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Anomalous anisotropic deformations of As_2S_3 flakes induced by linearly-polarized bandgap illumination

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ABSTRACT

Semi-free As_2S_3 flakes undergo visible-scale anisotropic deformations when exposed to linearly-polarized bandgap illumination. We investigate the behavior and also those in amorphous Se, GeS_2, $AgAsS_2$, and crystalline As_2S_3. These results suggest that the deformation occurs through photo-induced birefringence, photo-induced fluidity, and optical force.

1. Introduction

Soft materials including dye-doped polymers and chalcogenide glasses are known to anisotropically deform when exposed to photo-electronic excitations [1,2]. The deformations in polymers are relatively prominent, which may be triggered by *trans–cis* conformation changes in dye molecules such as azo-benzene [1]. On the other hand, illumination of linearly-polarized bandgap light upon As–S(Se) films induces transitory deflection of cantilevers [2,3], permanent M-shape deformation [2,4], and so forth [2]. Mechanisms of these phenomena in the chalcogenide are speculative, while almost all the deformations have been accounted for using some photo-electro-atomic (ionic) processes [2–4].

In the beginning of 2007, Asao, who was a student in the authors' group, noticed an anomalous deformation when investigating known anisotropic deformations [5]. Fig. 1 shows his result, in which (a) cracked flakes of annealed As_2S_3 films on a slide glass change to (b) horizontal bars after an exposure of linearly-polarized (vertically) bandgap light. The bar direction was always orthogonal to the electric field of the light, while the deformation shape was not reproducible. For instance, the right-hand photograph, which appears as an eye glass, shows a side view of the central thick bar in (b). In other cases, however, the shape was circular, snake-like, etc. Nevertheless, to the authors' knowledge, no such dramatic photo-induced deformations had been reported for any solids, except photo-synthetic plant growth, and the feature should be worth exploring.

Later experiments have succeeded in obtaining reproducible deformation by using semi-free flakes as described in 2 [6]. The non-reproducibility was caused by spontaneous sticking of the flakes to glass plates. Tanaka has also proposed that motive force of the deformation seems to arise, not from atomic forces as commonly suggested [2–5], but from the optical force [6]. However, the idea is challenging, which still contains qualitative and quantitative problems [7]. In the present work, therefore, we re-examine some features of the photo-induced anisotropic deformation in chalcogenide glasses.

2. Experiments

Typical experimental conditions were as follows: Samples were semi-free As_2S_3 flakes with thicknesses of 1–5 μm and lateral dimensions of ~0.1 mm. The flake was obtained through peeling As_2S_3 ($E_g \approx 2.4$ eV) films, which had been evaporated in vacuum and annealed at ~200 °C, off glass substrates. Then, the As_2S_3 flake was put on silicone grease or frosted glass, which made the flake semi-free. An exciting light source was a solid-state laser emitting linearly-polarized 2.3 eV ($\lambda = 532$ nm) photons with intensity of 50 mW. The beam was unfocussed, giving rise to a spot of ~0.5 mm in diameter, and accordingly, it provided nearly uniform illumination of ~10 W/cm^2 to the flake.

3. Results

Fig. 2 shows a deformation sequence. A circular flake with lateral dimensions of ~0.1 mm and a thickness of 4 μm is put on sil-

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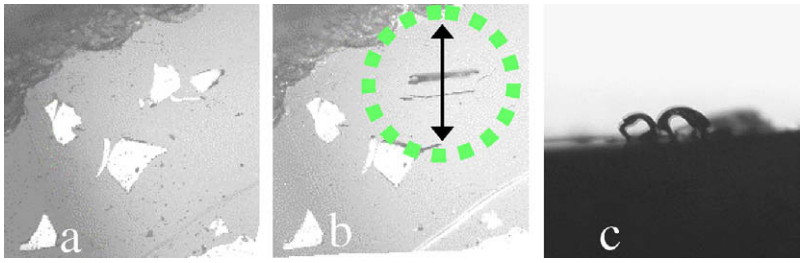

Fig. 1. (a) As_2S_3 flakes on a slide glass and (b) after an exposure to linearly-polarized (vertical) 2.3 eV light with intensity of 40 mW and a spot diameter (dotted circle) of ~0.5 mm for 80 min (c) shows a side view of the thick horizontal sample near the center in (b).

Fig. 2. A sequence of photo-deformation of a circular As_2S_3 flake laid on grease upon illumination to linearly (vertically) polarized 2.3 eV laser light of 40 mW at exposure times of (a) 0, (b) 10, (c) 80, and (d) 300 min. The green bar in (d) represents the direction of light polarization, and the length is 0.1 mm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

icone grease (a), and is exposed to the excitation light, which is vertically-polarized in these photographs. The sample first curls as a U-shape along the electric field (b), folds and elongates to the directions orthogonal to the electric field (c), and finally screws (d). Prolonged illumination continues to lengthen the screw to ~0.2 mm, which seems to be limited by the size of light spot. On the other hand, thinner flakes with a thickness of ~1 μm tended to become thread-like [6,7].

Spectral dependence has been measured using several lasers emitting photons of 1.8–2.6 eV [6]. A deformation efficiency, which is defined as the inverse of absorbed photon numbers ($\alpha Nt \geqslant 10^{23}$ photons/cm^3) for inducing a fixed U deformation, shows a broad peak at ~2.2 eV, just below the Tauc gap of 2.4 eV. That is, bandgap illumination is effective to the deformation, which suggests that photo-electronic excitation is required.

Behaviors in other materials have been investigated. First, polished thin (10–20 μm) flakes of melt-quenched GeS_2 glass ($E_g \approx 3.2$ eV) have undergone the U-shape deformation and orthogonal elongation upon illumination of 3.1 eV light with intensity of 10–40 W/cm^2. (We employed the polished bulk flakes, because evaporated GeS_2 films are more defective, even being annealed [8].) However, the spiral (Fig. 1(d)) and thread did not appear within exposure times of ~16 h, which might be insufficient. The deformation efficiency, which was examined at $\hbar\omega$ = 2.3–3.8 eV, showed a peak at 3.2 eV, the feature being consistent with that in As_2S_3 [6]. $AgAsS_2$ films, which were prepared through photodoping, also exhibited the U-shape deformation upon illumination of 2.0 eV light of ~10 mW for a few hours. These results suggest that the photo-deformation, or at least the U-shape deformation, is universal to chalcogenide glasses. Second, however, upon illumination of 1.8 eV light, amorphous Se films have undergone different deformations, which are isotropic or anisotropic [6]. The difference may be due to the low glass-transition temperature of ~30 °C. Third, as shown in Fig. 3, flakes of crystalline As_2S_3 (orpiment), which is known to be a layer-type crystal, have provided interesting responses [6]. The flakes laid on grease have rotated so that the layer plane becomes perpendicular to the electric field of linearly-polarized light of 2.3 eV.

4. Discussion

What is the mechanism of the anisotropic deformation? At least, two phenomena must contribute. One is the photo-induced fluidity [9,10], which will convert generated stress to deformation. However, this phenomenon is scalar, i.e. isotropic, and some anisotropic phenomena such as photo-induced birefringence [11,12] should take a certain role. In addition to these, we need some triggering force for the deformation. Several possibilities are examined as follows:

Since the deformation is anisotropic, it is difficult to envisage thermal force. In addition, it should be mentioned that for the U-shape deformation the reciprocity law between light intensity and exposure time holds at intensities of 0.4–40 mW [6], which evinces that some kind of non-thermal deformation occurs.

Optical gradient force [4,5] can be a candidate. We already know that illumination of tightly-focused (~5 μm) linearly-polarized beams to As_2S_3 films provides an anisotropic M-shape deformation [4]. The mechanism is controversial [13], while it is undoubtful that the light-intensity gradient is responsible for motive force. By contrast, the present deformation occurs when the light spot (~0.5 mm) is greater than the sample lateral size (~0.1 mm), which strongly suggests that the intensity gradient cannot govern the present observation.

We may envisage some electro-static force. For instance, the flake anisotropically charges under illumination with unknown mechanisms such as carrier diffusion [14] or photo-emission, and then, Coulombic attraction or/and repulsion stresses the flake. However, the deformation has appeared also in As_2S_3 flakes laid on Al foils, although with worse reproducibility in shape, which is probably due to flake-foil sticking (Fig. 1). Therefore, the electro-static mechanism seems to be less plausible.

Anisotropic photo-crystallization may occur. Since crystalline As_2S_3 is a layer type, the crystallization may cause anisotropic deformations. However, X-ray diffraction and micro-Raman-scattering spectroscopy could detect no appreciable atomic changes. For instance, as shown in Fig. 4, Raman-scattering spectroscopy of elongated flakes such as the one in Fig. 2(d) provides the conven-