LUMINESCENCE AND TRANSPORT PROPERTIES OF ELECTRON-HOLE DROPS IN HIGHLY EXCITED GERMANIUM

Arao Nakamura* and Kazuo Morigaki

Institute for Solid State Physics,
University of Tokyo,
Roppongi, Tokyo 106, Japan

ABSTRACT

Luminescence and electrical measurements have been performed in pure and As-doped germanium at 1.6 - 4.2 K under intense optical excitation. Under extremely high excitation of pure germanium, it is found that the electron-hole liquid phase is uniformly generated in the whole volume of the sample. From the observation of the giant fluctuating current, the electron-hole drops turn out to be negatively charged as a whole. Even in heavily doped germanium, it is found that the EHD is formed stably in an atomosphere of metallic electrons released from donor impurities.

I. INTRODUCTION

Since Keldysh[1] predicted the existence of the electron-hole drop (EHD) in germanium, the properties of EHD have extensively been investigated by various kinds of means at low temperatures in germanium.[2] In this paper, we present the results of luminescence and electrical measurements of EHD in pure and As-doped germanium. Here, main emphases are laid on the following three problems; one of them is concerned with the density-dependent luminescence properties of EHD in pure germanium. Secondly, we are concerned with the transport properties of EHD, especially, its net charge in pure germanium. Thirdly, an attention is paid on the existence of EHD in heavily doped germanium whose donor concentration exceeds critical concentration for the metal-nonmetal transition. The second section is mainly devoted to the description of the second problem. As regards the first and third problems, only the

---

* Present address: Laboratoire de Physique de la Matière Condensée, Ecole Polytechnique, Plateau de Palaiseau - 91120 Palaiseau, France.

essential results are summarized in section II.

II. EXPERIMENTAL RESULTS AND DISCUSSION

A. Density-dependent Luminescence Properties of EHD in Pure Germanium

In a previous paper[3] we have pointed out that when the average density of electron-hole(e-h) pairs, N_p, over the sample exceeds the equilibrium density of e-h pairs contained within an EHD, the electron-hole liquid(EHL) phase occupies the whole volume of the sample and thus a remarkable change with the variation of the average density of e-h pairs could be observed in the luminescence due to EHD. Also we have shown that this expectation actually occurs in the luminescence line due to EHD under an intense optical excitation at low temperatures. Furthermore, from an analysis of the line shape, we have obtained the ground state energy of EHL as a function of N_p. Such a change of the luminescence line with N_p can be seen in the time-resolved luminescence spectra of EHL which are taken after an optical excitation pulse is turned off. Figure 1 shows the time-resolved spectra of the LA(large peak) and TO(small peak) phonon-assisted luminescence from EHL at 1.6 K. The magnitude of N_p at the end of the excitation pulse, which is generated by a Nd-doped yttrium aluminum garnet Q-switched laser, with the pulse width of 11 nsec, is 6.4×10^{17} cm^{-3}. The spectra are taken for the delay time ranging from 1 μsec to 60 μsec. As seen from this figure, the peak position is shifted to the low energy side and the line width is decreased when the delay time is increased. However, when the delay time exceeds 40 μsec, the peak position and the line width do not change with time. The increase in the delay time corresponds to the decrease in the average density of non-equilibrium e-h pairs in the crystal. Therefore, this result can be interpreted as follows; after the laser pulse is turned off, the e-h pair density of EHL, which occupies the whole volume of the sample, decreases, so the line width gradually decreases with time and also the peak position is shifted

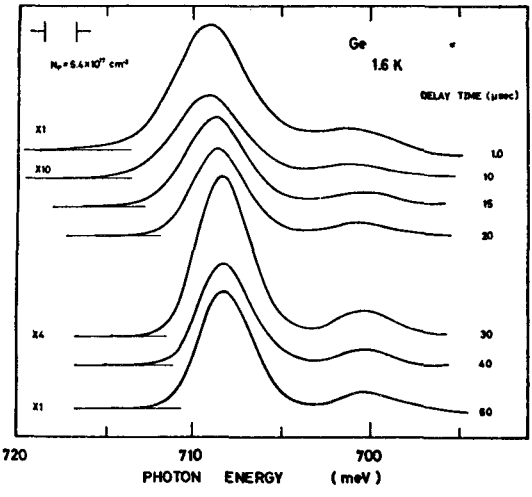

Fig.1. Time-resolved spectra of EHL at 1.6 K in Ge with the delay time of 1.0 μsec to 60 μsec. The magnitude of N_p is 6.4×10^{17} cm^{-3} at the instant of the end of the excitation pulse.

towards the low energy side. After the e-h pair density of EHL reaches the equilibrium density of EHD, the EHL phase exists as drops in the crystal, so that the peak position and the line width do not change with time.

In germanium, in addition to the main recombination mechanism which involves an LA-phonon, there is also a TA-phonon assisted process which is forbidden for an e-h pair at the band extrema. It is expected that the ratio of the integrated intensities of the TA lines and LA lines as a function of N_p is dependent of the e-h pair density of EHL phase with power of 2/3.[4] As shown in Fig.2, the ratio of the integrated intensities of the TA lines and LA lines as a function of N_p is critically increased at $N_p = 2.6 \times 10^{17}$ cm^{-3}. This result also suggests that the EHL phase occupies the whole volume of the sample when N_p exceeds its critical density ($\simeq 2.6 \times 10^{17}$ cm^{-3}), being consistent with the observations mentioned before.

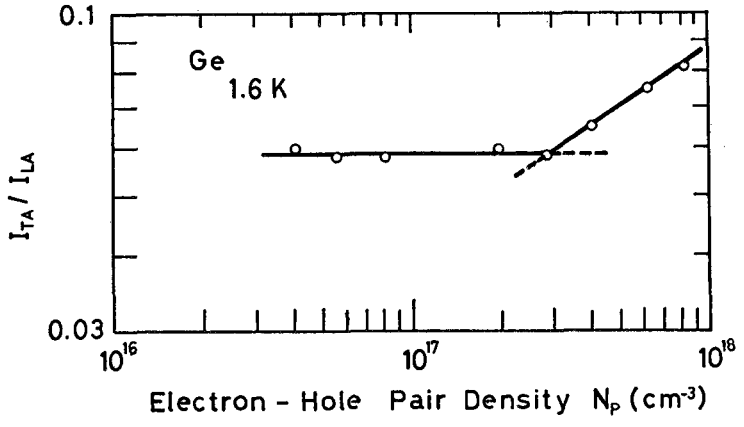

Fig.2. The ratio of the integrated intensities of the TA lines and LA lines as a function of N_p.

B. Transport Properties of EHD

In what follows, we summarize previous results[5] of the transient photoconductivity measurements in pure germanium. We have observed an anomalous profile of the transient decay curve of the photocurrent, as shown in Fig.3. The sample is excited by a pulsed dye laser with the

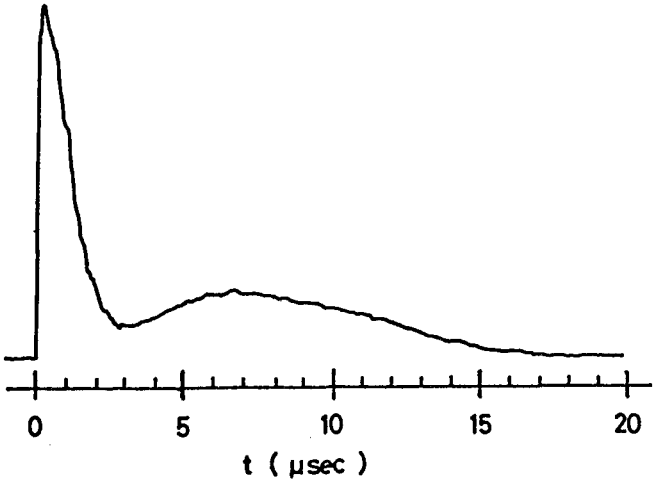

Fig.3. Decay profile of the photocurrent at $N_p = 2\times10^{15}$ cm^{-3} and 4.2 K. The magnitude of applied electric field is 1.1 V/cm.

pulse width of 5 nsec and the wavelength of 630 nm. The first peak which appears after being delayed by the response time ($\sim$0.5 μsec) of the apparatus is due to free electrons created by the band to band excitation, while the second peak arises from the contribution of free electrons ejected from EHD as a result of the Auger recombination of EHD. The N_p-dependence of the photoconductivity given by the second peak shows that the Auger recombination rate of EHD rapidly increases with N_p above $N_p \simeq 10^{15}$ cm^{-3}.

As was pointed out previously, the spike-like giant fluctuating photocurrent has been observed as superposing in the second peak, when the temperature is below 2.6 K. One pulse of the fluctuating photocurrent gives the charge of about 4×10^{-10} coulomb. Since this value is consistent with the results of p-n junction experiments,[6,7] such a spike-like giant fluctuating photocurrent is interpreted as being due to dissociation of an EHD containing $N \sim 2 \times 10^9$ electron-hole pairs. In order to understand the possible mechanism of such a giant fluctuating photocurrent observed in the sample with ohmic electrodes, we have performed the following measurement; samples of pure germanium (residual donor concentration $\lesssim 10^{13}$ cm^{-3}) were used and the beam of the laser (Nd:YAG Q-switched laser with the width of 11 nsec) was focused with a spot of diameter of 0.6 mm into a face of the sample with the electrode whose separation was 4 mm. The delay times for the appearance of the first giant fluctuating pulse were measured as a function of the distance between the electrode and the laser spot. This distance was changed by moving the lens along the direction normal to the laser beam. From this measurement, we have found that the delay time at which a photocurrent pulse first appears in the decay curve changes when the laser spot is moved towards the electrode. Figure 4 shows the delay time of the first pulse as a function of the relative distance between the electrode and the laser spot at both polarities of applied voltages. In this experimental condition, the EHD's are

generated in the vicinity of the laser spot, so that the delay time corresponds to the drift time of an EHD towards the electrode. As shown in Fig.4, it is decreased when the laser spot is shifted towards

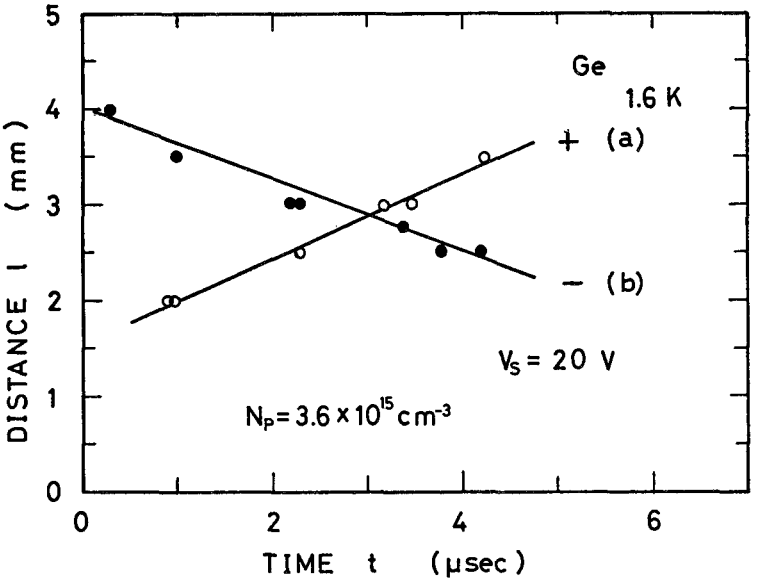

Fig.4. The time of the first giant fluctuating pulse as a function of the relative distance between the electrode and the small spot of the laser light. (a): the cathode on the upside of the ordinate; (b): the anode on the upside of the ordinate. The applied voltage is 20 V.

the anode. This result allows us to conclude that an EHD is negatively charged as a whole, consistently with the experimental result of Pokrovskii and Svistunova[8] and also with the theoretical result of Rice.[9]

In what follows, let us consider an equation of motion of an EHD regarding it as a classical particle. We assume that the diffusion of EHD which arises from its density gradient is negligible compared with the drift motion by applied electric fields. Assuming that the electric field is uniform over the sample, we can write the equation of motion of EHD as follows:

$$M\left(\dot{v} + \frac{v}{\tau_p}\right) = Ze\,\frac{V_s}{d} \quad , \tag{1}$$

where M, v, τ_p, and Ze are the mass, the drift velocity, the collision time, and the net charge of EHD, respectively, and V_s and d are the applied voltage and the distance between electrodes, respectively. If the drift time of EHD between the laser spot and the anode is long enough compared with the collision time, the motion of EHD becomes a constant velocity motion. Thus, the following equation of motion of EHD is obtained from eq.(1),

$$v = \frac{Ze\tau_p}{M} \cdot \frac{V_s}{d} \quad . \tag{2}$$

The slope of the straight line of the relative distance versus the delay time of the first pulse in Fig.4 gives the drift velocity of EHD. Thus, the drift velocity obtained from such a procedure should depend linearly on the applied voltage if eq.(2) holds. We have observed that this is the case in our experimental condition (V_s is between 18 V and 26 V). From eq.(2), we can derive the value of the net charge of EHD. The mass of EHD is estimated by using the magnitudes of the effective masses of electrons and holes and the number of electron-hole pairs contained in an EHD, which is known from the charge giving one photocurrent pulse. Since the experimental value of τ_p is not available at present, we take τ_p as 5×10^{-7} sec, which is by Bagaev *et al.*[10] Then, inserting these values of the parameters and also the experimental values of V_s, d and v into eq.(2), we can derive the magnitude of the net charge as a function of N_p as follows; Ze = -18000 e at $N_p = 4.3 \times 10^{14}$ cm^{-3} and Ze = -2300 e at $N_p = 3.6 \times 10^{15}$ cm^{-3}, and the net charge is linearly dependent of N_p in the range of $N_p = 4.3 \times 10^{14}$ cm^{-3} to 3.6×10^{15} cm^{-3}.

These values are large compared with the previous experimental result[8] and theoretical one.[9] However, we consider that this discrepancy is due to the large radius of EHD and the high electric fields applied to the sample in this experiment; in the range of applied voltages of this experiment, excitons and residual impurities in the

crystal are fully ionized (in this sample, the threshold field for the impact ionization of impurity and exciton is about 10 V/cm and 3 V/cm, respectively), so that the EHD exists in a gas of free carriers rather than in an exciton gas. Since the ionized carriers outside the EHD form a screening cloud around a charged EHD, it is expected that the EHD has a large value of net charge, depending on the density of ionized carriers. If we follow the formula of Rice[9] which contains the temperature, the radius of EHD and the density of free carriers as the parameters, we can estimate a net charge of EHD in case of the presence of free carriers outside the EHD. For $N_p = 4.3 \times 10^{14}$ cm^{-3}, we can obtain an almost consistent value of net charge with the experimental one, using the density of free carriers of 10^{13} cm^{-3}, and the radius of EHD of 13 μm.

C. EHD in Heavily Doped Germanium

As was reported previously,[11] the luminescence measurement allows us to conclude that EHD stably exists even in metallic samples of As-doped germanium whose donor concentrations exceed the critical concentration for the metal-nonmetal transition, that is, $N_D \simeq 4.7 \times 10^{17}$ cm^{-3}. This conclusion is consistent with recent theoretical results.[12,13]

In heavily As-doped germanium, the peak position of the EHD luminescence is shifted towards the low energy side with the donor concentration in comparison with the case of pure germanium. This shift is interpreted as being due to the interaction of electrons with donor impurities. The line width of the EHD luminescence depending on the donor concentration which has been observed in the samples of the metallic concentration region ($N_D \gtrsim 4.7 \times 10^{17}$ cm^{-3}) is mainly determined by the sum of the Fermi energies of electrons and holes. An additional broadening observed in the intermediate concentration region for the impurity conduction (1×10^{17} cm$^{-3} \lesssim N_D \lesssim 4.7 \times 10^{17}$ cm^{-3}) could be account-

ed for by the fluctuation of impurity potentials. The luminescence measurement of EHD as a function of the donor concentration will be useful to study the nature of the metal-nonmetal transition in doped germanium.

REFERENCES

1) L. V. Keldysh: *Proc. Int. Conf. Physics of Semiconductors, Moscow* (1968) ed. S. M. Ryvkin (Nauka, Leningrad, 1968) p.1303.

2) Ya. E. Pokrovskii: Phys. Status solidi (a) 11 (1972) 385, and numerous references contained therein.

3) A. Nakamura and K. Morigaki: Solid State Comm. 14 (1974) 1212.

4) C. Benoît à la Guillaume, M. Voos and F. Salvan: Phys. Rev. B5 (1972) 3079.

5) A. Nakamura and K. Morigaki: Solid State Comm. 14 (1974) 41.

6) V. M. Asnin, A. A. Rogachev and N. I. Sablina: ZhETF Pis. Red. 11 (1970) 162. [Soviet Phys. JETP Lett. 11 (1970) 99.]

7) C. Benoît à la Guillaume, M. Voos, F. Salvan, J. M. Laurant and A. Bonnot: C. R. Acad. Sc. Paris t272 (1971) 236.

8) Ya. E. Pokrovskii and K. I. Svistunova: ZhETF Pis. Red. 19 (1974) 92. [Soviet Phys. JETP Lett. 19 (1974) 56.]

9) T. M. Rice: Phys. Rev. B9 (1974) 1540.

10) V. S. Bagaev, T. I. Galkina, O. V. Gogolin and L. V. Keldysh: ZhETF Pis. Red. 10 (1969) 309. [Soviet Phys. JETP Lett. 10 (1969) 195.]

11) A. Nakamura and K. Morigaki: *Proc. Int. Conf. Physics of Semiconductors, Stuttgart* (1974) ed. M. H. Pilkuhn, (Teubner, Stuttgart, 1974) p.86.

12) G. Mahler and J. L. Birman: Phys. Rev. B12 (1975) 3221.

13) B. Bergersen, P. Jena and A. J. Berlinsky: J. Phys. C, Solid State Phys., 8 (1975) 1377.