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Photo-induced deformations in chalcogenide glass: Atomic or optical force?

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After an overview of photo-deformations in chalcogenide glasses, we study vector deformations appearing in semi-free As_2S_3 flakes and films with a few micron thicknesses. Upon illumination of linearly polarized bandgap light with a spot diameter of ~0.5 mm, powders (~10 μm in lateral size) of As_2S_3 laid on viscous grease rotate so that the film plane becomes orthogonal to the polarization direction. The flake (~0.1 mm) undergoes U-shape folding and spiral elongation, while the film (» 0.5 mm in lateral size) exhibits a large sinusoidal corrugation. We propose that these rotation and deformations in the powder, flake, and film are triggered not by microscopic atomic forces but by macroscopic optical forces.

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1. Introduction

It is known that the photon exerts microscopic and macroscopic forces. In an insulating solid, a photon having an appropriate *energy* excites an electron, which may give rise to an atomic or molecular distortion through electron-lattice interaction. Such photoinduced processes may produce marked structural changes, the examples being found in organic materials and chalcogenide glasses [1-4]. On the other hand, the photon also has *momentum* (wavenumber) and *spin* (polarization). The momentum has been widely utilized for optical trapping in laser tweezers [5] and more recently for actuation of nano-machines [6]. The spin can rotate macroscopic materials [7,8], which is promising for nano-motors and so on. In addition, Tanaka has recently discovered that a surprising photo-deformation, as a biological growth, of semi-free As_2S_3 flakes, which seems to be caused by the momentum and spin [9]. It is therefore valuable to explore further the role of radiation forces in photoinduced deformations of glasses and other viscous materials.

In the present work, after briefly reviewing the photoinduced (non-thermal) deformations in covalent chalcogenide glasses, we study new anisotropic deformations in As_2S_3. It seems that the photon provides, not only electro-atomic changes as extensively studied [1-4], but also exerts purely optical forces [5-8], which trigger drastic deformations.

2. Overall features

2. 1. Classification

The chalcogenide glass exhibits a variety of photoinduced phenomena, as listed in Table 1 for the deformations appearing in covalent compositions such as As(Ge)-S(Se). The change can be classified in respects of directionality and stability. Note that interesting deformations produced under two-beam interferences with several polarization states [10] are excluded here for focused descriptions

Table 1. Scalar and vector deformations of irreversible, reversible, memorable, and dynamic (transitory) processes in covalent chalcogenide films, and (speculated) mechanisms.

Directional	*Process*	*Observation*	*Mechanism*
SCALAR	irreversible	contraction (-1% in As_2S_3 [16]), (-10% in obliquely-deposited Ge-Se [17])	polymerization void collapse
	reversible	expansion (+0.4% in As_2S_3 [14], +0.3% in Se [34])	disordering
	dynamic	stress relaxation [24], fluidity [28] expansion [30]	bond interchange? electronic/thermal?
VECTOR	memorable	M-shape [37] scratch [27] crack [11] monolithic OM [11] U-shape and spiraling elongation [9] wrinkling [present]	oriented layer? optical torque? optical torque? optical torque? optical torque & pressure? optical pressure?
	dynamic	OM effect [33]	atomic or optical?

The directionality is specified as "scalar" or "vector". The scalar indicates isotropic changes induced by un-polarized, or even by polarized, light [11]. The vector includes anisotropic changes induced by linearly polarized light [12,13]. Effects of circularly polarized light such as photoinduced gyrotropy remain to be studied [13], and no related deformations have been known, to the author's knowledge.

The other classification is made as "irreversible", "reversible", "memorable", or "dynamic (transitory)". The irreversible change appears as a kind of stabilization process of as-prepared films. The reversible change is a de-stabilization process, which adds some structural disorder to annealed films and bulk glasses. Accordingly, the change can be recovered in principle by annealing, as demonstrated for volume changes [14]. However, deformations such as giant photo-expansion accompany macroscopic material flows [15], so that complete thermal recovery may be practically difficult due to sample vaporization. On the other hand, for the vector change, classification into the irreversible and reversible is confusing, since a polarization-dependent change appears under well-illuminated states of both as-prepared and annealed films. We here refer it as "memorable". Lastly, the dynamic (transitory) scalar or vector changes may occur during light irradiation, when electrons and holes are photo-excited.

2-2. Scalar deformation

The irreversible scalar deformation appears as a volume contraction [11]. For instance, as-evaporated As_2S_3 films on to room-temperature substrates undergo a contraction of ~1% in volume [16], which can be related to photopolymerization of molecular fragments as As_4S_4, S clusters, and so forth. Such a process has been commercially utilized also in organic photoresists. In obliquely-deposited Ge-Se films, which contain a large fraction of voids, the contraction amounts to ~10% [17,18], which is ascribed to void collapsing [18], probably arising from photo-reduced surface tension (viscosity). Vateva has reported irreversible expansion in Ge-chalcogenide films [19], while it may be governed by photooxidation, a photochemical reaction, not a bulk physical effect.

The reversible scalar deformation appears as volume expansion or contraction [14,15,20-23], which depend upon materials. Such opposite changes can be understood as manifestation of dense or loose atomic packing of the material [20]. For instance, As_2S_3 glass is relatively dense, and accordingly, the de-stabilization process accompanies an expansion of ~0.4% at room temperature [14]. The expansion can become seemingly greater than ~5% [15], if focused sub-gap illumination induces volumetric viscous flows. This giant volume expansion, which occurs with an *increase* in refractive index, has been employed for fabrication of self-positioned spherical and aspherical micro-lenses [11].

The dynamic stress relaxation has long been studied, since a pioneering report by Vonwiller for Se [24]. Some researchers employed bimetallic structures [25,26], and others applied indentation methods [3,27] to the measurements. However, most of these studies shed bandgap light (on Se), in which case it is difficult to distinguish photon and temperature effects upon observed characteristics. On the other hand, Hisakuni and Tanaka have demonstrated volumetric stress relaxation, i. e., photoinduced fluidity or glass-transition, using sub-gap light [28,29]. The fluidity becomes greater at lower temperatures, which unambiguously demonstrates an athermal effect.

The dynamic scalar deformation has been demonstrated in Shimakawa's group [30]. In $As_2S(Se)_3$ and Se, the volume expands during bandgap illumination, which is qualitatively consistent with the electro-structural expansion computer-simulated for Se [31] and phenomenologically modeled [30,32]. However, a clear distinction between electronic and thermal expansions in experiments seems to be difficult.

2-3. Vector deformation

The first vector deformation, a dynamic "opto-mechanical (OM) effect" has been discovered by Krecmer et al. [33]. They use bilayer samples consisting of small elastic cantilevers and As-Se(S) films (Fig. 4). The sample deflects up and down in response to the direction of the electric field of incident linearly polarized bandgap light. This polarization dependence manifests that the temperature rise, which gives a greater contribution to the deflection [34], cannot be responsible for the OM effect. Krecmer et al. suggest an atomic orientation model, which may be compared with in situ atomic structural changes [35,36].

For the memorable, Saliminia et al. [37] have found an anisotropically M-shaped deformation. They report that, when a film is not very thick, the scalar expansion [15] appearing under illumination with linearly polarized bandgap light gradually changes to an M-shaped deformation along the electric field (see, Fig. 1). They also propose a model assuming a gradient-intensity force, a

kind of optical forces, as a trigger of the deformation.

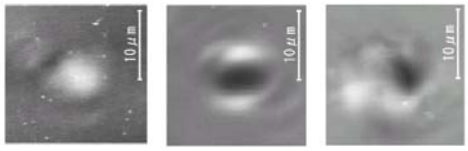

Fig. 1. A deformation sequence (0.5, 30 min, 25 h) in an annealed As_2S_3 film (thickness of ~2 μm) deposited upon a glass substrate under illumination with focused linearly (vertical) polarized light of 2.3 eV and 0.1 mW (~200 W/cm^2) [38]. The illumination gives a scalar expansion (0.5 min, left) which changes to an anisotropic M-shape deformation (30 min, center), and ultimately to a chaotic deformation after a prolonged illumination (25 h, right).

Tanaka and Asao have studied relationships between the scalar expansion, the M-shape deformation, and the OM effect [34,38]. Dependences upon light intensity and so forth suggest that the scalar expansion and the M-shape deformation have similar atomic motions. A difference lies in the directions of material flows, which are toward the free surface in the scalar and along the film surface in parallel to the electric field in the M-shape deformation [38]. They also have criticized the Saliminias' optical model, and propose an atomic disordering model on the premise of layer orientation [38]. In addition, on the basis of detailed experimental results, they have suggested that the M-shape deformation and the OM effect, only the known vector deformations at that time, have different origins [34].

Very recently, Trunov et al. [27] and Tanaka et al. [12] have discovered anomalous deformations. Trunov et al. demonstrate that a scratch made on the surface of As-Se films gives a vector response; scratches parallel and orthogonal to the electric field of linearly polarized light becoming fainter and greater, respectively. Tanaka et al. point out a similar response for cracks in annealed As_2S_3 films.

It is noted here that the dynamic and memorable changes arise through different mechanics. For instance, the dynamic OM effect is possibly governed by the elasticity of cantilevers made from Si_3N_4 etc. On the other hand, in all the memorable changes, it is reasonable to assume that a stress is converted to a strain through the photoinduced fluidity [28,29], or the change is resulted from viscous (or viscoelastic) deformations. Although the atomic mechanism of the photoinduced fluidity remains speculative, more problematic is the triggering force.

Is the motive force in these vector deformations atomic, optical, or anything else? To get insight into the force in simpler sample forms, we investigate the response of As_2S_3 films having different lateral dimensions. As_2S_3 may be an ideal material in this kind of optical experiments for obtaining reproducible results, due to its stability in glassy and compositional states.

3. Experiments

Samples were annealed As_2S_3 films with a thickness of ~2 μm laid on silicone grease (Toray, SH111) layers with thicknesses of 20-30 μm. These thicknesses were measured from interference fringes in optical transmittance for the film and from microscope inspections for the grease. Note that the grease was stable under annealing treatments at ~180 °C. Excitation light, obtained from a solid state laser (Uniphase, 4601), was linearly polarized with a photon energy of 2.3 eV (λ = 532 nm, $\alpha^{-1} \approx$ 20 μm), giving an irradiance of 40 mW to an unfocussed spot of ~0.5 mm in diameter (~20 W/cm^2). Deformations were inspected using a digital microscope (Keyence, VHX-100).

4. Results

Fig. 2 summarizes photoinduced deformations of As_2S_3 films with different lateral dimensions laid on grease. It is plausible that the laser illumination heats As_2S_3 films, while a temperature rise can spread to grease, and accordingly, thermal effects may be neglected in the following behaviors.

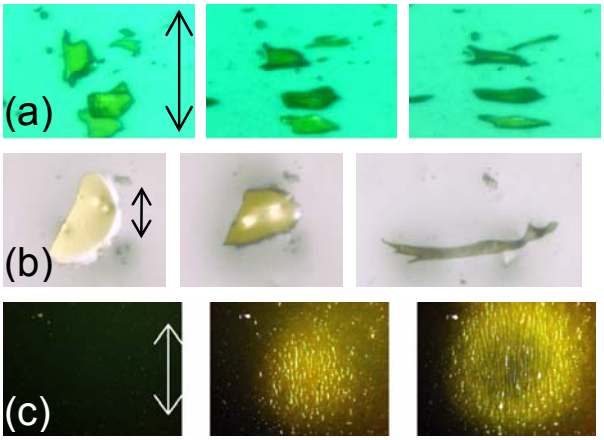

Fig. 2. Exposure-time sequences showing photo-deformations (motions) of As_2S_3 on grease in (a) powders (0, 15, 30 min), (b) a flake (0, 10, 120 min) [39], and (c) a film (0, 8, 60 min) [40]. The vertical arrows represent the direction of light polarization, the lengths corresponding to (a, b) 50 μm and (c) 0.5 mm.

As shown in Fig. 2(a), As_2S_3 powders (~10 μm) rotate to an orientation in which the film plane is orthogonal to the electric field of light. After the rotation, the powder tends to elongate laterally. A flake (~100 μm) on grease in

(b) undergoes, as reported previously [9], U-shape deformation along the electric field and successive orthogonal elongation with screwing. Similar deformations appear in flakes laid on frosted glass [9] and in cantilever-like samples [12,39]. On the other hand, (c) a wider film than the light spot laid on grease has undergone a wavy corrugation in an irradiated spot, the wave direction being orthogonal to the electric field [40]. Note that there exist three differences between this corrugation and the M-shape deformation (Fig. 1, center); the film being laid on grease here and deposited to glass there, the light being unfocussed and focused, and the most contrastive being the present corrugation *orthogonal* to the electric field and the M-shape deformation *parallel* to it.

5. Discussion

5-1. Radiation-force model

We suggest that all the photoinduced changes in As_2S_3 on grease in Fig. 2 (except the spiraling in (b)) can be understood, at least qualitatively, as triggered by radiation forces. The radiation force considered here is the optical torque and the optical pressure.

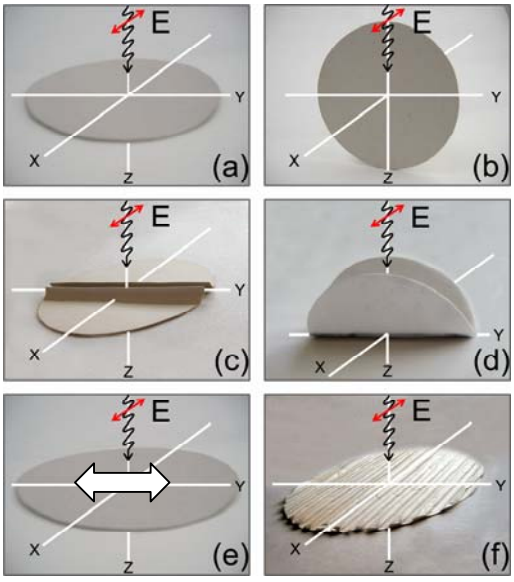

Fig. 3. Schematic illustrations of rotation and deformations of As_2S_3 induced by radiation forces. (a) Upon As_2S_3, linearly polarized bandgap light having a wider spot than the sample impinges. (b) The optical torque, arising from photon momentum and spin, rotates the disk if it is free, (c) lifts up the cracked edges in the film on substrates, and (d) deforms the flake on grease as a U shape. (e) The optical pressure, or the photon momentum, of scattered light elongates a flake orthogonal to the electric field. The elongation may appear as (f) a wrinkling in a circular spot of a wide film laid on grease.

The optical torque [7,8], arising from the photon momentum and spin, forces an As_2S_3 disk to rotate to an orientation in which the disk plane is orthogonal to the electric field (Fig. 3(b)). In this orientation, the film dimension along the electric field is minimal, and accordingly, the electromagnetic energy proportional to $\int\varepsilon_x|E_x|^2dV$ (ε_x and E_x are the dielectric constant and the electric field along the x-direction in the film, an V is the film volume) is minimal due to the so-called negative photoinduced birefringence ($\varepsilon_x = n_x^2$) [41] and maximal depolarization fields [12]. That is, this orientation is energetically the most stable. The rotations of As_2S_3 powders in Fig. 2 and of orpiment powders [9] can be ascribed to this rotational force.

The U-shape deformation of a flake on grease in Fig. 2 is also understandable (Fig. 3(d)). In this case, the flake on grease is difficult to freely rotate due to its lateral dimensions of ~0.1 mm, being greater than the grease thickness. Instead, through the photoinduced fluidity [28,29], the flake deforms as a U-shape, in which an effective sample thickness along the electric field becomes smaller.

The crack deformation reported in Ref. 11 can also be accounted for straightforwardly (Fig. 3(c)). The edge is lifted up, becoming orthogonal to the electric field by the optical torque. The scratch deformation [3,27] may be understood in a similar way.

On the other hand, as known from the Rayleigh scattering, the incident light on the film is scattered more strongly to the orthogonal direction (y-axis in Fig. 3) to the electric field. The strength may be estimated from a cat-whisker pattern appearing on illuminated Ag-chalcogenide films [2,42]. And, the scattered light exerts optical pressure upon the side edges in Fig. 3(e), forcing the disk to elongate in the y direction.

The elongation by optical pressure can give rise to several deformations. First, it is plausible that this force causes the orthogonal elongation after the U-shape deformation (Fig. 2(b)). (The helical deformation appearing with the elongation may be related to the photoinduced gyrotropy [13].) Second, if a film is wider than a spot size of light, such an orthogonal elongation is suppressed by surrounding un-illuminated regions of the film. Then, the elongation is converted to a wrinkling pattern, Fig. 3(f), in a film-on-grease system [43-45]. The present study has also demonstrated that an As_2S_3 film (not a flake) laid on a frosted glass surface, where no viscous layer exists, undergoes a buckling vector deformation upon illumination, which is consistent with the wrinkling process. Third, the chaotic deformation appearing after the M-shape deformation in the film on a glass substrate (Fig. 1, 25 h) [38] may be influenced by this optical pressure.

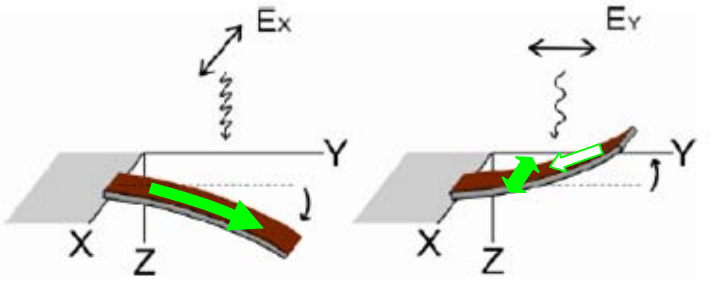

Fig. 4. Schematic illustrations of opto-mechanical effects with the optical pressure (green) and contraction (white). Thermal expansion is neglected for clarity.

Finally, it is suggested that the optical pressure can also give an explanation for the OM effects [12,33,34,39]. A difference between the dynamic deflection in bilayer cantilevers and the memorable in monolithic As_2S_3 cantilevers is that the former is governed by the elasticity of thick substrates (such as Si_3N_4 and mica) and the latter occurs through the photoinduced viscous deformation [39]. However, the motive forces in both deflections are ascribable to the optical pressure. When the electric field is perpendicular to the cantilever axis (Fig. 4, left), strongly scattered light along the axial direction produces the optical pressure upon the end, forcing to elongate As_2S_3. The dynamic OM effect appears as the consequence. In the monolithic sample, the As_2S_3 cantilever has a thickness of ~10 μm, which is not much smaller than the penetration length (~20 μm) of bandgap light (~2.3 eV). Accordingly, the irradiated surface tends to more elongate than the rear surface, and the cantilever deflects toward the propagation direction of light. On the other hand, when the electric field is parallel to the cantilever axis (Fig. 4, right), the chalcogenide film tends to widen with the optical pressure, which may shorten the film along the cantilever axis with a magnitude determined by the Poisson ratio. In addition, the optical torque can assist such a movement, in a similar way to the lifting-up of the cracked edge (Fig. 3(c)). In a monolithic cantilever, these optical effects are prominent again on the irradiated surface, and as the result, the cantilever bends toward the direction of incident light.

5-2. Quantitative analyses

Can we quantitatively understand the rotation and deformations using the radiation-force model? The rotation of As_2S_3 and orpiment [9] powders can be assumed to be governed by the optical torque and the viscosity of grease. And, rough calculations have suggested that the rotation speed is reasonable with the present model [9,46].

On the other hand, the deformation remains to be studied. The problem for the optical torque has been considered previously [12,39], and we here discuss the optical pressure. The optical pressure P is estimated, under neglection of the refractive index [5,6,47], as $P \sim I/cA$, where I is the light intensity, c the light velocity in vacuum, and A a pressurized area. This equation gives, for I = 10 mW and A = 50 μm^2, P ~ 1 N/m^2, which is far insufficient to produce a visible deflection of an *elastic* cantilever of mm sizes (~10^5 N/m^2 in experiments in Ref. 34). We should then take the photoinduced fluidity into account, in which accumulated strains through viscous motions may cause the deformation.

Hence, further analyses depend upon the value of photoinduced fluidity, or the viscosity. In [28,29], we have obtained a viscosity of 10^{12} poise, while a recent experiment on the monolithic OM effect, under estimated optical forces, gives 10^1 poise (= 1 Ns/m^2) [39]. There exists a surprising difference of more than ~10 digits off. However, such a difference may owe to the motive sources, which are externally applied in the photoinduced fluidity [28,29] and internally photo-generated in the present self-deformations. Some cooperative dynamics with the optical force and photoinduced fluidity in microscopic scales may be responsible for the present deformations. For instance, we may speculate that the both concurrently occur at selected atomic positions.

6. Conclusions

We have shown that several vector deformations in As_2S_3 can be interpreted, at least qualitatively, as triggered by the optical force, not by commonly-suggested atomic motions. However, for elucidation of the present idea, we need further quantitative studies.

The optical force has been widely utilized for laser tweezers [5] and is demonstrated to be promising for actuation of nano-machines [6]. The present study suggests its potential for athermal optical processing of viscous solids, including photo-fluid chalcogenides, heated oxide glasses, and so forth.

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