Formation of Electron-Hole Liquid in Optically Excited Si: Results of Fast Time-Resolved Spectroscopy

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We present the first measurements of time-resolved luminescence *spectra* during the growth of electron-hole liquid in Si excited by 15-nsec optical pulses. The results clearly show that at high excitation intensities, the electron-hole liquid forms directly from a hot, dense plasma rather than from a gas of excitons.

We report in this Letter the first measurements of time-resolved luminescence *spectra* obtained during the growth of electron-hole liquid[1,2] (EHL) in Si, following excitation by a fast (15 nsec) optical pulse. The intensity of luminescence from EHL reaches a peak ≈ 55 nsec after the beginning of the laser pulse. An analysis of the spectral shape at various times during this growth process allows us to determine the dominant form of excitation (plasma, excitons, and/or EHL) in the crystal at these times. In particular, the data clearly show that in Si, following excitation by short pulses, the EHL forms directly from a hot, dense plasma rather than through nucleation from an excitonic gas. Theories considering homogeneous nucleation from an ideal excitonic gas are available,[3,4] but direct formation of EHL from the optically excited plasma has not yet been considered theoretically. The time evolution of the luminescence without spectral resolution has been previously measured in Ge,[5,6] but the lack of spectral resolution has limited the amount of information obtainable from such studies. The time-resolved spectra reported here are essential in studying the changes that occur during the transformation of the initial optically excited electrons and holes into the final EHL.

A Syton-polished crystal of 1000-Ω-cm Si was immersed in superfluid He (~ 1.8°K) and excited by 15-nsec pulses (~ 0.5 μJ/pulse) from a cavity-dumped Ar^+ laser focused on the sample to a spot ~ 100 μm in diameter. The luminescence was collected from the front face and analyzed by a double spectrometer with ≈ 1.2-meV spectral resolution. The data presented here were obtained by using an FW 118 S1 photomultiplier followed by a photon counter with a 10-nsec gate. The 10–90% rise time of the laser pulse, as measured by this detection system, was ≈ 17 nsec.[7]

The low-temperature luminescence spectrum of Si is dominated by TO-LO- and TA-assisted recombination from the EHL and the TO-LO-assisted free-exciton recombination.[8] The time-dependent behavior of the two EHL bands is identical, and so we will concentrate on the stronger TO-LO-assisted EHL band which occurs at ≈ 1.080 eV, and the TO-LO-assisted exciton band at ~ 1.097 eV. The time evolutions of the luminescence signals with the spectrometer set at 1.080 and 1.097 eV are shown in Fig. 1 as curves marked 1 and 2, respectively. For curve 1, the peak in the luminescence is reached ≈ 55 nsec after the beginning of the laser pulse while for curve 2 it is reached at ≈ 35 nsec.[7] The remarkable shape of the luminescence signal in curve 2 leads one to the assumption of two distinct phases: The early phase starts at $t = 0$, reaches a peak at 35 nsec, and then decays to zero at $t \approx 55$

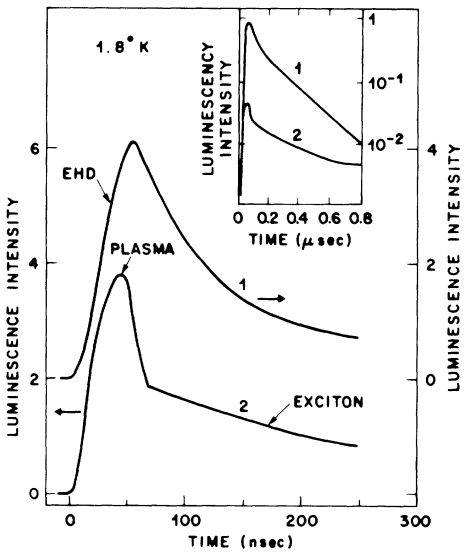

FIG. 1. Time evolution of luminescence intensity in Si excited by a 15-nsec laser pulse. The spectrometer was set at 1.080 eV, corresponding to the peak of the EHL luminescence, for curve 1, and at 1.097 eV, corresponding to the peak of excitonic luminescence, for curve 2. Spectrometer resolution is 1.2 meV. The zero in time corresponds to the beginning of the laser pulse.

nsec. The second phase starts somewhat later, and has a long decay time characteristic of free excitons.[9] Later in our discussion of the time-resolved spectra we will show that the two-phase assumption is correct, and we will identify the early phase as the initial hot, dense plasma and the second phase as the excitonic vapor associated with the electron-hole liquid. The time evolution over a larger range is shown on a semilog plot in the inset. Decay characteristics of EHL and free excitons have been studied previously[9] and will not concern us here. The delay between the 15-nsec-wide laser pulse and the peak of curve 1 has been reported previously using wider excitation pulses and/or slower detectors.[7,9,10]

In Fig. 2, we present normalized luminescence spectra at various delays with respect to the excitation pulse. Spectrum 1, corresponding to the time gate beginning at the peak of the laser pulse, is very broad with large high- and low-energy tails and no resolvable exciton structure. Spectrum 2, taken 20 nsec after 1, is narrower and shows a shoulder at the exciton energy (1.097 eV). Spectrum 3, taken 60 nsec after 1, has a smaller high-energy tail and a well-resolved exciton peak. Spectra taken at longer delays are similar to spectrum 3 on the low-energy side but have steeper high-energy tails and relatively stronger exciton peaks in accordance with Fig. 1.

Before proceeding to a discussion of the significance of these results, we describe briefly the expected theoretical shape of the luminescence

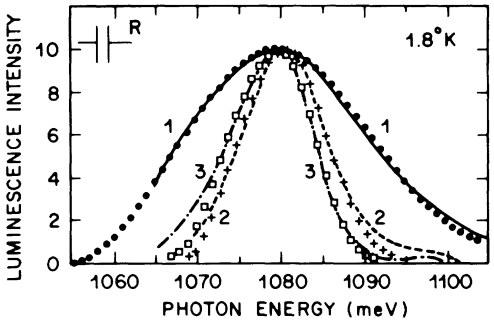

FIG. 2. Normalized luminescence spectra of optically excited Si obtained at different times during the growth of EHL. The curves 1, 2, and 3 are experimental and were obtained with a 10-nsec gate centered at 20, 40, and 80 nsec, respectively, after the beginning of the 15-nsec (full width at half-maximum) laser pulse. The points are calculated using equations in text taking $n=7.5\times10^{18}$ cm^{-3}, $T=45$°K (solid circles); $n=2.65\times10^{18}$ cm^{-3}, $T=18$°K (crosses); and $n=3.0\times10^{18}$ cm^{-3}, $T=12$°K (squares). The free-exciton peak occurs at ≈ 1.097 eV. The relative intensities of the spectra may be obtained from curve 1, Fig. 1.

spectrum from an electron-hole plasma of density n. The low-energy edge of the luminescence is well defined and occurs at $E_g' - \hbar\omega_{TO}$, where E_g' is the reduced band gap and $\hbar\omega_{TO}$ is the TO phonon energy. The reduced gap decreases with increasing density but its value is expected to be insensitive to increases in temperature up to ~ 50°K. The magnitude of the reduced gap can be either calculated theoretically[2,10] (see below) or obtained from published experimental curves at 2°K.[8,9] One finds that $E_g' - \hbar\omega_{TO} = 1.067$ eV for $n = n_d$, the electron hole density in EHL.[11] The high-energy tail of the luminescence spectrum is a sensitive function of the temperature T and extends to higher energies with increasing T.

Let us now consider what qualitative conclusions can be derived from the spectra in Fig. 2. The observation that spectrum 1 extends to energies considerably lower than 1.067 eV can only be explained if the excitation is in the form of a liquid or a plasma whose density is significantly larger than n_d. The long high-energy tail implies that the temperature of the plasma is considerably higher than the helium-bath temperature. Furthermore, the high-energy tail does not show any sign of exciton luminescence which leads to the conclusion that no excitons are present in the crystal during the intense optical excitation.

Three dramatic changes are apparent in spectrum 2 (Fig. 2), taken immediately after the end of the laser pulse. The low-energy edge has come closer to the expected value of 1.067 eV for the condensate, the exciton has begun to emerge, and the high-energy tail has become steeper. These observations indicate that EHL has already been formed and that its temperature is considerably lower than the temperature of the plasma in spectrum 1. The emergence of the luminescence from excitons shows that at least partial phase separation between EHL and free excitons has taken place. The intensity of the exciton luminescence is considerably smaller than that of the EHL luminescence, implying that the number of excitons is much smaller[12] than the total number of pairs in the liquid phase. Thus the formation of EHL has occurred directly from a hot, dense liquid without going through an excitonic phase.

Another important change occurs in spectrum 3, which was taken 40 nsec after spectrum 2. Its low-energy edge is close to that of spectrum 2 and covers an intermediate range lying between spectra 1 and 2. This leads to the conclusion that both spectra 2 and 3 are indeed coming from

an EHL with the liquid in 2 at higher temperature, and hence of a lower density, than the liquid in 3. Because of the lower temperature, the exciton peak has become well resolved in spectrum 3. At this point in time, only the excitons contribute to the time-decay curve 2 in Fig. 1. This qualitative discussion leads us to conclude that intense optical excitation initially produces a hot, dense plasma and that the EHL is formed directly from this hot, dense plasma in tens of nanoseconds.

Keeping this discussion of time-resolved spectra in mind, let us return to the time evolution curve 1 of Fig. 1. First we wish to stress again that this time evolution curve does *not* represent the total luminescence intensity integrated over the spectra shown in Fig. 2 but represents the luminescence intensity in a 1.2-meV energy window at 1.080 eV. Since the spectral distribution changes with time, the time evolution of the total integrated intensity will be quite different from curve 1, Fig. 1. Combining the data in Figs. 1 and 2, one easily finds that the total integrated intensities under spectra 1 and 2 are approximately the same. Since the total integrated intensity is proportional to ρn, where ρ is the enhancement factor[13] and n the density of the plasma or liquid, one finds that $\rho_2 \approx 2\rho_1$, where the subscripts correspond to spectra numbered in Fig. 2. This increase in ρ with time is expected for the following reasons. The enhancement factor is a result of the exchange and correlation effects between carriers and is expected to decrease with increasing kinetic energy of the carriers.[13] A decrease in the density or the temperature of the carriers leads to a decrease in their kinetic energy and hence an increase in ρ.

In order to put this discussion on firmer theoretical grounds, we note that the average energy per pair $\langle E(n)\rangle$ has been calculated[2] for Si at 0°K as a function of density of particles in the liquid. The chemical potential of the system is given by $\mu^0(n) = d[N\langle E(n)\rangle]/dN$ and the high-energy edge of the luminescence from the liquid is given by $\mu^0(n) - \hbar\omega_{TO}$. Here N is the total number of particles and $\hbar\omega_{TO} = 57.3$ meV is the energy of the TO phonon participating in the recombination.[14] The reduced band gap is given by $E_{g0}'(n) = \mu^0(n) - (E_{Fe}^0 + E_{Fh}^0)$, where E_{Fe}^0 (E_{Fh}^0) is the electron (hole) Fermi energy at $T = 0$°K. For temperatures small compared to the exciton binding energy (14.7 meV),[14] we assume that $E_g'(n) = E_{g0}'(n)$ and $\mu(n) = E_{g0}'(n) + (E_{Fe} + E_{Fh})$, where the Fermi energies at finite temperature T are such that

$$E_{Fe}/kT = (1.563\times 10^{-21} n^{4/3}/T^2 - 1.7)^{1/2},$$

and

$$E_{Fh}/kT = (5.915\times 10^{-21} n^{4/3}/T^2 - 1.7)^{1/2},$$

for Si,[15] where n is in inverse cubic centimeters and T in degrees kelvin. Under these conditions the shape of the liquid luminescence band is given by[16]

$$I(h\nu', n, T) \propto \int_0^{h\nu'} \frac{\epsilon^{1/2}(h\nu' - \epsilon)^{1/2} d\epsilon}{\{1+\exp[(\epsilon - E_{Fe})/kT]\}\{1+\exp[(h\nu' - \epsilon - E_{Fh})/kT]\}},$$

where the emitted photon energy $h\nu$ is

$$h\nu = h\nu' + E_g'(n).$$

Using these equations, we have fitted the observed spectra with theory treating n and T as adjustable parameters. The best-fit curves are shown by dots in Fig. 2. The fit with measured spectra is very good and supports the qualitative arguments given above. In particular, the initial plasma (spectrum 1) is dense ($\cong 7.5\times 10^{18}$ cm^{-3}) and hot ($\cong 45$°K). This plasma cools and expands to $T \cong 18$°K and $n_g \cong 2.65\times 10^{18}$ cm^{-3} as shown in spectrum 2. From the recent measurements of Hammond, Smith, and McGill,[16] we know that these values of n_d and T correspond to a point on the liquid-gas coexistence curve of the phase diagram. Thus these results show for the first time that EHL forms directly from a hot, dense plasma. They also show that the temperature-density trajectory of the plasma crosses the coexistence curve of the phase diagram on the liquid side first, and phase separation into EHL and excitons then becomes possible. The fit to spectrum 3 shows that n_d has *increased* to 3×10^{18} cm^{-3} while T has decreased to 12°K. These values of T and n_d also correspond to a point on the coexistence curve. Thus the liquid phase formed follows a trajectory along the coexistence curve where its density increases as its temperature decreases. However, the average density of pairs presumably continues to decrease because of decay and expansion.

In conclusion, the time-resolved spectra presented here clearly show that in silicon, following excitation by an intense short pulse, the for-

mation of excitons does not precede the formation of droplets and that the electron-hole liquid forms directly from the hot, dense plasma generated by the optical excitation pulse.

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[2]See, for example, W. F. Brinkman and T. M. Rice, Phys. Rev. B 7, 1508 (1973).

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[7]With a faster photomultiplier (response time ~2 nsec) and the electronics described here, the laser-pulse rise time was ≈ 10 nsec and the luminescence peaks occurred <10 nsec sooner than shown in Fig. 1. The quantum efficiency of this photomultiplier was more than a factor of 10 lower than that of FW 118. Hence the faster photomultiplier was unsuitable for detailed studies.

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[10]A. F. Dite, V. G. Lysenko, and V. B. Timofeev, Phys. Status Solidi (b) 66, 53 (1976).

[11]We use the term EHL or condensate for the liquid along the liquid-gas coexistence curve. n_d is the density of pairs in EHL and is a function of temperature.

[12]From Ref. 9, one can infer that the radiative recombination rate for excitons is only about an order of magnitude smaller than that for EHD. Therefore, the conclusion that the number of excitons is considerably smaller than the number of pairs in the condensate still holds.

[13]The enhancement factors for Si and Ge at 0°K have been calculated by P. Vashishta, S. G. Das, and K. S. Singwi, Phys. Rev. Lett. 33, 911 (1974). We acknowledge a helpful discussion on variation of ρ with n and T with M. Combescot and P. Vashishta.

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[15]To obtain these expressions, we have used density-of-state effective masses $m_{de}=1.07m_0$ and $m_{dh}=0.55m_0$ and the formula (C 3.20) given by Blakemore [J. S. Blakemore, *Semiconductor Statistics* (Pergamon, New York, 1962)].

[16]This equation calculates only the TO-assisted EHD recombination spectrum. The energy of the LO phonon is only 2 meV less than that of the TO phonon in Si, with the result that the LO-TO bands overlap. The ratio of the LO to TO coupling strengths is 0.11 [R. B. Hammond, D. L. Smith, and T. C. McGill, Phys. Rev. Lett. 35, 1535 (1975)]. In the actual curve fitting, we have calculated the theoretical curves by taking into account both the TO and LO contributions. For details, see R. B. Hammond, T. C. McGill, and J. W. Mayer, Phys. Rev. B 13, 3566 (1976). We thank Professor McGill for a preprint of this work.

Halogen Charge-Transfer States and the Optical Threshold Profile in Metals

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Charge-transfer excitations of halogen impurities in potassium have been detected by optical methods. The data are used to establish experimentally that optical threshold profiles in metals are determined by chemical properties of optical centers.

Halogen impurities are known to exist as *negative ions* in alkali metal hosts (i.e., F^-, Cl^-, Br^-, and I^-).[1] They adopt $(p^6)^-$ configurations with full outer shells bound well below the host band edge.[2] In this Letter we report the first observation of neutral halogen $(p^5)^0$ configurations in a metal. The new states were produced by photon absorption in the vacuum uv. The possible occurrence of these charge-transfer states as resonances in the local excitation spectrum has been suggested[3] but not previously confirmed. We account quantitatively for the threshold energy and relate the threshold broadening to the Stokes shift. Novel features of the results that bear on the spectroscopy of other materials are mentioned briefly. The most important consequence of this work is that the present results, when compared to other impurity and host spectra, establish experimentally for the first time that *the threshold profile in metals is determined by chemical features* of the ground and excited electronic structures.

Figures 1(a)–1(d) show the optical absorption *per ion* for F^-, Cl^-, Br^-, and I^- in potassium