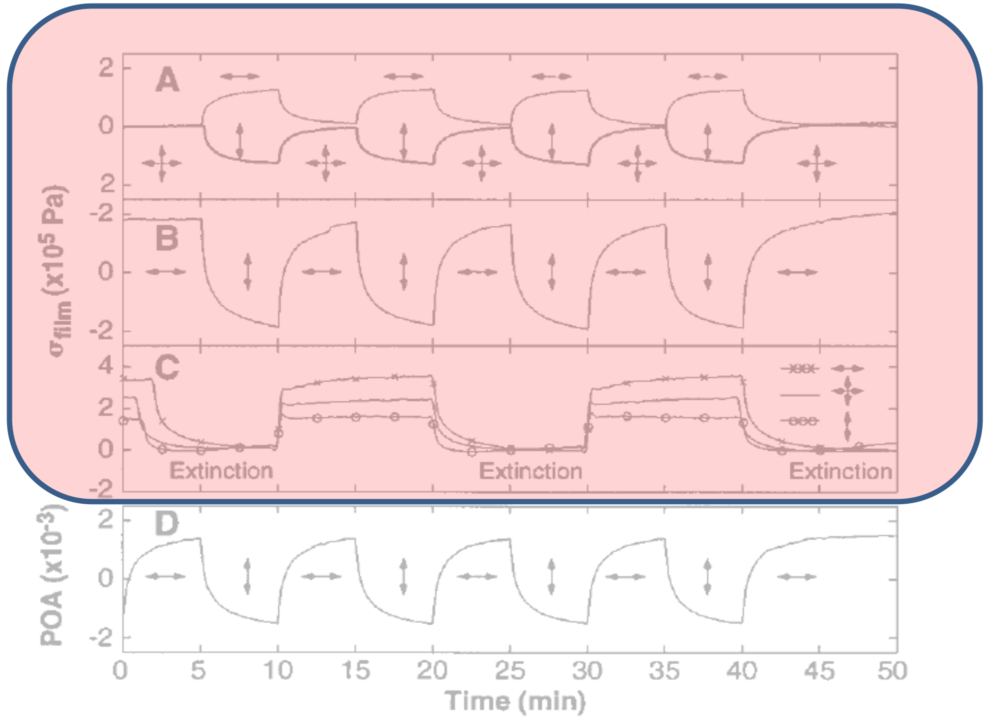
Slide provided by D. Zhao

Photoinduced deformations

Reversible nano-contraction & dilation induced by polarized light



$As_{50}Se_{50}$ film on SiN cantilever



Transient nano-contraction & dilation

Recovered by unpolarized light

Alternated by switching light polarization

P Krecmer, Science, 1997

Slide provided by D. Zhao

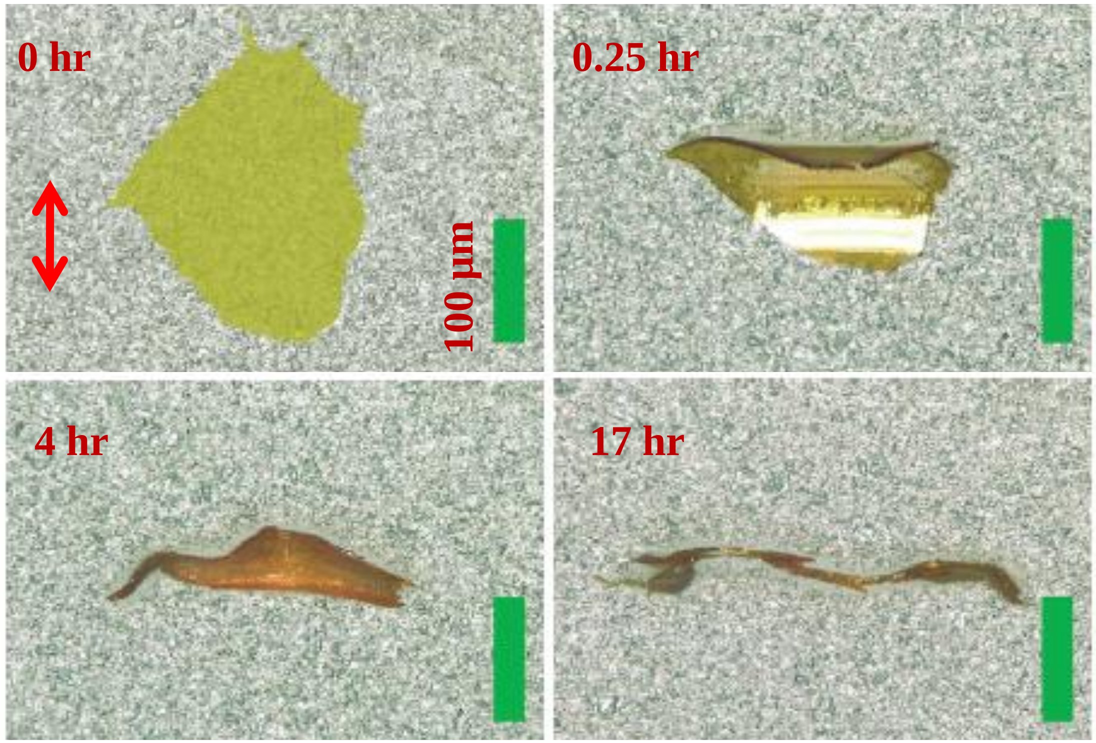
Photoinduced deformations

Visible anisotropic deformation by polarized light

Pump: $\hbar\omega$ = 2.3 eV ~ E_g

I= ~4W/cm^2

free-standing As_2S_3 film



This phenomenon also occurs in crystalline As_2S_3

K Tanaka, Appl. Phys. Exp., 2008

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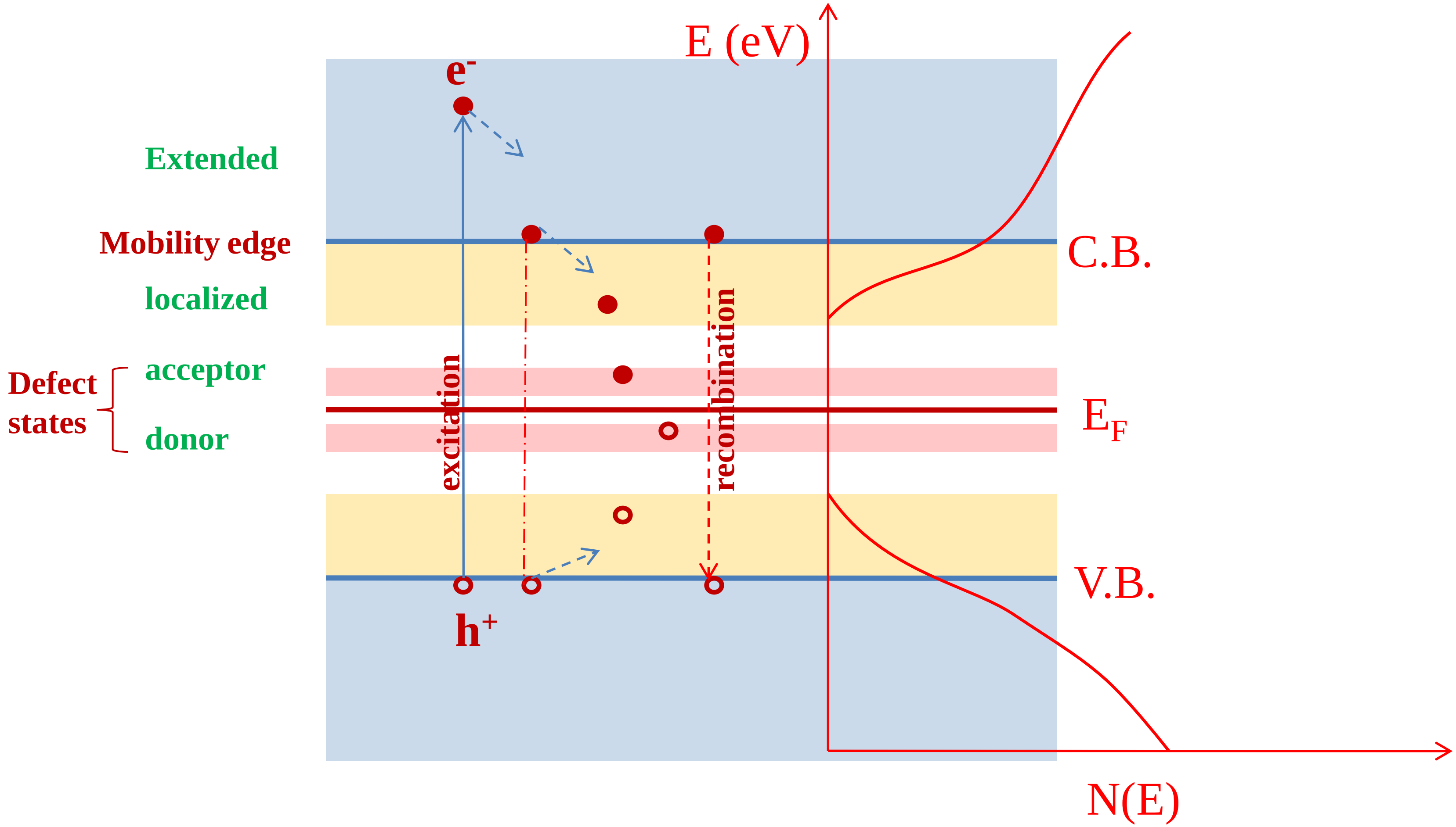
Electronic process in the photoexcited chalcogenide glasses



- ❑Photoexcited carriers (electrons and holes) are quite mobile at extended states;
- ❑Thermallize into localized states, low mobility.

- ❑Excitons, low mobility;
- ❑Polarons, local atomic rearrangement;
- ❑Trapped by defects, hopping conduction;
- ❑Recombination: radiative & non-radiative;

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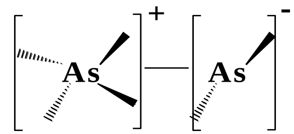
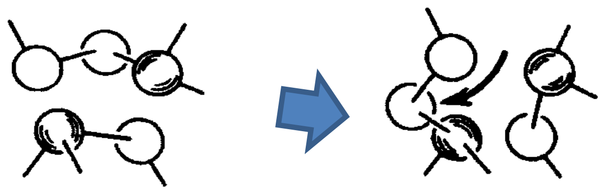
Mechanisms of photoinduced effects

Local atomic structure changes

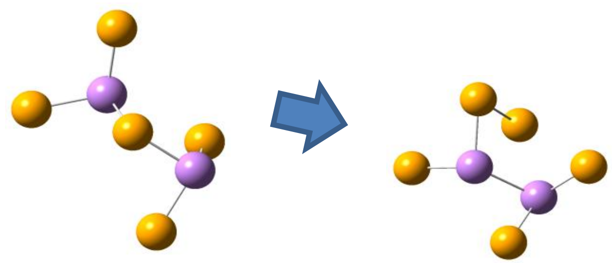
Valence alternation pairs (VAP): D^{+}-D^{-}



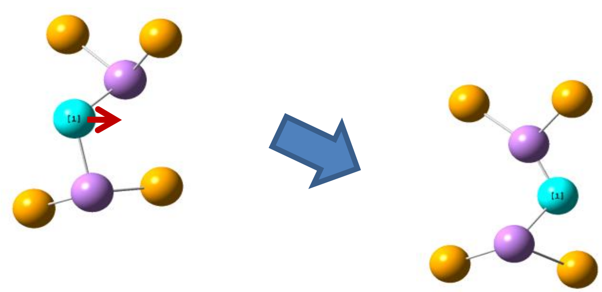
bond switching



(homopolar) bond creation



bond twisting



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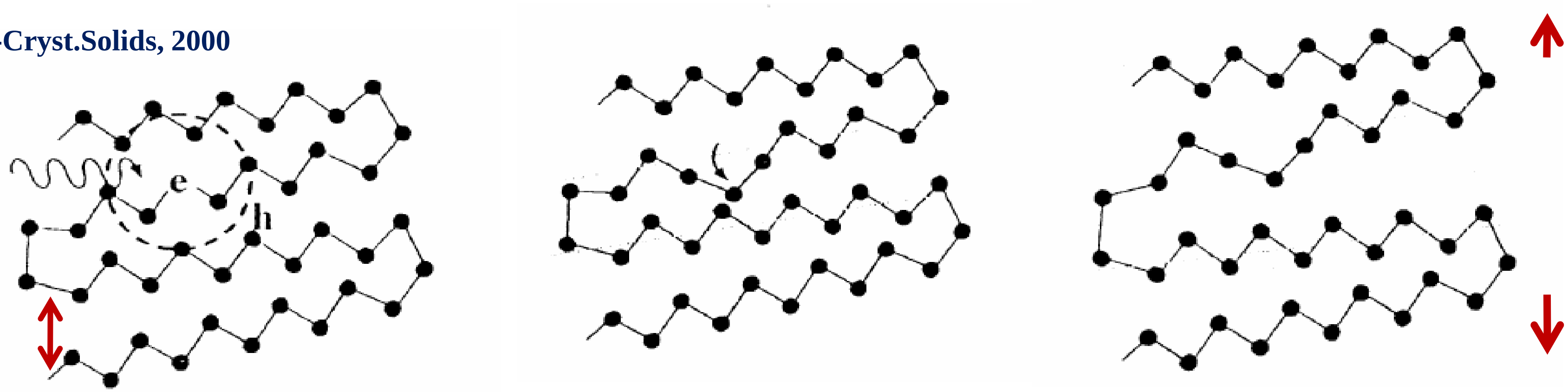
Intermolecular changes

K Tanaka, J.Non-Cryst.Solids, 2000



Van der Waals

e-h pair creation

Relaxation of carriers

→ Bond twisting

→ Interlayer strain

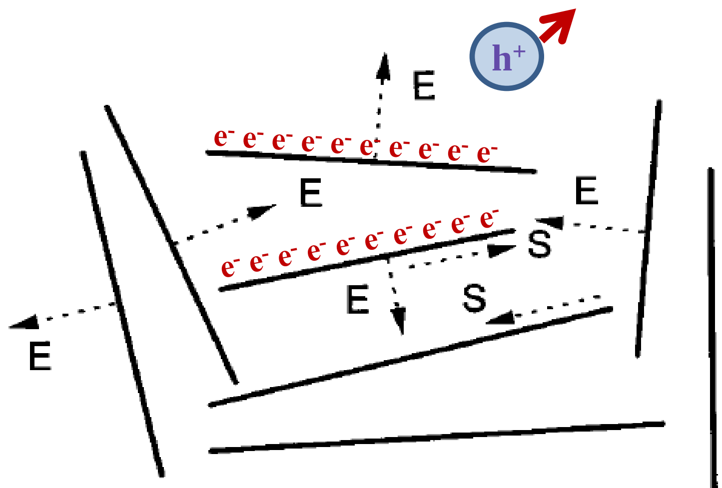
Strain relaxation

Interlayer spacing expand

Weakening van der Waals force

K Shimakawa, Philo.Mag.Lett., 1998

Repulsive Coulomb force between layers



Holes: higher mobility, drift away

Electrons: localized

Slip and Expansion of layers

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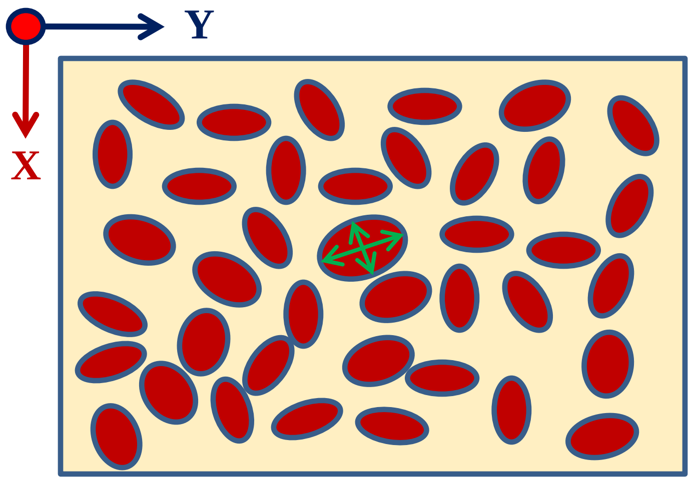
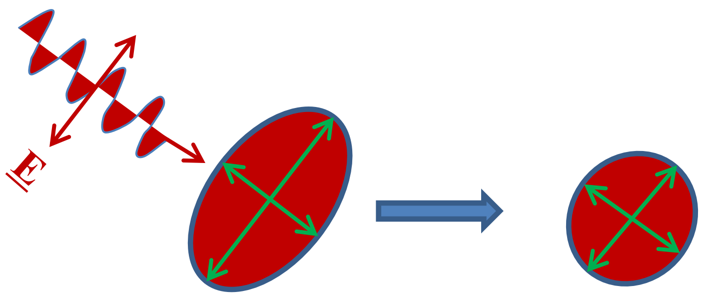
Mechanisms of photoinduced anisotropy

S R Elliott, J.Non-Cryst.Solids, 1996

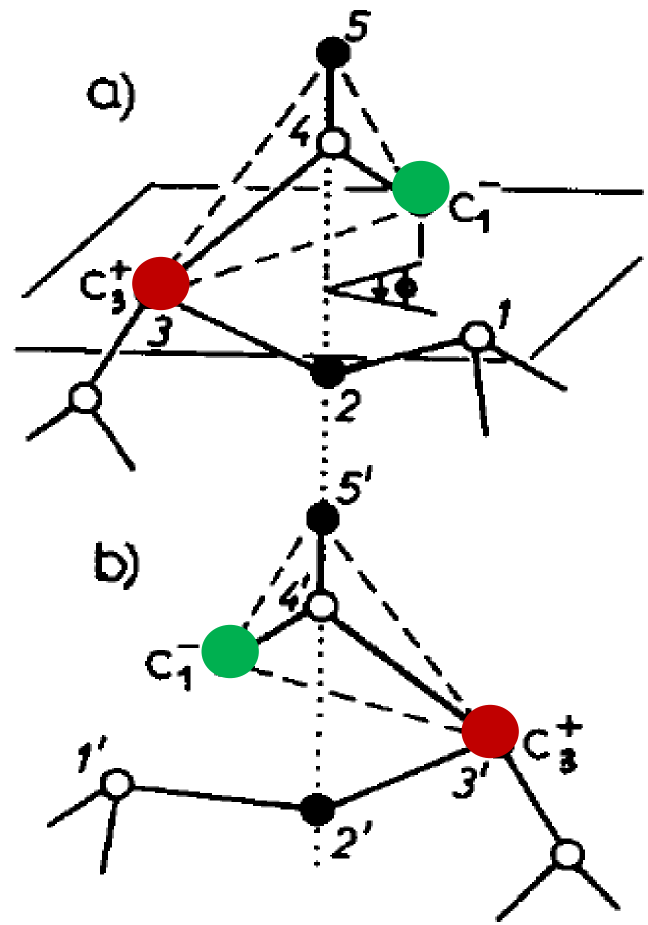
H Fritzsche, Phys.Rev.B, 1995

Anisotropic microvolumes (AMV)





Realignment of IVAP



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