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Photoinduced deformations in chalcogenide glasses: What are the driving forces?

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ABSTRACT

Chalcogenide glasses including As_2S_3 and Se are known to exhibit a variety of photoinduced deformations such as volume expansions, anisotropic shape changes, and surface ripples. These deformations are produced by photoinduced viscous material flows which are caused by some driving forces, while the origins are controversial. We propose a guiding idea that the driving force arises from atomic and optical mechanisms; the former from structural disordering and intermolecular alignment and the latter from radiation force and torque. Previously proposed models such as Coulombic and electric-gradient forces are criticized. We also compare these deformations with those in azobenzene-containing organic materials.

1. Introduction

Light exposure induces conspicuous deformations in chalcogenide glasses, with the features abounding in variety [1,2]. Some deformations grow to visible scales, which are promising for direct (without etching) fabrication of relief structures such as micro-lenses and gratings [2]. It should also be mentioned here that electron beams [3–9] and tunneling currents [10,11] can deform chalcogenide glasses. Nevertheless, why such stimuli are able to produce deformations remains speculative, or none of the mechanisms proposed so far can deliver unified explanations for various experimental observations.

It has also been known that dye-containing organic materials exhibit a variety of photo-deformations [12–14], the features being compared with those in the chalcogenide [15–17]. Specifically, extensive studies have been focused on azobenzene-containing (with densities of 0.5–50 mol%) polymers and liquid crystals, which may be prepared as spin-coated or Langmuir-Blodgett films. Although these materials are infrared-opaque, some deformations are surprisingly dramatic, probably reflecting molecularly-engineered structures. And, in those organic films it is doubtless that photoinduced trans-cis isomerization of azo-dyes triggers successive structural changes. By contrast, it is difficult to identify such a seed in the photo-deformation in chalcogenide glasses, which has made our understanding rudimentary.

We here consider the mechanisms of several photoinduced deformations (Table 1), from unified points-of-view. To make the dealt phenomena concise, we will deal with memorable deformations in covalent chalcogenide glasses such as As_2S_3, Se, and As-Se [18], rarely touching transitory motions [19–21] appearing *during* exposure to light. We also focus upon behaviors in annealed films and/or thin bulk flakes, which seem to undergo similar photoinduced responses. Little descriptions are given to photo-deformations in as-evaporated As(Ge)-S(Se) films [1,22] and ionic compositions such as Ag-As-S films [23], in which the origins are ascribable to photoinduced stabilization (polymerization) and ionic motions, respectively. We also exclude deformations produced using (pulsed) intense light, which may cause ablation [24–26].

The present study commences with a presumption that the photoinduced memorable deformation emerges as a result of visco-elastic mass flows. The flow rate is expressed as $\partial\gamma/\partial t = \sigma/\eta$, where γ is the shear strain, σ the stress, and η the viscosity ($1/\eta$ the fluidity), so that the subject to be answered is how light illumination can generate σ and reduce η. Probably, the σ generation and the η reduction occur cooperatively under illumination, while separated considerations will provide clear insights into the photo-deformation mechanism. And, for the η reduction, which is experimentally demonstrated as the photoinduced fluidity [18,27–29], Tanaka and Shimakawa have recently proposed a photo-fragmentation model, including chain breakages and crossing in Se clusters, the concept probably being applicable to other

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Table 1
Summary of photoinduced memorable deformations (at room temperature) in the three materials (the Tauc optical gap) [with original or representative references] and proposed forces. Stars (*) concern scalar phenomena/effects, and the others are vector. The forces underlined have atomic origins.

	As_2S_3 (2.35 e*V*)	As-Se (~1.9 eV)	Se (2.05 eV)	Forces
Volume expansion*	0.4% [64,66]	~0.2% [73]	0.3% [21]	Disordering* (gradient?)*
M deformation (*//**E***)	$L \approx 3\,\mu m$, $d \approx 50\,\mu m$ [55]	$L \approx 1\,\mu m$, $d \approx 10\,\mu m$ [73]	$L \approx 1\,\mu m$, $d \approx 5\,\mu m$ [21]	Alignment Radi. force Torque
Sinusoidal corrugation (*//**E***)	$\Lambda \approx 20\,\mu m$, $\Delta h \approx 0.2\,\mu m$ [74]	$\Lambda \approx 10\,\mu m$, $\Delta h \approx 0.1\,\mu m$ [75]	Not appear [74]	Alignment Radi. force
Scratch/crack deformations	L-deformation for $\perp$*E* [63,78]	Growth for $\perp$*E* [77]	Unclear [63,79]	Alignment Torque
Slit (with assisting beam)	Concave and convex [80]			Alignment Radi. force Torque
Deflection of monolithic cantilever	Up and down [61,63]			Disordering* Alignment Radi. force Torque
Curling and elongation of semi-free flake (film)	U-deformation & elongation, (wrinkling) $\perp$*E* [83,84]	U-deformation & elongation, (wrinkling) $\perp$*E* [85]	Elongation //*E* [63,85]	Torque Radi. force Se ???
Gratings by two interfering beams, assisting beam effect	$\Lambda \approx 1$–$40\,\mu m$ and $\Delta h \leq 1\,\mu m$ [55,94]	[89]*, [57,95]	[90]* [95]	Disordering* Alignment Radi. force Torque

chalcogenide glasses [30]. A sub-gap photon may efficiently excite atomic sites having smaller local gaps, which triggers such polaronic transformations. The model seems to be contrastive to the η-reduction mechanisms including cooperative motions in azo-systems [31,32].

The present work therefore focuses upon the *driving force*. We first list a few candidates for the forces in Section 2, which are then applied to interpret known photoinduced deformations, with critiques of other models, in Section 3. Finally, we will point out remaining problems and future perspectives in Section 4, and Section 5 concludes with Table 1. The unified model sketched henceforth, although still qualitative, will pave a way for grasping various photoinduced deformations, not only in chalcogenide glasses but in other solids, e.g., oxide glasses, dye-polymers, and biological materials.

2. Motive forces

At the outset, it would be helpful to delineate light-propagation conditions. Throughout the present work, the electric field of incident plane-wave light is written as $\boldsymbol{E}\exp\{i(\omega t + \boldsymbol{k}\cdot\boldsymbol{r})\}$ with the angular frequency $\omega = 2\pi c/\lambda$ and the wavenumber $k = 2\pi n/\lambda$, where c and λ are the velocity and the wavelength of light in vacuum, and n the refractive index of a material, which may reduce the light intensity ($\propto E^2$) with an absorption coefficient of α. In addition, we may need to take secondary, deflected light into account. The one component is *scattered light* [33]. If the film surface is not optically flat, and if the incident light is linearly polarized, scattered light propagating orthogonal to the electric field becomes stronger, the feature characteristic to dipole radiation. Actually, traces of scattered light have been detected as cat-whisker like Ag patterns in Ag-As-S films after exposure to linearly-polarized light [23]. The other component is *diffracted light*, which is likely to occur if sample surfaces are wavy. Specifically, if the shape is of sinusoidal gratings, the diffracted light tends to propagate parallel to the grating vector, irrespective of the electric-field direction, with a conversion efficiency being formulated by a grating-coupler theory in waveguide optics [34].

In the following, we assert that the motive force originates from two kinds of mechanisms; atomic and optical. The former may vary with the amorphous structure such as one-dimensional Se chains and two-dimensional As-S(Se) layer segments [18], and the latter depends upon the dielectric constant (with anisotropy) and the external shape of a sample.

2.1. Structural disordering

Photo-electronic excitation tends to induce volume expansion through enhancement of structural disorder. Numerical analyses for Se have demonstrated that photo-generated electrons and holes undergo polaronic states, which partly relax to defective, more disordered structures, causing expansions and contractions, respectively [35,36]. Besides, it has been documented that disorder enhancement in a compact material increases its volume [37]. For instance, the transformation from a face-centered-cubic packing of spheres to the dense random packing accompanies a fractional volume increase by ~16% [38]. Alkali-halide crystals expand through formation of Schottky defects. It is also reported that a structurally relaxed vitreous Se is tighter by 0.14% than a melt-quenched disordered state [39]. These observations manifest that the dense solid expands with disorder enhancements. On the

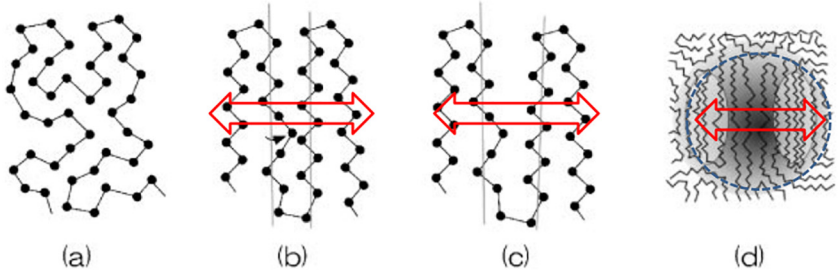

Fig. 1. Schematic illustrations of segmental structures in (a) annealed, (b) locally aligned under linearly polarized illumination, and (c, d) anisotropically relaxed states, with the double arrows indicating the ***E*** vector. (d) illustrates a top view of M deformations with the circle representing a light spot, which is assumed to have a Gaussian (gray) intensity distribution, and (enlarged) segmental structures. (Modified from [44].)