Transient direct-current conductivity of liquid selenium: an indication of the photoinduced

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Transient direct-current conductivity of liquid selenium: an indication of the photoinduced semiconductor–metal transition

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Abstract. The transient dc conductivity of liquid selenium after illumination with a pulsed laser has been investigated as a function of temperature over the range 285–580 °C and as a function of the laser intensity over the range 2–20 mJ/pulse. For the measurements, a new type of cell, made of quartz, of the authors' design was developed. We found that the conductivity increased up to $12 \, \Omega^{-1} \, cm^{-1}$ when the pulsed laser illuminated liquid selenium at 580 °C with the intensity of 20 mJ/pulse, which suggests that a photoinduced semiconductor–metal transition occurs. We also observed three types of relaxation, depending on the laser intensity and the temperature. The existence of these relaxations may suggest that there are several types of photoinduced structure in liquid selenium. We discuss the observed photoinduced effects in terms of the photoinduced structural changes.

1. Introduction

Liquid selenium in the vicinity of its melting point consists of long polymeric chains which each contain as many as 10^5 atoms and exhibits semiconducting behaviour. With increasing temperature, the chain length becomes short [1, 2], electrical conductivity increases [3] and the optical gap decreases [4]. It is known that further increase of temperature with application of pressure gives rise to the semiconductor–metal transition near the liquid–gas critical point ($T_c = 1615$ °C, $P_c = 385$ bar, $\rho_c = 1.85 \, g \, cm^{-3}$ [5]) [6–11]. NMR study [2] revealed that the chain molecule contains about ten atoms on average when the semiconductor–metal transition occurs. Recently, Tamura and collaborators carried out x-ray diffraction measurement and EXAFS measurement [12–15] for fluid selenium up to the supercritical region, including the semiconductor–metal transition. It was found that the local structure changes with the transition, preserving twofold-coordinated chain structure. Moreover an *ab initio* molecular-dynamics simulation up to the metallic region has been made by Shimojo *et al* [16]. They found that the chain-like structure persists even in the metallic state, although the chain structure is substantially disrupted. In this way, 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

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helical structure [17, 18]. 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 with an energy of about 2 eV, so trigonal selenium behaves as a semiconductor. The characteristic feature of the structural and electronic properties of liquid selenium near the melting point is considered to be essentially the same as that of the proprerties of the crystalline state. The thermal excitation of LP electrons to σ^*-orbitals, therefore, may affect the properties of liquid selenium, changing the strength of bonds, the conformation of the chain or the interaction between chains. The semiconductor–metal transition may be related to such an instability of the chain structure. As far as we know, there is no experimentally direct evidence to show the role of the LP electrons in the semiconductor–metal transition in liquid selenium. Recently, we carried out transient absorption spectroscopy of liquid selenium after illumination with a pulsed laser which excites LP electrons to σ^*-orbitals [19]. We observed an enormous change in the transmitted light upon illumination with the pulsed laser. In addition, the results of detailed analysis suggested that the optical gap decreases with time and disappears at about 0.5 μs when the pulsed laser illuminates liquid selenium at 350 °C with the intensity of 15 mJ/pulse. But to establish whether a photoinduced semiconductor–metal transition really occurs or not, another measurement such as that of the dc conductivity is needed. In this paper, we report the results of measurements of the transient dc conductivity of liquid selenium using a specially designed optical cell.

2. Experimental apparatus and method

In order to measure the laser-excited transient dc conductivity of liquid selenium, it is necessary to use an optical cell which has electrodes and a thin sample space. For this purpose, we have developed a specially designed optical cell made of quartz, as shown in figure 1. As seen in the figure, two quartz plates with round shapes face each other. The diameter of the round surface is about 1 cm. On each plate, there are two ditches which are the spaces in which to put the electrodes. The distance between the ends of the ditches is 0.3 mm. The round edges of these two plates were connected together by the glass-fusing work. A very thin and uniform sample space was made between the two plates. The thickness of the sample space was determined by the optical interference method. In the present experiment we made the thickness 1.2 μm. The pulsed laser illuminated the round surface from the normal direction. The plate and tubes in the figure were also connected by the glass-fusing work. Gold electrodes with a diameter
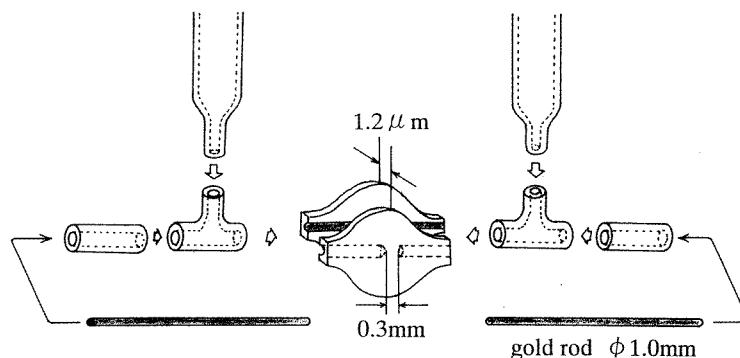
Figure 1. The optical cell made of quartz used for the transient dc conductivity measurement of liquid selenium.

of 1 mm were put into the ditches. The end of each electrode was attached to the end of the ditch. The other end of the gold electrode and the quartz tube were sealed with glue. A more detailed description of the cell construction will be given elsewhere [20].
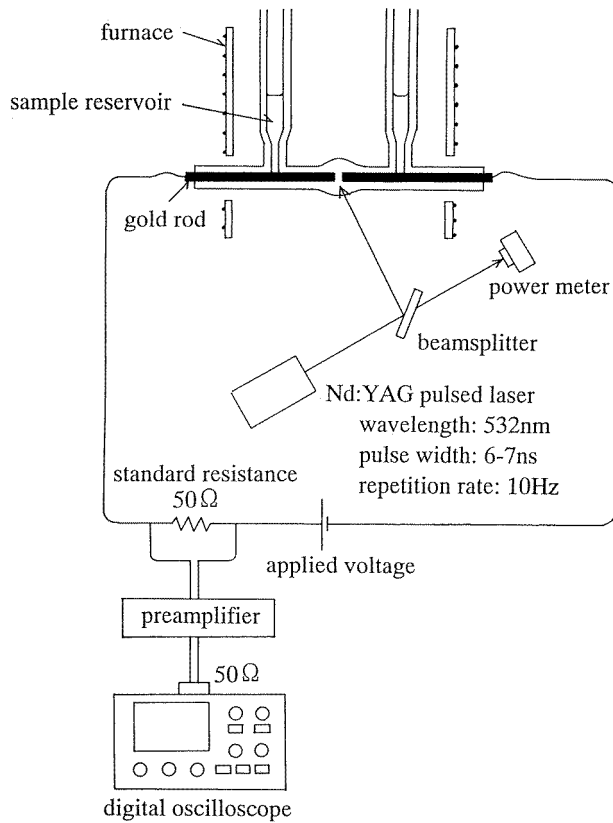
Figure 2. The experimental arrangement for the transient dc conductivity measurement of liquid selenium.

The experimental arrangement is illustrated in figure 2. The second harmonics (532 nm) of the pulsed Nd:YAG laser (Spectra Physics Lasers, Incorporated, Quanta-Ray GCR-165) were used for the excitation of the LP electrons in liquid selenium. The width of a pulse was 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 was reflected by a mirror and illuminated an area of diameter 8 mm of the liquid specimen contained in the quartz cell. There are two windows on the side wall of the furnace which are used for the illumination with the pulsed laser. As seen in the figure, we applied the dc voltage and put a standard resistance of 50 Ω between the electrodes of the cell. We measured the voltage across the standard resistance with a wide-band preamplifier (NF ELECTRONIC INSTRUMENTS BX-31A) and a digital oscilloscope (SONY Tektronix TDS350). The change of the voltage is related to the change of the conductivity of the liquid selenium. The laser shots were repeated 64 times to obtain final data with less noise. Before making the transient measurements, we measured the resistance of the sample without illumination using a digital multimeter. The value is close to that estimated from the literature [3]. In order to establish the time at which the pulsed laser illumination occurs, we used a Si PIN photodiode (Electro-Optics Technology ET 2000) and detected the scattered light from the pulsed laser.

3. Results and discussion

We measured the time variation of the voltage across the standard resistance after the laser illumination, changing two parameters: the temperature over the range from 285 to 580 °C and the intensity of the pulsed laser over the range from 2 to 20 mJ/pulse. We discuss the laser intensity dependence of the voltage change, fixing the temperature, first, in section 3.1, and then the temperature dependence of the voltage change, fixing the laser intensity, in section 3.2.

3.1. Laser intensity dependence

3.1.1. Laser intensity dependence at 450 °C. Figure 3 shows the voltage across the standard resistance versus time when the pulsed laser illuminates liquid selenium at 450 °C. The intensities of the pulsed laser are marked on the right-hand side of each curve in the figure. The curves which each have a peak at 0 ns indicate the pulse shapes as a function of time. The applied voltage in the electric circuit was 3.06 V (about 102 V cm^{-1}). This voltage is much smaller than the value at which the switching phenomena occur [21, 22]. There is a small oscillation in the observed curves, which is considered to result from the conditions of the electric circuit used in the present experiment such as the shield or the length of the cable. As seen in the figure, we could observe photoinduced change upon the illumination with a 6.2 mJ/pulse. With increasing laser intensity, the maximum voltage increases. The conductivity corresponding to the maximum voltage for the intensity of 19.8 mJ/pulse is
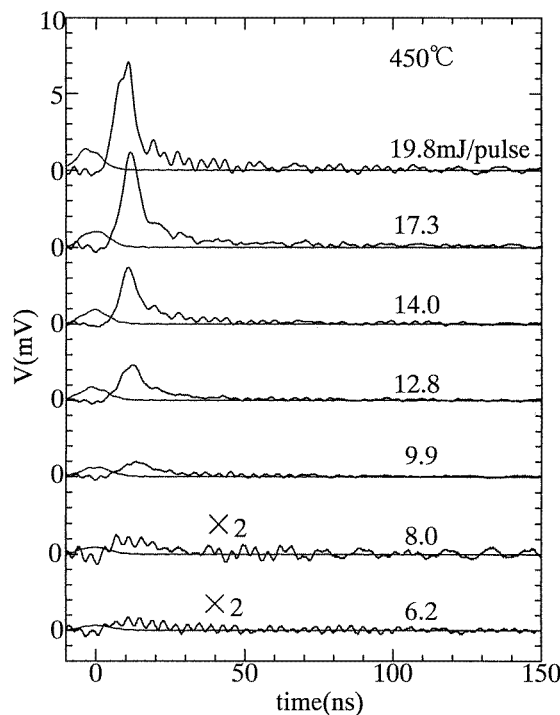
Figure 3. The voltage across the standard resistance versus time when the pulsed laser illuminates liquid selenium at 450 °C. The intensities of the pulsed laser are given on the right-hand side of each curve in the figure. The curves which have peaks at 0 ns indicate the pulse shapes as a function of time.
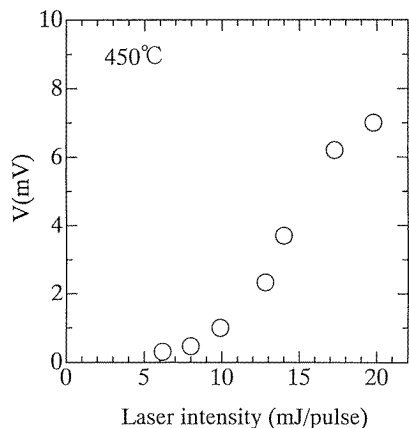
Figure 4. The maximum voltage versus laser intensity at 450 °C.

estimated to be 3.1 $\Omega^{-1}\text{cm}^{-1}$ by assuming that the photoinduced change takes place in the region of the penetration depth (885 Å) at 532 nm and at 450 °C [4], and using the value of the conductivity $\sigma = 9.9 \times 10^{-5}$ Ω^{-1} cm^{-1} [3] at 450 °C without illumination. It should be noticed that the conductivity changes by more than four orders of magnitude. The process of reaching the maximum voltage after illumination, which we call the 'generation' process, takes about 5 ns for the illuminations of 6.2 mJ/pulse and 8.0 mJ/pulse. On the other hand, it takes about 10 ns for illuminations stronger than 9 mJ/pulse. Since the time required to reach the maximum voltage is of the order of a nanosecond, the increases of the voltage cannot be considered to result from the photocurrent, in which case the photo-excited electrons would directly contribute to the conduction. So long a time reminds us of the possibility that the voltage may increase with increasing conductivity of liquid selenium accompanying some structural changes in the chains. Warren and Dupree [2] obtained the correlation time for the molecular reorientation of liquid selenium over the temperature range from 193 to 250 °C by means of NMR measurements. When we extrapolate their data, the correlation time at 450 °C is estimated to be about 10 ns. It is reasonable to consider that it needs rather a long time to change the structure of the polymeric chains in liquid selenium.

Figure 4 shows the laser intensity dependence of the maximum voltage at 450 °C. As seen in the figure, there seem to be two thresholds in the laser intensity. One threshold is at about 4 mJ/pulse. Around this point, the photoinduced change starts to occur. The other is at about 9 mJ/pulse. At this intensity, the effect of the illumination becomes larger. According to the results of photoconductivity measurement for liquid selenium by Rabit and Perron [22, 23], the photocurrent is proportional to the photon flux. The existence of such thresholds supports the view that the photoinduced phenomena observed here are not due to the photocurrent.

Figure 5 shows the time variation of the voltage in the relaxation process shown in figure 3, plotted on semilogarithmic scales. The points are obtained from the smooth curve following the experimental data in figure 3. It should be noticed that two relaxation processes are clearly observed when the intensity of the pulsed laser is stronger than 9 mJ/pulse. The relaxation times are 12 ns for the fast one and 94 ns for the slow one. The existence of two relaxation processes indicates that there are two types of electrical conduction and suggests that two different types of structure were formed after the illumination with the pulsed laser. On the other hand, there seems to be a single relaxation process with the relaxation time of 25 ns when the intensity of the pulsed laser is less than 9 mJ/pulse. The relaxation time of the relaxation
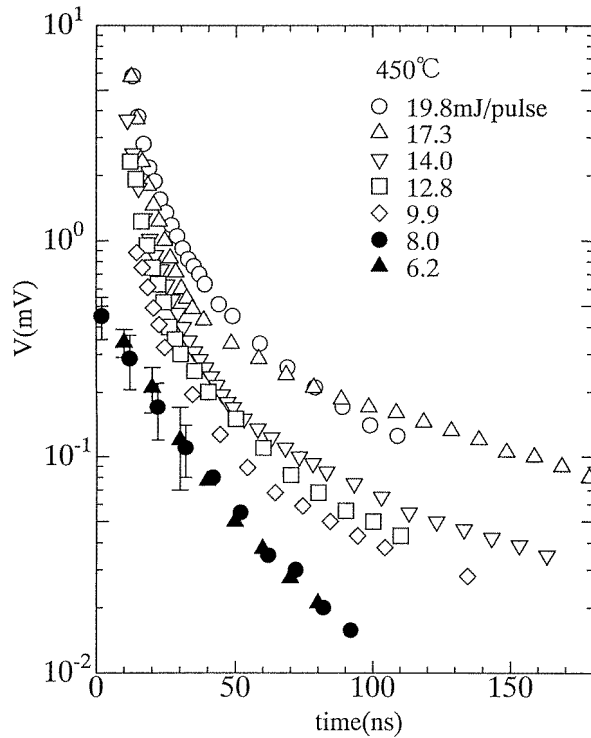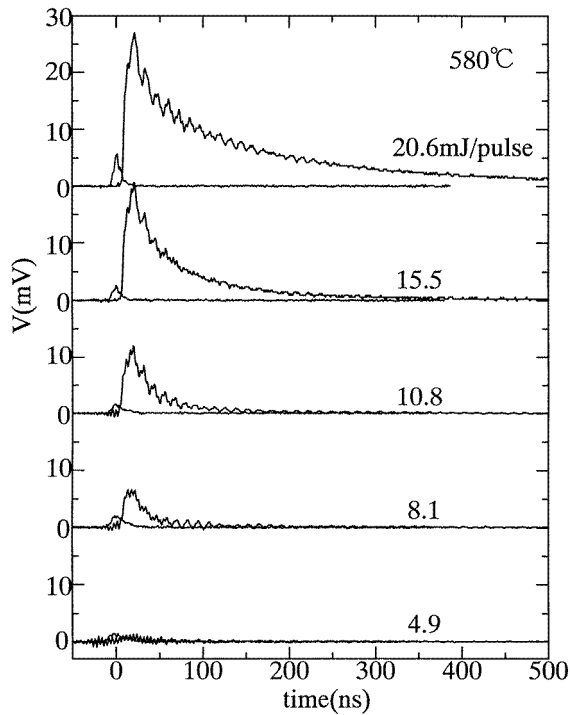
Figure 5. The time variation of the voltage in the relaxation process in figure 3 plotted on semilogarithmic scales. The points are obtained from the smooth curve following the experimental data.

process after the illumination with an intensity less than 9 mJ/pulse is different from both of the relaxation times which appear for illumination stronger than 9 mJ/pulse.

We can summarize the photoinduced phenomena at 450 °C as follows. When the pulsed laser illuminates it with an intensity below 9 mJ/pulse, the structure changes to a certain structure (A) and then relaxes to the initial one at thermal equilibrium. When the pulsed laser illuminates it with an intensity above 9 mJ/pulse, the structure changes to another type of structure (B), and relaxes to a further type of structure (B′) and then relaxes to the initial one.

3.1.2. Laser intensity dependence at 580 °C. Figure 6 shows the voltage across the standard resistance versus time when the pulsed laser illuminates liquid selenium at 580 °C. The applied voltage in the electric circuit was 3.47 V. The photoinduced change is larger than that at 450 °C. For the illumination of 20.6 mJ/pulse, the maximum voltage after the illumination reaches about 26 mV. The conductivity corresponding to this voltage is estimated to be 12 Ω^{-1} cm^{-1} on assuming that the photoinduced change takes place in the region of the penetration depth (787 Å) at 532 nm and at 580 °C [4], and using the value of the conductivity $\sigma = 3.7 \times 10^{-4}$ Ω^{-1} cm^{-1} [3] at 580 °C without illumination. It should be noticed that the conductivity changes by five orders of magnitude. According to Mott and Davis [24] and Mott [25], the minimum metallic conductivity of liquid selenium is about 20 Ω^{-1} cm^{-1}, which is much smaller than that of systems such as fluid Hg or Cs. The value of the conductivity which we observed here is very close to this value. Moreover, the maximum voltage becomes large with increasing laser intensity as seen in figure 6. We expect to get much larger conductivity and to clearly observe the photoinduced semiconductor–metal transition when the laser illuminates liquid selenium at 580 °C more intensely. As for the generation process, it takes about 20 ns and

Figure 6. The voltage across the standard resistance versus time when the pulsed laser illuminates liquid selenium at 580 °C. The intensities of the pulsed laser are given on the right-hand side of each curve in the figure. The curves which have peaks at 0 ns indicate the pulse shapes as a function of time.

saturation is observed before the maximum voltage is reached for illuminations of 10.8, 15.5 and 20.6 mJ/pulse. Note that this behaviour was not observed at 450 °C.

Figure 7 shows the time variation of the voltage in the relaxation process shown in figure 6 plotted on semilogarithmic scales. The points are obtained from the smooth curve following the experimental data in figure 6. Two relaxation processes are observed even for the illumination of 8.1 mJ/pulse, while they were not observed for the same intensity of illumination at 450 °C. However, for the illumination of 15.5 mJ/pulse, the crossover of the two relaxations becomes unclear. Note that at 20 mJ/pulse, there appear another two types of relaxation, whose relaxation times are 42 ns and 206 ns. These relaxation times are different from those observed for the weaker illumination. The appearance of such a new relaxation process at 20 mJ/pulse may be related to the appearance of a photoinduced 'metallic' state. In particular, it should be noticed that the relaxation time in the slow relaxation process is extremely long compared with that for the weaker illumination. This may suggest that the structure in the photoinduced highly conducting state hardly relaxes towards the thermal equilibrium state.

3.2. Temperature dependence

Figure 8 shows the voltage across the standard resistance versus time for different temperatures. The laser intensity is fixed at 20 mJ/pulse. The generation process at 580 °C seems to be different from the others. At 580 °C, it takes about 20 ns to reach the maximum voltage and saturation is observed before reaching the maximum voltage. For the others, it takes about
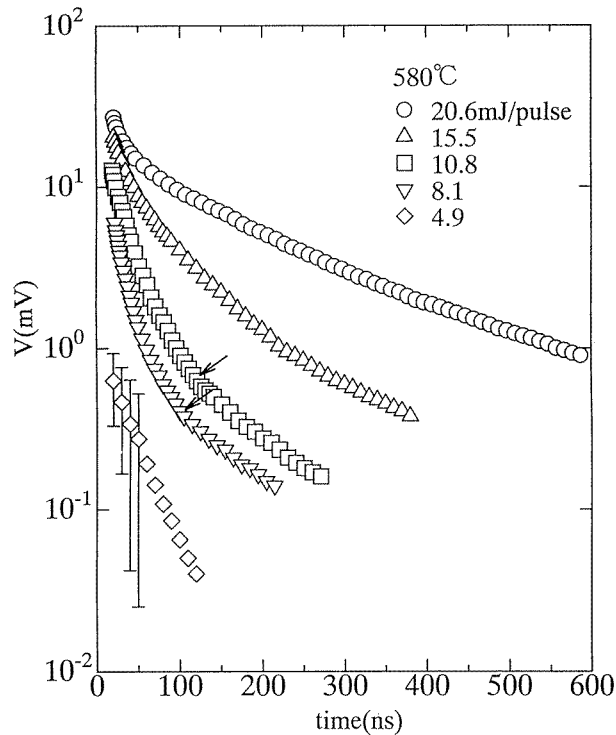
Figure 7. The time variation of the voltage in the relaxation process in figure 6 plotted on semilogarithmic scales.

10 ns to reach the maximum voltage. Such a long generation time as 20 ns observed at 580 °C is also observed for weaker laser intensities when we keep the temperature at 580 °C, as seen in figure 6.
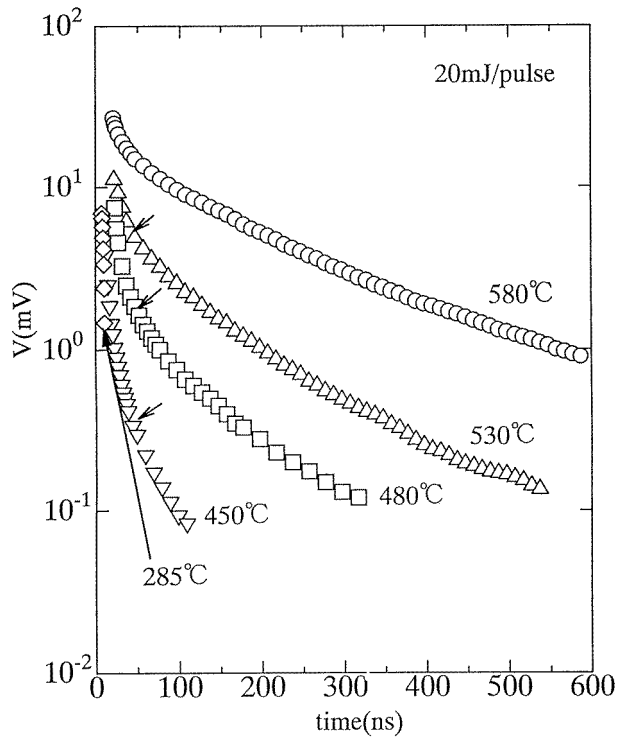
Figure 9 shows the time variation of the voltage in the relaxation process in figure 8 plotted on semilogarithmic scales. It is obvious that there are two relaxation processes at 450 °C and 480 °C. At 530 °C, the crossover becomes unclear. At 580 °C, there are two relaxation processes, but their relaxation times are different from those at 450 °C and 480 °C. As clearly seen in the figure, the increase of temperature assists the photoinduced change. It seems that the effect of the temperature increase on the photoinduced change is similar to that of the increase of laser intensity. However, we find a difference between the relaxation processes when we compare figure 9 with figures 5 and 7. In figure 9 the temperature is changed with fixed laser intensity while in figures 5 and 7 the laser intensity is changed with fixed temperature. In figure 9 the points at which the crossover from the fast relaxation process to the slow one takes place are indicated by the short arrows. Note that the voltage of the point increases with increasing temperature. Here the temperature variation of the voltage without laser illumination corresponding to the temperature change of the conductivity at thermal equilibrium was less than 10^{-2} mV over the temperature range from 285 °C to 580 °C. As seen in figures 5 and 7, in contrast, the voltage in the region where the crossover occurs is almost unchanged with increasing laser intensity; this is much clearer in figure 5. Thus the effect of laser illumination differs from that of the increase of temperature.

Figure 10 shows the plots of the maximum voltage after illumination with the pulsed laser
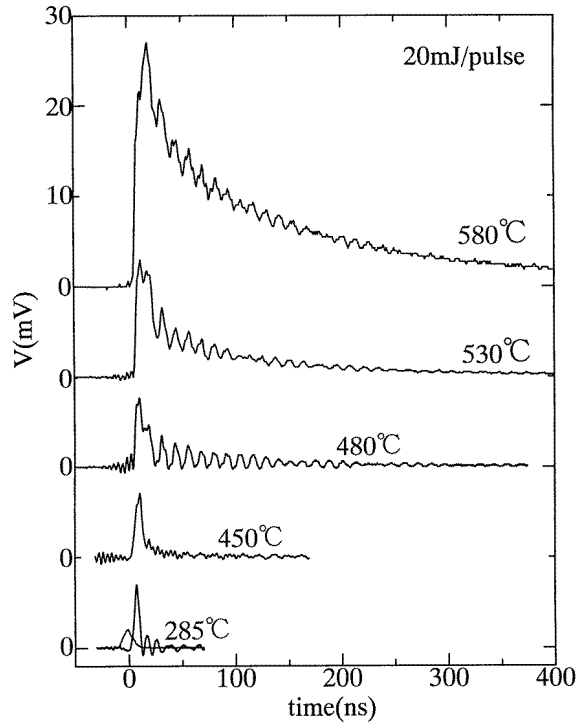
Figure 8. The voltage across the standard resistance versus time for different temperatures. The laser intensity is fixed at 20 mJ/pulse. The applied voltage was 3.06 V for the data at 285 °C and 450 °C, and 3.57 V otherwise. The curve which has a peak at 0 ns indicates the pulse shape as a function of time.

versus temperature, for different laser intensities. It is clearly found that the maximum voltage becomes extremely large above 500 °C for the laser intensities of 10, 15 and 20 mJ/pulse. For the laser intensity of 5 mJ/pulse, on the other hand, the rate of the increase of the maximum voltage above 500 °C is small compared with the rate for the laser intensity above 10 mJ/pulse. As regards the behaviour below 500 °C, an offset is observed for the laser intensities of 15 and 20 mJ/pulse. Figure 11 shows plots of the maximum voltage after illumination with the pulsed laser versus laser intensity, for different temperatures. As we have seen in section 3.1.1, there is a threshold of laser intensity at which the increase of the maximum voltage becomes large. At 450 °C, it is about 9 mJ/pulse. The threshold does not change so much at temperatures below 500 °C. Above 500 °C, however, the threshold shifts to the low-intensity side. In addition, the value of the maximum voltage becomes large above 500 °C for laser intensity over the range 8–20 mJ/pulse. Thus, it can be concluded that the photoinduced effect is changed at around 500 °C. Gobrecht *et al* [3, 26] and Mahdjuri [27] reported that three ranges of temperature can be distinguished in which the conductivity of liquid selenium behaves differently. In the temperature range below 500 °C, the main conduction comes from the defects and impurities. Between 500 °C and 720 °C, the conduction is intrinsic. Above 720 °C, the conduction with higher activation energy is observed. The thermal equilibrium state without photo-excitation below 500 °C is different from that above 500 °C. As regards the structure of the selenium chain, at 500 °C, one selenium chain contains about 3000 atoms on average according to the estimation by Warren and Dupree [2]. When the pulsed laser illuminates liquid selenium at

Figure 9. The time variation of the voltage in the relaxation process in figure 8 plotted on semilogarithmic scales.
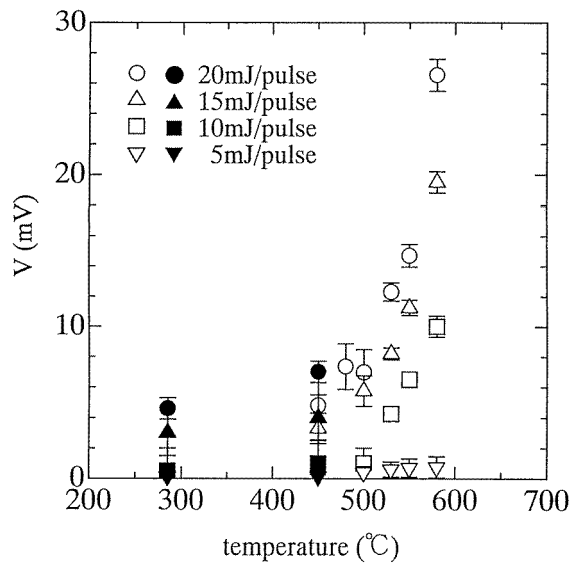
Figure 10. The maximum voltage versus temperature for different laser intensities. The applied voltage in the electric circuit was 3.06 V for the data indicated by closed symbols and 3.57 V for the data indicated by open symbols.

500 °C with the intensity of 20 mJ/pulse, the ratio of the number of photons to the number of Se atoms in the illuminated region is estimated to be 1/2. Therefore, if the excitation of LP electrons causes the bond breaking, the chain length becomes short. Intense illumination from the pulsed laser may produce short chains in which a small number of Se atoms—less than ten atoms—are contained. In such a short chain, the electronic state at the chain end is considered
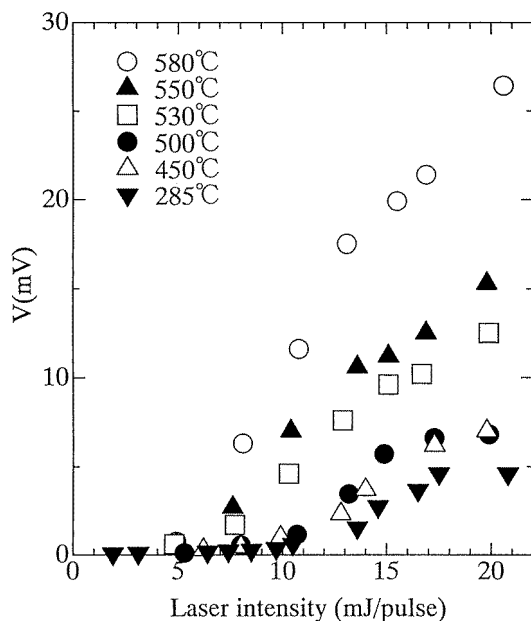
Figure 11. The maximum voltage versus laser intensity for different temperatures. For the data at 285 °C and 450 °C, the applied voltage in the electric circuit was 3.06 V; otherwise, it was 3.57 V.

to affect the whole chain, resulting in a change of the chain conformation. As mentioned in the previous section, such short chains appear in fluid selenium near the liquid–gas critical point and show metallic character.

In this study, we have reported several types of photoinduced change in liquid selenium. Such changes must be caused by the excitation of LP electrons. It is difficult to see how the observed phenomena could be caused by a photoinduced effect, and not a thermal effect. Quite recently, an *ab initio* molecular-dynamics simulation for a single infinite Se chain after excitation of the LP electrons has been carried out by Hoshino *et al* [28]. It was found that the excitation of the LP electrons causes structural instability of the chain and bond breaking. This result supports the possibility of producing a new structure with metallic properties by laser illumination.

4. Summary

We have presented results on the transient dc conductivity of liquid selenium after illumination with a pulsed laser for the first time. We have found that the conductivity increases up to 12 Ω^{-1} cm^{-1} when a pulsed laser with the intensity of 20 mJ/pulse illuminates liquid selenium at 580 °C, which suggests a photoinduced semiconductor–metal transition. Three types of relaxation were observed depending on the temperature and the intensity of the pulsed laser. When the temperature is 450 °C and the pulsed laser intensity is less than 9 mJ/pulse, we observed the first one, which is described with one exponential curve. When the pulsed laser intensity or temperature is higher, the second type of relaxation appears, which is described with two exponential curves. When the temperature is 580 °C and the pulsed laser is at 20 mJ/pulse, the third type of relaxation appears, which has two relaxation processes whose relaxation times are different from those in the second type of relaxation. The third type may be connected with a photoinduced semiconductor–metal transition. We attribute the existence of such a variety of types of relaxation to the existence of a variety of photoinduced structures.

We finally found that there is a difference between the results from the transient absorption spectroscopy in our previous study and those from the transient dc conductivity in the present study. The results of the transient absorption spectroscopy show that the photoinduced semiconductor–metal transition occurs 0.5 μs after illumination with a pulsed laser. On the other hand, from the transient dc conductivity measurement, the photoinduced semiconductor– metal transition is considered to occur about 20 ns after the illumination. Further investigation is required to resolve this discrepancy.

Acknowledgments

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