

Transient absorption spectra of liquid selenium: a possibility of photoinduced semiconductor-metal transition

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1998 J. Phys.: Condens. Matter 10 2209

(<http://iopscience.iop.org/0953-8984/10/10/005>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 12/05/2010 at 23:20

Please note that [terms and conditions apply](#).

Transient absorption spectra of liquid selenium: a possibility of photoinduced semiconductor–metal transition

Yoshifumi Sakaguchi and Kozaburo Tamura

Faculty of Integrated Arts and Sciences, Hiroshima University, Higashi-Hiroshima 739, Japan

Received 30 May 1997, in final form 22 October 1997

Abstract. Transient absorption spectra of liquid selenium after illumination with a pulsed laser have been investigated. It was found that a giant photodarkening occurs and the optical gap disappears when the pulsed laser illuminates liquid selenium at 350 °C with the intensity of 15 mJ/pulse. The possibility of a photoinduced semiconductor–metal transition is discussed.

1. Introduction

Liquid selenium in the vicinity of its melting point consists of long polymeric chains which contain as many as 10^5 atoms and exhibits semiconducting behaviour. With increasing temperature, the chain length becomes short, electrical conductivity increases and the optical gap decreases [1]. It is known that further increase of temperature with application of pressure gives rise to a semiconductor–metal transition near the liquid–gas critical point ($T_c = 1615$ °C, $P_c = 385$ bar, $\rho_c = 1.85$ g cm $^{-3}$ [2]) [3]. NMR study [4] revealed that the chain molecule contains about ten atoms on average when the semiconductor–metal transition occurs. Recent measurements of x-ray diffraction and EXAFS [5, 6] revealed that the structure of the chain molecules changes at the transition. The semiconductor–metal transition in liquid selenium seems to be strongly related to the instability of the chain structure.

Trigonal selenium, the most stable crystalline form under normal conditions, consists of helical chains. It is well known that lone-pair (LP) electrons, which are localized around selenium atoms and do not participate in covalent bonding, play a crucial role in stabilizing the helical structure [7, 8]. LP electrons occupy the highest filled state, forming the valence band, while the empty anti-bonding σ^* -states form the conduction band. Between the valence and conduction bands there is a gap of energy of about 2 eV, so trigonal selenium behaves as a semiconductor. The characteristic features of the structural and electronic properties of liquid selenium near the melting point are considered to be essentially the same as those for the crystalline state. The thermal excitation of LP electrons to σ^* -orbitals, therefore, may affect the properties of liquid selenium, changing the strengths of the bonds, the conformation of the chain or the interaction between the chains. The semiconductor–metal transition may involve such an instability of the chain structure. As far as we are aware, there is no experimentally direct evidence of the role of the LP electrons in the semiconductor–metal transition in liquid selenium. In this paper, we report the results of the measurement of transient absorption spectra taken after illuminating the selenium with

a pulsed laser which excites LP electrons to σ^* -orbitals. We discuss the possibility of a photoinduced semiconductor–metal transition in liquid selenium.

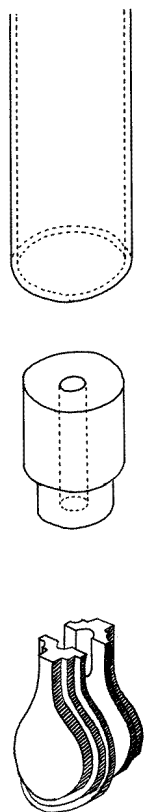


Figure 1. An optical cell made of quartz. Three separate parts are connected together. In the lowest part two quartz plates with rounded shapes face each other. The edges of these two plates are connected together and a very thin and uniform gap is made between them.

2. Experimental details

In order to measure the spectra in the high-absorption region with an absorption coefficient exceeding 10^4 cm^{-1} , which provide information about interband transitions, it is necessary to use an optical cell with a very thin space for the liquid sample. We have developed a specially designed optical cell made of quartz as shown in figure 1. As seen in the lowest part of the figure, two quartz plates with rounded shapes face each other. The diameter of the round surface is about 1 cm. The edges of these two plates were connected together by glass-fusing work. A very thin and uniform sample space was made between them. This part was connected to another two pieces as shown in the figure. The thickness of the sample space was determined by the optical interference method. The pulsed laser illuminated the rounded surface from the normal direction. A more detailed description of the cell construction will be given elsewhere [9]. In the present experiment we have used the cell with the thickness set at $1.0 \text{ }\mu\text{m}$.

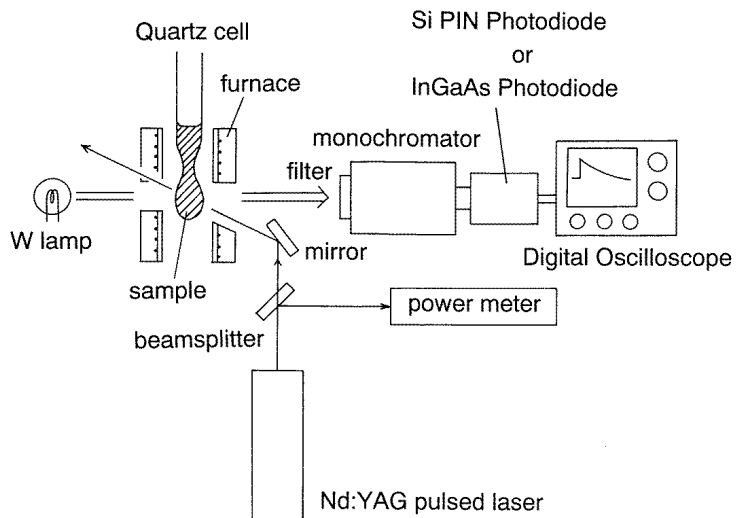


Figure 2. A schematic diagram of the apparatus used for the present experiment.

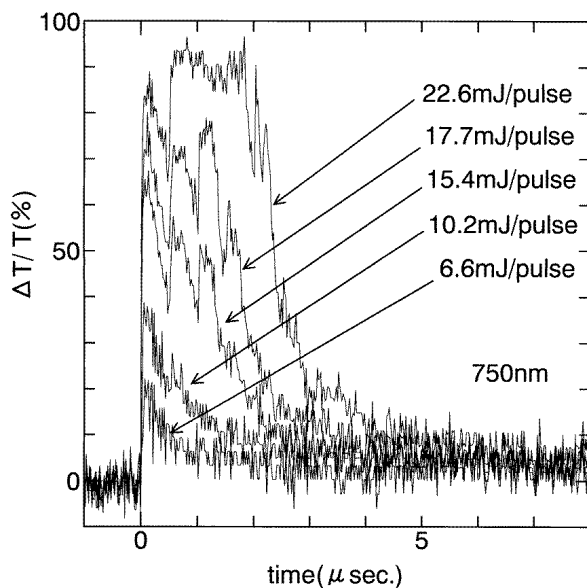


Figure 3. Plots of $\Delta T/T$ versus time for liquid selenium at 350 °C after illumination with a pulsed laser with varying power. The wavelength of the probe beam is 750 nm.

Figure 2 is a schematic diagram of the apparatus used in the present experiment. The second harmonic (532 nm) of the pulsed Nd:YAG laser (Spectra Physics Lasers, Incorporated, Quanta-Ray 16) was used for the excitation of LP electrons in liquid selenium. The widths of the pulses were 6–7 ns. The repetition rate was 10 Hz. The intensity of the pulsed laser was measured by using a power meter (Ophir Optronics, Incorporated, Nova and 03A-P) combined with a beam splitter. The pulsed laser beam was reflected by

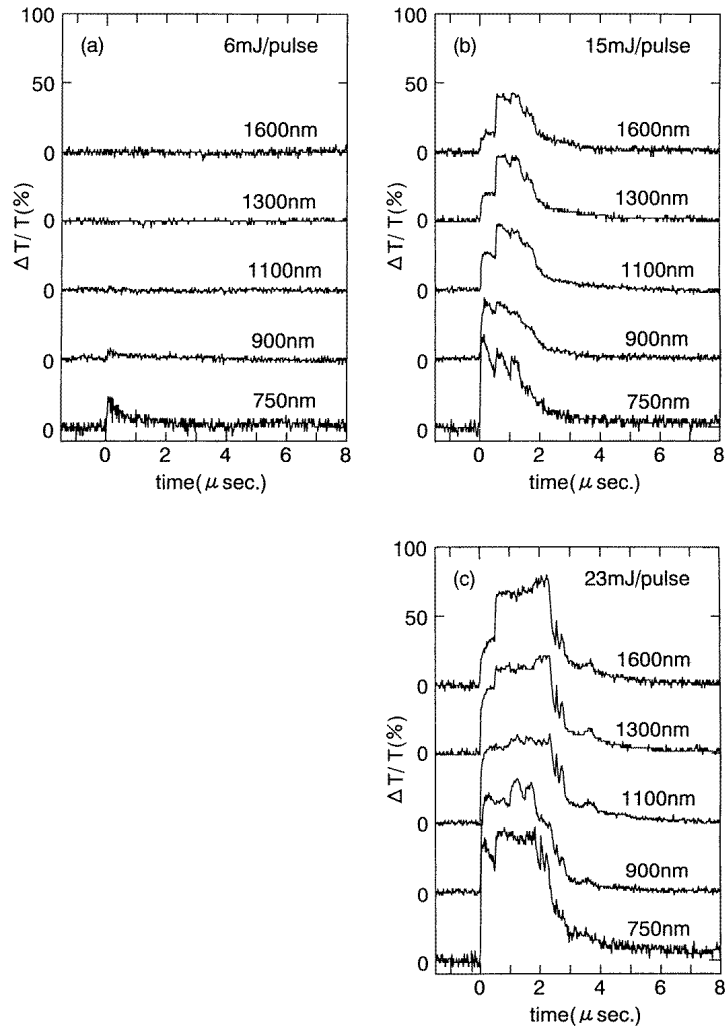


Figure 4. Plots of $\Delta T/T$ versus time at different wavelengths of the probe light for the laser power fixed at 6, 15 and 23 mJ/pulse. The temperature of the liquid selenium is 350 °C.

a mirror and illuminated an area 8 mm in diameter of the liquid specimen contained in the quartz cell. There are two windows in the side wall of the furnace which are used for the illumination with the pulsed laser and also for the transmission of a probe light. A tungsten lamp with a power of 30 W was used as the probe light. The light transmitting through the sample was monochromatized by a monochromator (Jasco CT25GD) and detected by a Si PIN photodiode (Hamamatsu Photonics K.K. S5531) or InGaAs photodiode (Hamamatsu Photonics K.K. G3476-03) combined with a digital oscilloscope (Sony Tektronix TDS350). The laser shots were repeated more than one hundred times to obtain final data with less noise. The ranges over which we made measurements were 680–1000 nm for the Si PIN photodiode and 950–1650 nm for the InGaAs photodiode. In front of the monochromator, a notch filter (Oriel instruments 53683) was placed to prevent the passage of stray light from the pulsed laser.

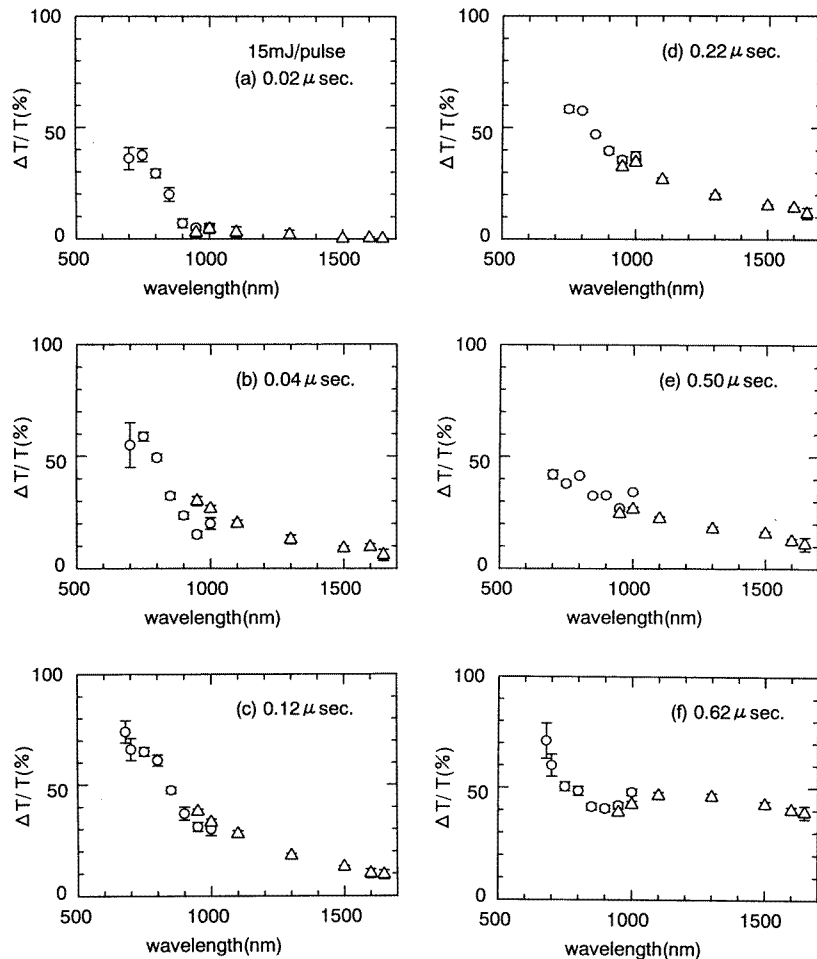


Figure 5. Plots of $\Delta T/T$ versus wavelength at different times after the illumination with the pulsed laser with the intensity set at 15 mJ/pulse, obtained from the data shown in figure 4(b). Open circles show the data obtained by using a Si PIN photodiode and open triangles the data obtained by using an InGaAs photodiode.

3. Results and discussion

3.1. Photodarkening and the relaxation in liquid selenium

Figure 3 shows the fractional change in the transmission of the probe light, $\Delta T/T$, versus time for liquid selenium at 350 °C, where T is the transmittance in the thermal equilibrium state and ΔT the photoinduced change of the transmittance. The wavelength of the transmitting probe light is 750 nm. The zero point on the horizontal axis indicates the time at which a pulsed laser illuminates the sample. As seen in the figure, when the pulsed laser illuminates the sample with the intensity of 6.6 mJ/pulse, an abrupt increase of $\Delta T/T$ is clearly observed and $\Delta T/T$ decreases monotonically with time but does not decay with a single-exponential curve. Here the increase of $\Delta T/T$ in the figure corresponds to the decrease of the transmitting probe light—that is, the photodarkening caused by the laser

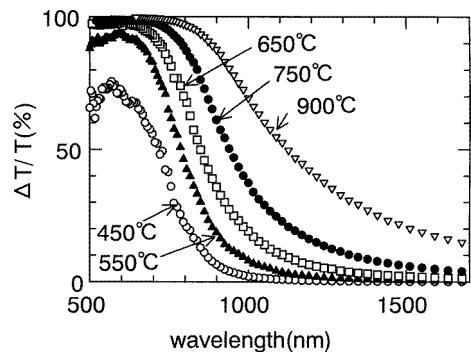


Figure 6. Plots of $\Delta T/T$ versus wavelength when the temperature of liquid selenium increases from 350 °C up to temperatures of 450, 550, 650, 750 and 900 °C. These data are obtained by using the static absorption spectra for liquid selenium [1].

illumination. With increasing laser power the value of $\Delta T/T$ at the time immediately after the illuminating increases. The value becomes more than 80% when the pulsed laser providing the illumination has an intensity of 22.6 mJ/pulse. It should be noted that $\Delta T/T$ does not decrease monotonically, and a second increase appears with a delay time of 0.5 μ s when the strength of the pulsed laser becomes higher than 10 mJ/pulse. The value of $\Delta T/T$ at the second absorption increases with increasing laser power and becomes more than 90% when the intensity of the pulsed laser is increased to 22.6 mJ/pulse. After the second absorption started to appear, an oscillation with a period of about 0.5 μ s was observed. The period of the oscillation remained almost the same when the laser power was changed.

It is important to confirm whether these photoinduced changes arise from a real absorption or not. In order to examine the possibility that the change arises from the photoluminescence, firstly, we measured the signal without any probe light after illumination with the pulsed laser. It was found that no signal was detected. Secondly, we examined the possibility that the change is due to the scattering of the probe light by some inhomogeneity appearing in the liquid sample. We measured the difference of $\Delta T/T$ caused by changing the width of the slit at the entrance of the monochromator. The values of $\Delta T/T$ were found not to change. Therefore, the change in $\Delta T/T$ observed must be due to the photoinduced absorption by the liquid sample itself.

It is also important to note whether the change arises from the temperature rise of the sample caused by laser heating or not. Recently, we have found photoinduced and athermal phenomena in liquid sulphur [10]. As is well known, sulphur belongs to the same group in the periodic table as selenium, and LP electrons play an important role in the structural and electronic properties. We have measured transient absorption spectra of liquid sulphur after illumination with the pulsed laser and found that photoinduced polymerization occurs, which is closely connected with the structural instability of sulphur molecules induced by the

Figure 7. (See facing page.) Transient spectra—that is, the time evolution of the plots of the optical absorption coefficient, α , versus the photon energy, $\hbar\omega$, after illumination with the pulsed laser at the intensity 15 mJ/pulse. Open circles show the data obtained by using a Si PIN photodiode and open triangles the data obtained by using an InGaAs photodiode. These data are calculated from the data shown in figure 5, taking into consideration the penetration depth of the laser. The solid curves are the static spectra [1].

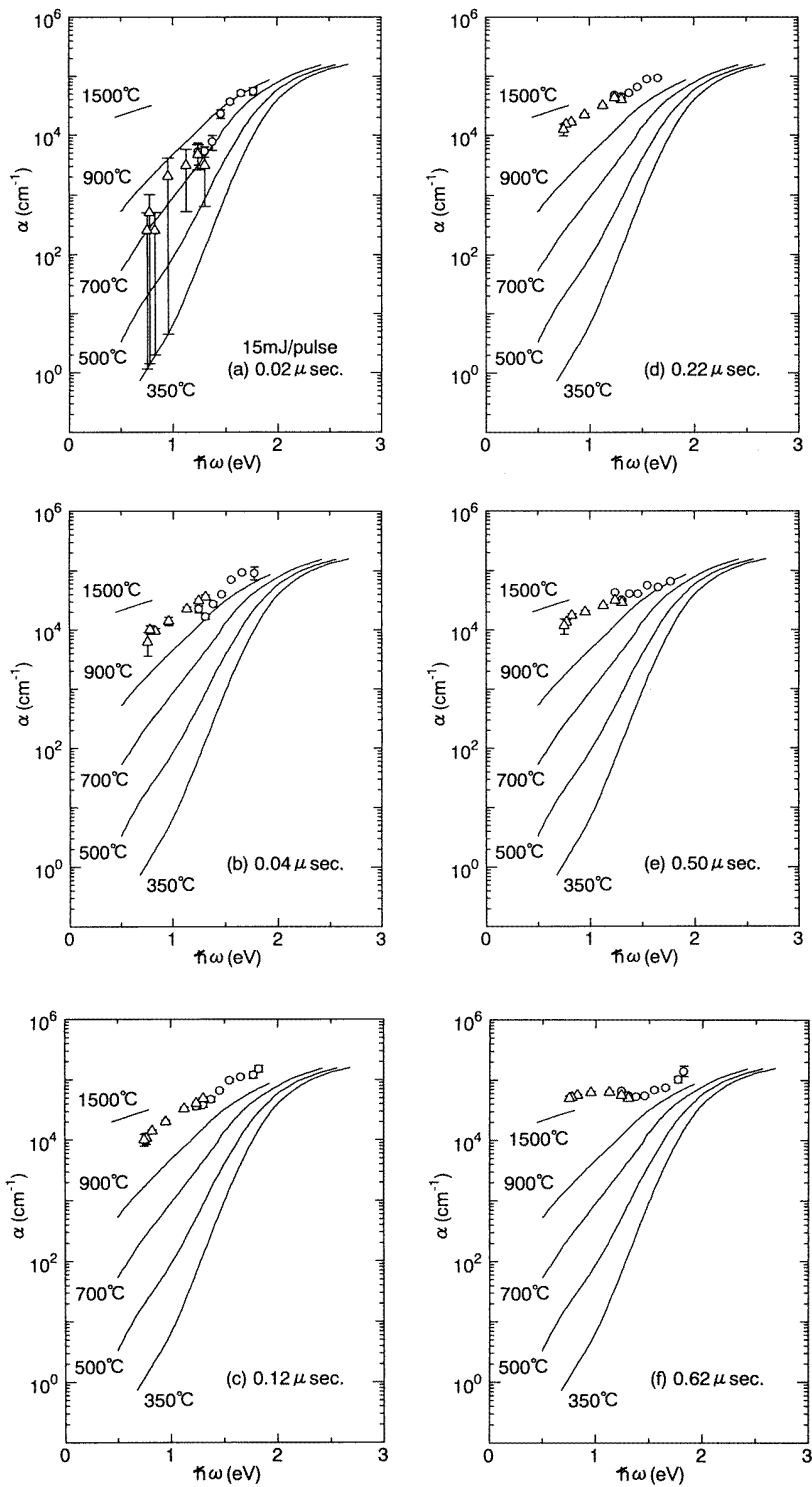


Figure 7. (See facing page for caption.)

excitation of LP electrons. The illumination with the pulsed laser possibly causes structural instability of the selenium chains. In the following section we will give an explanation of why these photoinduced changes are not caused by the temperature increase.

3.2. Transient absorption spectra of liquid selenium

Figure 4 shows plots of $\Delta T/T$ versus time at different wavelengths of the probe light with the laser power fixed at 6, 15 and 23 mJ/pulse. The values of the laser power are stated in figures 4(a), 4(b) and 4(c). The temperature of the liquid selenium is 350 °C. When the pulsed laser providing the illumination has the intensity 6 mJ/pulse, as seen in figure 4(a), a monotonic decay is observed at 750 nm and no change is observed at wavelengths longer than 1300 nm. When the pulsed laser providing the illumination has the intensity 15 mJ/pulse, as seen in figure 4(b), the increase of $\Delta T/T$ immediately after the illumination is clearly observed even at longer wavelengths. The value of $\Delta T/T$ is about 10% at 1600 nm. As is clearly seen in the figure, the second absorption with a delay time of 0.5 μ s appears at 1600 nm as well as at 750 nm. It should be noted, moreover, that at longer wavelengths, such as 1600 nm, $\Delta T/T$ gradually increases over time and seems to be saturated until the second absorption starts to appear. This behaviour is completely different to that at short wavelengths, such as 750 nm, where $\Delta T/T$ decreases over time. In addition, the value of $\Delta T/T$ for the second absorption at 750 nm is smaller than that for the first one, while the value for the second absorption at longer wavelength is much larger than that for the first one. Figure 4(c) shows the time variation of $\Delta T/T$ when the pulsed laser providing the illumination has the intensity of 23 mJ/pulse. In the time variation of $\Delta T/T$ up to the point at which the second absorption appears, we can see the gradual increase more clearly at longer wavelengths, and essentially the same characteristic behaviour as is shown in figure 4(b).

On the basis of these data we can obtain the transient absorption spectra. Spectral changes with time up to the point at which the second absorption appears are of particular interest. Figure 5 shows plots of $\Delta T/T$ versus wavelength at different times up to the point at which the second absorption appears after the illumination with the pulsed laser with the intensity at 15 mJ/pulse, obtained from the data shown in figure 4(b). Open circles show the data obtained by using a Si PIN photodiode and open triangles show the data obtained by using an InGaAs photodiode. The time is stated in each panel. At 0.02 μ s, just after the illumination, as seen in figure 5(a), $\Delta T/T$ is large for the range of wavelengths shorter than 950 nm and almost zero at longer wavelengths. After that, as seen in figures 5(b) and 5(c), $\Delta T/T$ at shorter wavelengths continues to increase and $\Delta T/T$ at longer wavelengths starts to increase. After 0.12 μ s, however, $\Delta T/T$ changes and begins to decrease at shorter wavelengths, while it continues to increase at longer wavelengths. When the second absorption starts to appear, as seen in figure 5(f), a distinct increase of $\Delta T/T$ to more than 40% is observed for all wavelengths.

It is interesting to compare the spectral changes shown in figure 5 with the temperature variation of static spectra. Figure 6 shows $\Delta T/T$ versus wavelength when the temperature of liquid selenium is increased from 350 °C up to the temperatures given in the figure. These data in figure 6 are obtained by using the static absorption spectra for liquid selenium [1]. As seen in the figure, $\Delta T/T$ increases for all wavelengths with increasing temperature. Note that $\Delta T/T$ in figure 5, in contrast, decreases at shorter wavelengths and increases at longer wavelengths over time, from 0.12 μ s to 0.50 μ s. The spectral change over time in figure 5, therefore, cannot be explained by assuming a temperature change of the sample.

Figure 7 shows the time evolution of plots of the optical absorption coefficients, α ,

versus the photon energy, $\hbar\omega$, after illumination with the pulsed laser at the intensity 15 mJ/pulse, which were calculated from the data shown in figure 5 taking into consideration the penetration depth of the laser light. The solid curves are the static spectra obtained from the literature [1]. As seen in figure 7(a), the shape of the transient absorption spectrum at 0.02 μs is different from those for the static spectra at higher temperatures. The data points on the high-energy side are initially located on the solid line obtained at 900 °C but move to that obtained at 700 °C with decreasing energy. Four data points on the low-energy side denoted by open triangles in figure 7(a) have large error bars because these data correspond to those on the long-wavelength side in figure 5(a) denoted by open triangles whose values are almost zero. The difference in the shape of the spectrum permits us to consider our photoinduced change to be athermal. In addition, the band structure must be changed because the photoinduced change occurs in the high-absorption region near the fundamental absorption edge. At 0.04 μs , as can be clearly seen in figure 7(b), α at low energies becomes extremely large. Over time from 0.12 μs to 0.50 μs , as seen in figures 7(c) to 7(e), the slope of the spectrum becomes small due to the decrease of α at higher energies and the increase at lower energies. It should be noted that the slope at 0.50 μs is almost the same as that of the static spectrum at 1500 °C where the optical gap becomes zero [1]. After the appearance of the second absorption, α increases enormously. The value is about $5 \times 10^4 \text{ cm}^{-1}$ even at lower energies.

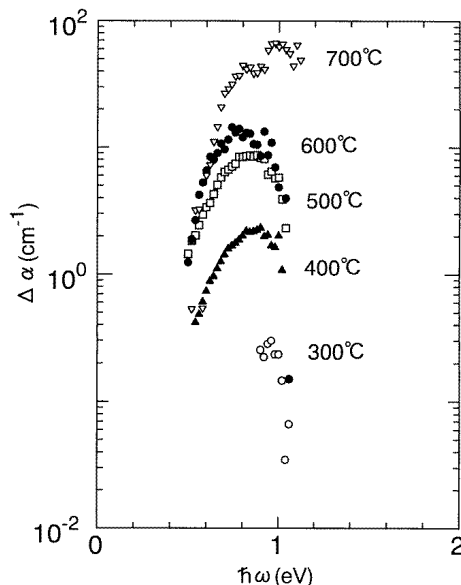


Figure 8. The difference spectrum of liquid selenium in the thermal equilibrium state—i.e. $\Delta\alpha$, which is the difference between the total absorption coefficient and the linear extrapolation of the Urbach tail in the low-energy region. These data were estimated using the static spectra [1].

A possible explanation for the large increase of α at lower energies apparent in figures 7(a) to 7(e) is as follows. Results of viscosity [11], magnetic susceptibility [12] and NMR [4] measurements suggest that the polymeric chains in liquid selenium break as the temperature is increased. Optical absorption spectra [1] indicate that additional absorption appears—in addition to the Urbach tail in the low-absorption region which originates from the unpaired electrons being generated by the thermal breaking of the bonds

of the chain. Figure 8 shows the difference spectrum in the equilibrium state—i.e. $\Delta\alpha$, which is the difference between the total absorption coefficient and the linear extrapolation of the Urbach tail in the low-absorption region. These data were estimated from the static absorption coefficient [1]. As is clearly seen in the figure, a maximum is observed and its position is at around 0.82 eV. The peak height increases with increasing temperature, which corresponds to the fact that the concentration of the dangling bonds increases with increasing temperature. The increase of α at lower energies in figures 7(a) to 7(e) may be related to a large number of dangling bonds being generated by the illumination with the pulsed laser.

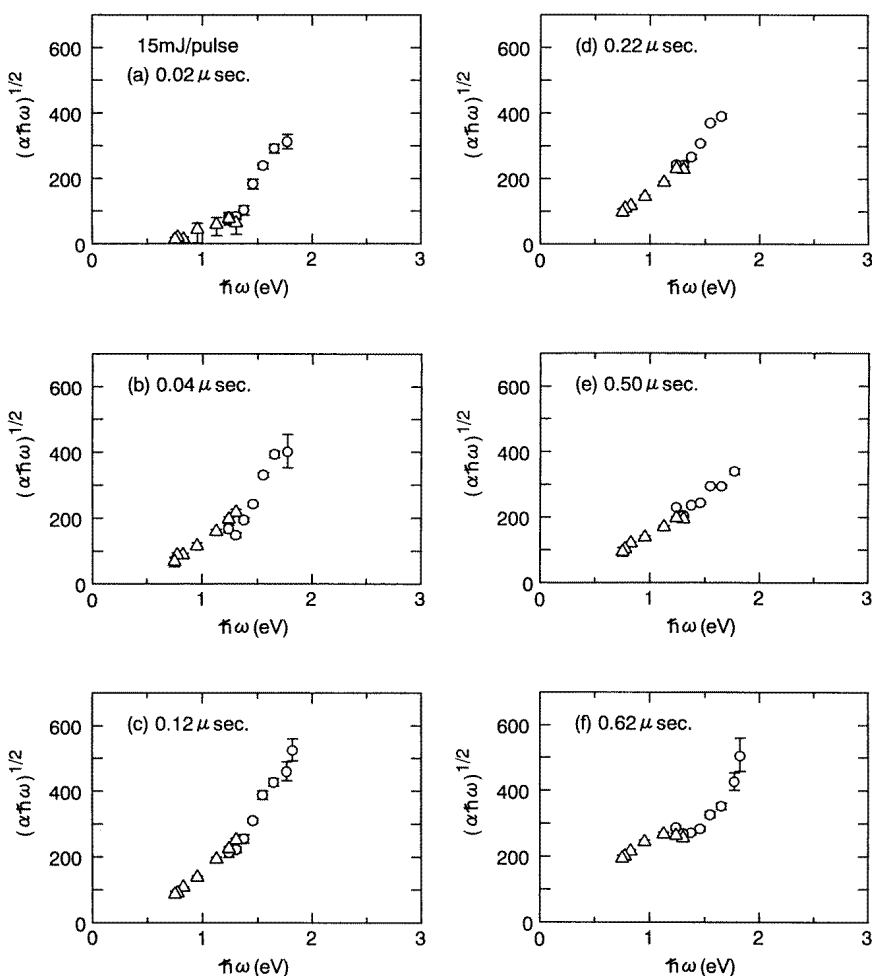


Figure 9. Tauc plots [13], $(\alpha\hbar\omega)^n$ versus $\hbar\omega$, of the transient absorption spectra in figure 7. Here we fix the index n at $1/2$.

3.3. Changes in the optical gap

Figure 9 shows Tauc plots [13], $(\alpha\hbar\omega)^n$ versus $\hbar\omega$, of the transient absorption spectra in figure 7. Here we fix the index n at $1/2$. As seen in the figure, we have a good linearity,

particularly for the plots at $0.50 \mu\text{s}$. As is well known, the optical gap, E_g , is deduced by the extrapolation of the plots in the high-absorption region. Figure 10 shows the time variation of E_g for different intensities of the pulsed laser from 6 to 23 mJ/pulse. Each data point has an error bar of $\pm 0.15 \text{ eV}$. The value of E_g at $350 \text{ }^\circ\text{C}$ in the thermal equilibrium state is about 1.5 eV when we fix n at $1/2$, which is indicated by the cross on the vertical axis in the figure. When the laser power is 6 or 10 mJ/pulse, E_g decreases down to about 1 eV and then seems to increase up to the value that it has in the thermal equilibrium state. In contrast, when the laser power is larger than 15 mJ/pulse, E_g decreases over time and becomes zero at around $0.50 \mu\text{s}$, which suggests that the photoinduced semiconductor–metal transition has occurred. It is interesting that the second absorption seems to appear when the gap becomes zero. There seems to exist a critical intensity of laser power at which the semiconductor–metal transition is induced. The critical intensity may lie in the range 10 to 15 mJ/pulse.

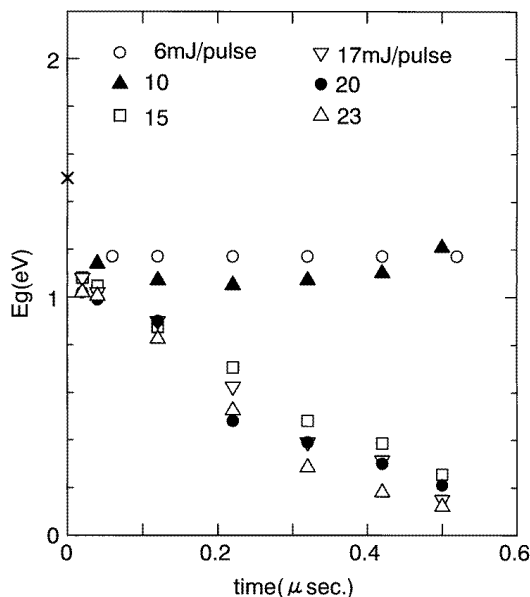


Figure 10. The time variation of E_g after the illumination with the pulsed laser at different intensities from 6 to 23 mJ/pulse for liquid selenium at $350 \text{ }^\circ\text{C}$. The value of E_g at $350 \text{ }^\circ\text{C}$ in the thermal equilibrium state is about 1.5 eV if n is fixed at $1/2$ as is indicated by the cross on the vertical axis. Each data point has an error bar of $\pm 0.15 \text{ eV}$.

It seems that the substantial decrease of E_g is strongly related to the large shift of the fundamental absorption edge combined with the rapid growth of α in the low-energy region, as seen in figure 7. The former may be related to the structural changes of chain molecules and the latter to the generation of defects. As mentioned in the previous section, comparison of the data in figure 7 with those in figure 8 leads us to the idea that the generation of a large number of dangling bonds may cause the decrease of E_g . *Ab initio* molecular-dynamics simulations for liquid selenium in the semiconducting region [14–16] suggest that there exist a variety of defects such as onefold dangling bonds and threefold ones. More advanced computer simulation for fluid selenium up to the metallic region would be helpful for the understanding of these photoinduced phenomena.

4. Conclusion

We present photoinduced absorption spectra of liquid selenium for the first time. We have found that the optical gap becomes zero when the illumination provided by the pulsed laser has an intensity higher than 15 mJ/pulse, which suggests a photoinduced semiconductor–metal transition in liquid selenium. For further understanding of the photoinduced phenomena, time-resolved measurements of the dc conductivity [17], and EXAFS and ESR studies would be helpful.

Acknowledgments

The authors are grateful to Professors M Inui, M Watabe, K Hoshino and C Li for valuable discussions. This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan, Iketani Science and Technology Foundation and the award of a PD Fellowship from the Japan Society for the Promotion of Science.

References

- [1] Hosokawa S and Tamura K 1990 *J. Non-Cryst. Solids* **117+118** 52
- [2] Hosokawa S, Kuboi T and Tamura K 1997 *Ber. Bunsenges. Phys. Chem.* **101** 120
- [3] Hoshino H, Schmutzler R W and Hensel F 1976 *Ber. Bunsenges. Phys. Chem.* **80** 27
Hoshino H, Schmutzler R W, Warren W W and Hensel F 1976 *Phil. Mag.* **33** 225
- [4] Warren W W Jr and Dupree R R 1980 *Phys. Rev. B* **22** 2257
- [5] Inui M, Noda T, Tamura K and Li C 1996 *J. Phys.: Condens. Matter* **8** 9347
- [6] Tamura K 1996 *J. Non-Cryst. Solids* **205–207** 239
- [7] Fukutome H 1984 *Prog. Theor. Phys.* **71** 1
- [8] Harrison W A 1980 *Electronic Structure and Properties of Solids* (San Francisco, CA: Freeman) p 93
- [9] Sakaguchi Y and Tamura K 1998 to be submitted
- [10] Sakaguchi Y and Tamura K 1995 *J. Phys.: Condens. Matter* **7** 4787
- [11] Perron J C, Rabi J and Riolland J F 1982 *Phil. Mag. B* **46** 321
- [12] Freyland W and Cutler M 1980 *J. Chem. Soc. Faraday Trans.* **76** 756
- [13] Tauc J 1969 *Optical Properties of Solids* ed F Abeles (Amsterdam: North-Holland) p 303
- [14] Hohl D and Jones R O 1991 *Phys. Rev. B* **43** 3856
- [15] Bichara C, Pellegatti A and Gaspard J-P 1994 *Phys. Rev. B* **49** 6581
- [16] Kirchhoff F, Gillan M J, Holender J M, Kresse G and Hafner J 1996 *J. Phys.: Condens. Matter* **8** 9353
- [17] Recently, we have performed transient dc conductivity measurements and obtained the result that the dc conductivity increases by more than four orders of magnitude from $6.8 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$ to $1.2 \times 10^0 \Omega^{-1} \text{cm}^{-1}$ when a pulsed laser with the intensity of 20mJ/pulse illuminates liquid selenium at 580 °C.