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A possibility of the photo-induced semiconductor–metal transition in liquid selenium

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Abstract

We have performed transient absorption measurements of liquid selenium after the illumination of a pulsed laser to clarify the possibility of the photo-induced semiconductor–metal transition. The intensity of the laser was increased up to 23 mJ/pulse and the temperature of the sample was increased up to 600 °C. By increasing the laser intensity and temperature of the sample, quite a large photo-induced change has been observed, which suggests the semiconductor–metal transition.

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Keywords: Electrical and electronic properties; Optical properties; Lasers; Optical spectroscopy; Photo-induced effects; Time resolved measurements; Phases and equilibria

1. Introduction

Selenium is known as an exotic material since photoconductivity was discovered in selenium by Smith in 1873 [1]. The phenomenon is commonly understood as a general feature of semiconductors nowadays. But at the time of the discovery, it was pointed out that the resistance of selenium is affected by the history of the illumination of light. This indicates that the structure of selenium is changed by the illumination and the slow relaxation affects its resistance. In this sense, selenium is an out of the 'ordinary' semiconductor. The optical properties of selenium are also attractive. Chalcogenide glasses, including amorphous selenium, exhibit a red-shift of the optical absorption spectra by the illumination of light, which is known as 'photodarkening' [2,3]. It is understood that this phenomenon is derived from the metastability of chalcogenide glasses [4]. Since the amorphous material is in the metastable state, the illumination of light can transform its state from one to another and the state is preserved by stopping the illumination. Selenium is the only element which is semiconducting in the liquid state. According to Russian researchers [5], who have made the pioneering studies in liquid semiconductors, semiconductors can exhibit two types of solid–liquid transition; semiconductor → semiconductor, or, semiconductor → metal. Moreover, an intermediate case, semiconductor → semiconductor → metal, is pointed out. Selenium belongs to the last category and the semiconductor–metal transition occurs in liquid state with increasing temperature [6,7]. According to the recent studies on the structural properties by means of X-ray diffraction and EXAFS measurements [8–10], it was found that the local structure also changes at the transition. Selenium exhibits such a dramatic change with increasing temperature in the liquid state, however, there was no research to see the effect of light in the 'liquid state' so far. It is interesting to study (I) whether the photodarkening occurs or not in the liquid state and (II) whether the photo-induced semiconductor–metal transition occurs as well as the thermally-induced one. Recently, we have made tran-

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sient absorption measurements and transient dc conductivity measurements for liquid selenium after illumination by a pulsed laser [11–13] to answer these questions. The results of those experiments are positive ones, that is, photodarkening was observed in the liquid state and an enormous change in electrical conductivity was observed after the illumination of pulsed laser. However, the observed results were not simple and the question for the 'photo-induced semiconductor–metal transition' has not been answered yet. In this paper, we report new results of transient absorption measurements and discuss the possibility of a photo-induced semiconductor–metal transition.

2. Experimental

To measure the transient absorption, it is necessary to use an optical cell which has thin sample space. For this purpose, we have developed an optical cell made of quartz [14]. In the present experiment we have used the cell with the thickness set at 1.0 μm. The second harmonics (532 nm) of the pulsed Nd:YAG laser was used for the photo-excitation. The width of a pulse was 7 ns. Repetition rate was 10 Hz. To know the time when the pulsed laser illuminates, we used a Si PIN photodiode and detected the scattered light of the pulsed laser. For heating the sample, we used a furnace which had two windows on the side for transmitting pulsed laser light. The transient absorption change was detected by monitoring the transmission of a probe beam of a Xe flash lamp or a tungsten lamp incident on the sample. The transmitted light was detected using a Si PIN photodiode, a InGaAs photodiode, a wide-band preamplifier, a digital oscilloscope and a delay generator.

3. Results

Fig. 1 shows the time variation of the photo-induced absorption, $\Delta T/T$, where T is the transmittance in the thermal equilibrium state and ΔT is the photo-induced change in the transmittance, in the delay time from 0 to 3 μs for liquid selenium at 450 °C. A positive change of $\Delta T/T$ shows photo-induced absorption, that is to say, a darkening induced by the laser illumination. The wavelength of the transmitted probe light is 800 nm. The peak of the laser-pulse is located at 0 in the horizontal axis. As seen in the figure, a photodarkening is clearly observed for the pulsed laser with the intensity of 4 mJ/pulse. It takes several microseconds or more to be the initial transmittance. Such slow decay may indicate that the photo-induced change is accompanied by a sort of structural change. A decay of $\Delta T/T$ in the time range from 0 to 0.5 μs in the curve for 10 mJ/pulse is faster than that for 4 mJ/pulse. When the intensity of the laser exceeds 10 mJ/pulse, a darkening of more than 20% is observed after the laser illumination and a sudden darkening appears at 0.5 μs. It appears that the sudden darkening occurs periodically and it resembles a beat. From the pre-

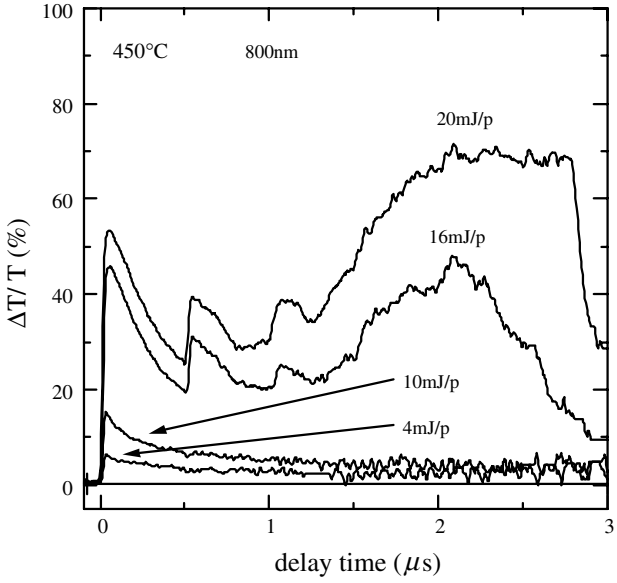

Fig. 1. Time variation of the photo-induced absorption, $\Delta T/T$, of liquid selenium at 450 °C for various laser intensities. The wavelength of the probe beam is 800 nm.

vious work, it was found that the sudden 'darkening' is caused by a light scattering [13]. It is considered that this phenomenon is related to a large and dynamical structural change in liquid selenium and it is worth studying the phenomenon itself. But such scattering disturbs for the exact evaluation of the optical absorption coefficient. Therefore, we focus on the photo-induced change in the time range before such scattering occurs. Fig. 2 shows the time variation of $\Delta T/T$ in the time from 0 to 180 ns for three different wavelength of the probe beam at various temperatures. The intensity of laser is fixed at 5 mJ/pulse in Fig. 2(a) while the intensity of laser is fixed at 15 mJ/pulse in Fig. 2(b). For the laser illumination of 5 mJ/pulse, $\Delta T/T$ linearly increases in the range from 0 to 20 ns and reaches the maximum value. After that, $\Delta T/T$ decreases monotonically. The maximum value increases with increasing temperature. For the laser illumination of 15 mJ/pulse, there are two time domains in the rise process; the rapid rise in the time range from 0 to 20 ns and the moderate rise which follows the rapid rise. It is noted that the total rise time is quite long compared with those of amorphous Se and other chalcogenide glasses [15]. Phillips pointed out the possibility of photo-induced metallization in glassy As_2Se_3 assuming the change at shorter time range of the order of picoseconds [16]. But we cannot expect that there exists such larger change in the picosecond range as long as we observe the present results. The total rise time depends on the wavelength; 30 ns for 680 and 800 nm and 50 ns for 1000 nm at 450 °C. The rise time becomes longer with increasing temperature. It changes to be 40 ns for 680 and 800 nm and 70 ns for 1000 nm at 580 °C. The maximum value of $\Delta T/T$ increases with increasing temperature; for the probe beam at 680 nm, the maximum values are 49% at 450 °C, 61% at 530 °C