Second Condensed Phase of Electron-Hole Plasma in Si

L. M. Smith and J. P. Wolfe

Department of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

(Received 7 July 1986)

Evidence for a condensed phase of plasma in Si above the electron-hole–liquid (EHL) critical temperature (≈ 24 K) is presented. The condensed plasma has a density of about one-tenth that of the low-temperature EHL phase and is observed both above and below the EHL critical point. This new low-density liquid appears in the region expected for the metal-insulator transition. A new phase diagram of excitonic matter in Si is presented which is radically different from previous work.

PACS numbers: 71.35.+z, 71.30.+h

Nearly two decades ago it was postulated by Keldysh[1] that at sufficient densities excitons in a cold semiconductor may condense into liquid droplets of electron-hole plasma. This is an unusual gas-liquid transition for a number of reasons. In the first place, the gas phase consists of photogenerated excitons (bound electron-hole pairs), which freely diffuse through the crystal from the excitation point. In the indirect-gap semiconductors Si and Ge, the excitons typically recombine in a few microseconds, producing a luminescence spectrum which reflects the distribution of kinetic energies within the exciton gas. The volume occupied by the excitonic gas is determined by the mean distance over which an exciton diffuses within its lifetime, which is typically about a millimeter. At sufficient optical powers the density of excitons equals the saturated gas density for which electron-hole droplets of much higher density begin to form.

Within the liquid phase, electrons and holes are completely dissociated because the liquid-gas (LG) transition is concurrent with a metal-insulator (MI) transition, also known as the Mott transition.[2] This significant departure from a simple liquid-gas transition (where the basic constituent, atom or molecule, remains intact in both phases) has raised speculation that the phase diagram could be qualitatively different from the usual Guggenheim form.[3] Citing earlier work by Landau and Zeldovich,[4] Rice[5] postulated that at elevated temperatuares the excitons may undergo a first-order MI transition to an electron-hole plasma, and then as the total density of pairs is raised, the electron-hole plasma would further condense into droplets of electron-hole liquid (EHL). This implies that the phase diagram would have *two* critical points, one at T_c(LG) associated with the liquid-gas (LG) transition and another at T_c(MI) associated with the metal-insulator transition. The gas density required for a metal-insulator transition is predicted to be 1 to 2 orders of magnitude smaller than the liquid density. Since Rice's suggestion, a number of many-body calculations have been made which seem to support these ideas,[6,7] but uncertainties arise in estimating the screening of the excitonic gas at intermediate densities.

Experimental evidence for separate LG and MI transitions has been reported for strain-confined excitons in Ge, where the stress significantly modifies the band structure.[8] Until now, no such phenomena have been observed in unstressed crystals, where the EHL properties are best characterized. Thomas, Mock, and Capizzi[9] concluded that the phase diagram in Ge was distorted by the Mott transition, but no separate first-order transition was observed. Likewise, a number of experimental phase diagrams[10–12] in unstressed Si show no sign of a separate MI transition of first order.

Since these studies several advances have been made in the spectroscopy of excitonic phases which call for another look at the problem. The principal technical difficulty lies in isolation of the overlapping recombination-luminescence spectra due to excitons, excitonic complexes (biexcitons or trions), and electron-hole plasmas. In the critical region for liquid condensation of all of these species may be present because the saturated gas density of excitons is very high. Fortunately, the (four-particle) biexciton line shape has now been accurately determined in Si, and it is likely that the trion (two electrons and one hole or two holes and one electron) has a similar luminescence line shape.[13] Also advances have been made in the calculation of the ground-state energy of electron-hole plasmas,[14] and so for a given pair density both the energy position and width of the spectrum are accurately predicted.

We have also chosen a somewhat different experimental approach which takes advantage of the differing lifetimes of the various phases. The spectral signature of each phase is extracted by time-resolved spectroscopy. In order to produce sufficient densities of electron-hole pairs, a cavity-dumped Ar^+ laser ($\lambda = 5145$, 4880 Å) with 12-ns pulse width and ~ 20 W peak power is focused to $\sim 50\,\mu$m on an ultrapure Si crystal ($N_A - N_D < 10^{12}$ cm^{-3}). Photoluminescence is integrated over the entire crystal volume, and single-photon counting with multichannel collection produces spectra as a function of time after the laser pulse.

Figure 1(b) shows the luminescence from the free excitons (FE) at a relatively long time after the laser pulse. The theoretical line shape (open circles) is simply

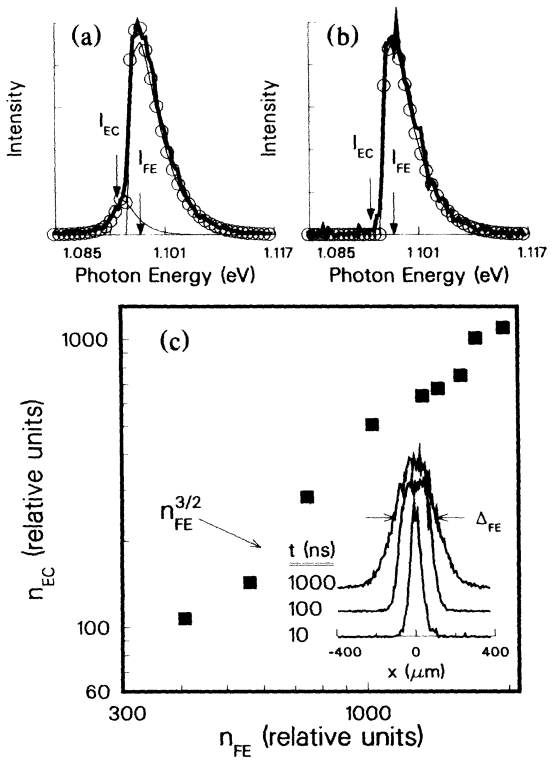

FIG. 1. Time-resolved luminescence spectra at $T=28$ K. Open circles are the sum of FE and EC components (fine lines). (a) 600 ns after laser pulse. (b) 2000 ns after laser pulse. (c) Relative densities of FE and EC as described in the text. Inset: Spatial profiles of FE luminescence.

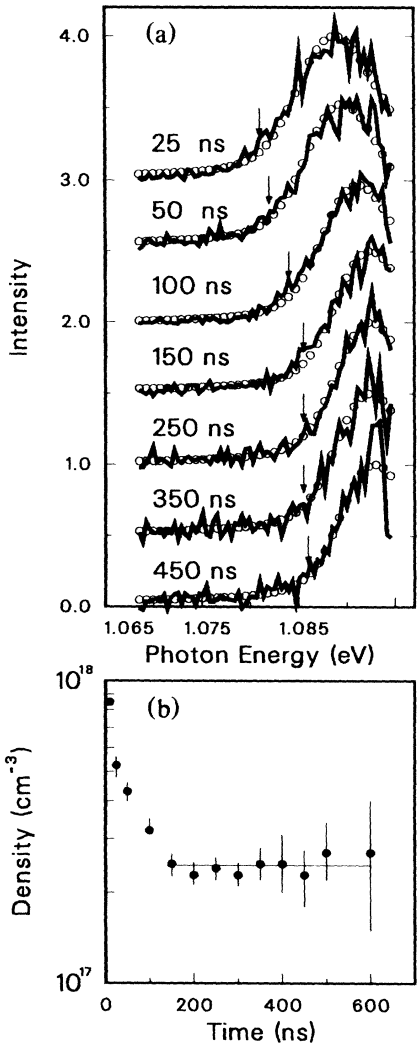

FIG. 2. (a) Time-resolved luminescence spectra at $T=28$ K with FE and EC components subtracted. Open circles are least-squares fit to data with arrows marking the "band bottom" energy of each spectrum. (b) Plasma density vs time obtained from (a). Error bars denote a 20% variation in the minimum χ^2 of the spectral fit.

$\sqrt{E}\exp(-E/kT)$, as expected for a Maxwell-Boltzmann distribution of particles. In this expression, E represents the kinetic energy and T is the temperature measured by a carbon resistor imbedded in the copper support for the crystal. In this case, the experimental temperature of 28 K is above $T_c(\mathrm{LG}) \approx 24$ K.

At somewhat earlier times, a low-energy tail appears on the exciton spectrum [Fig. 1(a)]. The intensity of this component increases with decreasing time (corresponding to increasing gas density), but the spectral shape remains unchanged for a wide range of delay times and can be accurately fitted by the known spectrum for excitonic molecules.[15,16] Using slit scans to determine the spatial full width at half maximum of the luminescence [e.g., Δ_{FE} in the inset of Fig. 1(c)], we determine the effective volumes $V_i \propto \Delta_{FE}^3$ associated with the EC (excitonic complex) and FE gases. In Fig. 1(c), we plot the relative densities $n_i \sim I_i/V_i$ for a range of delay times, where I_i are the intensities at the respective wavelengths indicated by the arrows in Fig. 2(a). The dotted line is $n_{EC} \propto n_{FE}^{3/2}$, suggesting that the excitonic complex is a three-particle trion.

For still earlier delay times (higher densities) a characteristic luminescence from electron-hole plasma is present at long wavelengths. This luminescence partially overlaps the EC and FE lines, and in Fig. 2(a) we have subtracted these two components from the total spectrum, using the intensity scaling determined above. At the earliest time (5 ns after the laser pulse) a broad luminescence line is observed, characteristic of plasma with $n \approx 8.5\times10^{17}$ cm^{-3}. With increasing time the plasma density decreases, as indicated by an increase in the "band bottom energy," E_{BB} [arrows in Fig. 2(a)], and a decrease in the width of the spectrum. For times ≥ 50 ns, the fits are well described by the lattice temperature. The circles are least-squares fits to the spectra with only one plasma density and intensity as adjustable parame-

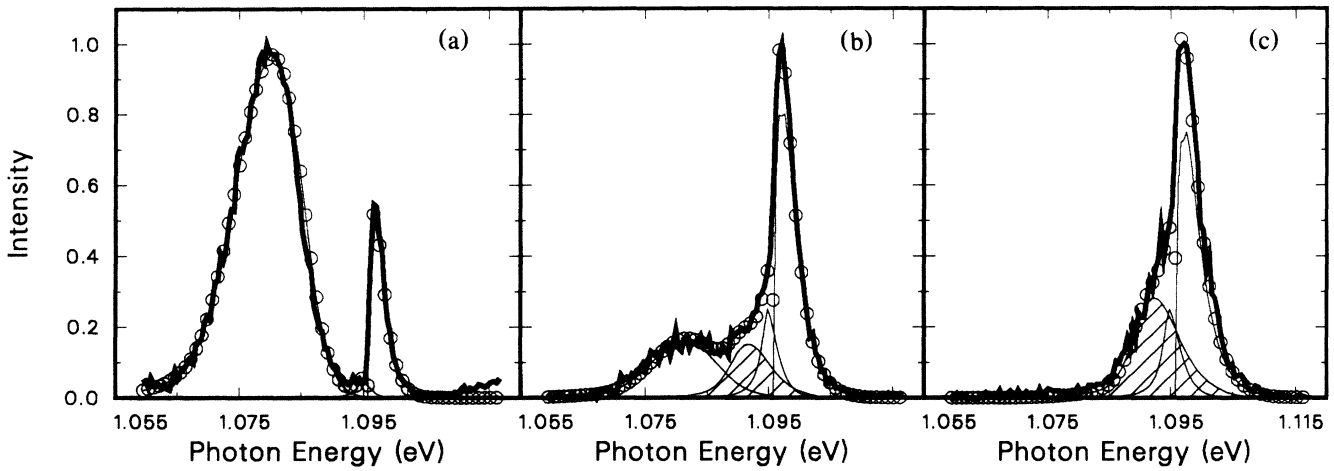

FIG. 3. Luminescence spectra 150 ns after the laser pulse. Open circles are composed of EHL, CP, EC, and FE components, shown in order of increasing energy position. Luminescence from the new condensed phase is shaded. (a) 14.5 K. (b) 21.7 K. (c) 25.2 K.

ters; the position and width of the spectra are related by the theory of Vashishta and Kalia.[14] The time dependence of the plasma density is plotted in Fig. 2(b).

The remarkable feature is that after 150 ns the plasma density remains constant with $n = 2.3 \times 10^{17}$ cm^{-3}. During the period of fixed density—from 150 ns to greater than 600 ns—the intensity of the plasma line decreases by about an order of magnitude.[17] To maintain a constant density with decreasing number of pairs, a spatial condensation must be occurring. Since the spatial profiles of the plasma luminescence are actually expanding during this period (as a result of phonon-wind forces[18]), we conclude that the volume condensation is in the form of plasma droplets.

Why have others missed this new excitonic state? The key seems to be the temporal resolution of our experiments. After the intense excitation pulse, a "settling time" of about 150 ns is required for the electron-hole plasma to reach an equilibrium state. Previous phase diagrams[10-12] were based on spectra sampled at earlier times, before the electron-hole plasma was sufficiently relaxed. Initially the plasma is formed as a continuous mass during the short excitation pulse, but it cannot expand instantly to an equilibrium density because of momentum damping forces, which are caused by electron-phonon scattering.[19]

The condensed plasma (CP) phase is observed even below the liquid-gas critical temperature (≈ 24 K). A temperature dependence of the entire spectrum is plotted in Fig. 3. At 14.5 K only EHL, EC, and FE components are required to explain the luminescence spectrum. At 21.7 K, well below T_c(LG), extra luminescence is present between EHL and FE. The previously determined CP line (shaded curves) can explain this discrepancy as shown. At 25.2 K, no liquid is observed, but the same three CP, EC, and FE components are adequate to describe the data.

What then is the critical point for the condensed plasma? At temperatures above 35 K the kT broadening of the spectra increases the uncertainty in the determination of the CP density. At present our best estimate for the disappearance of the constant-density plasma is 45 ± 5 K.

With this information we have attempted to construct a new excitonic phase diagram for Si. The EHL and CP boundaries are fixed by the measured plasma densities at $t \geq 150$ ns as a function of temperature, as are shown with the solid dots in Fig. 4. The dashed curve shows the

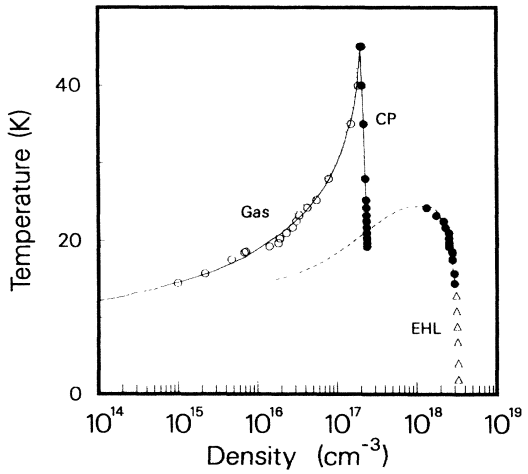

FIG. 4. Proposed phase diagram of excitonic matter in Si. Solid circles are densities of EHL and CP determined from the data. The dashed line is a Guggenheim fit to the EHL densities. Open circles and shaded region are calculated total gas pair densities, as described in the text. Triangles are low-temperature EHL data from Ref. 20.

standard Guggenheim curve. We estimate a triple point $T_3 = 18.5 \pm 1$ K which defines the only point on the phase diagram where gas, liquid, and CP can coexist. [The three phases are simultaneously observed in the spectrum of Fig. 3(b) because we are spatially integrating over a range of pair densities.]

The total gas density n_g is the sum of the partial pair densities of FE, EC, and the free carriers, which can be calculated from thermodynamic expressions,[9] given the chemical potentials of the condensed phases. The relative densities of the various species depend on the form of the carrier screening, which determines the excitonic binding energy and thus the amount of ionization. The open circles of Fig. 4 are obtained by use of the screening approximation of Ebeling and co-workers[6] with $c = 0.2$, which is chosen to equalize the gas and CP densities at 45 K. The shaded region to the left of these points indicates the variation in predicted n_g as C is increased to 0.6. Of course, the true shape of the phase diagram above T_c(LG) depends on the precise form of the screening.

The thesis of this paper rests upon the interpretation that the spectra after 150 ns in Fig. 2(a) are due to electron-hole plasma—not an excitonic complex. Previous experimental studies have wrestled with the difficulties in distinguishing these two phases. The time-resolved spectra presented here, together with the positive determination of the excitonic-molecule spectra in Si, seem to separate the two phases neatly. This analysis has indicated a radical departure from the previously determined excitonic phase diagram in Si. The microscopic structure of the new condensed phase and its relation to the metal-insulator transition remain as important problems.

We thank W. Keller of Siemens AG for the Si crystal. This work was supported in part by National Science Foundation Grant No. NSF-DMR-80-24000, with facility support by Materials Research Laboratory Program Grant No. NSF-DMR-85-16981. One of us (L.M.S.) acknowledges the support of a National Science Foundation Graduate Fellowship.

[1]L. V. Keldysh, in *Proceedings of the Ninth International Conference on the Physics of Semiconductors, Moscow, 1968,* edited by S. M. Ryvkin (Nauka, Leningrad, 1968), p. 1303.

[2]N. F. Mott, *Metal-Insulator Transitions* (Taylor and Francis, London, 1974).

[3]E. A. Guggenheim, J. Phys. Chem. **13**, 253 (1945).

[4]L. D. Landau and G. Zeldovich, Acta Physicochim. URSS **18**, 194 (1943).

[5]T. M. Rice, in *Proceedings of the Twelfth International Conference on the Physics of Semiconductors, Stuttgart, 1974,* edited by M. H. Pilkuhn (Teubner, Stuttgart, 1974), p. 23.

[6]W. D. Kraeft, K. Kilimann, and D. Kremp, Phys. Status Solidi (b) **72**, 461 (1975); W. Ebeling, W. Kraeft, and D. Kremp, in *Ergebnisse der Plasmaphysik und der Gaselektronik Vol. 5,* edited by R. Kompe and M. Steenback (Akademie-Verlag, Berlin, 1976); W. Ebeling, W. D. Kraeft, D. Kremp, and K. Kilimann, Phys. Status Solidi (b) **78**, 241 (1976); R. Zimmerman, K. Kilimann, W. D. Kraeft, D. Kremp, and G. Ropke, Phys. Status Solidi (b) **90**, 175 (1978).

[7]I. Balslev, Phys. Status Solidi (b) **101**, 749 (1980).

[8]L. J. Schowalter, F. M. Steranka, M. B. Salamon, and J. P. Wolfe, Phys. Rev. B **29**, 2970 (1984).

[9]G. A. Thomas, J. B. Mock, and M. Capizzi, Phys. Rev. B **18**, 4250 (1978).

[10]A. F. Dite, V. D. Kulakovsky, and V. B. Timofeev, Zh. Eksp. Teor. Fiz. **72**, 1156 (1977) [Sov. Phys. JETP **45**, 604 (1977)].

[11]J. Shah, M. Combescot, and A. H. Dayem, Phys. Rev. Lett. **38**, 1497 (1977).

[12]A. Forchel, B. Lourich, J. Wagner, W. Schmid, and T. L. Reinecke, Phys. Rev. B **25**, 2730 (1982).

[13]G. A. Thomas and T. M. Rice, Solid State Commun. **23**, 359 (1977).

[14]P. Vashishta and R. K. Kalia, Phys. Rev. B **25**, 6492 (1982).

[15]K. Cho, Opt. Commun. **8**, 412 (1973).

[16]M. L. W. Thewalt and J. A. Rostworowski, Solid State Commun. **25**, 991 (1978).

[17]This is not apparent from Fig. 2(a) because we have increased the sampling interval at later times.

[18]F. M. Steranka and J. P. Wolfe, Phys. Rev. Lett. **53**, 2181 (1984); J. P. Wolfe, J. Lumin. **30**, 82 (1985).

[19]M. A. Tamor and J. P. Wolfe, Phys. Rev. B **26**, 5743 (1982).

[20]R. B. Hammond, T. C. McGill, and J. W. Mayer, Phys. Rev. B **13**, 3566 (1976).