Photo-induced phenomena in chalcogenide glass:
Comparison with those in oxide glass and polymer

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Two topics, the both being related with localized states in non-crystalline solids, are studied. One is a comparison of photo-induced phenomena in oxide, chalcogenide, and organic materials. Despite of different inorganic and organic structures, there exist many similarities in photo-induced phenomena, which can be ascribed to excitation of localized electronic states. The other topic concerns photo-induced phenomena induced by linear and non-linear excitation. A result on As_2S_3 demonstrates that band-gap excitation by one- and two-photon processes provides different changes. It is suggested that the two-photon process occurs resonantly at around localized states in amorphous materials, and the process plays important roles in the structural change.

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1. Introduction

The chalcogenide glass, consisting of S, Se, and Te in the group VIb elements, presents a variety of photo-induced phenomena [1, 2]. For instance, sulfide and selenide glasses show athermal photo-structural changes, some of which appear only under illumination and others remain after illumination, the latter being irreversible or reversible in a sense if the change can be recovered with annealing. In some photo-induced phenomena, the electric field of excitation light provides anisotropic changes [2, 3]. These phenomena have been applied to optical devices such as holographic memories [4], waveguide switches [5], micro-lenses [6], and photonic structures [7, 8]. On the other hand, telluride films exhibit photo-thermal changes such as the phase change, which has been utilized in DVD (digital versatile disk) systems [2].

The reason why the chalcogenide glass exhibits many kinds of photo-induced phenomena can be ascribed to unique electronic and atomic structures [1]. Electronically, the glass is a kind of semiconductors with the energy gap of 1 – 3 eV, and accordingly, it can be photo-excited by visible light. In addition, excited carriers are effectively localized in disordered and defective glass structures, and the carriers undergo strong electron-lattice interaction. Structurally, the glass has moderate atomic connectivity, which is not so rigid as in oxide glasses and not so flexible as in organic polymers. For instance, typical chalcogenide glasses such as $As_2S(Se)_3$ and $GeS(Se)_2$ are assumed to have distorted covalent-layer structures with average atomic coordination numbers of 2.4 – 2.67, and the glass-transition temperatures distribute at 200 – 400 °C. Therefore, the electron-lattice interaction can cause some structural changes, which are stable at room temperature and may be recovered with annealing. Despite of these general views, however, detailed mechanisms of each photo-induced phenomenon have not been elucidated, the main reason being the glass structure, which is difficult to determine explicitly.

To get further insight into the mechanisms, we here take a comprehensive approach. In the first part, the phenomena are compared with those in other materials. Specifically, a comparison with those in organic materials is valuable, since their photo-structural mechanisms have been understood more deeply [9, 10]. In the latter part, we investigate a change in As_2S_3 induced by intense mid-gap excitation. So far, many studies have dealt with one-photon (sub-)band-gap excitation [1-3], and if one- and two-photon band-gap excitations can give the same structural change is ambiguous. Through these studies, we will see a universal role of electronic localized states in the photo-structural phenomenon.

2. Photo-induced changes in inorganic and organic systems

We already utilize inorganic and organic products which employ some photo-structural changes. The most famous may be Bragg-reflector fibers of oxide glasses, DVDs of chalcogenides, and CD-R (compact disk recordable) and photo-resists of organic films. These products represent characteristic features of each material. The Bragg reflector must be stable and have long life times (~20 years). The DVD should retain good durability for repeated crystalline-amorphous phase changes. Organic films can be obtained with simple coating, which may be the cheapest way for thin-film preparations.

Table 1 compares some characteristics of a photo-sensitive polymer, Ge-doped SiO_2, and As_2S_3. The polymer is molecular, consisting of dyes and back-bone chains [9-11]. The concentration of dyes is typically ~10 mol.%, and the chain may be amorphous or liquid-crystalline with molecular weights (degree of polymerization)

greater than 10^3. For such organic systems, we can select more-or-less artificially the dye and the back-bone chain. The dye has a fairly sharp absorption spectrum, so that optical excitation can be analyzed as an isolated unit in a similar way to that in a small molecule [12]. In addition, responses of back-bone structures are predictable from the molecular structures. Therefore, we can delineate relatively easily the photo-induced mechanism. For instance, photons excite the dyes, which may undergo trans-cis conformation changes, which in many cases cause successive structural (orientation, translational, etc.) changes in the back-bone chains. It should be mentioned here that similar excitation processes can be proposed for photo-structural changes in Ge-doped SiO_2, in which Ge plays the same role as that of the dye [13]. In short, it is reasonable to assume that, in these sensitizer-doped systems, the photo-structural processes are triggered by the excitation of sensitizers.

Table 1. Comparison of typical photo-induced optical changes in As_2S_3 [2], Ge-doped SiO_2 [13], and azo-polymers [9-11]. $\hbar\omega_{exc}$ shows the energy of photons which can excite the photo-induced changes, T_g the glass-transition temperature, $\Delta\alpha$ the induced absorption change, Δn the isotropic (scalar) and birefringent (vector) refractive-index changes, and ΔV the photo-induced volume change.

Material	$\hbar\omega_{exc}$ [eV]	T_g [°C]	$\Delta\alpha$	Δn	ΔV[%]
azo-polymer	~3.5	~100	increase in dye absorption	0.1 (vector)	20
Ge-doped SiO_2	~6	1200	increase in defective absorption	0.001 (scalar)	0.1
As_2S_3	2.0 – 2.4	200	red-shift of absorption edge ΔE	0.03 (scalar) 0.002 (vector)	1

Then, how can we treat a homogeneous chalcogenide system such as As_2S_3? There still exist a lot of similarities in photo-structural behaviors in the chalcogenide and the dye-polymer system (see, Table 1) [14, 15]. For instance, in both systems, induced changes disappear at the glass-transition temperatures [2, 9, 10]. Photo-induced birefringence appears in chalcogenide glasses and in dye-polymers upon illumination of polarized [3, 10, 16, 17] and unpolarized light [3, 18]. Marked volume changes [9, 10, 15], anisotropic deformations [10, 15, 19], fluidity [20, 21], and mechanical motions [22, 23] can be induced commonly.

Having seen these many similarities, we are tempting to propose some universality in the photo-structural mechanisms. Since the roles of dyes and back-bones in organic systems have been understood [9, 10], the corresponding elements in the homogeneous glass should be sought, which are probably localized gap states and normal-bonding networks [1, 24]. The localized state can be directly photo-excited or it may trap excited carries, which will trigger successive structural changes in the disordered network. A big problem for such homogeneous systems, however, is that many kinds of defective structures can be envisaged as the gap state [1, 24].

3. Excitation-energy dependence

Fig. 1 summarizes reported photo-induced phenomena in As_2S_3 glass ($E_g \approx 2.4$ eV) as functions of

excitation photon-energy and light intensity [2, 25]. For comparing pulsed and cw results in a single frame, the (peak) light intensity is plotted on the vertical axis, while the overall tendency does not change if the dose is taken for pulsed exposures.

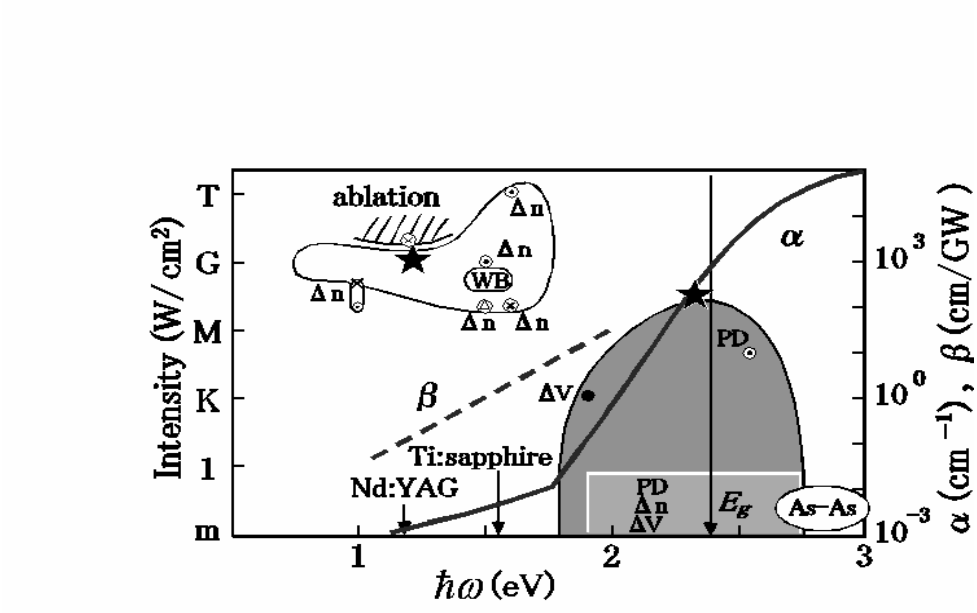

Fig. 1. Photo-induced phenomena scaled with excitation photon-energy and (peak) light intensity. The left-hand side vertical axis is scaled with a unit of 10^3. The abbreviations WB, PD, Δn, and ΔV represent, respectively, wrong-bond formation, photo-darkening, refractive-index change, and volume change. The two solid stars indicate the experimental conditions described in 4. One- (α) and two-photon (β) absorption spectra are also shown by a solid and a dashed line with the right-hand side scale.

We see in the figure that several kinds of photo-induced phenomena appear. Photo-darkening (photo-induced red-shift ΔE in absorption edge) PD and related phenomena (Δn and ΔV) are induced by cw band-gap illumination ($\hbar\omega \approx 2.4$ eV) with intensities lower than ~0.1 W/cm^2 and by intense (~100 W/cm^2) sub-gap illumination ($\hbar\omega \approx 2.0$ eV) as well [2]. Specifically, longer penetration depths (≤ 1cm) of sub-gap light are favorable to produce prominent volume expansions [2]. Note that temperature rise, which necessarily occurs with illumination, can be neglected here. On the other hand, there are several studies which demonstrate some photo-induced changes upon pulsed (ps – ns) mig-gap ($\hbar\omega \approx 1.2 \sim 1.5$ eV) exposures [25], which may provide two-photon excitation. When the light intensity is increased to ~10^{10} W/cm^2 (~1 J/cm^2), laser ablation occurs.

However, it is not straightforward to ascribe the mid-gap exposure effects to two-photon excitation. Because, the glass is likely to possess gap-states, which absorb mid-gap photons, as actually seen in Fig. 1 by finite α (~10^{-3} cm^{-1}) at $\hbar\omega \approx 1.2 \sim 1.5$ eV. For obtaining deeper insights, therefore, well-defined experiments for one- and two-photon excitations are needed.

4. Experiments and results on As_2S_3

The samples were annealed flakes of *high-purity* As_2S_3 glass. The one- and two-photon absorption spectra,

$\alpha(\hbar\omega)$ and $\beta(\hbar\omega)$, of this ingot were evaluated previously [26], the results being shown in Fig. 1. The samples were exposed to band-gap ($\hbar\omega$ = 2.33 eV) and mid-gap ($\hbar\omega$ = 1.17 eV) pulses emitted from a Nd:YAG laser (5 ns and 5 Hz), in which only the photon energy and the intensity were changed in keeping other exposure conditions fixed as possible. For instance, total absorbed photon numbers were held at 10^{23} – 10^{24} cm^{-3}. Then, before and after light exposures, absorption spectra, refractive indices at $\lambda \approx$ 800 nm, and Raman-scattering spectra were inspected.

Important results are summarized in Table 2 [27]. Here, it should be mentioned that the 1.17 eV light intensity I of 10^9 W/cm^2 has been selected after repeated trials. If $I \approx 10^8$ W/cm^2, no detectable changes appeared with exposure durations of several hours. On the other hand, 10^{10} W/cm^2 pulses were likely to damage the sample. As is known from Table 2, the selected intensity satisfies a condition of $\beta I \gg \alpha$, so that we can assume that two-photon processes govern photo-electronic excitation. In addition, a quantitative analysis suggests that photo-thermal effects can be neglected. It is mentioned here that measurements of detailed light-intensity dependence were difficult due to intensity fluctuation of the pulsed laser and so forth.

Table 2. Photo-induced changes (ΔE, Δn, and Raman scattering) in As_2S_3 glass by pulsed 1.17 and 2.33 eV light at absorbed photon numbers of 10^{23} - 10^{24} cm^{-3} in comparison with those induced by cw band-gap light [2]. Related parameters (α, β and peak intensities) for 1.17 and 2.33 eV light are also listed. β at $\hbar\omega$ = 2.33 eV cannot be evaluated. Accuracies for ΔE and Δn are ±5 meV and ±0.001. Note that Δn in the present pulse and the previous cw experiment are evaluated at wavelengths of ~800 nm and 633 nm.

$\hbar\omega$ [eV]	ΔE [meV]	Δn	Raman scattering	α [cm^{-1}]	β [cm/W]	intensity [W/cm^2]
1.17	0	0.005	wrong bond	10^{-3}	10^{-10}	10^9
2.33	20	0.003	no change	300	x	10^7
cw	50	0.02				

In Table 2, two contrastive features should be emphasized. One is that the two-photon band-gap excitation (1.17 × 2 eV) does not provide noticeable photo-darkening, in spite of the refractive-index increase. Then, taking the Kramers-Kronig relation into account, we may envisage an absorption increase at band-tail regions (1.6 – 2.4 eV), while it has been difficult to examine the change because the two-photon excitation makes the sample frosty. The other is that the Raman-scattering measurements demonstrate that the two-photon excitation gives appreciable density increases (1 – 2 at.%) in wrong bonds (As-As and S-S), which may cause the light scattering. Interestingly, such wrong-bond increases have also been induced by cw super-band-gap excitation [28].

5. Discussion

The one-photon and the two-photon absorption coefficient, $\alpha(\hbar\omega)$ and $\beta(\hbar\omega)$, can be written down approximately for disordered semiconductors as;

$$\alpha(\hbar\omega) \propto |\langle\varphi_f|H|\varphi_i\rangle|^2 \int D_f(E+\hbar\omega)D_i(E)\,dE, \quad (1)$$

and

$$\beta(\hbar\omega) \propto |\sum_n \langle\varphi_f|H|\varphi_n\rangle\langle\varphi_n|H|\varphi_i\rangle/(E_{ni}-\hbar\omega)|^2 \int D_f(E+2\hbar\omega)D_i(E)\,dE, \quad (2)$$

where φ is the electron wavefunction, H the electron-light interaction Hamiltonian, D the density-of-state, E the energy, and the subscripts i, n, and f represent initial, intermediate, and final states. We see that the convolution integrals in these expressions are practically the same, just $\hbar\omega$ in (1) being replaced to $2\hbar\omega$ in (2). In contrast, the transition probabilities have different forms, which may govern material dependence. Actually, for many glasses, it can be pointed out that maximal α above the absorption edge is commonly ~10^5 cm^{-1}, while maximal β varies at 10^0 - 10^2 cm/GW [29]. The interpretation will be reported elsewhere.

Here, it is important to note that, different from an ideal semiconductor, the amorphous material possesses gap states. The gap state provides three effects upon optical absorption. First, one-photon absorption to the gap state occurs. Second, the two-photon absorption can occur in resonance with the gap state if the photon energy satisfies $E_{ni} - \hbar\omega \approx 0$ in Eq. (2), i.e., when the gap state (n) is located at mid-gap. This is contrastive to the situation, $|E_{ni} - \hbar\omega| \geq E_g/2$, in the ideal semiconductor exposed to mid-gap excitations. In addition, since the gap state has a localized wave-function, *the resonant two-photon absorption occurs spatially selectively at around the gap state*. Third, the gap state may cause two-step absorption, which consists of successive one-photon absorptions via the gap state. Here, the two-photon and the two-step absorption could be distinguished from light-intensity dependence. For instance, in the present As_2S_3 glass, the two-step absorption can be practically neglected when $2\hbar\omega \approx E_g$ [26].

The spatially-localized resonant two-photon excitation is assumed to provide distinct effects upon the photo-structural change. That is, the excitation energy can be efficiently transferred to the localized state, which will be a source of successive structural changes, as illustrated in Fig. 2. In As_2S_3, the localized state seems to be produced by As-As bonds [30], and accordingly, the wrong bond may grow to As clusters through presently-unknown mechanisms, which can give the Raman-peak increase (Table 2). Such structural changes necessarily produce more inhomogeneous and stressed structures consisting of As-As and S-S bonds, and accordingly, the refractive index may increase through photo-elastic effects.

On the other hand, it is reasonable to assume that one-photon (sub-)band-gap illumination provides more extended excitation. Excited carriers may cause bond-twisting atomic motions, resulting in more disordered interaction among lone-pair electrons [2], which form the top of the valence band. Such disorder enhancements can therefore provide the photo-darkening, as illustrated in Fig. 2, and the refractive-index increase, which are consistent with the Kramers-Kronig relation.

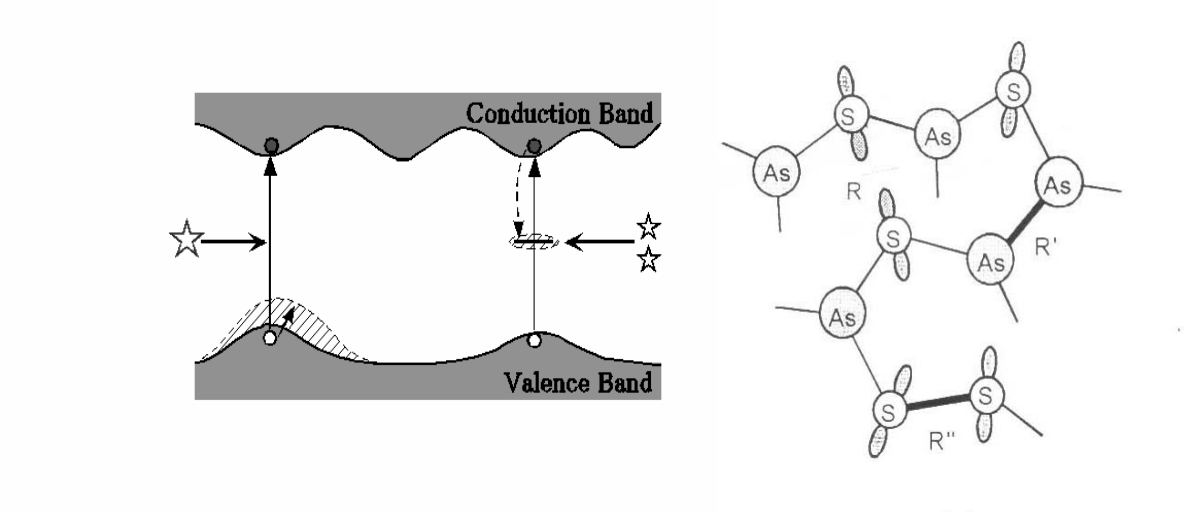

Figure 2. A schematic illustration of band-gap excitations (left) through a one-photon (left) and a localized resonant two-photon (right) process, and related atomic structures (right) including As-As and S-S homopolar bonds.

It may be valuable to consider if other materials have similar nonlinear responses to that observed in As_2S_3. Naturally, homogeneous oxide glasses such as SiO_2 may follow the same situation [13]. On the other hand, in inhomogeneous systems such as dye-polymer and Ge-SiO_2, the sensitizer is always likely to absorb photons, irrespective of linear and nonlinear processes. In such cases, unique photo-structural changes may appear.

6. Conclusions

In many photo-induced phenomena, the localized state becomes a source of strong electron-atom interaction. In inhomogeneous systems the state is produced by dyes or dopants, and in homogeneous glasses it is produced by defective structures. In nonlinear optical excitation processes, the state is responsible for spatially-localized resonant absorption, which is likely to provide different structural changes from those induced by linear optical excitation.

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