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Photoinduced structural changes in amorphous semiconductors

© *Keiji Tanaka*

Department of Applied Physics, Faculty of Engineering, Hokkaido University,
Sapporo 060, Japan

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A variety of photostructural changes observed in tetrahedral and chalcogenide amorphous semiconductors are reviewed from physical and chemical points-of-view. Specifically, observations of the photodarkening and related phenomena in chalcogenide glasses are summarized, and structural models proposed so far are criticized.

1. Introduction

It is known that many substances exhibit structural changes when exposed to visible light. A well-known example in inanimate science may be the photographic reaction, in which migration of Ag^+ ions is induced in Ag-halide crystals by photoelectronic excitation [1].

Recently, it becomes known that amorphous semiconductors exhibit a variety of photoinduced phenomena [2–8]. The followign three features inherent to amorphous semiconductors appears to be responsible for the observations: 1) valence electrons in semiconductors are liable to be optically excited, 2) electron-lattice interaction appears to be strong in flexible networks, and 3) amorphous materials can possess a number of metastable structures.

The phenomena observed in amorphous semiconductors can be classified into two groups. The one is bulk effects, or photoinduced phenomena in single amorphous phases [3–8]. The other is a kind of photo-chemical reaction such as the photodoping, the photoinduced oxidation and so forth, for which the reader may refer to some publications [2,4,6,9].

The present paper aims at giving a description focused upon the bulk photoinduced phenomena. First, unified views common to tetrahedral and chalcogenide systems are pointed out, and then characteristic differences are discussed. Second, the reversible photodarkening and related phenomena induced in chalcogenide glasses with illumination and annealing are considered.

2. Perspective of bulk photoinduced phenomena

2.1. Observations

As shown in Table, the bulk photoinduced phenomena observed in tetrahedral and chalcogenide systems can be classified into some groups, depending upon the densities of atomic sites involved [10].

Photoinduced crystallization is the most dramatic phenomenon, observed in both tetrahedral [11] and chalcogenide amorphous semiconductors [12,13]. The phenomena appear to be induced electronically [13,14] and thermally [11,12], and the thermal process has been utilized as phase-change erasable memories [12]. Clearly, the photocrystallization is irreversible, in the sense that the initial amorphous state cannot be recovered with annealing,[1] since the illuminated state is thermodynamically more stable (see, the inset in Table).

The number of covalent bonds interchanged in the photocrystallization processes seem to depend upon the material of interest. For instance, in amorphous Se, which is composed with distorted chain molecules [16,17], interchange of a few atomic bonds ($\sim 1\%$) seems to be sufficient to align the distorted chains into hexagonal crystals.[2] In contrast, in a ternary compound such as Ge–Sb–Te [12], bond breakage and reconstruction of a greater number ($\sim 10\%$) may be needed to produce polycrystals, since compositional disorder is inherent in compound materials. In Table, therefore, the atomic density contributing to the photo-crystallization is represented roughly as $10^{22}\,\mathrm{cm}^{-3}$. The phenomena is understood to accompany structural changes in the long-range order, since crystals are produced.

Also observed in tetrahedral and chalcogenide systems are reversible phenomena involving sturctural changes at atomic sites of $10^{17} \div 10^{18}\,\mathrm{cm}^{-3}$, approximately ppm order [5]. The density is comparable to that of point defects in crystals, e. g. color centers in alkali halides [1], and it is far below a detection limit of experimental techniques such as X-ray diffraction which can provide direct structural information. Accordingly, mechanisms of these photoinduced phenomena are largely speculative, specifically when related sites are ESR-inactive. The Staebler–Wronski effect, which refers to a degradation of photoconductive properties in amorphous hydrogenated Si, is a reversible phenomenon most extensively studied [5]. In chalcogenide glasses held at low temperatures ($\leqslant T_g/2$), illumination generates unpaired electron spins (photoinduced ESR), which accompany an increase in optical absorption (photoinduced mid-gap absorption) and decrease in the photoluminescence intensity (photoinduced photoluminescence fatigue) [5]. Common to all these phenomena is that dangling bonds are assumed to be photocreated [5].

Between the high- and low-density photoinduced phenomena described above, there exist several phenomena

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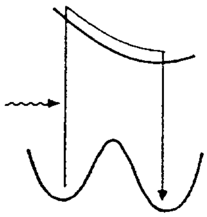
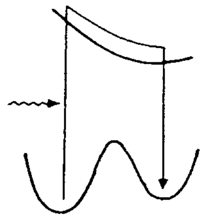
[1] The phase-change process can be reversible with thermal annealing and quenching, which are induced with pulsed illumination with different light intensities and pulse widths. In the reversible photoamorphization of crystalline $As_{50}Se_{50}$ films, substrates are responsible for the peculiar phenomenon.

[2] Breaking of covalent bonds and reptile motion of chain fragments are probably needed, like the crystallization process in chain polymers (see [18]).

A classification of bulk photoinduced phenomena observed in tetrahedral (a-Si:H) and chalcogenide amorphous semiconductors. The atomic densities are representative. SRO, MRO and LRO stand for short-, medium- and long-range orders

Atomic density, cm^{-3}	Structural change	Material		Reversibility
		a-Si:H	Chalcogenide	
$\sim 10^{22}$	LRO	Photo-crystallization	Photo-crystallization Giant photo-contraction Photo-polymerization Photo-decomposition	Irreversible 
$\sim 10^{20}$	MRO		Photo-darkening Photo-induced anisotropy	Reversible 
$\sim 10^{18}$	Defective SRO	Staebler–Wronski	Photo-induced ESR	

involving atomic sites of $\sim 1\%$ [5]. Interestingly, this kind of phenomena is demonstrated only in chalcogenide glasses. In tetrahedral materials, such photostructural changes seen to be still speculative [19,20]. In these photoinduced phenomena in chalcogenide glasses, some are irreversible and others are reversible, and in general irreversible phenomena exhibit greater structural changes. A well-known irreversible change is the photo-polymerization phenomenon observed in as-evaporated As_2S_3 films [7,8]. On the other hand, at least, two reversible changes, i. e. the photodarkening and the photoinduced anisotropy, are known to exist [3,5,6,8]. The details will be discussed in 3.

2.2. Discussion

It is interesting to note in Table that all the photoinduced phenomena involving atomic sites less and more than $\sim 10^{20}$ cm^{-3}, $\sim 1\%$ of the total atom density, are reversible and irreversible. It can be understood that the irreversible phenomena can involve greater atom numbers, since the changes occur toward more stable atomic structures (see Table). Then, why should the atomic sites be less than 1% in the reversible changes?

This fact can be accounted as follows: The density of 1% reads one photoinduced stomic site per cube with a side length of $5 \div 6$ atoms, which is $1 \div 3$ nm, depending upon the atomic bonds involved, i. e. covalent and/or Van der Waals bonds. This length implies that, in a reversible change, a photoinduced atomic configuration can be metastable, provided that produced strain is confined in this cube. It can than be relaxed into a stable structure with thermal relaxation induced by annealing. Alternatively, if more defective sites were generated in the cube, interaction between the defective sites would be stronger, and hence cooperative relaxation (annihilation) might occur towards stable atomic configurations. We can thus assume that the defective atomic density of 1% is the limit arising from the structures which can localize photoinduced strains.[3] It is interesting to note here that the critical length of $1 \div 3$ nm is comparable to the medium-range structural length in chalcogenide glasses [16,17]. We can envisage one photoinduced defect in a crystalline structure with a scale of $1 \div 3$ nm.

Then, why should the site density of the photoinduced dangling bonds be less than 10^{18} cm^{-3}? The density may be related to a nature of nonequilibrium disordered structures [10].

It may also be valuable to consider the photoinduced phenomena from a chemical point-of-view. We note in Table that chalcogenide glasses exhibit a variety of photoinduced phenomena, while the tetrahedral material possesses a fewer. How can we understand these contrastive features?

The origin can be sought in the chemical bonding structures. As illustrated in Fig. 1, chalcogenide glasses are assumed to be composed with covalent clusters held together with weak intermolecular forces of the Van der Waals type [16]. That is, the glass possesses the dualistic bonding nature and $2 \leqslant Z \leqslant 3$, where Z is the covalent coordination number averaged over constituent atoms [16]. This flexible structure with the low coordination number seems to cause

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[3] In order to confirm this speculation, however, lattice dynamical calculation in large amorphous networks is needed.

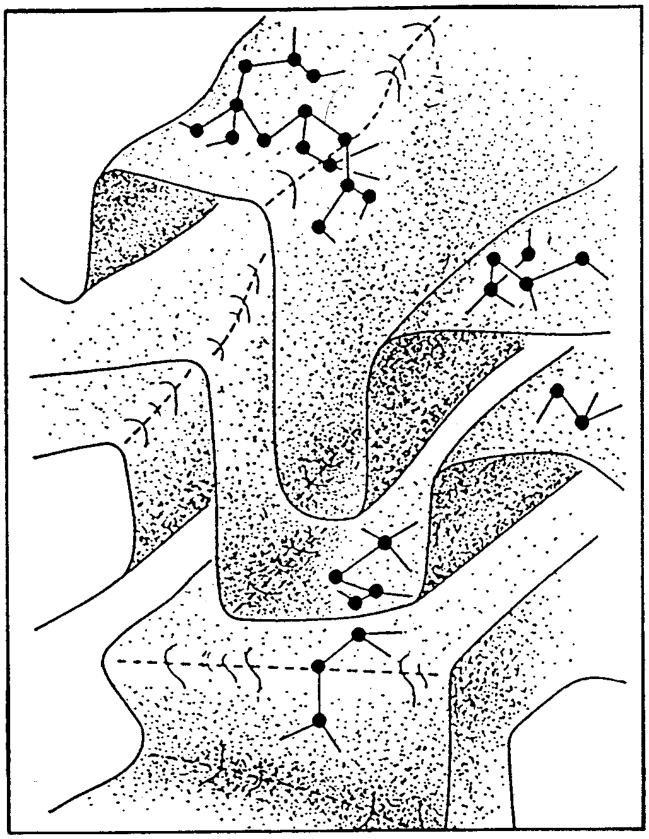

Figure 1. A schematic illustration of a chalcogenide glass composed with four- (Ge), three- (As,Sb) and two-fold (S,Se,Te) coordinated atoms.

many kinds of photoinduced phenomena. For instance, the photo-polymerization mentioned in 2.1 can occur because there exist intra- and inter-molecular bonds [7,8]. We will also see in the next section that the photodarkening can be related to the existence of strong and weak bonds. In contrast, the atomic bond involved in the tetrahedral material is of one kind, i. e. only covalent, and accordingly photoinduced changes are restricted in variety. Actually, Shimizu argues that the Staebler–Wronski effect could not occur if all Si atoms were tetrahedrally bonded with each other ($Z = 4$) [5].

Here, it is tempting to consider if photoinduced phenomena appear in amorphous rare-gas solids. The material contains only Van der Waals bonds ($Z = 0$) and it may be very soft [16,21]. Unfortunately, as the author knows, photoinduced phenomena in such materials have not been studied so far. However, it is plausible that only photoinduced crystallization can occur, since the Van der Waals bond is non-directional and flexible. Phenomena similar to the Staebler–Wronski effect cannot appear, since there exist no covalent bonds and local bistable configurations cannot be sustained.

Summarizing these considerations, we conclude that the existence of two kinds of bonds in chalcogenide glasses is responsible for a variety of photoinduced phenomena. That is, the low Z is essential.[4]

3. Photodarkening and related structural changes

So far the photodarkening phenomenon observed in chalcogenide glasses attracts considerable interests, and the structural changes have been extensively studied. In the following, we will give a brief review of the photodarkening and related phenomena, and then consider some structural models proposed so far.

3.1. Observations

When a chalcogenide glass such as As_2S_3, which has been annealed at T_g in advance, is illuminated at room temperature, or at temperatures substantially lower than T_g, the sample exhibits reversible changes in volume, optical, electrical, photoelectrical, mechanical, chemical, and thermal properties [4–6,8]. Here, the optical change includes the photodarkening, which refers to the feature that illuminated materials appear to be darkened. As shown in Fig. 2, this darkening is caused by a reduction of the optical bandgap energy. An increase in the refractive index ($\Delta n/n \simeq 0.03/2.6$ in As_2S_3) accompanies this absorption change. The electrical change appears as an increase in the *ac*-conductivity [5], while *dc*-conductivity change cannot be examined, since the material is nearly insulating [17]. As for the photoelectrical change, photoconductive degradation is demonstrated to affect upon the spectral change [5,22]. It is not conclusive if the hole mobility undergoes some modifications with illumination [6,7]. The mechanical, chemical and thermal changes imply that the material becomes more soft and unstable with illumination [5]. Also consistent with these rigidity changes is the volume expansion ($\Delta V/V \simeq 0.5\%$ in As_2S_3) with illumination. More surprisingly, Tanaka et al. have demonstrated giant volume expansion with sub-bandgap illumination, which can be utilized to produce microlenses [6]. However, the expansion does not occur if a sample is illuminated under hydrostatic compression, despite the photodarkening appears [5]. Hense, we can assume that the photoexpansion and the photodarkening are not directly related [23].

To obtained insight into microscopic sturctural changes accompanying the photodarkening, diffraction, extended X-ray absorption fine structure (EXAFS) and vibrational spectroscopic studies habe been performed [3–8]. However, it seems difficult to extract a unified model for the structural change from these studies, since the structure itself is controversial [16,17]. In addition, as implied above, it is plausible that different kinds of structural changes are induced by illumination.

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[4] In this sense, photoinduced phenomema can appear also in oxide glasses, as they do [5]. Nonetheless, the atomic bond is more ionic, and the dualistic bonding nature is not prominent. Accordingly, they exhibit a fewer kinds of photoinduced phenomena, like *a*-Si : H.

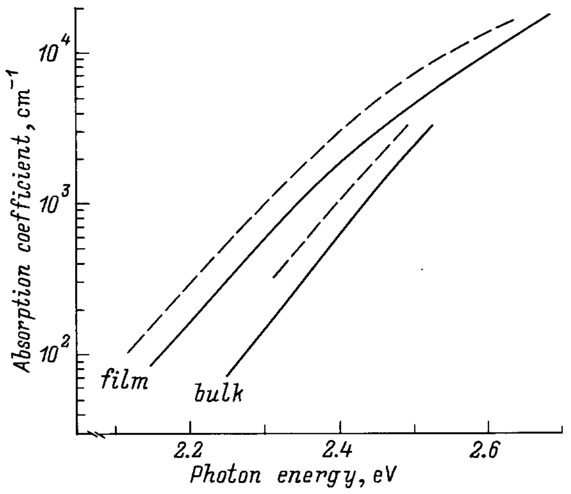

Figure 2. Photodarkening in deposited and bulk As_2S_3 at room temperature. Solid and dashed lines show annealed and illuminated states. The film characteristics are measured using the photothermal spectroscopy [K. Tanaka, Y. Ichimura, K. Sindoh. J. Appl. Phys., **63**, 1815 (1988)].

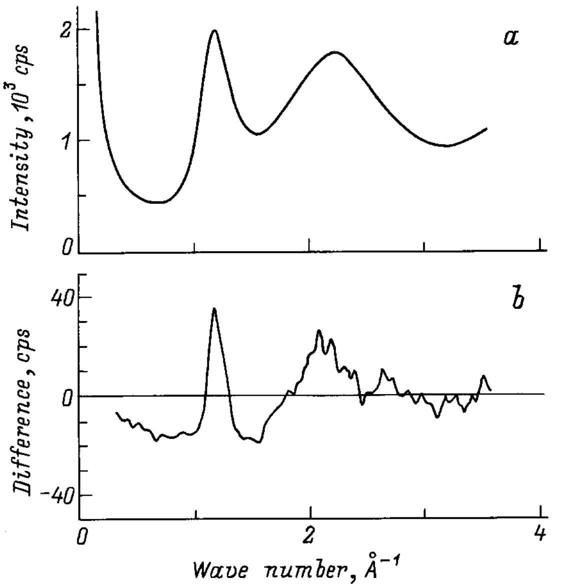

Figure 3. X-ray diffraction patterns of an As_2S_3 bulk glass before and after illumination. *a* — shows the annealed state, and *b* — shows the difference obtained by subtracting the X-ray intensity of the illuminated pattern from that of the annealed pattern.

Diffraction studies using X-ray and neutron have been reported from some groups [3,5]. Fig. 3 shows an X-ray result reported by the present author using bulk As_2S_3 glass [23]. Illumination and diffraction measurements have been performed at room temperature *in situ*, which is important to exclude thermal expansion effects and to detect minute changes. We see that the X-ray intensity difference (annealed–illuminated) is positive at around the first sharp diffraction peak (FSDP), which indicates the photoinduced disordering in the medium-range order. This experimental result is confirmed by some researchers [3,5], while the interpretation of the FSDP remains controversial [16,17]. The author devotes the so-called distorted-layer model [16], while others insist three dimensional models and so forth [17].

Some EXAFS studies have been reported [3,5,24]. However, the results reported for binary glasses are not necessarily consistent [3,5]. Creation of homopolar bonds and fluctuation enhancement of As–S–As bond angles are pointed out. Kolobov et al. report *in situ* investigation for amorphous Se [24].

Vibrational spectra have been obtained through Raman and infra-red (IR) studies [4–8]. In Raman scattering spectra of illuminated As_2S_3 films, a trace of As–As bonds is detected at 231 cm^{-1}, and the intensity of the low-frequency Raman peak located at $\sim$25 cm^{-1}, the so-called Boson peak, is substantially reduced [5,7,8]. No marked changes in the As–S vibrational band centered at 340 cm^{-1} are reported. By contrast, in the IR spectroscopy, which may be more feasible to quantitative evaluation, slight broadening of the As–S vibrational band is detected [4].

3.2. Discussion

How can we understand these macroscopic and microscopic changes? Taking the reversible features into account, we should assume a configuration-coordinate diagram such as shown in Table [5], in which an illuminated state is depicted as quasi-stable. Then, the problem turns to the structural element involved.

Here, as illustrated in Fig. 4, structural models proposed so far can be classified into two groups. In all models, relatively- ordered structures are assumed to be the annealed state. For illuminated state, the defect models (*a*) and (*b*) presume creation of some kinds of defects, and in contrast the distortion models (*c*) postulate randomness increases in normal bonding configurations.

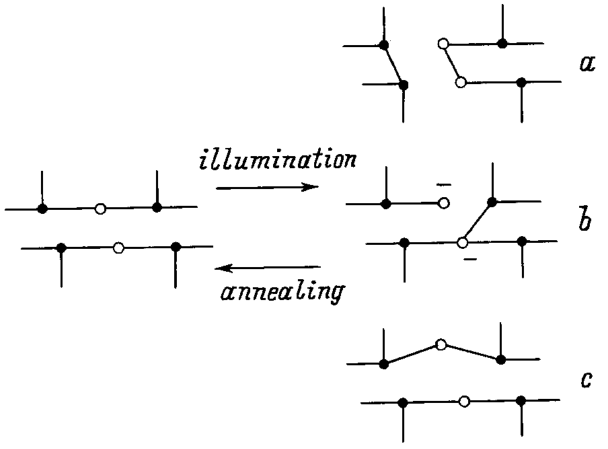

Figure 4. Schematic illustration of structural models proposed for the photodarkening and related phenomena. *a* and *b* — show defect models, and *c* — represents distortion models.

3.2.1. Defective structure models. Owen and others have emphasized through their Raman scattering measurements that As–As bonds are formed in illiminated states (Fig. 4, *a*) [5,7,8]. It is theoretically predicted that As–As bonds provide electronic states in the bandgap [3,17], and hence the photodarkening may appear, if the homopolar bonds are created. Nonetheless, the model cannot be a universal explanation of the photoinduced change, since the photodarkening appears in elemental materials, S and Se [5]. In addition, no evidence of photoinduced Ge–Ge bonds is obtained throught Raman studies [23].

Street and others have developed defective models using the charged-defect concept originally proposed by Mott [5]. The charged defects are assumed to produce electronic states in the band-tail regions [17], and hence the bandgap will be reduced with illumination. These defects with the density of $\sim 1\%$ would manifest specific vibrational peaks, which are investigated by Kolobov et al. [25].

3.2.2. Distorted structure models. In the last model illustrated in Fig. 4, some kinds of photoinduced distrotions in normal bonding configurations are assumed. Since modifications of covalent bond lengths will require substantial energy and the strained structures may not be quasi-stable, such distortions cannot be envisaged in the reversible photodarkening.

Then, plausible structural changes can be sought in distortions in bond angles, dihedral angles and Van der Waals distances. For instance, Utsugi and Mizushima emphasize the angular distortion in the short-range order, on the basis of their IR studies [4]. Angular fluctuation will increase the width of the conduction band, since the conduction band in chalcogenide glasses are composed with the antibonding state of covalent bonds [16,17]. As a consequence, the photodarkening can appear.

On the other hand, distortions in the dihedral angle and the Van der Waals distance will enhance the randomness in the medium-range structural order. Pfeiffer et al. assume distortion of dihedral angles on the basis of their EXAFS studies [3]. In contrast, the present author has proposed the intermolecular distortion through bond twisting motion of chalcogen atom [5]. These two kinds of structural changes appear to be consistent with the FSDP weakening and broadening shown in Fig. 3. The structural changes will modify the width of the valence band, since the width of the valence band is strongly influenced with the interaction between lone-pair *p*-orbital electrons of chalcogen atoms [16,17].

At present, it difficult to elucidate which structural change is the most responsible. We expect that further insight can be obtained if it will be disclosed that the photodarkening is caused by the changes in the bottom of the conduction band and/or in the top of the valence band. However, the accuracy of the photoelectron spectroscopy capable to determine the position of the band edges is not sufficient to resolve a shift of ~ 50 meV. Alternatively, we can assume that the three structural changes are interrelated, since the structural relaxation is characteristic to chalcogenide glasses possessing the low *Z*. That is, if an intermolecular bond is distorted with illumination, structural relaxation will necessarily occur, leading to appreciable angular distortions.

3.2.3. Miscellaneous. When dealing with the photodarkening in As_2S_3 and similar materials, we should note characteristic differences and similarities between the bulk and the annealed films. In general, structures of the bulk and the annealed films are assumed to be similar, while it has been demonstrated that the annealed film still contains an appreciable number ($\sim 1\%$) of As–As bonds [7,8]. In fact, Fig. 2 shows that the absorption edges of an annealed film and the corresponding bulk are clearly different. Wrong bonds (homopolar bonds in stoichiometric compounds) seem to cause the difference. However, surprisingly, the photoinduced red-shifts are nearly the same, ~ 50 meV, in both materials.

We should also note that when As_2S_3 is exposed to linearly-polarized light, the photodarkening and the photoinduced anisotropy appear simultaneously. The mechanisms of these phenomena are demonstrated to be different [5,26,27], and accordingly it is doubtless that at least two kinds of structural changes are induced with illumination. Further studies are needed in order to obtain one-to-one correspondences between macroscopic changes and microscopic structural changes, in which the latter is largely speculative.

4. Summary

Overall features of the photoinduced phenomena observed in amorphous semiconductors are considered from two aspects. From the atomic density, it appears that the reversible phenomena cannot accompany structural changes at atomic sites more than $\sim 1\%$ of the total atom density. From a chemical point-of-view, the reason why chalcogenide glasses exhibit a variety of phenomena can be sought in the dualistic bonding nature composed with covalent and Van der Waals bonds.

The photodarkening and related phenomena are critically reviewed. Many macroscopic features have been revealed, while the mechanism remains speculative. This is because the structural changes appear to extend to medium-range scales, for which no convincing experimental tools have not yet been available. By contrast, the phenomena appear to be promising for fabrication functional devices [5,6].

This manuscript is dedicated to Professor Kolomiets, who is undoubtedly the founder of amorphous semiconductor physics. He also brought up many able scientists such as Professor Lyubin and Dr. Kolobov. I cannot forget his stout and warm hands in Ioffe Institute in 1987.

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