Dynamics of photodarkening in amorphous arsenic chalcogenide

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We have performed transient optical absorption measurements for amorphous As_2Se_3 and As_2S_3 using a nanosecond pulsed laser and specially designed optical cells, which prepared melt-quenched amorphous film of micrometer and sub-micrometer size. From the measurements, we have observed (I) transient photodarkening in the nano- and microsecond domain, which is a photo-response for one pulse of the laser, (II) accumulative photoinduced absorption for repeated pulsed illumination, (III) a decay of the accumulated photoinduced absorption after stopping the illumination and (IV) a saturation of the decay. Temperature dependence of these photoinduced effects was examined from room temperature to 430 °C for As_2Se_3 , 300 °C for As_2S_3 including liquid state. Dynamics of the photodarkening is discussed on the basis of the experimental results.

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1. Introduction

Amorphous arsenic chalcogenide such as As₂Se₃ and As_2S_3 exhibits photodarkening, which is characterized by red-shift of optical absorption edge after prolonged bandgap illumination [1]. The change is semi-permanently preserved at room temperature. This phenomenon is unique to amorphous phase and was not observed in crystal. The change accompanies a structural change. The characteristic of the structural change is that a whole bulk of the sample is involved in the change as volume expansion suggests [2]. The change is quite different from a spatially limited local change such as creation of defect. A great interest in clarifying the mechanism of the photodarkening has been shown by many researchers since the phenomenon was discovered in 1970s [3]. However, the mechanism has not been clarified yet.

The photodarkening process is explained in terms of metastability of amorphous chalcogenide. In amorphous materials, there are many metastable states while there is one free energy minimum in crystal. A state can be transferred from one metastable state to another by bandgap illumination. By the prolonged illumination, a state can reach the most stable state under illumination among these metastable states. After stopping the illumination, a state is trapped in the metastable state. Hence, the photoinduced effect is semi-permanently preserved. By annealing the sample, a state can be transferred to the most thermally stable state. This picture explains the reversibility of this phenomenon.

As for a driving force to transfer a state by bandgap illumination, it is pointed out that the excitation of lone-pair electrons plays an important role since the photodarkening effectively occurs for the illumination of light whose energy is greater than the energy gap [1]. However, the role of the excitation of lone-pair electrons on the occurrence of the photodarkening has not been clarified from dynamical point of view. Since the prolonged illumination is used as the excitation light source, there might be an immediate response for the excitation of lone-pair electrons and an evolutional change during the illumination. In addition, we should notice that the photodarkening is observed "after stopping" the illumination. This means that there might be a photo-response under the illumination, its decay and the durable change after stopping the illumination. To clarify the mechanism of the photodarkening, all of these processes should be examined. For this purpose, we have performed the transient photoinduced optical absorption spectra measurements for amorphous (a-) As₂Se₃ and As_2S_3 throughout the time domain between the nanosecond and the minute using a nanosecond pulsed laser. The measurement in the nano- and microsecond domain has been performed using weak pulsed laser, where accumulative photoinduced effect can be ignored. The measurement in the second and minute domain has been performed using relatively stronger repeated pulsed laser to observe the accumulative photoinduced change and its decay. In this article, we show our recent experimental results [4,5] and discuss the origin of the photoinduced change.

2. Experimental

It is noted that photodarkening is observed at absorption edge. Therefore a film with micrometer or sub-micrometer size should be prepared to observe the change. In this experiment, melt-quenched amorphous films with the thicknesses of 0.4 μ m for As₂Se₃ and 1.5 μ m for As₂S₃ were prepared using specially designed optical cells [6]. Liquid films could also be prepared using the cells. For a-As₂Se₃, the second harmonics (532 nm=2.33 eV) of the pulsed Nd:YAG laser operated at 10 Hz was used as an excitation light source. For a-As₂S₃, the third harmonics (355 nm=3.49 eV) was used. These energies are large enough to excite lone-pair electrons to the anti-bonding states in the samples [7, 8]. The pulse-width was 6 ns.



Fig. 1. Time decay of the photoinduced absorption, $\Delta T/T$, where T is the transmittance in the thermal equilibrium state and ΔT is the photoinduced change in transmittance, in As₂Se₃ at temperatures between room temperature and 430 °C.

The measurement of photoinduced absorption in the nano- and microsecond domain has been performed in two ways; time variation measurement of the absorption at a fixed wavelength and spectrum measurement at a fixed time. For the measurement of time variation of the absorption at a fixed wavelength, we used a tungsten lamp as a probe beam, a silicon PIN photodiode, a wide amplifier, and a digital oscilloscope. The measurements have been performed for As₂Se₃ at temperatures from room temperature to 430 °C including the liquid state. To avoid the accumulation of the photo-induced effect, weak illumination of pulsed laser was used. The intensity was 1.1mJ/cm^2 · pulse for the measurements at 28, 130 and 230 °C, 1.4 mJ/cm² \cdot pulse for the measurements at 430°C. The spectrum measurement for a-As₂Se₃ at room temperature has been performed using a Xe flash lamp as a probe beam, ICCD camera, a gate generator and a delay generator. The gate width was 5 ns. The intensity of the pulsed laser was $1.1 \text{mJ/cm}^2 \cdot \text{pulse}$.



Fig. 2. Time evolution of the photoinduced absorption spectrum for a-As₂Se₃ at room temperature. The delay time is indicated in the figure. The gate width is 5 ns.

The measurements in the second and minute domain have been also performed in the two ways. The time variation of the absorption at a fixed wavelength was measured using a tungsten lamp as a probe beam, a silicon photodiode as a detector and a digital voltmeter for monitoring the signal. The transmitted light was monochromatized at 650 nm for a-As₂Se₃ and 520 nm for a-As₂S₃ in order to monitor a change in the absorption edge. The pulsed laser with the intensity of 5 mJ/cm² \cdot pulse was repeatedly illuminated for 30 s. The signal of the monochromatized transmitted light was acquired at 1-second intervals. The measurement was performed at temperatures from room temperature up to 130 °C for As₂Se₃ and 300 °C for As₂S₃. Annealed sample was used for each measurement at a constant temperature. Photoinduced absorption spectra for both a-As₂Se₃ and a-As₂S₃ at room temperature were measured using a Xe flash lamp as a probe beam and ICCD camera as a detector. The time to obtain one spectrum was 50 s. The pulsed laser with the intensity of 8 mJ/cm² \cdot pulse was repeatedly illuminated for 10 min for the measurement.

3. Results and discussion

3.1. Photodarkening in the nano- and microsecond domain

Fig. 1 shows the time variation of the photoinduced absorption, $\Delta T/T$, where *T* is the transmittance in the thermal equilibrium state and ΔT is the photoinduced change in transmittance, for As₂Se₃ at temperatures from 28 °C to 430 °C in the nanosecond and microsecond domain. The observed change indicates a photo-response after one shot of the pulsed laser, that is, an immediate response for the excitation of lone-pair electrons, where accumulative photoinduced effect is excluded. In the curve at 28 °C, about one percent of photodarkening is observed at 200 ns. This indicates that there is a transient

photodarkening in the nanosecond domain. There is a long decay tail to be millisecond. With increasing temperature, the tail becomes shorter. In this experiment, the pulsed laser is shot every 10^{-1} s. At 28 °C, the photoinduced change at 10^{-1} s is estimated to be 10^{-2} % from an extrapolation of the experimentally obtained curve. We can expect that such long decay time causes an accumulative photoinduced change with the repeated pulsed illumination, which will be discussed in the next section. It should be noticed that the transient photoinduced absorption in the nano- and microsecond domain is also observed at 230 °C, where the sample is in the supercooled liquid state, and even at 430 °C, where the sample is in the liquid in the thermal equilibrium state. This is the different point from the durable photodarkening, which is observed only in amorphous state after stopping the prolonged bandgap illumination and is not supposed to be observed above glass transition temperature, T_{g} .



Fig. 3. The optical absorption spectra of As₂Se₃ at temperatures between room temperature and 430 °C.
The spectra are obtained by using the data of optical absorption coefficients in [7].

Fig. 2 shows the time evolution of the photoinduced absorption spectrum for $a-As_2Se_3$ at room temperature. The photoinduced absorption is remarkably observed in the shorter wavelength. In Fig. 3, optical absorption spectra at different temperatures are shown together with the range of the wavelength where the photoinduced absorption is observed in Fig. 2. Apparently, the photoinduced absorption occurs at the absorption edge. This means that the band edge structure changes by the pulsed laser illumination so that the optical gap decreases. There is an oscillation in each spectrum. We attribute the oscillation to the optical fringe caused by the change of refractive index.

3.2. Accumulative photoinduced change and its decay

3.2.1 Time variation of the photoinduced absorption and its temperature dependence

Fig. 4 shows the time variation of the photoinduced change of the transmitted light intensity for annealed a-As₂Se₃ and a-As₂S₃ at room temperature from starting repeated pulsed illumination to about 10 minutes after stopping the illumination. Pulsed laser was repeatedly illuminated from 30 to 60 s. The wavelength of the probe beam is 650 nm for a-As₂Se₃ and 520 nm for a-As₂S₃, which monitors the change in the absorption edge. The intensity of the transmitted light decreases starting the illumination. This suggests that there is photoinduced absorption for one pulse of the laser and the photoinduced effect is accumulated by the repeated illumination. Accumulative process is different between a-As₂Se₃ and a-As₂S₃. In a-As₂S₃, there are a fast decrease of the transmitted light, which appears in the first 10 s period after starting the illumination, and a next slow decrease, which appears after the fast decrease. After stopping the illumination, a decay of the photoinduced effect and a saturation of the decay are observed. The former indicates the presence of transient photodarkening and the later indicates the durable photodarkening. These features are consistent with the previous results of the transient photo-induced optical absorption in a-As₂Se₃ measured by Ganjoo et al. [9, 10] and in a-As₂S₃ measured by Frumer et al. [11] using a CW laser.



Fig. 4. Time variation of the intensity of the transmitted light in annealed a- As_2Se_3 (a) and a- As_2S_3 (b) at room temperature for repeated pulsed illumination from starting illumination to about 10 minutes after stopping the illumination. Pulsed laser was repeatedly illuminated from 30s to 60 s. The wavelength of the probe beam is 650nm for a- As_2Se_3 and 520 nm for a- As_2S_3 . The change in the illuminated time is shown in each inset.

The photoinduced change for one experimental of 30s-illumination procedure composed and 10min-non-illuminated period was repeatedly examined. The results at different temperatures are shown in Fig. 5. It is found in the curves at room temperature for both of the samples that the photoinduced effect related to the durable photodarkening decreases with increasing the number of experimental run and there seems to be a saturated level. The level must be related to a most stable state under fully illuminated condition among many metastable states. After reaching the level, the durable photodarkening effect is no more induced by the same illumination. In contrast, the accumulated photoinduced absorption is almost constant except the first run. Even after reaching the light saturated level related to the durable photodarkening, there is a photoinduced effect by the illumination. This change is related to the only transient photodarkening.



Fig. 5. Time variation of the intensity of transmitted light for 10 times repeated procedure composed of 30s-illumination and 10min-non-illuminated period in a-As₂Se₃ (a) and a-As₂S₃ (b) at several temperatures between room temperature and the temperature near the glass transition temperature, T_{s} . The value of the vertical axis indicates the electric signal obtained from a silicon photodiode, which is proportional to the intensity of light. The values are indicated for ease of comparison of the change of the intensity with the initial intensity. The inset in (b) shows the change in the supercooled liquid As₂S₃ at 250 °C. The intensity of the probe beam is multiplied by 4.6.

In Fig. 6, the results in Fig. 5 are plotted in $\Delta T/T$, where T is the transmittance before starting illumination, for both a-As₂Se₃ and a-As₂S₃ at each temperature. The number of experimental run dependence on the photoinduced effect is clearly observed in the figure. The effect of durable photodarkening decreases by repeating experimental run. The effect also decreases with increasing temperature. The total photodarkening effect for 10 times of the illumination is plotted as a function of temperature in Fig. 7. The data points of the durable photodarkening effect extrapolate to zero at the temperature below T_g ; 105 °C for a-As₂Se₃ and 155 °C for a-As₂S₃. Above the temperature, there is no photoinduced change related to durable photodarkening. This indicates that the light saturated level is no more stable above such temperature.



Fig. 6. Time variation of the photoinduced absorption $\Delta T/T$ in a-As₂Se₃ and a-As₂S₃.

temperature, accumulative At constant the photoinduced effect, which is the maximum value of $\Delta T/T$ during the illumination, is almost constant regardless of the number of run. Only the value for the first run is different from those of other runs. This is caused by a large contribution of the durable photodarkening in the first run. The accumulative photoinduced effect is plotted as a function of temperature in Fig. 7. For a-As₂Se₃, the accumulated effect decreases photoinduced with increasing temperature and it is expected to be zero near T_g . For a-As₂S₃, the value for the first run decreases with increasing temperature while that of other run does not decrease so much. It is considered that this temperature insensitivity is responsible for the strong covelency of a-As₂S₃ compared with a-As₂Se₃. The datum point of the first run and that of the other runs meet at temperature near T_g . This temperature coincides with the temperature where the durable photodarkening effect disappears. Above this temperature, the photoinduced effect is only related to the transient photodarkening. It should be noted that there is accumulative photoinduced absorption above T_g , that is, in the supercooled liquid state. We attribute the change to the stronger covalency in As₂S₃. Such strong covalency would make a slow structural relaxation of the order of second even in the supercooled liquid state. The accumulative photoinduced effect rapidly decreases above T_g and we have checked that

there is no accumulative photoinduced absorption at 300 °C. The structural relaxation is supposed to be faster with the aid of the thermal vibration and the fluidity above T_g .



Fig. 7. Temperature variation of the photoinduced effect represented by $\Delta T/T$ in $a-As_2Se_3$ and $a-As_2S_3$. Closed circles indicate the photoinduced effect related to the durable photodarkening (DPD), where ΔT is estimated by the total change of transmittance for the 10 times experimental runs. Other symbols are indicated in the figure.

3.2.2. Spectra measurements

Photoinduced absorption spectra during repeated laser illumination and after stopping the illumination for a-As₂Se₃ and a-As₂S₃ at room temperature are shown in Fig. 8. For both of the samples, photoinduced absorption with a peak appears after starting the illumination, and the peak grows by the subsequent illumination. After stopping the illumination, the peak decays with time and there is a saturation of the decay. This saturated spectrum indicates the change related to the durable photodarkening. It should be noted that the peak maximum is located at the energy (590 nm=2.10 eV for a-As₂Se₃, 460 nm=2.70 eV for a-As₂S₃) higher than the optical gap (1.7 eV for a-As₂Se₃, 2.4 eV for a-As₂S₃ [7,8]) in both of the spectra during and after stopping the illumination. The range of the wavelength where photoinduced absorption is observed in the spectrum (550-700 nm for a- As₂Se₃, 440-550 nm for a- As₂S₃) is in the energy region of the absorption edge in the optical absorption spectrum. Therefore, the photoinduced change indicates the change of the band edge structure so that the optical gap decreases.

3.3. Photodarkening process

We have observed three types of photodarkening; (1) transient photodarkening in the nano- and microsecond domain (2) transient photodarkening in the second and minute domain, which is observed after accumulative photoinduced change for repeated pulsed illumination (3) the durable photodarkening. The result of the photoinduced effects for repeated experimental run can be understood using free energy diagram as shown in Fig. 9. With one pulse of the laser, a state is excited to higher

energy level and relaxes toward the initial level. But it is temporary trapped on a higher level than the initial level (the inset in Fig. 9). This procedure corresponds to the photodarkening in the nano- and microsecond domain. By repeating the pulsed laser illumination, a state goes higher and higher as the accumulative photoinduced change suggests. In this process, the total photoinduced change is determined by two factors; the increase of the level for one pulse of the laser and the number of pulses. After stopping the laser illumination, a state goes lower and lower passing through the temporary trap levels. This process corresponds to the transient photodarkening in the second and minute domain. A state is finally trapped on the level which is related to the durable photodarkening. If there is no illumination or no thermal change, a state is semi-permanently trapped on this level. With the next laser illumination, a state goes higher and higher again passing through the temporary trap levels. Total increase of the level is also determined by the above two factors. That is why the accumulative photoinduced change is almost constant regardless of the number of experimental run. On the other hand, there is a saturation level in finally trapped levels, which are related to the durable photodarkening.



Fig. 8. Time evolution of the photoinduced absorption spectrum for a-As₂Se₃ and a-As₂S₃ at room temperature.

The temperature dependence of the three types of photodarkening is summarized as follows. (1) The durable photodarkening is observed below T_g . (2) The transient photodarkening in the second and minute domain is observed only below T_g for As₂Se₃ and in both amorphous and supercooled liquid states for As₂S₃. (3) The transient photodarkening in the nano- and microsecond domain is observed in amorphous, supercooled liquid and liquid state. From these results, we can expect that the structure under a given temperature condition affects the photoinduced changes. In crystal, As₂Se₃ and As₂S₃ have a stacked layer structure. It is considered that the layer structure is primarily preserved in amorphous and liquid state

[12,13,14]. At higher temperature, such as the temperature above 450 °C, the layer structure collapses [12,15]. Since the transient photodarkening in the nanoand microsecond domain is observed in both amorphous and liquid states, it is supposed to be a common structural unit in both amorphous and liquid state where the photostructural change occurs. A cluster composed of two-dimensional network of covalent bonds is a plausible candidate as the structural unit. The interaction between the clusters seems to be related to the durable photodarkening since the effect is quite affected by temperature variation and it disappears above T_g , where the clusters can move.



Fig. 9. Schematic diagram of free energy levels in amorphous arsenic chalcogenide. The photoinduced change for one pulsed of the laser is indicated in the inset.

It should be noted that all of these photoinduced changes are observed in the absorption edge. This indicates that the band edge structure changes by the illumination. Since the energy where the photoinduced changes are observed is larger than the optical gap $(1.7 \text{ eV} = 729 \text{ nm for } a-As_2Se_3, 2.4 \text{ eV} = 517 \text{ nm for}$ a-As₂S₃ at room temperature [7, 8]) as seen in Fig. 2 and Fig. 8, the shift of the band edge is supposed to occur, rather than the broadening of the band tail. There are two possibilities to make the optical gap decrease; lowering anti-bonding band, which is the lowest conduction band, and raising lone-pair band, which is the highest valence band. The former can be explained by weakening of covalent bond. The weakening of the covalent bonds results in the shortening of the distance between the centre of the bonding band, which is the second highest valence band, and the centre of the antibonding band. This causes the shift of the antibonding band to lower energy. Raising lone-pair band is suggested by Watanabe et al. [16] considering the intermolecular interaction, namely, the repulsive interaction between the lone-pair electrons located at different layers. The conclusive model should be carefully made after performing further experiment. However, we can describe a scenario of the photoinduced change by summing up our present experimental results as follows.

With the bandgap illumination, lone-pair electrons on chalcogen atoms excite to antibonding orbitals on the cluster. By this excitation, the As-Se or As-S covalent bonds are weakened. The change of the bond length produces the distortion to surrounding atoms. The distorted configuration affects the strength of the bond in the surrounding atoms, resulting in the change of the bond length. In this way, the effect can propagate to the next surrounding atoms and spreads all over the cluster. Once such effect spreads all over the cluster, it takes a long time with the orders of nanosecond or microseconds to recover to the initial state. This must be the reason why the photoinduced change is observed in the microsecond domain even in the liquid state. The cluster must be a grafted chain (a 1.5 dimensional network) in the high temperature liquid [15], or a two dimensional network in the low temperature liquid and amorphous. With decreasing temperature, the size of the cluster might be larger and the interaction between the clusters might be larger. Above T_g , the clusters can move. Below T_g , the arrangement of the clusters is quenched. Although there is no long range order in the amorphous state, the arrangement of the clusters after quenching must be the most thermally stable one. We expect that deviation of the arrangement of the clusters is induced by the bandgap illumination. The structural change on the cluster must affect neighboured cluster and the effect results in the change of the arrangement of the clusters. After making the deviation, the cluster stays at the metastable site rather than to get back to the initial site. This can be realised because of the randomness of the arrangement. Flipping to the other site is supposed to be made with small energy. This change corresponds to the durable photodarkening. The transient photodarkening observed after the accumulative photoinduced change may be related to the distortion of the cluster. The distortion can be accumulated by repeated pulsed illumination. When the covalency in the cluster is strong and the interaction between the clusters is strong, the accumulative effect on the distortion can be insensitive to the temperature variation. Above T_{g} , the cluster can move and the interaction between the clusters considerably decreases. It is expected that the accumulative distortion in the cluster is easy to relax due to the weakening of the interaction between the clusters. A rapid decrease of the accumulative photoinduced change above T_g in Fig. 7 seems to suggest such picture.

4. Conclusion

We have measured transient photoinduced optical absorption for a-, $1-As_2Se_3$ and a-, $1-As_2S_3$. Three types of photodarkening, namely, transient photodarkening in the nano- and microsecond domain, the transient photodarkening in the second and minute domain and the durable photodarkening, were observed from the

measurement. The difference of the three photodarkening clearly appeared in the results of repeated experimental run and the temperature dependence. The transient photodarkening in the nano- and microsecond domain was observed even in the supercooled liquid and the liquid state. For As₂S₃, accumulative photodarkening in the supercooled liquid state was observed. A clear peak at the energy higher than the optical gap was observed in the photoinduced absorption spectra. It is considered from the result that the photodarkening is related to the change in the covalent bond or interaction between clusters. We expect that the change occurs involving a whole system of the sample which should be distinguished from locally limited change such as creation of defect. Validity of the described scenario should be examined by making further experiments.

In the end, we wish Prof. Radu Grigorovici a happy 95th birthday and wish him good health in the years to come.

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