PHYSICAL REVIEW B VOLUME 56, NUMBER 1 1 JULY 1997-I

Photoinduced anisotropic crystallization of amorphous Se

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(Received 13 December 1996)

Birefringence can be induced in Se films photocrystallized by linearly polarized light at ~350 K. The birefringence reaches ~0.1, which is approximately 1/10 of that in the hexagonal Se. X-ray-diffraction investigations suggest that the photothermally induced birefringence is caused by alignment of Se chain molecules. [S0163-1829(97)05425-8]

I. INTRODUCTION

Chalcogenide glasses are known to exhibit a variety of photoinduced phenomena.[1–3] Among these phenomena, photocrystallization[4] and the photoinduced anisotropy[5] are of special interests here.

Photocrystallization in amorphous (*a*-)Se has been studied by Dresner and Stringfellow.[4] They demonstrate that the crystallization rate of *a*-Se into hexagonal crystals can be enhanced as much as an order of magnitude by light illumination. Photocrystallization is also investigated in other materials such as As-Se (Ref. 6) and $GeSe_2$ (Ref. 7) using Raman scattering experiments. The mechanism of photocrystallization is believed to be photoelectronic; i.e., amorphous-to-crystalline structural changes are enhanced by photoexcited carriers, while the details of the electron-lattice interaction are still ambiguous.[6–9]

On the other hand, Zhdanov *et al.* have discovered that optical anisotropy can be induced in chalcogenide glasses subjected to the exposure of linearly polarized light.[5] For instance, in As_2S_3, illumination of linearly polarized light at room temperature can induce a dichroic shift of ~5 meV in the optical absorption edge and a birefringence of ~0.002.[1,10,11] Note that As_2S_3 possesses an optical band-gap energy of 2.4 eV and a refractive index of 2.6,[12] so that the induced anisotropies are relatively small. The photoinduced anisotropy is assumed to be induced through the orientation of some atomic units, while the structural entity of the units has been controversial.[13] The present authors have suggested on the basis of some experimental observations that the entity is considered to be anisotropic quasicrystalline segments,[11] the idea being originally proposed by Zhdanov *et al.*[5]

Taking these two phenomena into account, we may envisage a phenomenon which will be referred to as photoinduced anisotropic crystallization (PAC). That is, illumination of linearly polarized light may transform isotropic amorphous structures into oriented crystalline structures. In such a PAC phenomenon, the anisotropy may be greater than that in the conventional anisotropy appearing in amorphous phases. In addition, if the PAC phenomenon exists, the quasicrystalline model[5,11] proposed for the conventional photoinduced anisotropy will be reinforced. With these motivations in mind, we will study the PAC phenomenon.

The present paper demonstrates the PAC phenomenon in Se. The observed birefringence in Se films is discussed in relation to structural changes from amorphous to crystalline phase.

II. EXPERIMENTS

Se films with thicknesses of 0.1–1 μm were evaporated onto silica-glass substrates held at room temperature. Then the samples were annealed at 310 K for 3 days, which might be effective for structural relaxation.

Photocrystallization of Se films was induced using linearly polarized light with a wavelength of 633 nm emitted from He-Ne lasers. The light intensity was varied at 30 mW/cm^2 to 5 W/ cm^2. The temperature of the samples under illumination was varied at 300–360 K.

Birefringence at a wavelength of 633 nm was evaluated using a transmission-type ellipsometer at room temperature.[11] In this instrument, the phase difference of orthogonally polarized light, which was transmitted through a sample, could be measured. The probe-light intensity was reduced to 1 mW/cm^2, and accordingly no appreciable photoeffect was induced under the monitoring processes. The phase difference normalized to the film thickness provided the birefringence.

The structure of illuminated Se films was investigated using x-ray diffraction at room temperature. The diffractometer system consisted of a Cu target operating at 50 kV and 250 mA, a pole-figure goniometer, and a scintillation counter fitted with a graphite monochromator.

III. RESULTS

A. Optical

Figure 1 shows the birefringence $\Delta n = n(\parallel) - n(\perp)$ photoinduced at some temperatures T as function of exposure time. Here $n(\parallel)$and $n(\perp)$ denote the refractive indices parallel and perpendicular to the electric field of inducing light. As a reference, the change at 295 K is plotted by a dotted line.[11]

We see that the characteristics at $T < T_g$ and $T > T_g$, where T_g [$\simeq$310 K (Refs. 2 and 14)] is the glass-transition temperature of Se, are different. At the lower-temperature region, $-\Delta n$ monotonically increases with the exposure time. In contrast, at the higher-temperature region, $-\Delta n$ increases first, showing a maximum, and then decreases. Note that the samples illuminated at $T < T_g$ are amorphous,[11] while as described in Sec. III B the samples illuminated at

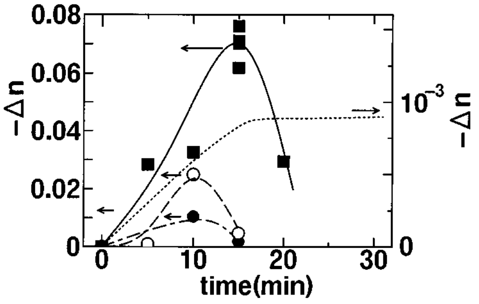

FIG. 1. Exposure-time dependence of the photoinduced birefringence $-\Delta n = n(\parallel) - n(\perp)$ in an a-Se film of 1 μm, 330 K (●), 340 K (○), and 350 K (■). For the 295 K result, which is plotted by a dotted line, the right-hand-side scale applies. The excited light intensity is 300 mW/cm^2.

$T > T_g$ exhibit crystalline diffraction peaks. Therefore, the high-temperature result is assumed to be a manifestation of the PAC phenomenon.

Figure 2 shows the maximal photoinduced birefringence as a function of T. At $T \simeq T_g$, no appreciable birefringence is induced. In contrast, at 350 K, Δn reaches ~ -0.07, which is much greater than that induced in the conventional photoinduced birefringence observed at $T < T_g$. Actually, the magnitude amounts approximately to 1/10 of the natural birefringence in hexagonal Se, 0.8.[14] At higher temperatures, conventional thermal crystallization,[4] which is inherently isotropic, seems to prevail. We can assume, therefore, that the PAC phenomenon critically depends upon photo and thermal effects.

Figure 3 shows the dependence of the maximal birefringence at 350 K upon the light intensity of illumination. Under intense illumination, the quantitative reproducibility of Δn becomes worse, which may reflect a sensitive influence of the photo and thermal effects. However, we can see a substantial increase in $-\Delta n$ with light intensity, which is likely to manifest a greater photoeffect.

Some comments may be needed here for the samples. First, the PAC phenomenon appeared similarly in Se films with thicknesses of 0.1–1 μm. In thicker films, the birefringence may decrease, probably because the penetration depth of 633-nm light is $\sim$1 μm.[2,14] Second, the PAC phenomenon could be induced only in Se films annealed beforehand at $\sim$310 K. If as-deposited Se films were exposed to illumination, e.g., at 350 K, the films were just crystallized, exhibiting the known spherulite morphology.[4] Naturally, no birefringence was detected, because the spherulite crystals were isotropic in the film plane. On the other hand, the films annealed at 310 K exhibited a different feature. That is, although the annealed film looked similar to the as-deposited films, after illumination, no appreciable spherulite crystals appeared. The films looked coarse textured and gray colored, accompanying a marked birefringence. Third, the birefringence obtained through PAC was retained stably if the sample was kept in the dark at room temperature. However, the anisotropy was reduced by illumination of circularly polarized light at temperatures above T_g. A reversible anisotropic change observed in conventional photoinduced anisotropy[5,10,11,13] was not demonstrated in the PAC phenomenon.

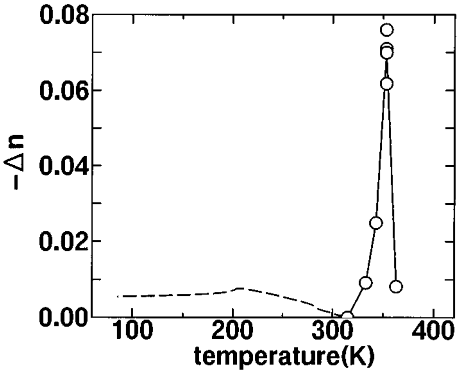

FIG. 2. Maximal photoinduced birefringence in Se as a function of temperature at which the sample is exposed to linearly polarized light of a wavelength 633 nm and an intensity of 300 mW/cm^2. The results at temperature below 320 K are also plotted (Ref. 11).

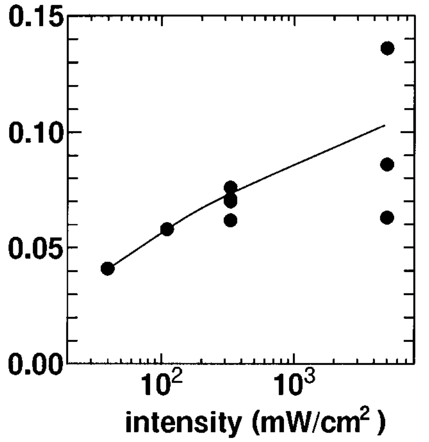

FIG. 3. Maximal birefringence $-\Delta n$ at 350 K as a function of the light intensity of illumination.

B. Structural

Figure 4 shows a series of x-ray-diffraction patterns of a photocrystallized Se film. The sample has been illuminated at 350 K for 15 min with linearly polarized light (300 mW/cm^2, 633 nm), which is demonstrated to provide a maximal birefringence (see Fig. 1). As illustrated in Fig. 1, in (a) and (b), the sample has been fixed to the goniometer in different ways: in (a), the electric field vector E of the light being horizontal, and in (b) it being vertical. In addition, diffraction patterns have been measured at some bowing angles γ, and accordingly, the diffraction pattern at $\gamma = 0°$ corresponds to the conventional Bragg arrangement.

We can see in Fig. 4 the four crystalline peaks at $2\theta = 24°$, 30°, 41°, and 45°. These peaks can be indexed, respectively, as 100, 101, 110, and 111 of the hexagonal Se crystal (see Fig. 5 for the unit cell).[15] As γ increases from 0° to 50°, the 100 peak dramatically decreases and the 101 peak exhibits a maximum. This γ dependence of 100 and 101 peaks indicates that Se chains orientate parallel to the film surface, since 100 planes are parallel to the c axis and 101 planes are inclined (Fig. 5). This chain orientation is consistent with previous macroscopic observations.[16] In these diffraction

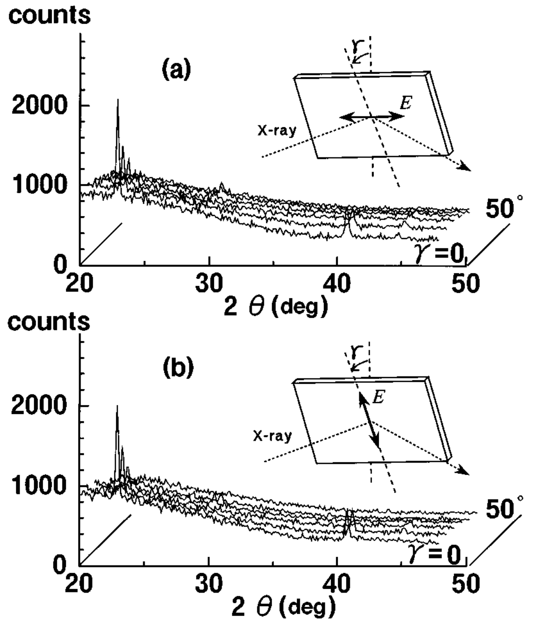

FIG. 4. X-ray-diffraction patterns of a photocyrstallized Se film fixed to the goniometer in two different ways: in (a), the electric field vector E of light being horizontal, and in (b) vertical. Diffraction patterns have been measured at some bowing angles γ, and accordingly, the diffraction pattern at $\gamma=0°$ corresponds to the conventional Bragg arrangement.

patterns, however, we can hardly see a plausible difference between the horizontal and vertical configurations.

To see whether anisotropic effects may exist, we plot the 100 and 101 peak intensities as a function of γ. Figure 6 shows that the 100 peak intensity decreases with γ, while the 101 intensity exhibits a peak at $\gamma=37°$. For the anisotropy, no appreciable difference is seen for the 100 peaks. However, for the 101 peak, the horizontal configuration (solid line) gives a higher intensity at $\gamma=37°$ by $\sim$10%. Note that these 100 and 101 characteristics have been confirmed in the two samples investigated.

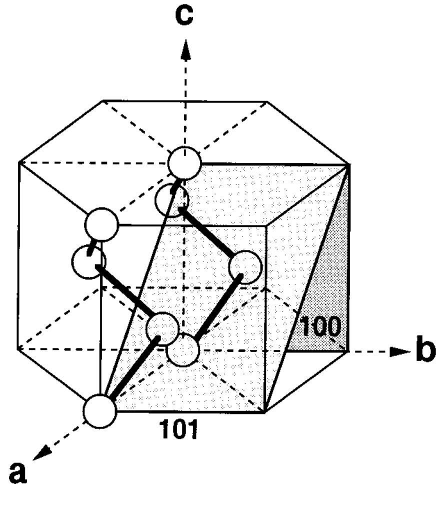

FIG. 5. Structural illustration of hexagonal Se with 100 and 101 planes. The 100 plane is parallel to the c axis, and 101 plane tilts 37° to the c axis.

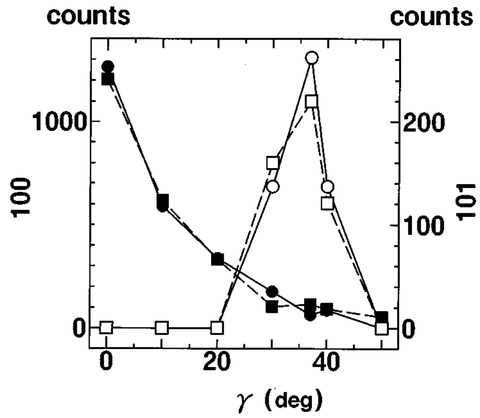

FIG. 6. γ dependence of x-ray intensities of 100 (solid symbols) and 101 (open symbols) peaks for the horizontal (circle) and vertical (square) configurations.

IV. DISCUSSION

Recently, Fritzsche has proposed a model for conventional photoinduced anisotropy.[13] He assumes that annealed chalcogenide glasses appear isotropic, since anisotropic elements contained in the glass align in random orientations. If such a glass is exposed to linearly polarized light, the anisotropic elements with the principal axis nearly parallel to the electric field vector of light will be excited preferentially. Then the excited elements may relax into other orientations. In consequence, after illumination, the anisotropic elements align so that the principal axes lie perpendicularly to the electric field vector of light, and accordingly $\Delta n<0$ appears.

On the other hand, properties of Se are known as follows:[14] The crystal, stable at room temperature, is the hexagonal form, which is illustrated in Fig. 5. Since the structure is uniaxial, it exhibits a birefringence of $n(E\parallel c)=3.6$ and $n(E\perp c)=2.8$, where E is the electric field vector of light. In contrast the structure of a-Se is known to depend upon preparation procedures and so forth, while annealed a-Se is most likely to be composed of entangled chain molecules.

Combining Fritzsche's model with the Se structure, we can predict for Se samples illuminated with linearly polarized light that Se chains tend to align perpendicularly to the electric field vector of light. This prediction is in harmony with a previous study for conventional photoinduced anisotropy.[11] Then we can further expect that oriented Se crystals can be produced with illumination at appropriate temperatures.

The present x-ray result supports the above idea. An important structural feature is that horizontal configuration gives rise to the higher 101 intensity at $\gamma=37°$ (Fig. 6). In the horizontal configuration, the above notion predicts that Se chain molecules align vertically. Then, since the c axis and 101 planes intersect at 37°,[14] when γ becomes 37°, the 101 peak becomes maximal. On the other hand, in a vertical configuration, the molecules are expected to align horizontally. Accordingly, the 100 peak can behave similarly to that in the horizontal configuration, which is consistent with the result in Fig. 6. However, in an ideal case such as in a single crystal, this configuration could not give the 101 diffraction peaks at any γ, since the 101 plane cannot become perpendicular to the plane defined by incident and scattered x rays, needlessly, since we are dealing with partially crystallized samples and the alignment is not ideal. However, the preferential alignment of the chain molecules perpendicular to the electric field vector of linearly polarized light can be inferred from the more intense 101 peak at $\gamma=37°$ in the horizontal configuration.

Quantitatively, as described in Sec. III B, the intensity difference between the horizontal and vertical configurations of the 101 peak at $\gamma=37°$ is $\sim$10%, and this value seems to be consistent with the observed birefringence. That is, the intensity difference can be used as a measured of crystalline orientation. Then, since the birefringence in the hexagonal crystal is 0.8,[14] the partially oriented crystal may show a birefringence of $\sim$0.08, which is nearly the same as the birefringence obtained through PAC. This agreement strongly suggests the existence of the PAC phenomenon in Se.

However, the atomic mechanism of the PAC phenomenon is largely speculative at present. For conventional photocrystallization processes, it is assumed that illumination enhances the crystal-growth rate by cessation and slippage of the chain molecules through photoexcitation and recombination of electrons and holes.[4] In the PAC phenomenon, a similar process can occur, while the growth rate should become anisotropic with linearly polarized illumination.

Effects of the annealing at 310 K for 3 days upon microscopic structures have not been known explicitly. Krisciunas *et al.*[17] have demonstrated that as-evaporated Se possesses columnar inhomogeneous structures, which may be effective to produce spherulite crystals. Such a film structure is unfavorable for the creation of anisotropic structures. The annealing can provide a kind of structural relaxation[18] or increases in molecular weight,[8] while the structural changes have not been demonstrated microscopically.

V. CONCLUSIONS

We have demonstrated that birefringence can be induced in evaporated Se films by photocrystallization with linearly polarized light. The photoinduced birefringence reaches to 1/10 of that in the hexagonal single crystal. This optical result seems to be consistent with the structural orientation which is inferred from x-ray-diffraction patterns. These results provide a demonstration of photoinduced anisotropic crystallization. In addition, the present result reinforces the quasicrystalline model for conventional photoinduced anisotropy.

ACKNOWLEDGMENTS

The present work was financially supported by grants from the Ministry of Education, Suhara Memorial Foundation, Casio Science Foundation, Showa Electric Wire and Cable Co. Ltd., and Hitachi Microcomputer Engineering Ltd.

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