ELECTRON-HOLE DROPS IN SILICON

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ABSTRACT

Two problems concerning the emission from Si under high-excitation have been investigated: One of them is the near-infrared emission from highly excited Si-surface by a Q-switched ruby laser. Time-resolved emission spectra make clear the electron-hole liquid phase extending uniformly over the crystal surface. The second problem is the far-infrared emission from Si under high-excitation. We observe the emission due to the 2p-1s transitions of the excitons in Si.

Up to present, the existence of electron-hole drops (EHD) has been believed only for the indirect energy gap semiconductors, Ge and Si, though there have been a fewer studies on EHD in Si comparing with Ge. The cause of a fewer studies for Si is that the carrier concentration inside EHD is one order of magnitude larger in Si than in Ge, and the life-times of excitons and EHD in Si are also one order of magnitude shorter comparing to Ge, so that for Si an appreciably stronger excitation is necessary for making the same state of EHD as for Ge. However, for making clear the whole aspect of EHD, the comparison between the condensed phase in Si and that in Ge is indispensably important.

Here we treat two problems concerned with the highly excited state in Si. (i) One of them is an experimental study of the highly excited state of Si produced by a Q-switched ruby laser.

The experiment was performed by using phosphorus-doped 1200 Ωcm Si samples. The resistivity corresponds to the doping level of 4×10^{12} cm^{-3} impurity concentration. In the measurements, the samples were cooled by being directly immersed in liquid helium or liquid hydrogen. The excitation by a GaAs laser of 1 watt/pulse produced the excited

carriers of about 10^{14} cm^{-3}, while in the case of a Q-switched laser, the excitation power was 200 kilowatt/pulse and the number of the excited carrier amounted to more than 5×10^{18} cm^{-3}.

Near infrared emission line from Si in the case of GaAs laser excitation is shown by the broken curve in Fig.1. This line was discovered by Haynes[1] and ascribed to EHD by Pokrovskii *et al.*[2] The emission produced by a Q-switched ruby laser excitation is indicated by

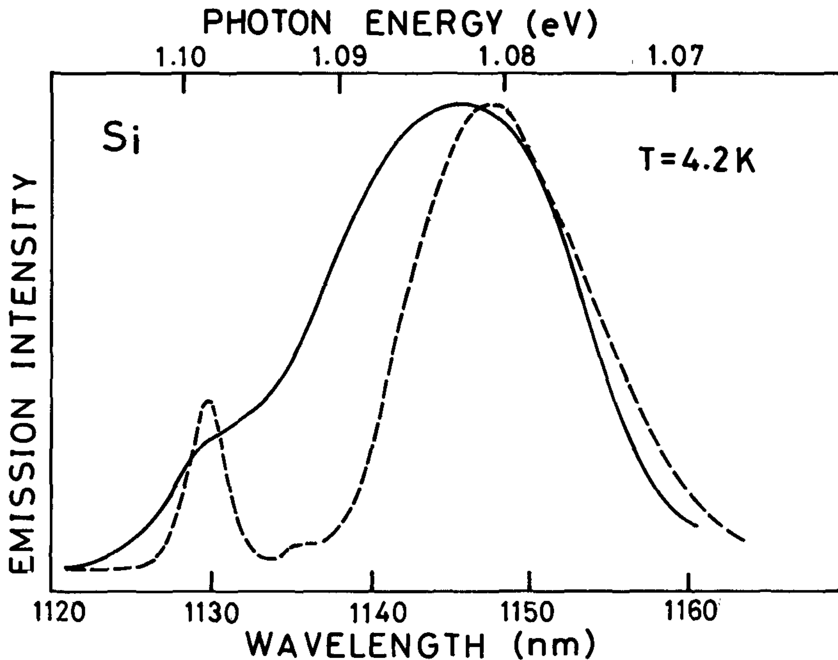

Fig.1. Comparison of near infrared emission spectra between two different excitation. The broken curve corresponds to a GaAs laser (relatively weak) excitation, while the solid curve to a Q-switched ruby laser (extremely strong) excitation.

the solid curve in the figure. By the extremely high excitation the spectral shape of the Haynes line changes and a new component grows between the free exciton (FE) line and the Haynes line (N-line). According to the conception of EHD, the spectral shape of EHD remains unchanged with the change of the excitation power; that is, the carrier density inside EHD is uniquely determined from the condition of the minimum free energy, so that higher excitation increases only the number

of EHD's or their radii, which yields the same spectral shape. Therefore, the new component produced at the higher energy side of the Haynes line cannot be interpreted as due to the emission from normal EHD.

On the other hand, as FE-component peaked at 1.098 eV changes with the excitation level, we must separate the contribution of the FE-line from the whole spectrum. Thus we study the time-resolved emission spectra of highly excited Si.

Figure 2(a) shows the time-resolved emission spectra at 4.2 K. It

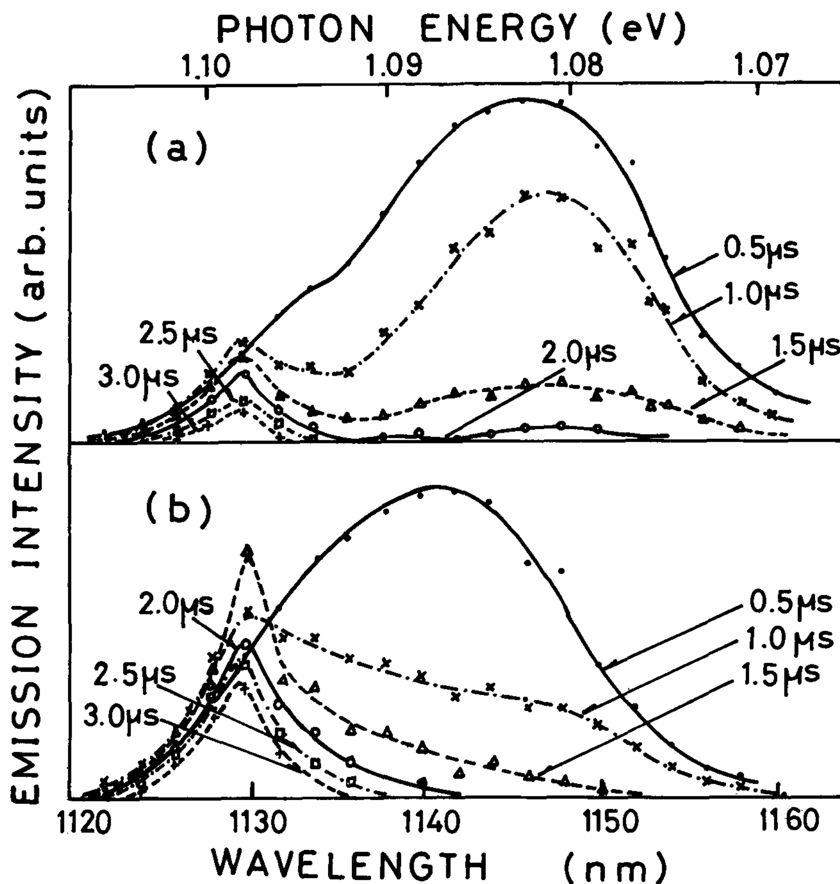

Fig.2. Time-resolved emission spectra at 4.2 K (a) and at 20 K (b). The time delays between excitations and observations are indicated in μsec units.

is seen in the figure that the new component (N'-line) decays faster than the N-line and the whole spectral shape tends to approach to the shape for the weaker excitation case (the Haynes line) as time passes. The decay time of the N'-line is within 1.5 μsec, while the FE-line grows after the decay of the N'-line and remains longer than the N'-line.

Figure 2(b) shows the time-resolved spectra at 20 K, where we hardly observe the N-line. As the spectral shape and the peak position of the line at 20 K peaked at 1.088 eV agree with those of the N'-line at 4.2 K, we regard the line as the N'-line. The line decays quickly within 1.5 μsec, which is close to the decay time of the N'-line at 4.2 K. A remarkable feature of the spectra at 20 K is that the FE-line requires about 1.5 μsec to reach its maximum after the excitation when the N'-line at 20 K disappears. This behavior of the FE-line is characteristic for high excitations and was not found in weaker excitation by Cuthbert[3)] whose injection level was about 10^{17} cm^{-3}. The coincidence of the decay time of the N'-line with the growing time of the FE-line suggests that a source of the N'-line is formed initially in the sample and then it dissociates to the free excitons.

We have assumed so far that the new component at 4.2 K and the line peaked at about 1.088 eV are the same one and they have been designated commonly as the N'-line. This assumption is reasonable because the peak energies, the line widths and the decay times are in agreement between them. The line shape analysis for the N'-line was performed according to the assumption of band-to-band transition by Pokrovskii *et al.*[2)] The density of state masses used are[4)] $m_c = 1.08\ m_0$, and $m_h = 0.55\ m_0$. As the result, we obtained the carrier density of $n_0 = 8.3 \times 10^{18}$ cm^{-3}, which is appreciably larger compared with the concentration in equilibrium EHD, $n_0 = 3.7 \times 10^{18}$ cm^{-3}.

We suppose from the above experimental results that the crystal surface is filled with the electron-hole plasma just after the extremely high excitation, which is the origin of the N'-line. Free excitons

cannot be generated at the initial stage because of the strong screening effect of the free carriers in the liquid.

From a phase-diagrammatical consideration,[5] the initial electron-hole liquid phase at 4.2 K by high-excitation changes to the coexistence phase of EHD and FE, which explains the time-resolved emission spectra of Fig.2(a), while at 20 K, the initial high pressure liquid phase passes through the coexistence phase of EHD and FE in a short time and runs into the single FE phase immediately, which can interpret the spectral figures of the time-resolved emission spectra of Fig.2(b).

The N'-line at 20 K might be also ascribed to EHD. However, this explanation cannot clarify the reason for the appearance of the FE-line after the decay of the N'-line as shown in Fig.2. If the N'-line is originated from EHD, it should coexist with FE, so that the post-excitation peak of FE cannot be observed. Besides, the carrier concentration inside EHD must decrease at higher temperatures, and therefore, the N'-line at 20 K must have a narrower line width compared with the N-line at 4.2 K. This is not the case in the present experiment.

(ii) The second problem is on the far-infrared emission from Si under high excitation. We expected the emission due to the plasma oscillation of EHD in Si as observed in Ge by Vavilov.[6]

Figure 3 shows the block diagram of the experimental set-up. The excitation power of the GaAs laser was 25 watt/pulse and supposed to make enough EHD in Si. We also used a halogen lamp of 150 watt. The light from the source was guided through a glass optical fiber to the Si sample which was set at the bottom of a metal cryostat. As the window of the cryostat we also used a pure Si plate which is transparent in the far-infrared region. The far-infrared luminescence from Si was introduced into a Michelson interferometer, Beckman model FS-720, then detected by the photoconductive semiconductor detectors of Ge-Sb or Ge-As. The interferometer was considered to be advantageous to measure the weak emission power less than 10^{-9} W. The Si samples

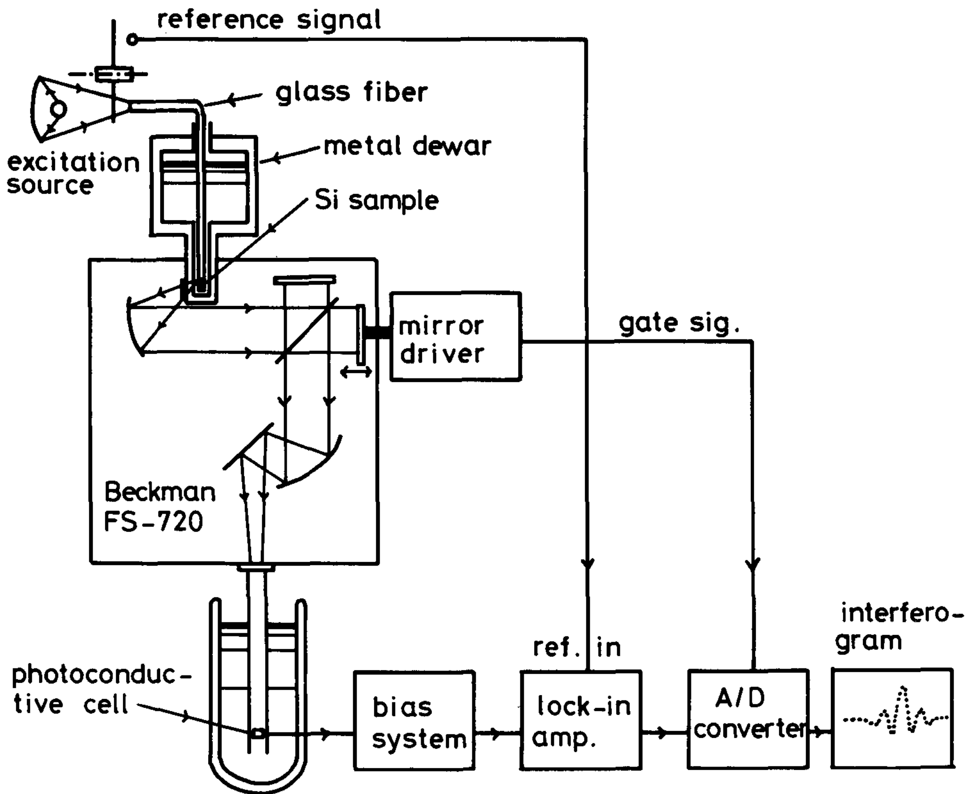

Fig.3. Block diagram of experimental system for measuring far-infrared emission spectra of Si under high-excitation using Michelson interferometer.

used were cut from the same ingot as that used in the experiment (i).

Figure 4 shows the far-infrared emission spectrum from the Si sample at 4.2 K, which is obtained by using the Ge-Sb detector. The spectrum has a sharp peak at 93 cm^{-1} (11.5 meV) and tails off toward the high energy side.

As the origin of this far-infrared emission, three possibilities can be considered; the emission from plasma in EHD, the transitions between the discrete levels of the impurity state, and those of the exciton. The first possibility is excluded by the following reasons. If we calculated the plasma frequency, $\omega_p^2 = e^2N/\varepsilon\mu$, by taking the carrier concentration in EHD of $N = 3\times10^{18}$ cm^{-3} and the reduced mass of μ =

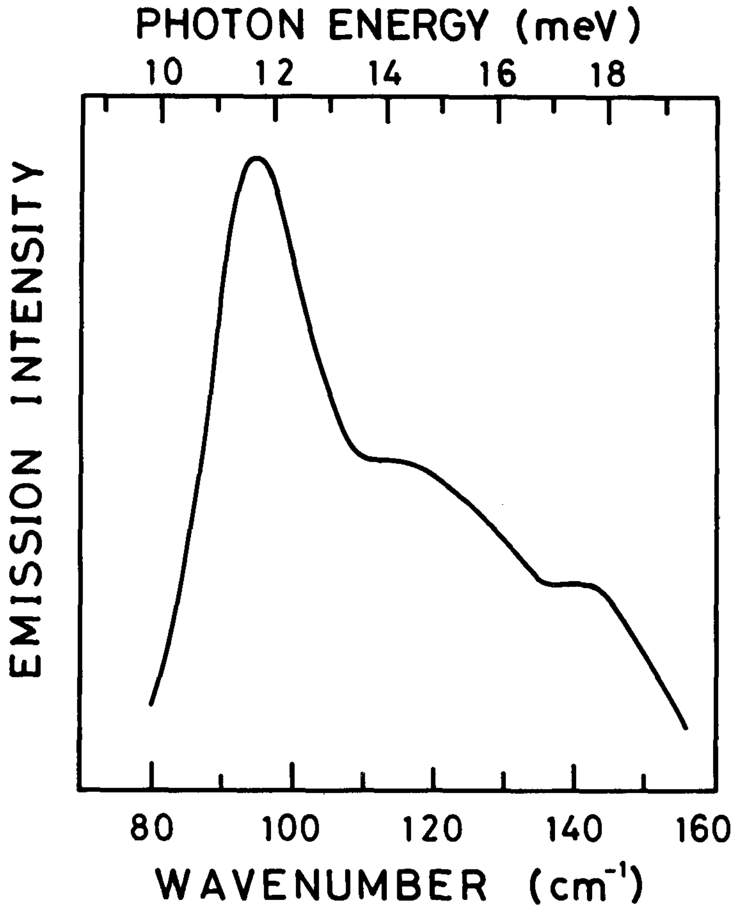

Fig.4. Far-infrared emission spectra of Si under high-excitation using Michelson interferometer and Ge-Sb detector.

0.15 m_0, then we have the theoretical peak frequency $\omega_p/\sqrt{3}$ as 227 cm^{-1}, which is too high compared with the experimental results. On the other hand, the emission remains above the liquid nitrogen temperature up to near the room temperature, though the intensity appreciably decreases. These facts exclude the first possibility of the emission from EHD. Secondary, the emission due to transitions between the discrete levels of impurity is not probable, because the impurity concentration in the present case is too small, 4×10^{12} cm^{-3} and also at 4.2 K the ground states of the impurities are occupied by electrons, so that such a

transition cannot occur.

The experimental information regarding the excited states of the exciton in Si was given by Shaklee and Nahory.[7] They gave the 1s-2s energy separation for TA phonon assisted transition to be 10.7 meV and the separation for LO and TO assisted transitions to be 11.0 meV. Our experimental peak energy of 11.5 meV is very close to these values. We therefore attribute our emission peak in Fig.4 to the exciton transition from the 2p state to the 1s ground state. The energy difference of 0.5 ~ 0.8 meV between their results and ours may be explained as the energy difference in the 2s and 2p levels of the n = 2 state, whose degeneracy is removed on account of the mass anisotropy in the conduction band and the degeneracy of the valence band.[8] In the case of the interband absorption,[7] the 2s state was observed, while in the case of the far-infrared emission, the 2p state must be the initial state according to the selection rule.

The reason that the far-infrared emission from the plasma in EHD was not observed in the present experiment may be ascribed to the weakness of the emission intensity or the weak sensitivity of the present detector in the region. Therefore, further investigations are required.

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