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Photoinduced Macroscopic Vector Deformations in Chalcogenide Glasses

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ABSTRACT

Photoinduced vector deformations in amorphous Se films on viscous and rigid substrates have been studied for comparison with those in As_2S_3 . In both the films, illumination of focused and unfocused linearly-polarized bandgap light produces, respectively, anisotropic M-shape deformations and wavy wrinkles. The M-deformations occur in parallel to the electric field, but the wavy directions are contrastive; parallel and orthogonal to the electric field in Se and As_2S_3 films on grease. The unfocused illumination also produces corrugations in As_2S_3 films on glass substrates. We assume that atomic and optical forces are responsible for these deformations.

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Chalcogenide

Photoinduced effect

Vector deformation

Light-matter interaction

1. Introduction

Soft materials such as biological cells [1], dye-doped polymers [2], and amorphous chalcogenides [3,4] are known to exhibit marked deformations upon light illumination. It has also been known for a long time that in many solids an exposure of a linearly-polarized laser beam produces surface ripples, in which the rippling direction and periodicity seem to be governed, respectively, by the electric field and wavelength of light [5-8]. Unified understandings of these photoinduced deformations are worth challenging, which may open a new scientific paradigm of light-matter interaction and applications to opto-deformable devices.

For the amorphous chalcogenide, recent studies have demonstrated several kinds of photoinduced vector (polarization-dependent) deformations, as reviewed in [3,4]. The deformations accompany no appreciable anisotropic changes in X-ray diffraction and/or Raman-scattering spectroscopy, and accordingly, we should explore the deformation mechanisms through other approaches. In addition, interrelations between some deformations are vague. For instance, the present authors have recently demonstrated that, in $\text{As}_2\text{S}(\text{Se})_3$ and Se films deposited upon silicone grease layers, the directions of photoinduced wrinkling are contrastive; orthogonal and parallel to the electric field of linearly-polarized bandgap light [9], while the reason remain highly speculative.

In the present work, we will comparatively study the photoinduced vector deformations in As_2S_3 and Se in more details. It is demonstrated that there exist similarities and differences in the deformations of these two materials. The deformation mechanisms and motive forces are discussed.

2. Experiments

Samples were amorphous Se and As_2S_3 films (1 – 10 μm in thicknesses) which were evaporated onto two kinds of substrates, oxide glass plates and silicone grease (Toray SH111) layers (a few tens of μm in thicknesses) covering the glass plates. The present measurements evaluated the grease viscosity as $10^3 - 10^4$ Pa's, which tended to decrease with an increase in shear rate. After evaporation, Se samples were stored for stabilization in the dark for a few days at room temperature, since the glass-transition temperature is $\sim 35^\circ\text{C}$. As_2S_3 samples were annealed in Ar atmosphere at $\sim 180^\circ\text{C}$, slightly below the glass-transition temperature. Light sources employed were several kinds of cw lasers emitting linearly polarized beams with photon energies of 1.8 – 2.6 eV, intensities of 10 – 50 mW, and (Gaussian) beam diameters of 0.7 – 2.0 mm. For investigation of temperature dependence, samples were stored in a vacuum cryostat, the temperature of which was controlled using a Peltier device. Surface deformations were inspected and photographed using a digital microscope (Keyence, VHX-100), as in previous experiments [9-12]. X-ray diffraction patterns were obtained using a rotating Cu anode (Rigaku, RU-300), a LiF monochromator (for the $\text{K}\alpha$ line), a Laue camera, and

high-sensitive photographic plates with exposure times of ~8 h.

3. Results

Fig. 1 shows photoinduced deformations in a-Se films with different thicknesses (1 – 10 μm) on grease. The samples have been exposed for 6 h to an unfocused 1.8 eV laser beam ($\sim 1 \text{ W/cm}^2$), which has a penetration depth of $\sim 30 \mu\text{m}$. As shown in the left-end photograph, the thinnest film ($\sim 1 \mu\text{m}$ thick) has undergone no anisotropic deformations under any exposure conditions. For all the other films we see corrugations, the wavy direction being *parallel* to the electric field (vertical in Fig. 1) of light [9], which is in marked contrast to that in $\text{As}_2\text{S}(\text{Se})_3$ [9,10]. We also see, as exemplified in a side view of the second photograph, that these sinusoidal corrugations are manifestations of wrinkling deformations, which suggests that the film elongates in the wavy direction. Since the elongation is restricted by peripheral un-illuminated regions, it becomes to be the wrinkle. A detailed analysis of Fig. 1 has shown that the periodicity (0.1 – 0.4 mm) and amplitude ($\leq 40 \mu\text{m}$) of the wrinkle increase with the film thickness. These thickness dependences are consistent with the idea predicted by the conventional wrinkling theory [13]. For instance, it is reasonable to assume that the thinnest film cannot generate sufficient stresses, which surmount the grease viscosity, and hence no deformations appear.

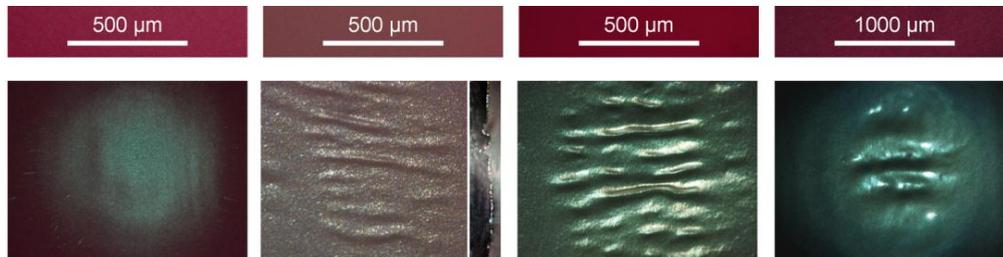


Fig. 1. Variation of photoinduced wrinkles in a-Se films on grease with an increase in the film thickness from 1 (left), 2, 3, and 10 (right) μm . The electric field of linearly polarized light is vertical in these photographs. The right-hand side view of the 2 μm film shows its cross section (side view).

Spectral dependence was investigated for 2 μm -thick Se films using 1.8, 2.0, and 2.2 eV laser beams. Under the same absorbed doses ($\sim 10^8 \text{ J/cm}^2$), 1.8 eV light produced the most prominent wrinkle with the highest efficiency, while 2.2 eV light yielded no deformations, which is attributable to a penetration-depth effect. The penetration depths of 1.8, 2.0, and 2.2 eV light are estimated, respectively, at 30, 2.5, and 0.2 μm , the last being much ($\sim 1/10$) smaller than the film thickness. Such spectral dependence seems to be consistent with that obtained for As_2S_3 films [10].

Light intensity was varied at $0.1 - 2 \text{ W/cm}^2$ (3 – 60 mW) for 2.0 eV light. Under the same incident doses ($\sim 10^4 \text{ J/cm}^2$), the wrinkle in 2 μm -thick Se films became finer with an increase in the

intensity; the periodicity decreasing from ~ 130 to ~ 70 μm with a nearly constant amplitude of ~ 15 μm . These values gave a fractional elongation, which was evaluated from the sinusoidal shape [10], ranging over 5 – 10%. Qualitatively the same behavior was obtained for 1 μm -thick As_2S_3 films under exposures to 2.3 eV light of 3 – 40 mW [10]. These intensity dependences suggest that the films become fluidal under intense illumination, which can be attributable to the intensity dependence of photoinduced fluidity [14,15].

Temperature, at which illumination and observation were made, was varied at $-30 \sim +35^\circ\text{C}$. In 2 μm -thick Se films, which were exposed to 1.8 and 2.0 eV light, the wrinkling appeared most efficiently at $\sim 20^\circ\text{C}$. It seems that deformations at -30 and 35°C are suppressed, respectively, by a viscosity increase of the grease and enhanced thermal relaxation of a-Se films. We also varied temperature at $-30 \sim +80^\circ\text{C}$ for 1 μm -thick As_2S_3 films, which were exposed to bandgap light (2.3 eV, 10 W/cm^2). The wrinkling efficiency was nearly constant at $-30 \sim +25^\circ\text{C}$, and it substantially reduced (to $\sim 1/5$) at $+80^\circ\text{C}$, which may also reflect thermal relaxation effects.

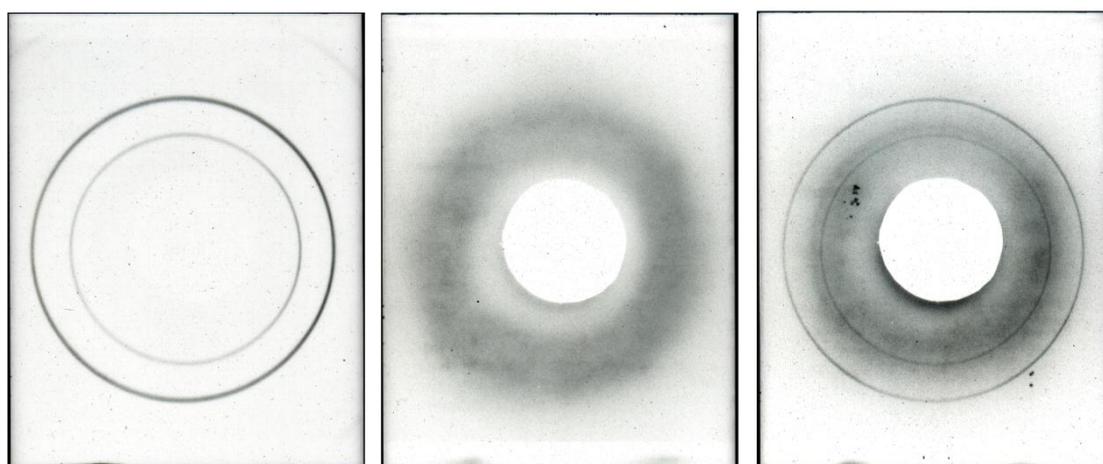


Fig. 2. X-ray diffraction patterns of c-Se (left), a-Se before illumination (center), and a-Se after photoinduced deformation (right), in which the elongation direction is vertical. The dots at upper left in the right photograph are noises.

We have also examined atomic structures using x-ray diffraction and Raman-scattering spectroscopy. Fig. 2 shows x-ray diffraction patterns obtained using transmission x-ray diffraction. We see two clear rings in c-Se (left) at $2\theta \approx 23^\circ$ (inner) and $\sim 30^\circ$ (outer), which are ascribed to $\langle 100 \rangle$ and $\langle 101 \rangle$ peaks of trigonal Se. A-Se before illumination (center) presents a broad halo ring at around $\sim 20^\circ$. The halo intensity may vary along the circular direction, which is due to instrumental artifact. The illuminated film (right) presents the halo and the weak two crystalline rings, but we cannot point out reliable anisotropy for these patterns (even after a few trials and numerical analyses of obtained photographs). Raman-scattering spectroscopy has neither given meaningful anisotropy.

In addition, we performed subsidiary experiments for flakes of a-Se and c-Se to those previously reported [9]. Upon illumination of un-polarized light, a-Se flakes appeared to isotropically shrink, which is similar to the behavior in a-As₂S₃ [11]. It was also confirmed that c-Se (trigonal) flakes on grease undergo no deformations.

Finally, Table 1 compares the variation of deformations in As₂S₃ and Se films with the substrate and the size of light spots. As shown in the upper left-hand cells, under exposures to focused (10 – 20 μm) linearly polarized bandgap light, both the films on glass substrates exhibit the anisotropic M-shape deformation [16-18]. The films on grease (upper rights) deform irregularly, while As₂S₃ tends to be M-shaped. On the other hand, exposures of unfocused laser beams to the films on grease (lower rights) produce wrinkles, the wavy directions being orthogonal to the electric field in As₂S₃ and parallel in Se, as reported previously [9]. The transition from the M to wrinkle patterns in As₂S₃ films on grease has appeared at the light-spot diameter of ~50 μm.

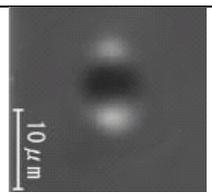
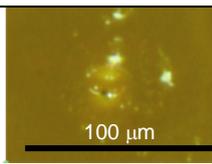
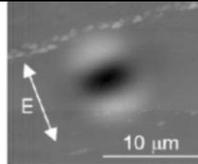
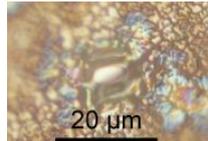
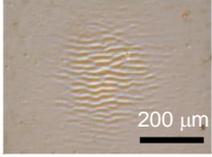
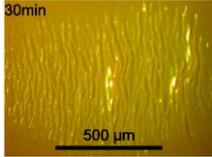
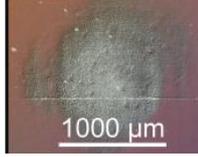
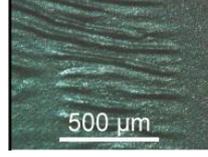
As ₂ S ₃	glass	grease	Se	glass	grease
focus			focus		
un-			un-		

Table 1. Typical photoinduced vector deformations of As₂S₃ (left) and Se (right) films with a few micron thicknesses on glass and grease. The films have been exposed at room temperature to focused (10 – 20 μm) and un-focused (0.5 – 1 mm) laser beams having photon energies of 2.3 eV for As₂S₃ and 1.8 eV for Se. Unless otherwise specified, the electric field is vertical in these photographs. The photographs of glass-focus As₂S₃ and Se are reproduced from [17] and [18], and the grease-unfocus Se is the same with that in Fig. 1. The photograph of glass-unfocus As₂S₃ corresponds to the state at 10 h in Fig. 3.

In addition, the present work has uncovered that As₂S₃ films on glass substrates exhibit low corrugations *parallel* to the electric field (glass-unfocus As₂S₃ in Table 1). As exemplified in Fig. 3, under illumination of linearly-polarized bandgap light, the height h linearly increases with the exposure time, while the periodicity Λ appears to approach a fixed value of ~25 μm. We also confirmed that these two values increase with an increase in the film

thickness of 1 – 5 μm . Under similar exposure conditions, a-Se films have shown no anisotropic deformations (glass-unfocus Se in Table 1), while there may be some photo-effects.

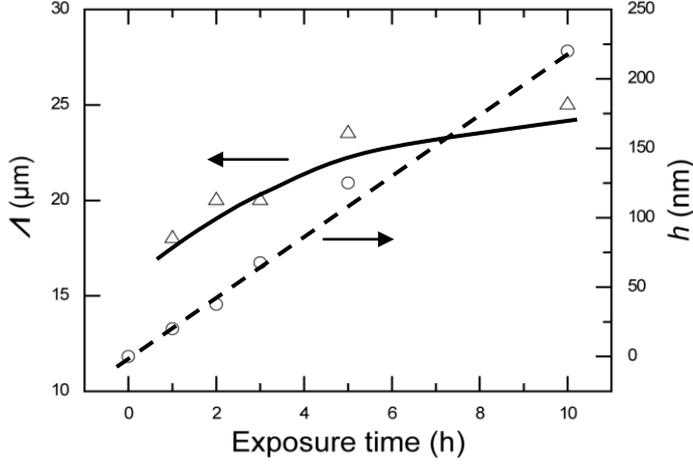


Fig. 3. Periodicity A and height h of a surface corrugation in an As_2S_3 film (5 μm in thickness) on glass as a function of exposure time of unfocused 2.3 eV and 10 W/cm^2 light. The deformation at 10 h is shown in Table 1.

4. Discussion

In short, we have seen similar features and a clear difference for the photoinduced vector deformations in Se and As_2S_3 . Under focused exposures, both the films on glass undergo the anisotropic M-shape deformation. For the film on grease under unfocused illumination, both the materials exhibit qualitatively the same wrinkling behaviors in respect of the film thickness, excitation photon energy, intensity, and temperature. However, the wrinkling directions are distinctly different; parallel and orthogonal to the electric field in Se and As_2S_3 .

Tanaka and colleagues have proposed an atomic orientation model for the M-deformation [3,12,17]. The atomic model can be applied also to the M-deformation in Se, since both the materials consist of covalent layer (or chain) segments held together by van-der-Waals forces. Otherwise, it is plausible that a polarization-dependent optical gradient force [19], which is suggested for organic polymers, is responsible for the M deformation.

The group has also proposed an optical-pressure model for the wrinkling (orthogonal elongation) in As_2S_3 [9-12]. The deformation is assumed to occur through viscous flows, which are exerted by the optical pressure. It is plausible that the viscous deformation leaves no traces of atomically detectable changes, which is consistent with the no x-ray anisotropy (Fig. 2). In this model, the wrinkle (material flow and elongation) appears *orthogonal* to the electric field, reflecting the direction of optical pressure exerted by intensely scattered light. Accordingly, this model cannot give an explanation for the *parallel* wrinkle in a-Se. To

understand the parallel elongation, we may envisage, for instance, that oscillations of trapped electrons under optical fields cause material flows through electron-lattice interaction [9], which remains to be studied.

In addition, the present result in Table 1 has posed another problem. How can we interpret the corrugation *parallel* to the electric field in As₂S₃ films on glass? We here note that the corrugation periodicity (~25 μm) is much longer than those previously reported [5-8], which are governed by some kinds of light interference [6]. Otherwise, it is tempting to relate the corrugation to the M-shape deformation or to the parallel wrinkling in a-Se, since these three deformations seem to arise from material flows in the same (parallel) direction with the electric field. Specifically, the corrugation and the M deformation have quantitatively similar heights and lateral peak-to-peak lengths (periodicity). Further studies remain.

5. Conclusions

It has been demonstrated that at least three kinds of vector deformations appear in Se and As₂S₃ films. Those are the M-shaped deformation under focused illumination [16-18], the sinusoidal corrugation in As₂S₃ on glass under unfocused illumination, which is presently uncovered, and the wrinkling deformation in the film on grease under unfocused illumination [9,10]. Many similarities exist in these vector deformations, while a marked difference in Se and As₂S₃ is the wavy directions in the wrinkles. These observations suggest that several motive forces are responsible for the vector deformations in amorphous chalcogenide films.

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