Photodarkening in the nano- and microsecond domain: measurements of transient photoinduced absorption spectra of amorphous and liquid As_2Se_3

LETTER TO THE EDITOR

Photodarkening in the nano- and microsecond domain: measurements of transient photoinduced absorption spectra of amorphous and liquid As$_2$Se$_3$

Yoshifumi Sakaguchi and Kozaburo Tamura

Graduate School of Engineering, Kyoto University, Yoshida-honmachi, Kyoto 606-8501, Japan

Abstract
Photodarkening in the nano- and microsecond domain was observed in amorphous As$_2$Se$_3$ from measurements of the transient photoinduced optical absorption spectra in the high absorption region using a specially designed optical cell which prepared a submicrometre-size melt-quenched amorphous film. This photodarkening was also observed in the liquid state. The observed optical change suggests the presence of a photoinduced structural change in the time domain. The origin of this photodarkening is discussed.

1. Introduction

It is well known that chalcogenide glasses exhibit reversible photodarkening, which is characterized by a shift of absorption edge to the low-energy side. The photodarkening is observed after prolonged illumination with bandgap light and the effect is semi-permanently preserved at room temperature. It recovers by annealing near and below the glass transition temperature, T_g. The phenomenon implies a photosensitivity of the materials with lone-pair electrons, which have been named *lone-pair semiconductors* by Kastner [1]. Also, it shows the presence of many metastable states, which originate from the structural randomness of the materials [2]. The state changes from one metastable state to another by bandgap illumination. After stopping the illumination, the state is trapped in a certain metastable state. Hence the photoinduced effect is preserved. The optical change is accompanied by a structural change, as the volume change [3] and the change of x-ray diffraction pattern [4] suggest. The structural change is not a local one such as the creation of defects but it involves the whole bulk of the sample. It has been pointed out that the excitation of lone-pair electrons plays a crucial role in the occurrence of photodarkening [2]. However, the effect of the excitation of lone-pair electrons is not clearly shown in this experimental procedure. Because prolonged illumination is used as the excitation light source, an evolutional change might occur during the illumination. The photodarkening observed is 'not' the 'immediate' effect caused by the excitation of lone-pair electrons but the final state after optical processes and structural changes are completed. To clarify the effect of the excitation of lone-pair electrons, any immediate response should be

examined. Recently, Li and Drabold performed first-principles molecular dynamics simulations for photoexcited glassy As_2Se_3 [5]. They showed a photostructural change in the femtosecond domain. They observed bond breaking, bond switching and the creation of defect pairs. They inferred that the non-local 'polaron-like' collective oscillation is related to the spatially non-local change. Measurements of the transient absorption spectra of amorphous (a-) As_2Se_3 using a nanosecond pulsed laser were made by Orenstein *et al* [6–8]. They measured the spectra only in the energy region associated with the defect states. However, the photodarkening is related to the non-local structural changes, which differ from local structural changes such as the creation of defects. In order to investigate the non-local structural changes, measurements of the absorption spectra in the high absorption region are required. For this purpose, we have performed measurements of the transient photoinduced optical absorption spectra in the high absorption region for a-As_2Se_3 using a specially designed optical cell which prepared melt-quenched amorphous film. The measurements were performed including the liquid state up to 703 K. In this letter, we show the experimental results of the measurements and discuss the origin of the observed photoinduced change.

2. Experimental details

We have used a specially designed optical cell which can prepare submicrometre-size liquid film [9]. In this experiment, we have prepared samples with a thickness of 0.6 μm. Melt-quenched amorphous film was obtained by inserting the liquid sample into the cell and quenching the sample. Using the film, the optical absorption spectrum in the high absorption region could be measured. Time-resolved optical absorption measurements were performed using a monochromator, a Si PIN photodiode, a wide-band amplifier, a digital oscilloscope, a delay generator and a W lamp as a probe beam. The second harmonics (532 nm = 2.33 eV) of the pulsed Nd:YAG laser were used as the excitation light source. This laser can excite lone-pair electrons to the anti-bonding states in the sample since the optical gap of a-As_2Se_3 at room temperature is 1.7 eV [2, 10, 11]. The pulse-width is 7 ns. The repetition rate was 10 Hz. Measurements at temperatures in the range from 301 to 503 K were made in a single run by using the pulsed laser with an intensity of 1.1 mJ cm^{-2}. The measurement at 703 K was made in a different run by using the pulsed laser with an intensity of 1.4 mJ cm^{-2}.

3. Results and discussion

3.1. Photoinduced change at room temperature

Figure 1 shows the time variation of the photoinduced absorption, $\Delta T/T$, at different wavelengths for a-As_2Se_3 at room temperature. T is the transmittance in the thermal equilibrium state and ΔT is the photoinduced change in transmittance. Photoinduced absorption and its decay are clearly observed at each wavelength. The data indicate that the pulsed illumination induces the change in absorption and that transient photodarkening exists in the nano- and microsecond domain. A larger darkening is observed in the region with a shorter wavelength. There are two decay processes in the observed time domain. One is observed in the time domain before 1 μs with a steeper change. The other is observed in the time domain after 1 μs with a long decay time. To cover the wide time domain, a double logarithmic plot of the photoinduced absorption, $\Delta T/T$, versus delay time is shown in figure 2. The fact that the photoinduced absorption is observed even at 1 ms shows that the decay is very slow. In the figure, the two decay processes are seen in the difference of slopes of the decay curves except that at 900 nm.
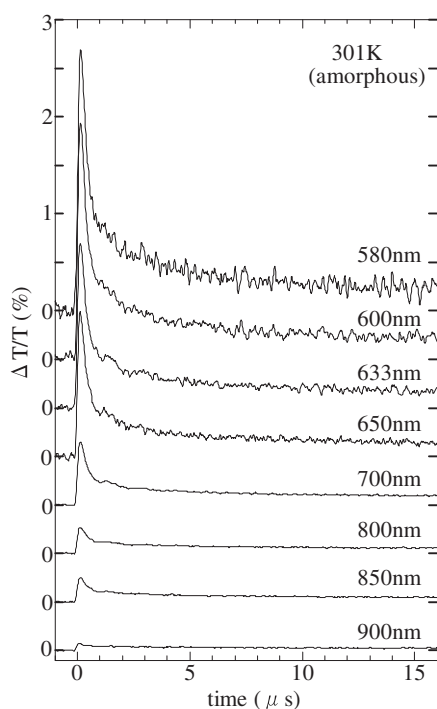
Figure 1. Photoinduced absorption change of a-As$_2$Se$_3$ at room temperature after illumination by a pulsed laser with the intensity of 1.1 mJ cm^{-2}.

In the inset of figure 2 we present the optical absorption spectrum at room temperature before illumination by the pulsed laser [11, 12]. Optical absorption spectra of amorphous semiconductors can be divided into three regions [13]: an exponential region, usually referred to as the Urbach tail; a high absorption region above the Urbach tail; and a weak absorption region below the Urbach tail. The high absorption region is in the range of optical absorption coefficient α greater than 10^4 cm^{-1} and is associated with the interband transitions. The Urbach tail is in the range from 1 cm^{-1} (or less) to 10^4 cm^{-1}. There are several models to explain the exponential change but the conclusive explanation has not been settled [14]. The weak absorption region is associated with defects and impurities. In the inset of figure 2, the wavelengths of the monochromatized probe beam and the corresponding optical absorption coefficients are indicated. As seen in the figure, α at 600, 650 and 700 nm lie in the high absorption region, α at 800 nm lies on the Urbach tail, and α at 900 nm lies in the weak absorption region.

Figure 3 shows the photoinduced absorption spectra for each decay process at 200 ns and at 2 μs which are deduced from the data in figures 1 and 2. As seen in the spectrum at 200 ns and also at 2 μs, large photoinduced absorption is observed at wavelengths less than 750 nm. It should be noted that the change occurs in the high absorption region, which means that the fundamental absorption edge substantially shifts to lower energy with the laser illumination. It is known that in photodarkening induced by prolonged illumination with bandgap light, the absorption edge shifts in accordance with the bulk structural change [2, 3]. The transient photodarkening observed in the high absorption region suggests that such bulk-oriented change takes place at the same time. The weak photoinduced change at 900 nm is connected with
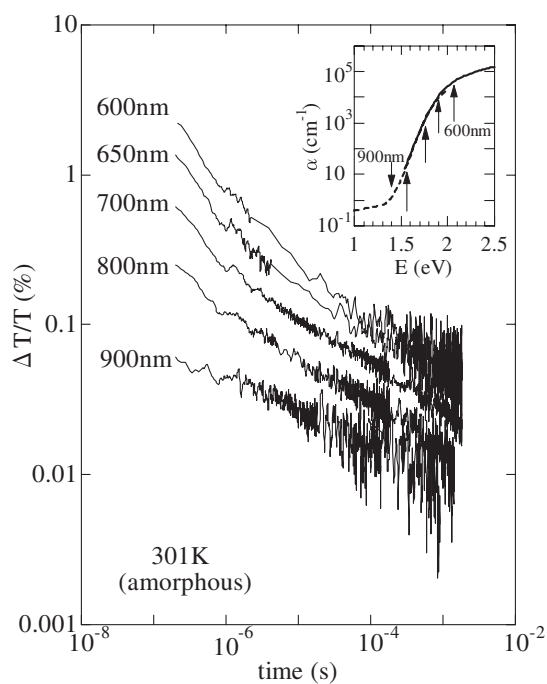
Figure 2. Time decay of the photoinduced absorption of a-As$_2$Se$_3$ at room temperature. Inset: the optical absorption spectrum at room temperature. Solid curve from [11] and dashed curve from [12]. The arrows indicate the optical absorption coefficients at 600, 650, 700, 800 and 900 nm respectively from the right-hand side.
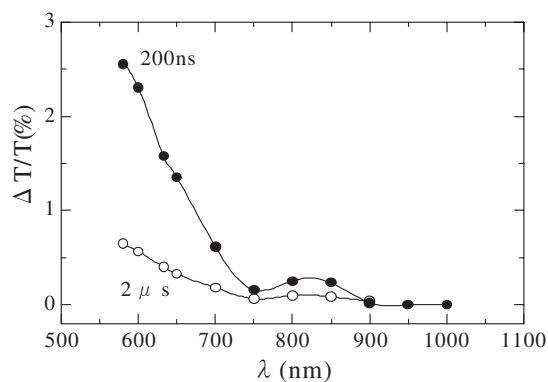

Figure 3. Photoinduced optical absorption spectra at 200 ns and 2 μs for a-As$_2$Se$_3$ at room temperature. The weak maxima appearing from 750 to 900 nm are due to the optical interference caused by the change of refractive index of the sample.

localized defect states. It is considered that the defects such as dangling bonds or *valence alternation pairs* are created by laser illumination.

3.2. Temperature variation of the photoinduced change

Figure 4 shows a logarithmic plot of the photoinduced absorption, $\Delta T/T$, versus delay time for the amorphous sample at higher temperatures and the supercooled liquid. The difference
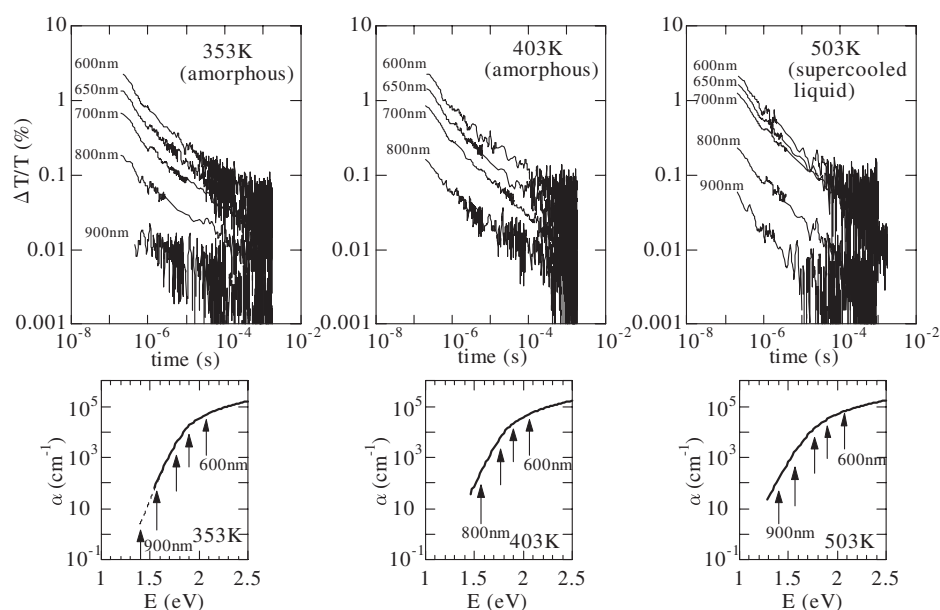
Figure 4. Time decay of the photoinduced absorption of amorphous (353 K, 403 K) and supercooled liquid (503 K) As_2Se_3. The optical absorption spectrum at the corresponding temperature is indicated below each figure. Solid curve from [11] and dashed curve from [12]. The arrows indicate the optical absorption coefficients at the energies of the monochromatized probe beam used. The longest and the shortest wavelengths of the probe beam are indicated in the figures.

of the slope of the photoinduced curve between the fast decay region (<1 μs) and the slow decay region (>1 μs) observed at room temperature becomes small at 353 K. At 503 K, there is no difference between them. The slope of the curve in the time domain from 10^{-5} to 10^{-3} s becomes steeper with increasing temperature. The photoinduced change at 900 nm of a-As_2Se_3 at 353 K is smaller than that at room temperature and the change at 900 nm was not detected at 403 K. We attribute this to a defect which relaxes immediately at high temperatures with the aid of thermal vibration. At 503 K, the photoinduced change at 900 nm appears again. In the optical absorption spectrum at 503 K, the absorption coefficient at 900 nm is 75 cm^{-1} and this is no longer in the weak absorption region. It lies on the Urbach tail. The origin of the photoinduced change is different from that of the change at 900 nm at room temperature although the wavelength is the same. It should be noticed that transient photodarkening is still observed in the supercooled liquid state in the nano- and microsecond domain. The photodarkening observed after stopping the prolonged illumination cannot be expected to occur above T_g, since it recovers by annealing below T_g. The origin of the photodarkening in the nano- and microsecond domain is different from the photodarkening observed after stopping the prolonged illumination.

3.3. Photodarkening in the liquid state

Figure 5 shows the time decay of the photoinduced absorption of liquid As_2Se_3 at 703 K in the thermal equilibrium state. The slope of the decay is steeper than that at lower temperatures. This indicates that the structural relaxation becomes faster with the aid of the thermal vibration. It should be noticed that the photoinduced change is observed in the nano- and microsecond domain even in the liquid state. Here the liquid is in the thermal equilibrium state. This is
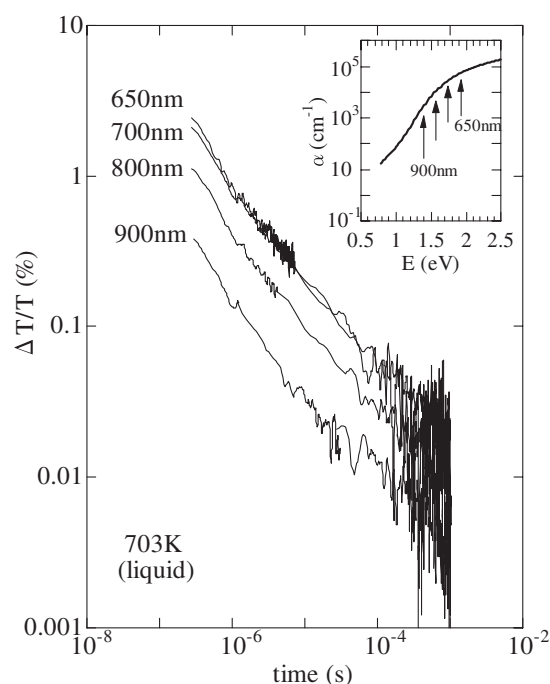
Figure 5. Time decay of the photoinduced absorption of liquid As_2Se_3 at 703 K. Inset: the optical absorption spectrum at 703 K [11]. The arrows indicate the absorption coefficients at 650, 700, 800 and 900 nm respectively from the right-hand side.

in contrast to the supercooled liquid state and amorphous state, which are in 'not' thermal equilibrium state. This suggests that the photodarkening in the nano- and microsecond domain is essentially different from the photodarkening observed after stopping the prolonged illumination, which originates from the metastability of the material.

Since a photoinduced change in the liquid state occurs in the high absorption region as well as a change in the amorphous state, it is considered that a non-local structural change also occurs involving the whole bulk of the liquid sample upon illumination by a pulsed laser. We infer that there are common initial and excited structures in both the amorphous and liquid state. As for such structure, we consider a two-dimensional network composed of covalent bonds since the nearest neighbour distance and the medium range order do not change from the amorphous state to the liquid state [15–17]. The size of the layer might be smaller with increasing temperature and the layer might also be more deformed with increasing temperature. We can regard such a sheet of the layer as a structural unit where the photostructural change occurs. The long decay time can be explained by such a structural unit in a following way. Photons excite lone-pair electrons in some of the atoms on the unit and induce instability in the covalent bond. It causes a change in the bond length. The effect is not limited to the local region, but it propagates to the surrounding atoms and spreads all over the unit. For instance, As–As or Se–Se wrong bond is produced from an As–Se bond by the excitation of lone-pair electrons. The created distortion propagates to the next atoms. New wrong bonds would be created on the next atoms in this process. Once such an effect spreads all over the unit, it takes a long time, with the order of nano- or microseconds, to recover to the initial state. This must be the reason why such slow decay is observed even in the liquid state.

We have already observed such a type of photoinduced absorption change in liquid selenium [18]. The photoinduced absorption decays in the microsecond domain. Fork *et al* have observed photoinduced absorption with a long tail beyond 25 ps in a-As_2S_3 in their picosecond spectroscopy [19]. We can expect that the change continues to the nanosecond domain. Photodarkening in the nano- and microsecond domain seems to be the common response for illumination which excites lone-pair electrons to the anti-bonding state in amorphous and liquid chalcogenides. Lone-pair orbitals or antibonding orbitals may play an important role in propagating the photoinduced effect.

4. Summary

We have found that transient photodarkening exists in the nano- and microsecond domain in amorphous and liquid As_2Se_3. Since the energy region where the darkening occurs is associated with the interband transitions, the photoinduced change exhibits a non-local structural change in the time domain. This structural change is essentially different from the structural change which is observed after stopping prolonged illumination in the sense that the former seems to be associated with the common nature of lone-pair semiconductors while the latter is associated with the metastability of amorphous chalcogenides. The extension of the temperature range and the time domain in the measurements will yield important information about these structural changes. The measurements for other chalcogenides will help to give a unified view of the photostructural response in chalcogenide disordered system.

References

[1] Kastner M 1972 *Phys. Rev. Lett.* **28** 355
[2] Tanaka K 1980 *J. Non-Cryst. Solids* **35/36** 1023
[3] Hamanaka H, Tanaka K, Matsuda A and Iizima S 1976 *Solid State Commun.* **19** 499
[4] Tanaka K 1975 *Appl. Phys. Lett.* **26** 243
[5] Li J and Drabold D A 2000 *Phys. Rev. Lett.* **85** 2785
[6] Orenstein J, Kastner M and Monroe D 1980 *J. Non-Cryst. Solids* **35/36** 951
[7] Orenstein J and Kastner M 1981 *Phys. Rev. Lett.* **46** 1421
[8] Orenstein J, Kastner M A and Vaninov V 1982 *Phil. Mag.* B **46** 23
[9] Sakaguchi Y and Tamura K 2000 *Rev. Sci. Instrum.* **71** 494
[10] Mott N F and Davis E A 1979 *Electronic Processes in Non-Crystalline Materials* 2nd edn (Oxford: Clarendon) p 290, 291 (The value of optical gap of a-As_2Se_3 measured by Felty and Myers (private communication) is presented in the textbook)
[11] Hosokawa S, Sakaguchi Y, Hiasa H and Tamura K 1991 *J. Phys.: Condens. Matter* **3** 6673
[12] Edmond J T 1966 *Br. J. Appl. Phys.* **17** 979
[13] Tauc J 1974 *Amorphous and Liquid Semiconductors* ed J Tauc (London: Plenum) p 172
[14] Several models are presented in
    Mott N F and Davis E A 1979 *Electronic Processes in Non-Crystalline Materials* 2nd edn (Oxford: Clarendon) p 273
    Tauc J 1974 *Amorphous and Liquid Semiconductors* ed J Tauc (London: Plenum) p 180
[15] Taylor P C, Bishop S G and Mitchell D L 1971 *Phys. Rev. Lett.* **27** 414
[16] Uemura O, Sagara Y, Muno D and Satow T 1978 *J. Non-Cryst. Solids* **30** 155
[17] Hosokawa S, Sakaguchi Y and Tamura K 1992 *J. Non-Cryst. Solids* **150** 35
[18] Sakaguchi Y and Tamura K 1998 *J. Phys.: Condens. Matter* **10** 2209
[19] Fork R L, Shank C V, Glass A M, Migus A, Bosch M A and Shah J 1980 *J. Non-Cryst. Solids* **35/36** 963