SOME LUMINESCENCE PROPERTIES OF EXCITED SILICON AT LOW TEMPERATURES

Thesis by

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ABSTRACT

Detailed studies of the luminescence due to the recombination of nonequilibrium electrons and holes in Si are reported for the temperature range 2-16°K. The properties of the exciton and electron-hole condensate luminescence are investigated in the spectral range from 1.11μ to 1.17μ. The Si was excited by laser pumping and by electrical injection.

The temperature dependence of the intensity ratio of the LO-to TO-phonon assisted exciton recombination luminescence in laser excited, high purity Si is reported. The ratio is found to differ from that observed in absorption and to vary from 0.3 at 2°K to 0.1 at 13°K. The variation of the ratio with temperature is shown to be due to the splitting of the ground state of the exciton by several tenths of a meV. The relevance of these results to the recombination from the electron-hole condensate in Si is discussed.

Detailed measurements and lineshape fits of the combined LO-to TO-phonon assisted electron-hole liquid luminescence lines from laser excited, high purity Si are reported. These data permit a determination of the liquid density, chemical potential, Fermi energy, and work function as functions of temperature. Results give support to the metallic model of the electron hole liquid in Si. The zero temperature condensate density is found to be $3.33 \pm .05 \times 10^{18}$ cm^{-3} and the zero temperature work function is measured as $8.2 \pm .1$ meV.

An investigation of luminescence from Si double injection diodes in the temperature range 5-16°K is also reported. Properties of the luminescence are compared with luminescence from laser excited, high purity Si and laser excited, Li doped Si. The peak position of the combined LO- and TO-phonon assisted electron-hole condensate lumin-

escence is observed at 1.082 eV in each of these cases. The density of the condensate, obtained by fitting the lineshape of this luminescence, was found to be 2×10^{18} cm^{-3} for both double injection and laser excitation of Li doped Si. This value is significantly smaller than the density found for the condensate in laser excited, high purity Si, 3×10^{18} cm^{-3}. Several features of the double injection luminescence suggest the influence of Li doping in the double injection diodes.

Finally, the effects of heating in the luminescence from Si double injection devices is discussed in an appendix.

Parts of this thesis either have been or will be published under the following titles:

Chapter 2: Observation of Splitting of the Indirect Exciton Ground State in Silicon, R. B. Hammond, D. L. Smith, and T. C. McGill, submitted to Physical Review Letters.

Chapter 3: Temperature Dependence of the Electron-Hole Liquid Luminescence in Silicon, R. B. Hammond, T. C. McGill, and J. W. Mayer, Physical Review. B, April 15, 1976.

Chapter 4: Properties of the Electron-Hole Liquid Luminescence in Silicon Double Injection Diodes, R. B. Hammond, T. C. McGill, and J. W. Mayer, submitted to Physica Status Solidi (b).

Appendix: Condensation of Injected Electrons and Holes in Silicon, R. B. Hammond, V. Marrello, R. N. Silver, T. C. McGill, and J. W. Mayer, Solid State Communications 15, 251 (1974).

Publications during the course of this work and not included in the thesis are:

Electron-Hole Condensate Radiation from Ge Double Injection Devices Between 1.5 and 4.2°K, V. Marrello, R. B. Hammond, R. N. Silver, T. C. McGill, and J. W. Mayer, Physics Letters 47A, 237 (1974).

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CHAPTER 1

INTRODUCTION

In this thesis we are concerned with the properties of nonequilibrium electrons and holes in Si. These excitations can exist in several states. Free electrons and holes are the states described in the one electron band theory of solids. Electrons and holes can also interact and form bound states. One electron and one hole can bind through their Coulomb attraction, $-e^2/\epsilon r$, to form a bound state called an exciton. It was conjectured by L. V. Keldysh(1), that a more tightly bound state than the exciton might exist in some semiconductors. This state would be a high density, metallic (Fermi degenerate) plasma of electrons and holes (electron-hole liquid) in which the positions of the electrons and holes are correlated. A large number of nonequilibrium electrons and holes would be necessary to produce such a state. Keldysh predicted that this plasma would condense from an "excitonic gas" and form in "electron-hole droplets". Keldysh's predictions have since been substantiated by the discovery of electron-hole droplets in both Ge and Si(2).

The states of nonequilibrium electrons and holes in semiconductors can be studied by observing the radiation emitted when they recombine. Nonequilibrium electrons and holes in indirect band gap semiconductors can recombine emitting a photon and a phonon which allow both energy and crystal momentum to be conserved, as shown in Fig. 1. The phonon can have one of four possible energies because there are four phonons; longitudinal acoustic (LA), longitudinal optical (LO), transverse acoustic (TA), and transverse optical (TO); which have the appropriate crystal

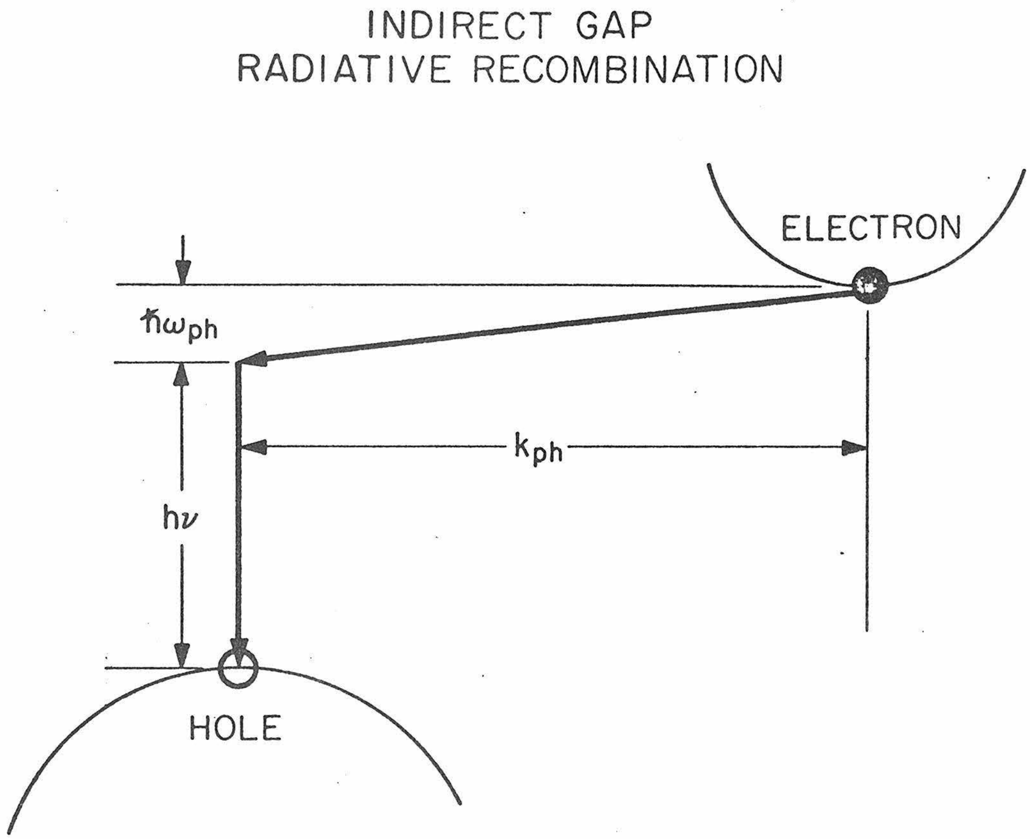

Figure 1. Schematic of radiative recombination of nonequilibrium electron and hole in an indirect band gap semiconductor.

momentum for the process. The energy of the emitted photon is just the energy of the electron and hole less the energy of the emitted phonon. In luminescence the exciton and electron-hole droplet state can be modeled just as free electrons and holes in the band model except that the effective band gap is decreased for these states. At low densities (the usual case) electrons and holes bound as excitons are spread in a Boltzmann distribution among the energy states near the band extrema. (At high densities, excitons lose their individual character and an electron-hole plasma forms which is described by Fermi-Dirac statistics.) The Boltzmann distribution among the low lying states (described in a spherical band approximation) leads to a luminescence lineshape of the form

$$I(h\nu) = (h\nu + \hbar\omega_{ph} - E_X)^{1/2}\exp((h\nu + \hbar\omega_{ph} - E_X)/kT) \qquad (3)$$

where E_X is the effective band gap for electrons and holes bound into excitons, $h\nu$ is the energy of the emitted photon, and $\hbar\omega_{ph}$ is the energy of the emitted phonon. Fits of the experimental exciton luminescence lineshape in Si with this function have verified this model(4) and also have permitted a determination of $(E_X - \hbar\omega_{ph})$. In the electron-hole droplet state, because the density of the electrons and holes is high and because these quasi-particles are fermions, electrons and holes are spread in a Fermi-Dirac distribution among the energy states near the band extrema. This Fermi-Dirac distribution among the low lying states (again described in a spherical band approximation) leads to a luminescence lineshape of the form (2)

$$I(h\nu) = \int d\varepsilon_e \varepsilon_h \rho_e(\varepsilon_e)\rho_h(\varepsilon_h) \{\exp((\varepsilon_e - \varepsilon_f^e)/kT) + 1\}^{-1}$$

$$\{\exp((\varepsilon_h - \varepsilon_F^h)/kT^{-1} \delta\{ E_g{}' + \varepsilon_e + \varepsilon_h - h\nu - \hbar\omega_{ph}\}$$

where ρ_e and ρ_h are the electron and hole density of states functions, ε_e and ε_h are the electron and hole energies relative to their respective band extrema, ε_F^e and ε_F^h are the electron and hole Fermi energies, and $E_g{}'$ is the modified band gap for the electron-hole condensate. A fit to the observed electron-hole droplet lineshape with this function permits a determination of $(E_g{}' - \hbar\omega_{ph})$, and the condensate density. Also, fitting both the condensate and exciton lineshapes allows one to measure the condensate-exciton gas work function:

$$\phi = \{ E_X - \hbar\omega_{ph}\} - \{\varepsilon_F^e + \varepsilon_F^h + (E_g{}' - \hbar\omega_{ph})\}$$

G. A. Thomas et al.[5] have made detailed line fits of the LA-phonon assisted electron-hole condensate luminescence lineshape in Ge. From these fits they have determined the temperature dependence of the chemical potential (the high energy edge of the luminescence line), Fermi energy (width of the line), and density of the electron-hole condensate in Ge. They found that the luminescence model gave an excellent qualitative fit to the condensate lineshape and that each of the parameters extracted from the line fits showed a temperature dependence consistent with Fermi liquid theory. These results give strong support to the electron-hole plasma model for the condensate in Ge.

Other properties of the electron-hole condensate in Ge have been measured by a wide variety of experiments. The decay of electron-hole drops by recombination and evaporation into excitons was measured as a function of temperature by monitoring cyclotron resonance of electrons and holes in the condensed state.[6] The work function was also measured in this experiment by measuring the laser pumping threshold for droplet formation as a function of temperature. Two investigators have observed large increases in the photoconductivity of Ge when the condensate is present.[7,8] Drop sizes for the condensate in Ge have been measured by Rayleigh scattering of light.[9,11] Depending on temperature, drop diameter measurements vary between 3μ and 10μ. The number of charges in an electron-hole drop in Ge has been measured by breaking them up in the field of a p-n junction and measuring the resulting current spike.[12] Far infrared absorption due to plasma excitations in the condensate has been observed.[13] Finally, the effects of strain[14], doping[15], magnetic field[16], and electric field[17] on the electron-hole condensate luminescence in Ge have been observed.

Properties of the electron-hole condensate in Si have not been studied as extensively as in Ge. Of the experiments described above for Ge, few have been performed in Si. The number of charges in an electron-hole drop in Si has been measured by current spikes in a p-n junction[18]; and the effects of doping on the condensate luminescence have been observed[15]. The work function has been measured by Pokrovsky[2] by measuring the relative exciton-condensate luminescence intensities for different excitation levels at 4.2°K. Also a single line fit to the Si condensate luminescence by Pokrovsky et al.[19] yielded a density of 3.7 x 10^{18} cm^{-3} for the condensate at 4.2°K. This strong condensate luminescence in Si is a superposition of replicas due to TO- and LO-phonon assisted re combination respectively. This fact was not included in the lineshape calculation by Pokrovsky et al; and thus, theirs is an overestimate of the condensate density. Also, the only spectroscopic determination of the work function was from this same data and again did not include the effects of the two phonon replicas in the luminescence.[20] To analyze the strong condensate luminescence in Si, it is necessary to know the relative contributions of the LO-and TO-phonon replicas. No estimate of this has appeared in the literature.

In Chapter 2 is described a systematic line fitting investigation of the LO-TO phonon assisted exciton luminescence in Si. This investigation yielded the first detailed measurement of the temperature dependence of the intensity ratio of the LO- and TO-phonon replicas in the exciton luminescence in Si. This data led to a theoretical model which implied that the temperature dependence of the LO:TO ratio was indirect evidence of the ground state splitting of the exciton in Si. The model also permitted an estimate of the ratio of the relative intensities of the LO- and TO-phonon replicas in the electron-hole condensate luminescence. This ratio is essential to the lineshape fitting of the electron-hole con densate luminescence discussed in Chapter 3. The theoretical model which has allowed a prediction of the LO:TO ratio in Si has since been substantiated in Ge for LA- and TO-phonon assisted luminescence of the electron-hole condensate and exciton.[21] In Ge the phonon replicas are well separated and the exciton ground state splitting has been measured directly. The intensity ratios predicted in the model agree with the observed values.

Chapter 3 describes a systematic line fitting investigation of the LO-TO phonon assisted electron-hole condensate luminescence in laser excited, high purity Si. This investigation comprises the first systematic measurement and analysis of this luminescence. The study yields the first detailed measurements of the condensate density, chemical potential, work function, and Fermi energy; and the first measurements of any kind of the temperature dependence of these parameters. The results give strong support to the metallic plasma model for the electron-hole condensate in Si.

Besides optical excitation, nonequilibrium electrons and holes may also be produced in a semiconductor by electrical injection. Chapter 4 describes a luminescence study of Si excited by current injection from p+ and n+ doped contacts. It is verified that the electron-hole condensate can be produced in Si by this method of excitation. Also the effects of dopant impurities introduced into the Si during the formation of the contacts is investigated.

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CHAPTER 2

LO- AND TO-PHONON ASSISTED FREE EXCITON RECOMBINATION RADIATION FROM LASER EXCITED SILICON

The emission and absorption of radiation due to indirect excitons in silicon at low temperatures has been the subject of a number of investigations[1-5]. Features identified with TA, LO-and TO-phonon assisted transitions have been identified. Dean *et al.*[3], and Shaklee and Nahory[4] and Nishino *et al.*[5], have studied the absorption at temperatures less than 10°K. Shaklee and Nahory[4] have correctly interpreted the two features at approximately 1.22 eV to be due to absorption with the emission of a LO or TO phonon. These two lines are split by approximately 2 meV. Dean *et al*[3] have studied the emission via LO- an TO-phonon processes at 2.5°K and 5.5°K. They observed that the ratio of rate for LO-and TO-phonon emission processes, γ_E, showed a distinct temperature dependence. However, their interpretation of these emission lines was based on a physically incorrect model[4].

In this letter, we report on a systematic investigation of the temperature dependence of the recombination processes via LO- and TO-phonon emission. We find that the ratio γ_E varies with temperature in agreement with the two experimental points given by Dean *et al*[3]. This variation of γ is shown to result naturally from the ground state splitting of the exciton into two 2-fold degenerate states Δ_6 and Δ_7 combined with the differences in selection rules for LO- and TO-phonon emission for the two exciton states. The splitting of the ground state of the exciton is due to the interaction of the hole at $\vec{K} = 0$ with the anisotropic charge density of the electron in the conduction band[6,7].

Analysis of the experimental data gives an energy splitting between the Δ_6 and Δ_7 states in qualitative agreement with the theoretical values given by McLean and Loudon[6], and Lipari and Baldereschi[7]. Although this splitting has been explored in detail theoretically, we believe this is the first experimental observation of the consequences of this splitting in silicon.

The emission spectrum from a sample of laser excited silicon is shown in Fig. 2. The silicon crystal was high purity p-type with a net impurity concentration $N_A - N_D \sim 2 \times 10^{11}\ cm^{-3}$. The spectrum was obtained by illuminating the sample with a GaAs laser which produced pulses of 2 μs duration with a repetition rate of 20 KHz. The optical power was approximately 3 watts. The luminescence was analyzed with a Spex 1400-II spectrometer, detected with an RCA 7102 S-1 photomultiplier tube operated at 195°K, and processed with a lock-in amplifier. The spectrum was independent of laser power and hence, showed no evidence of heating.

The luminescence lineshape was fit with the expression proposed by Elliott[(8)]. The intensity was assumed to vary as

$$I(E) \sim (E-E_x)^{1/2} \exp[-(E-E_x)/k_B T] \qquad (1)$$

where E_x is the threshold energy. This theoretical expression for the intensity was modified to include the effects of detector sensitivity, spectrometer transmission and broadening, and a Gaussian broadening due to phonon lifetime.

The theoretical curve in Fig. 2 was obtained using this procedure with energy broadening due to phonon lifetime characterized by a standard deviation of 0.34 meV; an energy separation between the TO and LO lines of 1.8 meV; a temperature of 2.1°K, the bath temperature; and γ_E of 0.33. The value of the broadening used here is in agreement with the value deduced from derivative absorption spectroscopy[5].

Spectra at other temperatures exhibit similar features except that

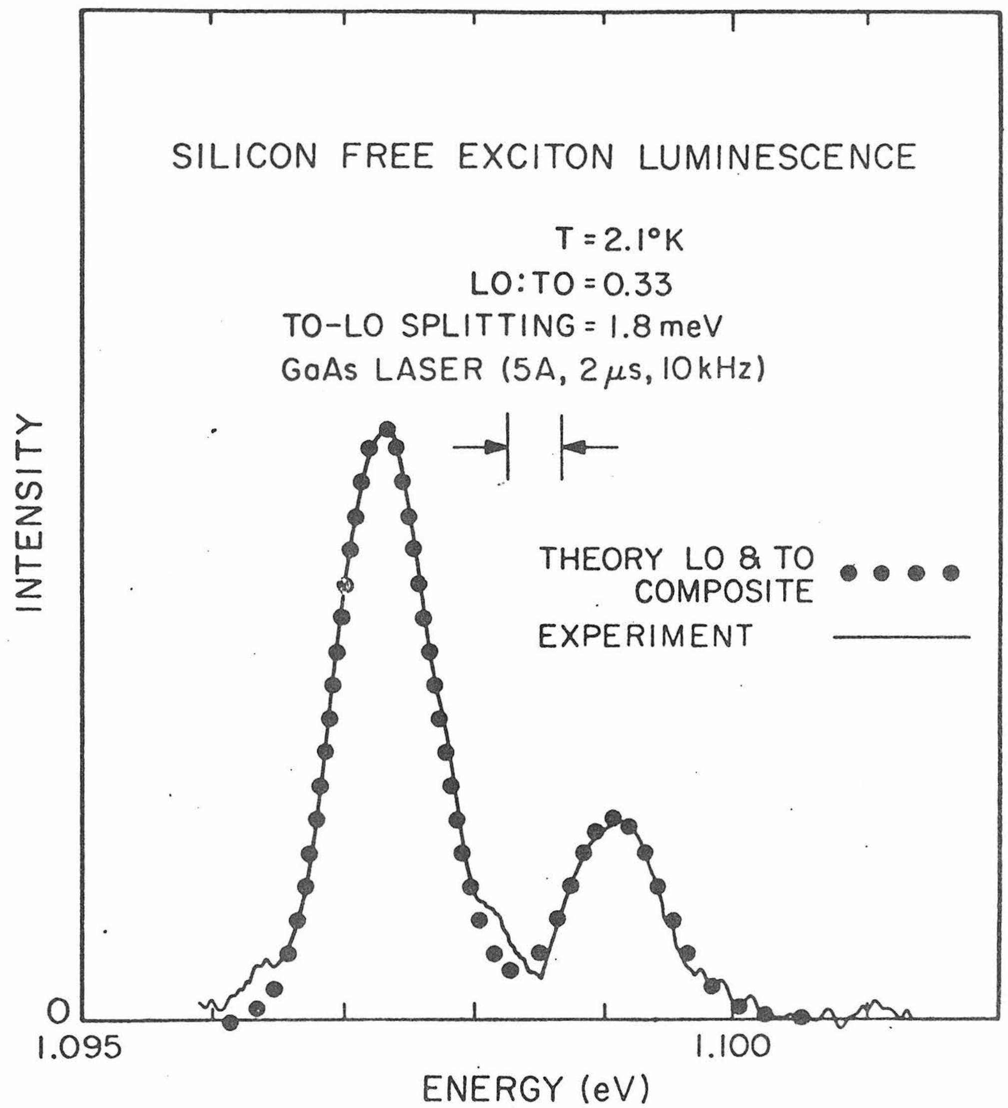

Figure 2 Luminescence spectrum of silicon at 2.1°K. The silicon was excited using a GaAs laser. The solid line is the experimental results. The TO-assisted recombination produces the line centered at ∿ 1.097 eV. The LO-assisted recombination produce the line centered at ∿ 1.099 eV. The dots are the theory produced by the procedure described in the text.

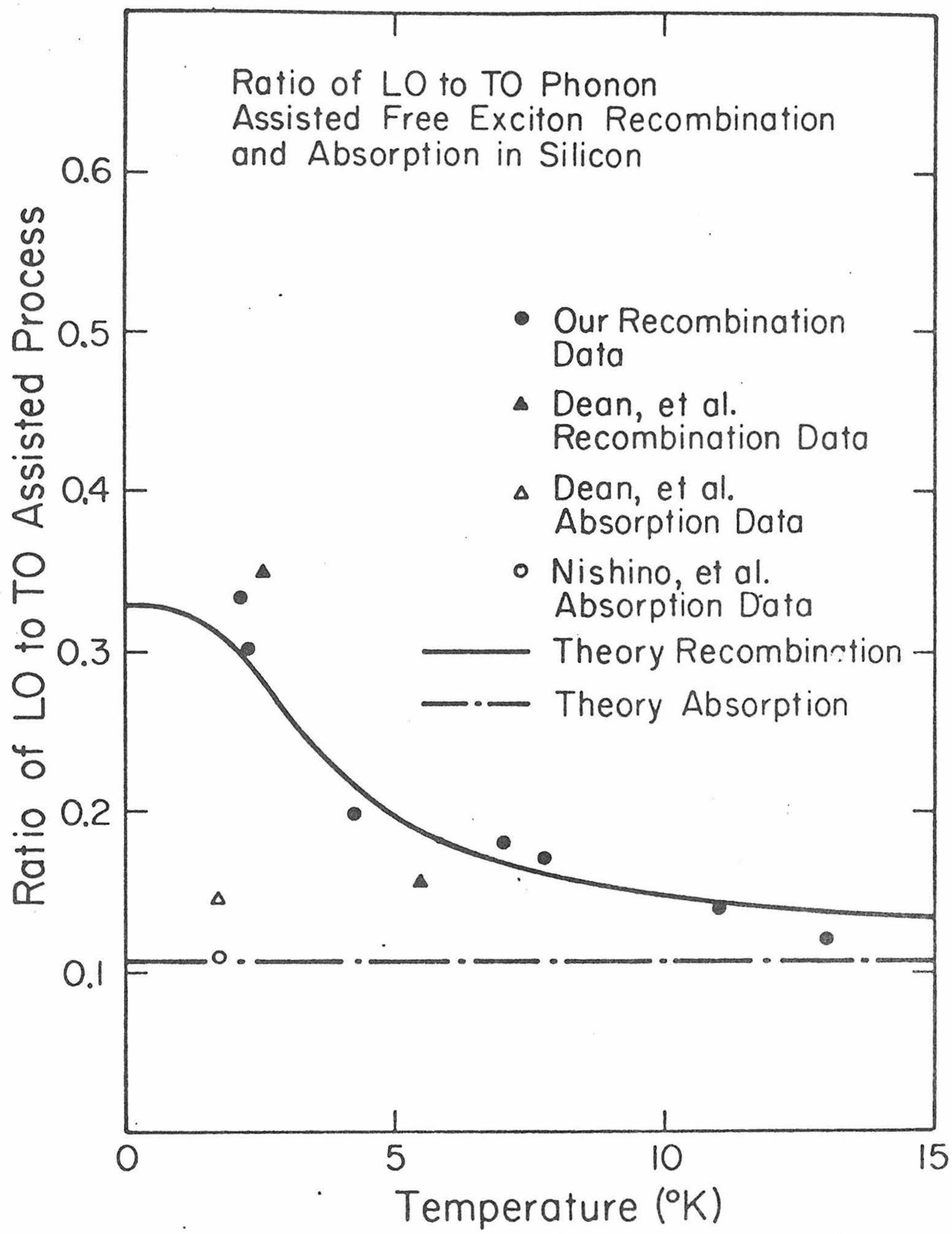

Figure 3 The ratio of LO-to TO-phonon assisted emission and absorption as a function of temperature. The experimental data labeled by (▲) and (△) is taken from Ref. 3. The data labeled by (o) is taken from Ref. 5. The theoretical curves are obtained by taking ΔE = 0.6 meV; and with A positive A = 2.2 and B = 1.3 or with A negative A = -0.4 and B = 0.2. Both of these sets of values produce identical curves.

as temperature is increased the separated lines tend to merge. The values of γ_E at other temperatures were obtained by the same line fitting procedure. The results of these experiments along with the results reported by other authors for emission and absorption[3,5] are given in Fig. 3. These results show that γ_E varies from ~ 0.3 at 2.1°K to ~ 0.1 at 13°K. The data also show that γ_E approaches the ratio for absorption γ_A at higher temperatures.

The variation of γ_E with temperature may be understood in terms of the splitting of the ground state exciton level into two levels separated by an energy ΔE. The ratio $\gamma_E(T)$ is given by

$$\gamma_E(T) = \frac{R_{LO}^{\Delta_6} + R_{LO}^{\Delta_7} e^{-\Delta E/k_B T}}{R_{TO}^{\Delta_6} + R_{TO}^{\Delta_7} e^{-\Delta E/k_B T}} \qquad (2)$$

where $R_{LO}^{\Delta_6}$ and $R_{LO}^{\Delta_7}$ are the rates for photon emission via LO-phonon emission for the mostly tightly bound state Δ_6 and the split off excited state derived from the ground state Δ_7, respectively. $R_{LO}^{\Delta_6}$ and $R_{TO}^{\Delta_7}$ are defined in an analogous way for the TO-phonon assisted process. In absorption the ratio γ_A is given by the ratio of the sum of the rates. For high temperatures such that $k_B T >> \Delta E$, we have that $\gamma_E(T)$ approaches γ_A in agreement with experiment.

From Eq. (2) it is clear that to predict $\gamma_E(T)$, we must know the ratios of the various rates. As illustrated in Fig. 3 the two most likely recombination paths are: (1) the electron emits a phonon and makes a transition from the Δ_1 state in the conduction band to the Γ_{15}^- state in the conduction band and then recombines with a hole in either the Δ_6 state in the case of the more tightly bound exciton or the

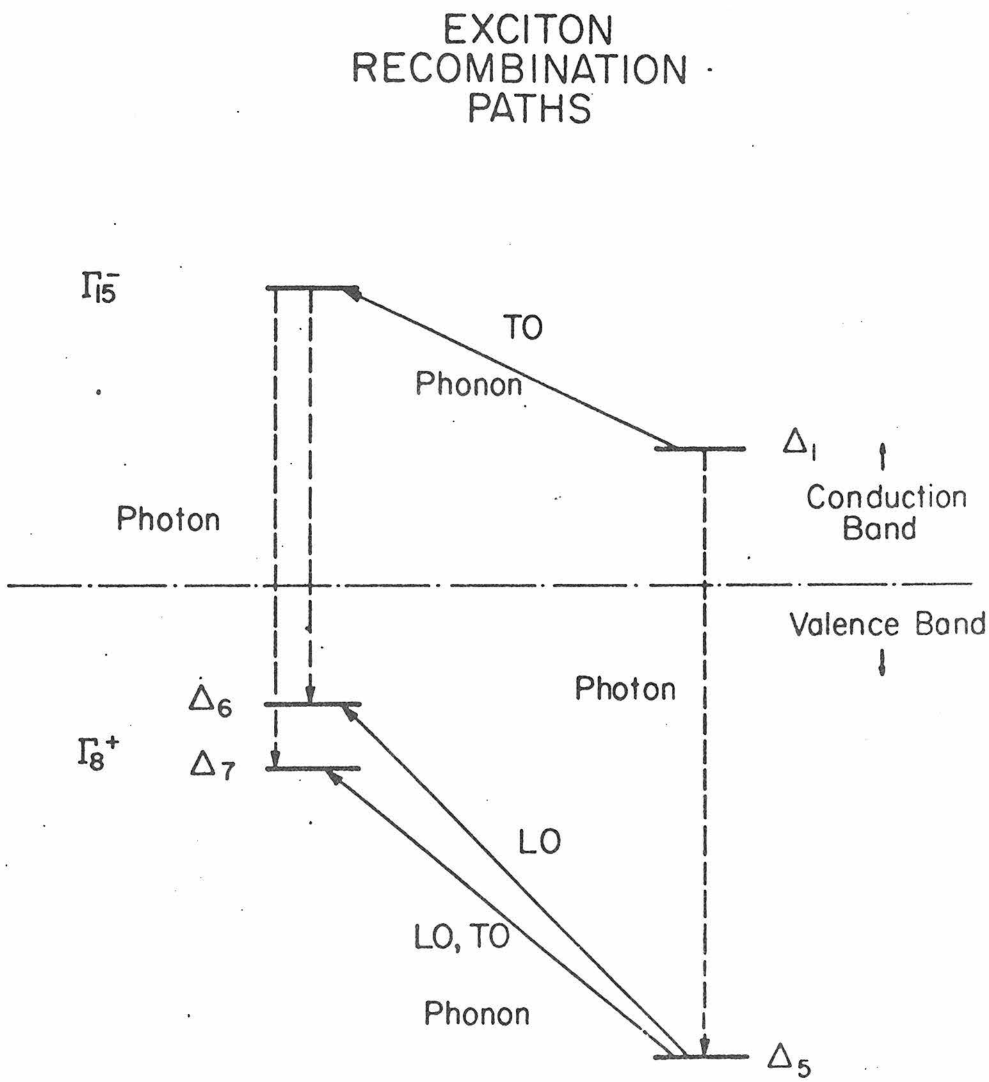

Figure 4. Schematic diagram of the two recombination processes in silicon. The splitting of the ground state of the exciton is shown in the hole band where the 4-fold degeneracy of the Γ_8^+ states is split into two 2-fold degenerate states Δ_6 and Δ_7 which are labeled according to the irreducible representations of the group of $\vec{K}$ for $\vec{K}$ along the Δ-direction.

Δ_7 state in the case of the less tightly bound exciton. The process is allowed for TO-phonon emission only[9]. (2) The electron in Δ_5 emits a phonon and recombines with a hole in the state Δ_6 or Δ_7, respectively. Then the electron in state Δ_1 in the conduction band recombines with the hole in Δ_5 emitting a photon. When the hole is in the Δ_6 state, this process is allowed for the LO phonon only, and is TO- and LO-phonon allowed when the hole is in the Δ_7 state. A group theoretical study of the relative rates[10] leads us to conclude that $\gamma_E(T)$ must be of the form

$$\gamma_E(T) = |B|^2 \frac{3+e^{-\Delta E/k_BT}}{3|A|^2 + [4|A+1|^2 + |A|^2]e^{-\Delta E/k_BT}} \tag{3}$$

where A and B involve ratios of energy denominators from the second order perturbation theory, the reduced matrix elements[11] of the momentum operator p, and the TO and LO part of the electron-phonon interaction Hamiltonian H_{ep}^{TO} and H_{ep}^{LO}, respectively.

$$A = \frac{\Delta E_V}{\Delta E_C} \frac{\Gamma_{25}^{+}||p||\Gamma_{15}^{-}}{\Delta_5||p||\Delta_1} \frac{\Gamma_{15}^{-}||H_{ep}^{TO}||\Delta_1}{\Gamma_{25}^{+}||H_{eo}^{TO}||\Delta_5} - 1 \tag{4}$$

where Δe_V and ΔE_C are the energy denominators for transitions through the Δ_5 and Γ_{15}^{-} states, respectively.

$$B = \frac{\Gamma_{25}^{+}||H_{ep}^{LO}||\Delta_5}{\Gamma_{25}^{+}||H_{ep}^{TO}||\Delta_5} \tag{5}$$

Since the space group for the diamond lattice contains the inversion symmetry and the states must be invariant under time reversal, then A and B may be taken to be real[12]. The sign of B is irrelevant in Eq. (3) but the sign of A is important. The exact values of A and B cannot be computed at the present time, but we expect A and B to be of order unity.

The comparison between the experimental results and theoretical results for both emission and absorption is contained in Fig. 2. The values of ΔE, A, and B were determined by a least-squares fit to the experimental data, excluding that obtained from Dean _et al._[3]. The value of ΔE which produced the best fit is 0.6 meV. If A is taken to be positive, then the best fit is obtained for A = 2.2 and B = 1.3. Identical curves are obtained by taking A negative with A = -0.4 and B = 0.2. The theoretical curves for γ_E and γ_A for these parameters are shown in the figure. The agreement between the experimental results and theoretical calculations is quite good. The value of ΔE taken here is in good agreement with the calculations of McLean and Loudon[6]. However, the agreement is not noticeably changed for a range of values of ΔE between 0.3 meV and 0.7 meV; A between 0.5 and 2.9, and B between 0.5 and 1.5. If we allow A to be negative, then A ranges between -0.2 and -0.4 and B ranges between 0.3 and 0.2. While there is a rather large range of parameters which provide a reasonable fit to the experimental data, the good agreement between theory and experiment provides the first experimental confirmation of the splitting of the ground state of the exciton in silicon.

The luminescence from the electron-hole condensate in silicon also possesses a strong line due to LO- and TO-phonon assisted recombination[13]. In this case, it is not possible to resolve the two lines since the intrinsic width of the condensate line, approximately 12 meV, is greater then the splitting between the TO- and LO-assisted lines. However, in fitting the condensate lineshape, it is essential to have a value for the ratio of these two processes. Since holes in the condensate should occupy the states Δ_6 and Δ_7 with equal probability the correct value of the ratio of LO to TO process is the value observed in exciton absorption, $\gamma = 0.11$.

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CHAPTER 3

TEMPERATURE DEPENDENT LUMINESCENCE FROM THE ELECTRON-HOLE LIQUID IN LASER EXCITED, HIGH PURITY SILICON

I. Introduction

The condensation of nonequilibrium electrons and holes into high density, metallic electron-hole droplets at temperatures $\lesssim 6°K$ in high purity Ge single crystals has been demonstrated by a wide variety of experiments.[1-7] The properties of this electron-hole plasma, first predicted by L. V. Keldysh[8], have been quite thoroughly studied. Using a simple but elegant model for the luminescence lineshape of electrons and holes recombining from this condensed phase [1], G. A. Thomas _et al._[2] have determined the density of the electron-hole liquid between 1.08°K and 4.25°K. Their results give condensate densities between 2.4 and 2.1×10^{17} cm^{-3} with a monotonically decreasing density for increasing temperature. The calculated lineshape agrees closely with the experimental lineshape over this range of temperatures. Besides the condensate density, this lineshape fitting procedure yields values for the chemical potential and Fermi level of condensate. Thomas _et al._ were able to show that within experimental error the chemical potential and the Fermi level for the electron-hole liquid in Ge have the T^2 dependences expected from Fermi liquid theory.

Although the condensation of nonequilibrium electrons and holes into metallic electron-hole droplets has been observed in Si, experimental investigations of this phenomenon have not been as extensive as in Ge. A single qualitative fit of the condensate luminescence lineshape in Si was reported by Kaminsky and Pokrovsky[9] and yielded a density of 3.7 $\times 10^{18}$ cm^{-3} for the electron-hole condensate at 4.2°K. Also, using this same luminescence lineshape from Kaminsky and Pokrovsky, other investigators,[10,16] have estimated the condensate-exciton gas work function to be ~7meV.

These estimates of the condensate density and work function assumed the presence of only one recombination process in the condensate luminescence. There are, however, two processes which contribute to this luminescence. These are due to TO and LO phonon assisted recombination, respectively. Because only the TO phonon assisted process was considered, Kaminsky and Pokrovsky's estimate of the condensate density is high and the estimate of the work function is low. Beyond these two results no attempt has appeared in the literature to apply the model employed by Thomas *et al*. in Ge to analyze Si luminescence spectra. The purpose of this work is to exploit this same model to obtain quantitative results for properties of the electron-hole liquid in Si. We have included the effects of both the TO and LO phonon replicas in our analysis of the condensate luminescence. We have analzyed Si photoluminescence spectra between 2.2°K and 13°K and determined the condensate density, chemical potential, Fermi level, and work function in this temperature range. We find that the variation with temperature of these parameters is consistent with the metallic plasma model for the condensate in Si.

II. Experimental

The photoluminescence experiment was performed on p-type, single crystal Si slices with net acceptor concentrations of: $N_A - N_D = 1.5$ and $7. \times 10^{11}\ cm^{-3}$. The higher purity crystal, on which all the line fitting data was taken, was 10mm x 20mm x 3mm thick and was laser excited in the middle of a 10mm x 20mm face which was mechanically polished and chemically etched. The sample temperature was controlled in a Janis variable temperature He Dewar and measured with a Ge resistance thermometer in contact with the Si sample. For laser excitation, a GaAs laser mounted inside the Dewar 4mm above the sample surface produced a circular excitation spot on the sample of ~0.5mm in diameter. To minimize heating in the Si, the laser was pulsed with 2μs pulses at a repetition rate of 20KHz. Instantaneous optical powers of 0.3 - 3.0 watts were used. The Si luminescence was analyzed with a Spex 1400-II double grating spectrometer, detected with a RCA 7102 S-1 photomultiplier tube operated at 195°K, and the electrical signal processed with a lock-in amplifier and recorded on a strip-chart recorder. The relative detector sensitivity-spectrometer transmission function and the total spectrometer-instrument broadening function were both measured over the wavelength range where line fitting was done. The effects of these functions were then included in the calculated lineshapes. The absolute energy position of the spectrometer was calibrated using a very sharp (< 1Å) luminescence line from a Hg lamp at 1.1287μ.

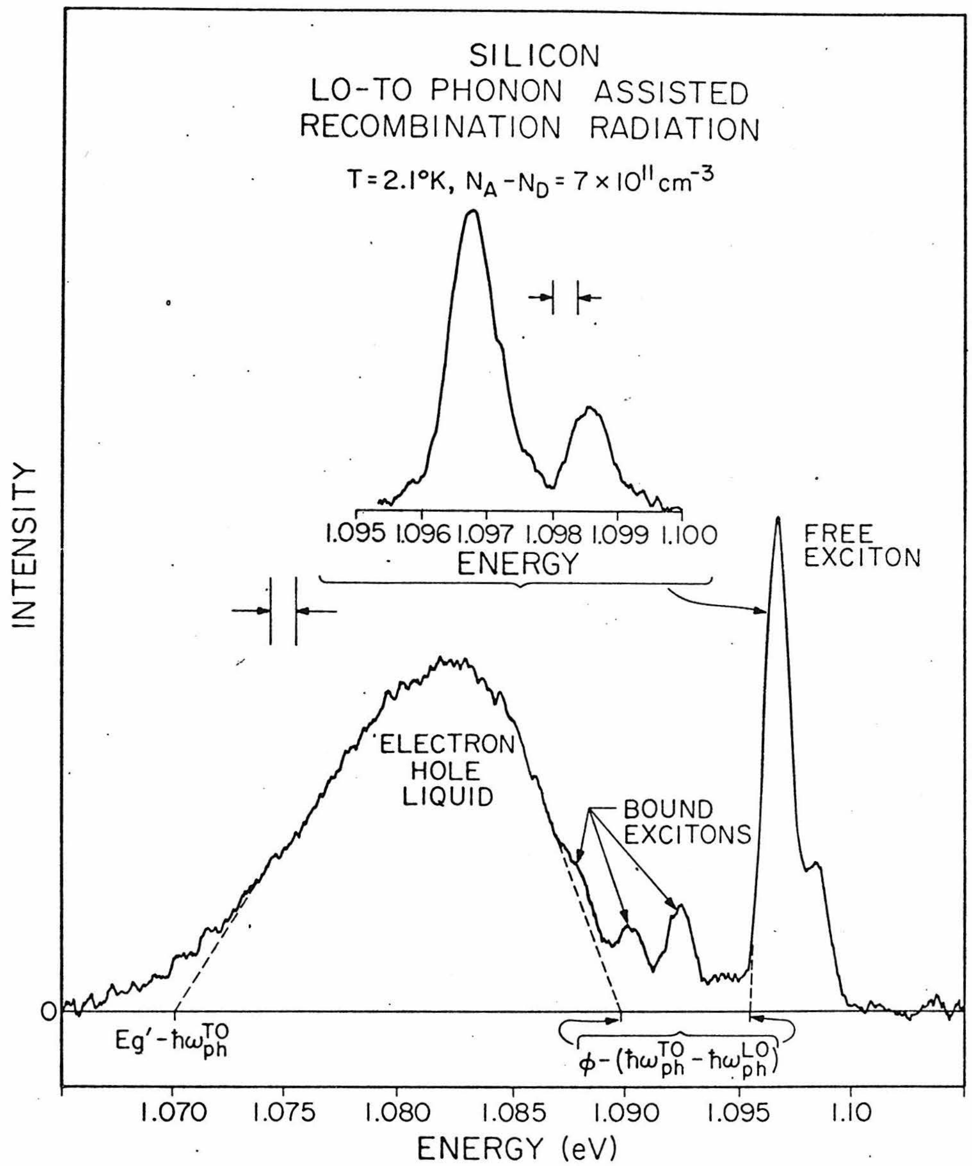
III. Silicon Luminescence Spectra

Si photoluminescence spectra at low temperatures consist of a number of different lines arising from electrons and holes recombining from states such as free excitons, excitons bound to impurities, and electron-hole condensate. Here we are primarily concerned with free exciton and condensate emission. Since Si is an indirect band gap semiconductor, radiative recombination is accompanied by phonon emission. There are two dominant phonon assisted recombination processes which emit longitudinal optical (LO) and transverse optical (TO) phonons, respectively. The recombination radiation spectrum is thus composed of two replicas separated by the TO-LO splitting of ~2meV.[(13)] To discuss the calculations, then, it is appropriate to present an experimental spectrum which illustrates the main features of this strong free exciton and condensate luminescence in Si. Such a spectrum is shown in Fig. 5 for laser excitation at 2.1°K. The free exciton recombination radiation line that occurs at 1.097 eV in Fig. 5 is composed of the two phonon replicas due to TO- and LO-phonon emission, respectively. The insert shown in the upper portion of the figure shows these replicas under high resolution. They are split by 1.8meV and their intensity ratio is LO:TO = .33. In exciton absorption measurements the observed ratio is LO:TO = .11.[(14)] The ratio in luminescence is temperature dependent and approaches the ratio from absorption at high temperatures.[(15)]

The LO- and TO-phonon replicas also occur in the emission from the electron-hole condensate centered at 1.082 eV. However, due to the intrinsic width of the condensate luminescence line (~12meV), it is not possible to resolve the two replicas. On the other hand since there are two superposed yet slightly split contributions to the condensate

Figure 5. LO- and TO-phonon assisted recombination radiation spectrum from laser excited, high purity Si at 2.1°K. The spectrum has strong free exciton luminescence which can be resolved into its LO- and TO-phonon components. The LO- and TO-phonon assisted condensate luminescence is a broad peak centered at 1.082 eV. The extrapolated low energy threshold of this luminescence yields the value of the modified band gap for the condensate less the energy of the TO-phonon. The magnitude of the separation of the extrapolated high energy edge of the condensate line and the low energy threshold of the free exciton line is shown. This value corrected for the difference in the LO- and TO-phonon energies is the condensate-exciton work function. The extrapolated low-energy threshold and high energy edge of these lines is determined by line fitting described in Section IV.

FIGURE 5



SILICON
LO-TO PHONON ASSISTED
RECOMBINATION RADIATION
T = 2.1°K, N_A - N_D = 7 × 10^11 cm^-3
1.095 1.096 1.097 1.098 1.099 1.100
ENERGY
FREE
EXCITON
ELECTRON
HOLE
LIQUID
BOUND
EXCITONS
INTENSITY
0
Eg' - ħω_ph^TO
φ - (ħω_ph^TO - ħω_ph^LO)
1.070 1.075 1.080 1.085 1.090 1.095 1.10
ENERGY (eV)

luminescence, the observed lineshape is modified and also shifted in line position depending on the relative intensities of the two phonon replicas in the condensate emission. As outlined in Sec. IV, these considerations are important in determining the electron-hole liquid density and the liquid-gas work function. For example, to determine the work function a 1.8meV correction must be added to the energy difference between the low energy edge of the TO free exciton line and the high energy edge of the LO condensate line. This is an appreciable (~20%) correction to the work function.

The effective energy gap for the condensate is determined by the extrapolated threshold of the low energy edge of the TO condensate line as shown in Fig. 5. This extrapolation is accomplished by a line fitting procedure discussed in the next section. Also in Fig. 5 three vertical arrows indicate the positions of bound exciton complex lines. These lines were observed and their origin was discussed by Sauer(11), and Kosai and Gershenzon(12) for p-type samples with higher doping levels ($>10^{13}cm^{-3}$). These doping levels were at least an order of magnitude higher than in the sample used to obtain the spectrum shown in Fig. 5. However, in the work reported below, it was necessary to use even higher purity material to eliminate the influence of these extraneous lines.

IV. Theoretical Lineshape

The basic concepts for the electron-hole liquid lineshape calculation are shown schematically in Fig. 2. In this diagram we have the conduction and valence bands which are displaced in k-space. The effective band gap, E_g', for the condensate is smaller than the one-electron band gap, E_g, due to the strong interactions between electrons and holes in this high density state. The bands are filled up to their respective quasi-Fermi levels ($\varepsilon_F^e, \varepsilon_F^h$) which are determined primarily by the condensate density but are also a weak function of the temperature. As shown in the diagram, an electron with energy ε_e may recombine with a hole of energy ε_h by emitting a phonon with energy $\hbar\omega_{ph}$ and a photon with energy $h\nu$. The lowest energy photon which can be emitted in such a recombination event is just $h\nu = E_g' - \hbar\omega_{ph}$ and occurs when an electron and a hole each at its band extremum recombine. On the other hand, the highest energy photon which can be emitted is $h\nu = E_g \; \hbar\omega_{ph} + \varepsilon_F^e + \varepsilon_F^h$ which occurs when an electron and a hole each at its respective quasi-Fermi level recombine. Thus, the total width of the condensate luminescence line is approximately determined by the sum of the two quasi-Fermi levels: $\Delta h\nu = \varepsilon_F^e + \varepsilon_F^h$.

The lineshape of luminescence due to recombination of electrons and holes in the electron-hole liquid in Si may be calculated for each phonon replica from

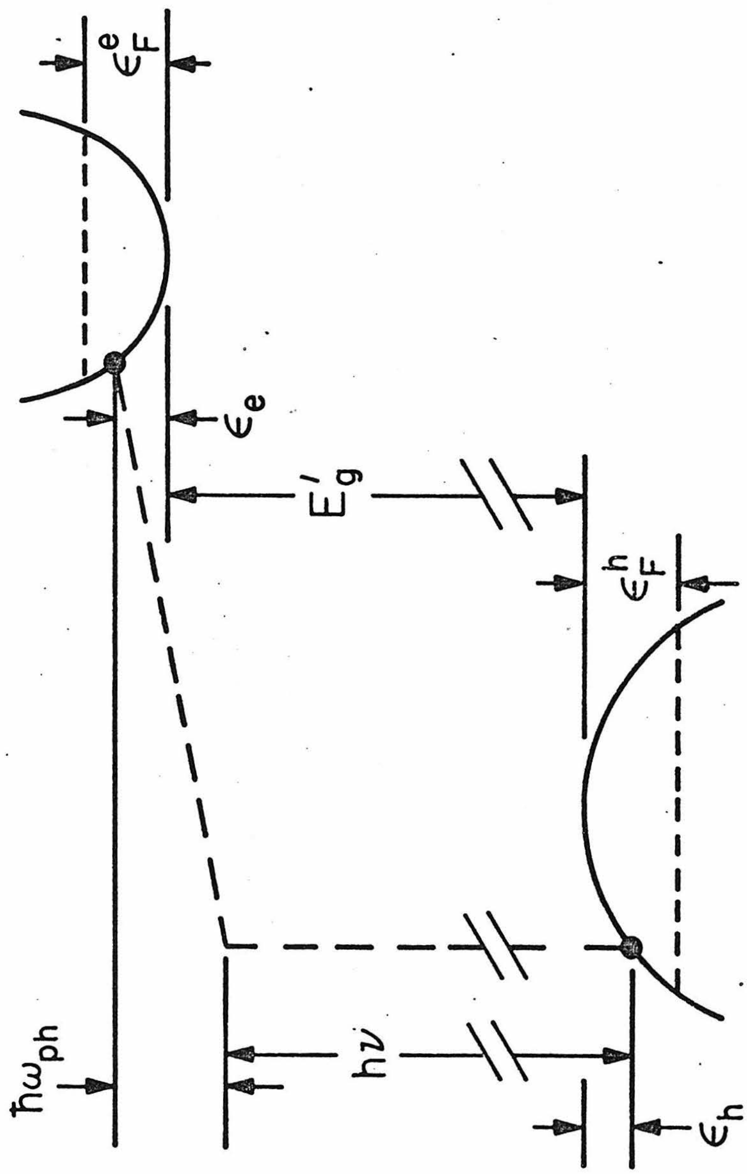
$$I_{cond}(h\nu) = A \quad d\varepsilon_e d\varepsilon_h \rho_e(\varepsilon_e)\rho_h(\varepsilon_h)\left(e^{(\varepsilon_e - \varepsilon_F^e)/KT}+1\right)^{-1}\left(e^{(\varepsilon_h - \varepsilon_F^h)/KT}+1\right)^{-1}$$

$$\delta(E_g' + \varepsilon_e + \varepsilon_h - \hbar\omega_{ph} - h\nu) \qquad (1)$$

Figure 6 Model for the radiative recombination of electrons and holes from the Fermi-degenerate electron-hole condensate. The valence and conduction bands are separated in energy and crystal momentum and are filled to their respective quasi-Fermi energies. E_g' is the energy gap for the condensate. An electron with energy ε_e above the band minimum and a hole with energy ε_h above the band maximum recombine emitting a phonon with energy $\hbar\omega_{ph}$ and a photon with energy $h\nu$.

FIGURE 6

LUMINESCENCE MODEL
FOR
ELECTRON-HOLE LIQUID



where ρ_e and ρ_h are the electron and hole density of states functions in the density of states effective mass approximation. The factor A contains the electron-hole matrix element and a number of other parameters and hence is dependent on which phonon replica is being considered. This model assumes that 1) the energy-wavevector relationship for the condensate is unmodified compared to the single electron band structure (except for the decrease in band gap already mentioned). 2) the matrix element for the recombination is independent of energy and crystal momentum, and 3) the recombination is adequately described in a single particle model. For convenience in the calculation presented below, we assume that the density of states varies as $E^{1/2}$.

With these assumptions, it is possible to calculate the form of one phonon replica. In Eq. (1), the density of states functions are calculated from the measured density of states effective masses for electrons and holes. The quasi-Fermi levels are determined by the density, the density of states effective masses, and the temperature.

In Si the total recombination intensity from the condensate is the sum of contributions from the LO and TO phonon replicas,

$$I_{cond}(E) = I^{TO}_{cond}(E) + I^{LO}_{cond}(E) \qquad (2)$$

where each contribution is described by Eq. (1). To calculate the condensate luminescence lineshape, it is necessary to know the relative intensity of these two contributions; i.e., we need to know the ratio A_{LO}/A_{TO}. This ratio has recently been estimated to be the value obtained from exciton absorption of .11.[(15)] We have chosen this ratio in the fits of the luminescence results reported in Sec. V.

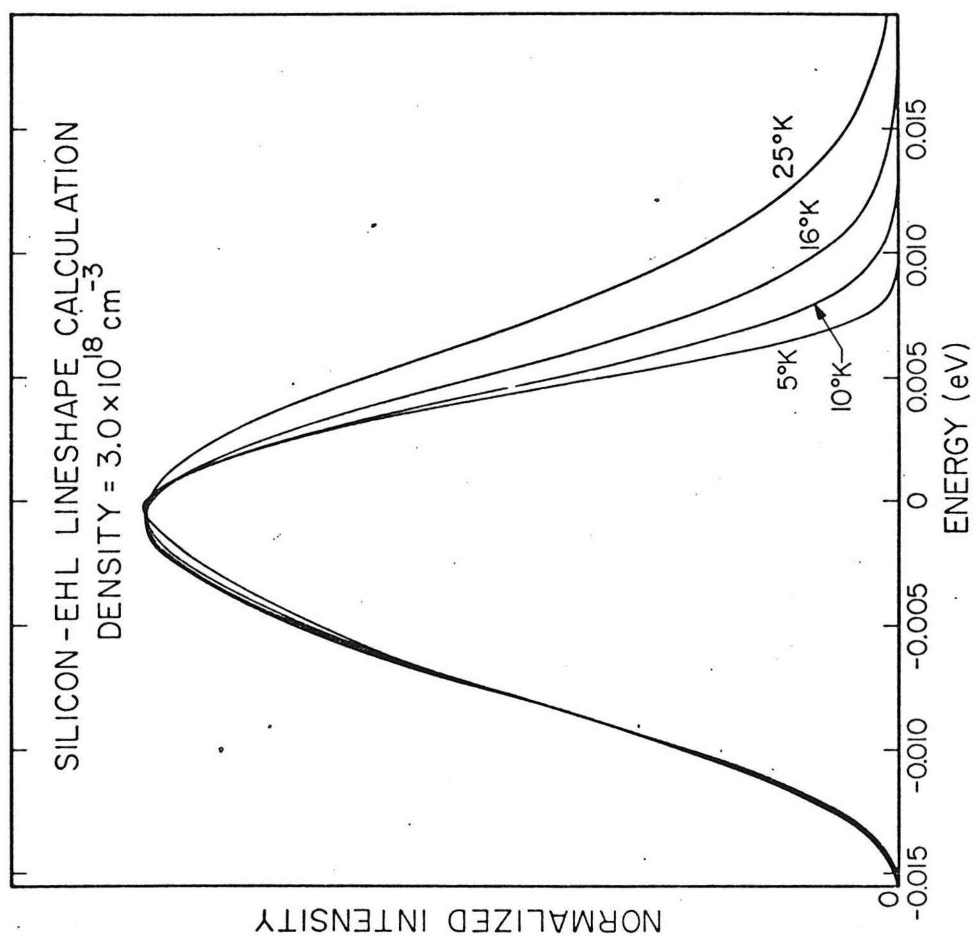


Figure 7. Silicon condensate luminescence lineshape calculations for 5, 10, 16, and 25°K at a density of 3 x 10^{18} pairs/cm^3.

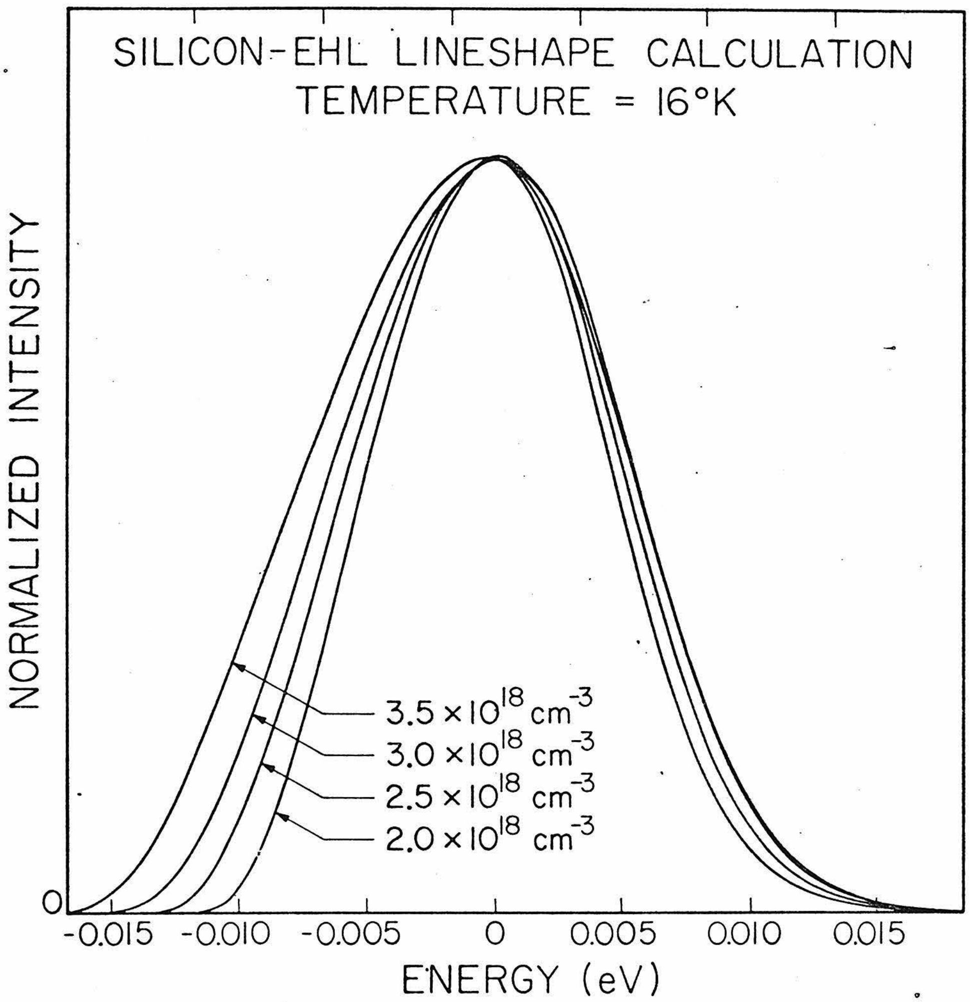


Figure 8. Silicon condensate luminescence lineshape calculations for densities of 2.0, 2.5, 3.0, and 3.5 x 10^{18} pairs/cm^3 at 16°K.

Before using Eq. (2) to calculate lineshapes and determine the electron-hole condensate density and work function spectroscopically, we will illustrate in Figs. 7 and 8 the effects of varying temperature and density on the qualitative form of the condensate luminescence lineshape. Since the work function is an adjustable parameter in these calculations, the absolute energy scale is not fixed. Therefore, in Figs. 7 and 8 we have chosen zero energy as the position of the maximum of the condensate luminescence. Figure 7 shows calculations according to Eq. (1) of the condensate lineshape for a density of 3. x 10^{18} cm^{-3} at several temperatures. The low energy side is essentially unchanged with temperature while the high energy side changes significantly. Fig. 8 shows calculations according to Eq. (1) of the condensate lineshape for various densities at a single temperature. Here we see that the low energy side varies considerably with density while the high energy side varies much less. These figures suggest several things important to the condensate line fitting. First, density and temperature changes each have very different effects on the lineshape so that one cannot be traded against the other to obtain a good fit. The correct density may be determined by fitting the low energy side of the line without regard to the temperature. Also, the temperature may be determined by fitting the high energy side of the lineshape.

V. Results

Figure 9 shows line fits at two temperatures of TO-LO phonon assisted recombination radiation due to electrons and holes in the electron-hole condensate in Si. These fits are calculations of Eq. (2) with corrections for spectrometer transmission, detector sensitivity,

TABLE I

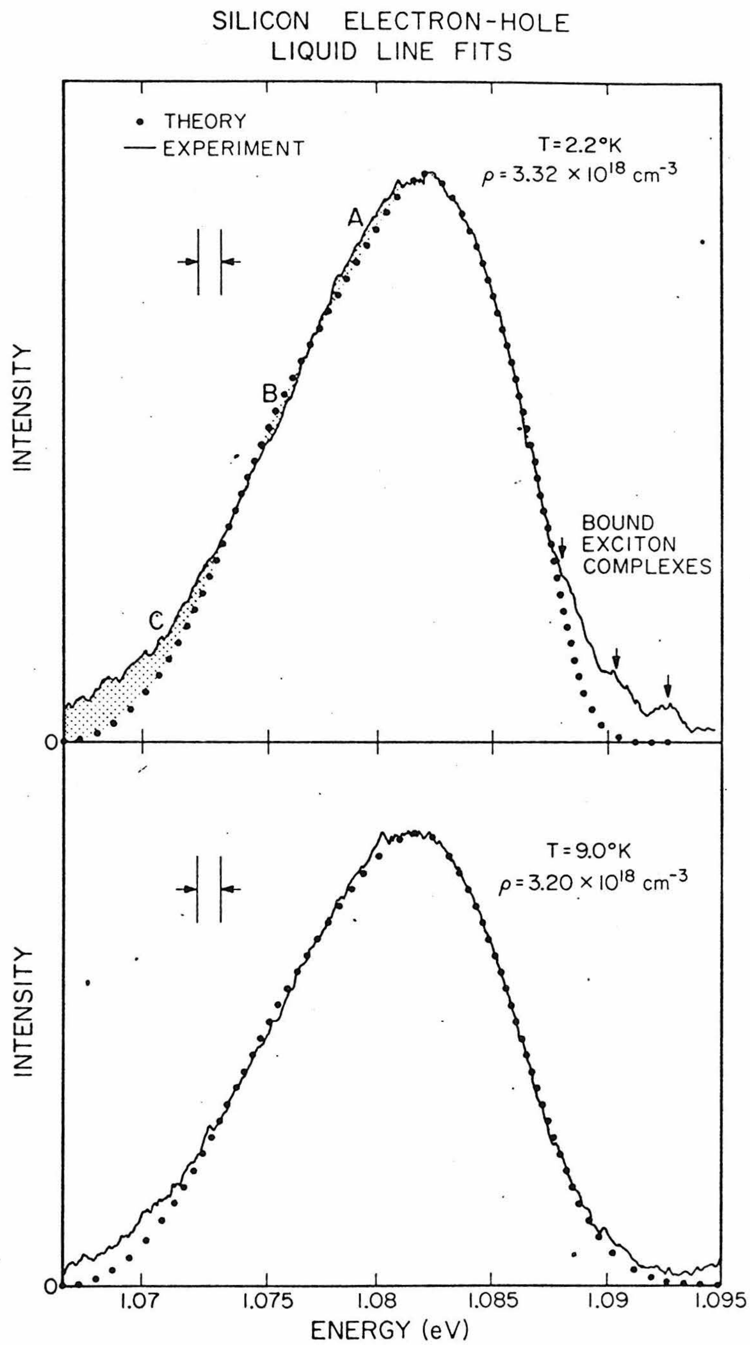
TEMP	LASER INTENSITY†	EHD FWHM	EHD POSITION
2.2°K	.3 watts	125 Å	1.1472 μ
	.6 watts	124 Å	1.1473 μ
	1.5 watts	124 Å	1.1473 μ
4.2°K	.6 watts	124 Å	1.1473 μ
	1.5 watts	124 Å	1.1474 μ
	3.0 watts	123 Å	1.1473 μ
7.0°K	.3 watts	124 Å	1.1473 μ
	.6 watts	124 Å	1.1475 μ
	1.5 watts	124 Å	1.1475 μ
9.0°K	.3 watts	125 Å	1.1475 μ
	.6 watts	126 Å	1.1476 μ
	1.5 watts	125 Å	1.1475 μ

For each temperature these numbers are the same within the noise level.

† Laser intensity is not corrected for the reflectance of Si.

Figure 9. LO- and TO-phonon assisted condensate recombination radiation from laser excited, high purity Si at 2.2°K and 9.0°K, with a laser intensity of 600 mW. Calculated line fits (dotted lines) to this luminescence yield condensate densities of 3.32 and 3.20 x 10^{18} cm^{-3} respectively. Discrepancy areas between the calculated lineshape and the experimental lineshape at 2.2°K are cross-hatched and labeled A, B, and C. These same discrepancy areas can be seen at 9.0°K; but they are diminished in size.

FIGURE 9

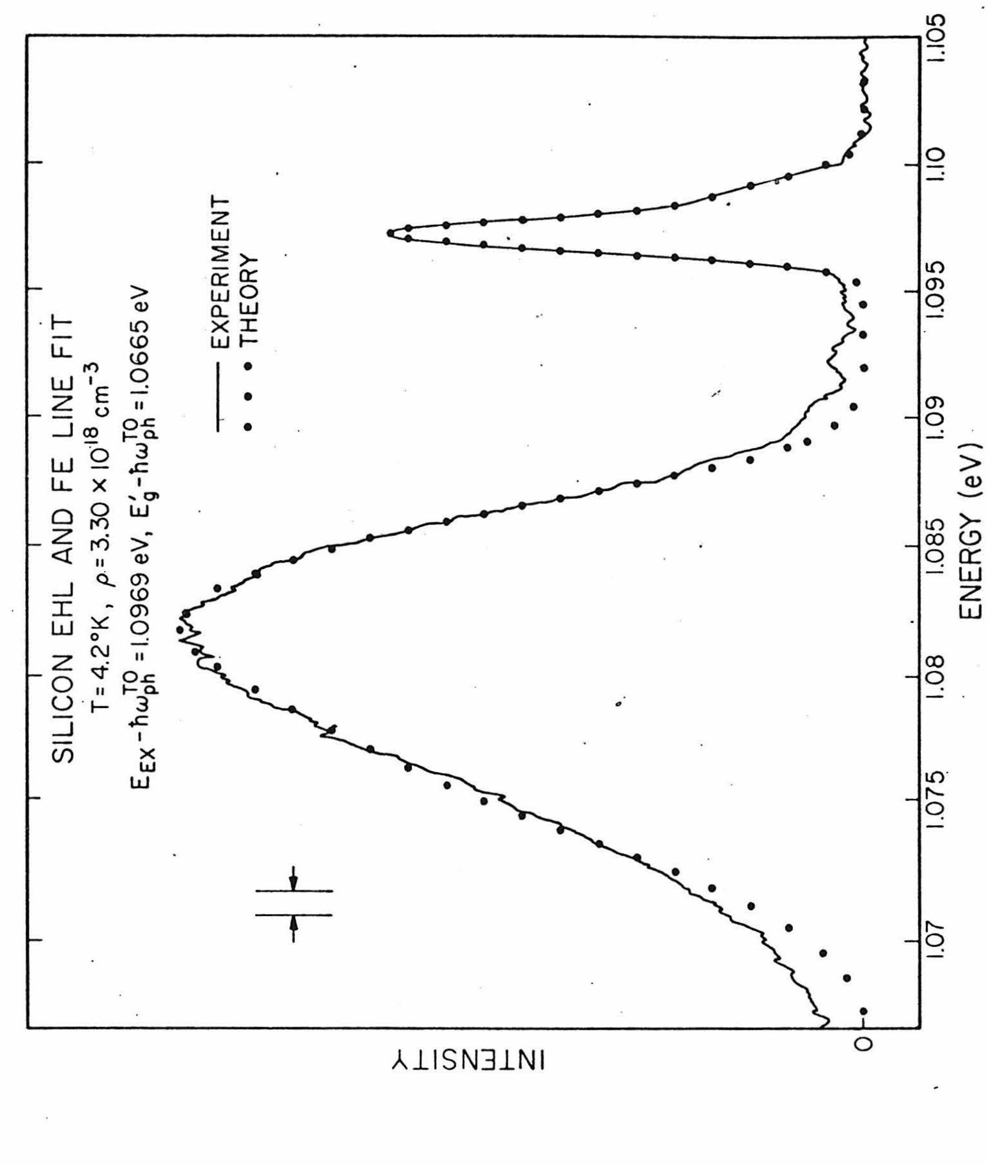


SILICON ELECTRON-HOLE
LIQUID LINE FITS
• THEORY
— EXPERIMENT
T=2.2°K
ρ=3.32 × 10^18 cm^-3
A
B
C
BOUND
EXCITON
COMPLEXES
INTENSITY
0
T=9.0°K
ρ=3.20 × 10^18 cm^-3
INTENSITY
0
1.07
1.075
1.08
1.085
1.09
1.095
ENERGY (eV)

and spectrometer-instrument broadening. The condensate density is found to be 3.32×10^{18} cm^{-3} at 2.2°K and 3.20×10^{18} cm^{-3} at 9.0°K. The condensate lineshape was fit and the density determined in this manner for temperatures between 2.2°K and 13.0°K. The lineshapes showed no change at different laser excitation intensities for temperatures between 2.2°K and 9.0°K. At higher temperatures, only the highest excitation levels produced the condensate radiation so it was not possible to vary the excitation intensity. The condensate line widths and positions at different pump powers and different temperatures are summarized in Table I. At each temperature these line widths and line positions are unchanged (within the noise) at different excitation levels. This is evidence for the lack of heating in the experiment. Also, for each temperature and excitation level, the value of the temperature was confirmed by fitting the free exciton luminescence. In each case, the LO-TO phonon assisted free exciton luminescence agreed with the resistance thermometer measurement. At high temperatures the width of the free exciton luminescence is a good indicator of the temperature since kT broadening is large compared to the LO-TO splitting. On the other hand at low temperatures, where the kT broadening is small the LO:TO intensity ratio is a strong function of temperature and is thus, a sensitive measure of the temperature.[15] Fig. 10 shows condensate and free exciton line fits to a spectrum at 4.2°K. Besides being a measure of the temperature, the free exciton fit also yields the value of the low energy exciton threshold which permits a determination of the exciton-condensate work function.

In the condensate line fit at 2.2°K in Fig. 9, three regions of discrepancy between the calculation and the experimental lineshape are

FIGURE 10


SILICON EHL AND FE LINE FIT
T = 4.2°K, ρ = 3.30 × 10^{18} cm^{-3}
$E_{EX} - \hbar\omega_{ph}^{TO}$ = 1.0969 eV, $E'_g - \hbar\omega_{ph}^{TO}$ = 1.0665 eV
EXPERIMENT
THEORY
INTENSITY
0
1.07
1.075
1.08
1.085
1.09
1.095
1.10
1.105
ENERGY (eV)

shaded and labeled respectively A, B, and C. These regions of discrepancy were noted in the line fits at all temperatures and all excitation levels. The discrepancy region C is evidence of the recombination of electrons and holes with lower energy than is allowed in the simple band model. This discrepancy at low energy in the line fit has also been observed in Ge by several investigators and is attributed to electrons and holes recombining from the condensate and leaving the condensate in an excited state which is different from that given by the standard band model. Thus the energy of the emitted photon is lowered by just the amount necessary to produce the excitation. The discrepancies between the calculated lineshapes and the experimental spectra decrease continuously at higher temperature. This effect can be seen easily by comparing the fits at 2.2°K and 9.0°K for the electron-hole condensate as shown in Fig. 5.

At 2.2°K (see Fig. 9), and 4.2°K (see Fig.10), weak lines due to recombination of excitons bound at impurity sites are observed on the high energy side of the condensate line. This is the first reported observation of these lines in high purity p-type Si (N_A - N_D - 1.5 x 10^{11} cm-3). They are shown prominently in the luminescence spectrum of Fig. 1 for Si doped 7 x 10^{11} cm^{-3}. For this work it was possible to reduce the intensity of these lines sufficiently that their effect on the lineshape fitting was not significant.

The quantitative results of the condensate luminescence lineshape fitting for Si are summarized in the graphs in Figs.11-14. Qualitatively, we see that the condensate density, Fermi level, and chemical potential each show an increase with decreasing temperature while the condensate-exciton work function decreases with decreasing temperature. These are the trends expected from the plasma model. In fact, theoretically, we expect the following dependences[18]

$$\mu(T) = \mu(0) - \alpha T^2$$
$$n(T) = n(0) - \beta T^2$$
$$E_F(T) = E_F(0) - \delta T^2$$
$$\phi(T) = \phi(0) + \alpha T^2$$

where μ is the condensate chemical potential, n is the density, E_F is the sum of the electron and hole quasi-Fermi levels and ϕ is the exciton-condensate work function. Since the exciton binding energy is independent of temperature, the T^2 dependence of the chemical potential implies this same dependence for the work function so the coefficient is the same for each of these parameters. Extrapolated values to zero temperature for each of the condensate properties are shown in Table II. These are derived from the graphs shown in Figs. 11-14. As shown in Figs. 11-14, the variation of each of the parameters is consistent with the T^2 dependences expected from theory. Since there was some contribution on the high energy side of the condensate line from the free exciton at 11°K and 13°K, the error in the lineshape fits increased for these two temperatures above the error at lower temperatures.

The Fermi liquid parameters obtained from our data are:

$$\alpha = 5.8 \pm 1.0 \times 10^{-3}\,\mathrm{meV}\text{-}°K^{-2}$$
$$\beta = 1.6 \pm 1.0 \times 10^{15}\,\mathrm{cm}^{-3}\text{-}°K^{-2}$$
$$\delta = 8 \pm 4 \times 10^{-3}\,\mathrm{meV}^{-}°K^{-2}$$

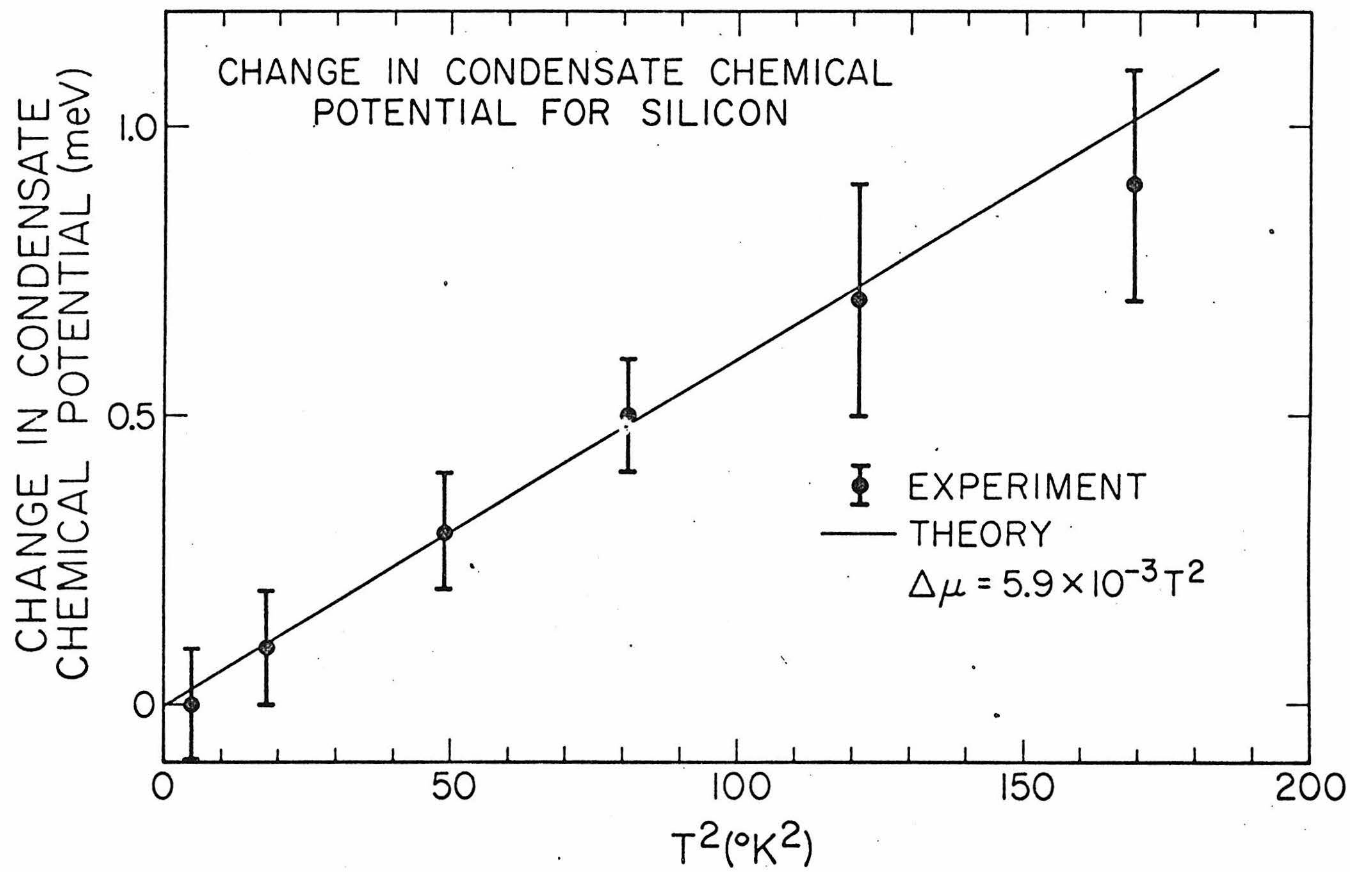


Figure 11. Results of lineshape fits to the LO- and TO-phonon assisted condensate luminescence for the chemical potential of the electron-hole liquid in laser excited, high purity Si.

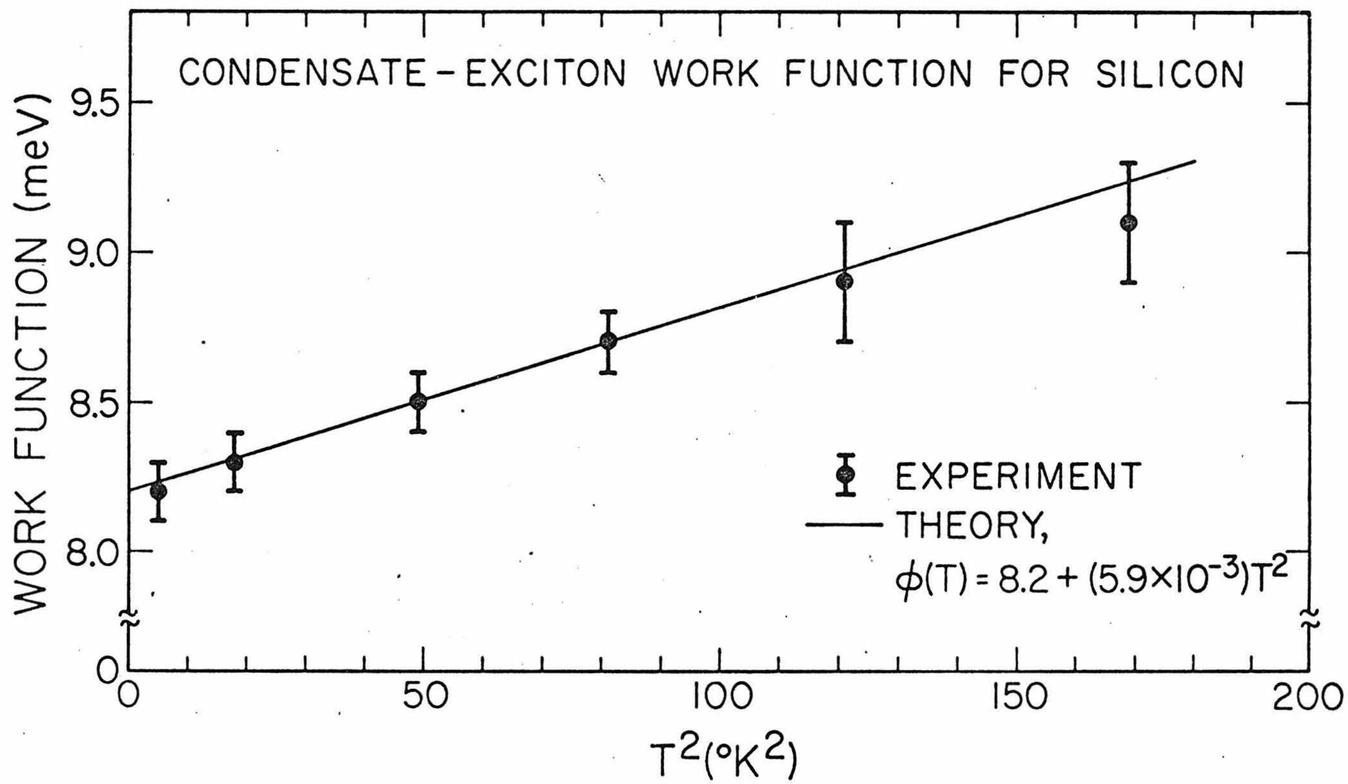


Figure12. Results of lineshape fits to the LO- and TO-phonon assisted condensate luminescence for the condensate-exciton work function in Si.

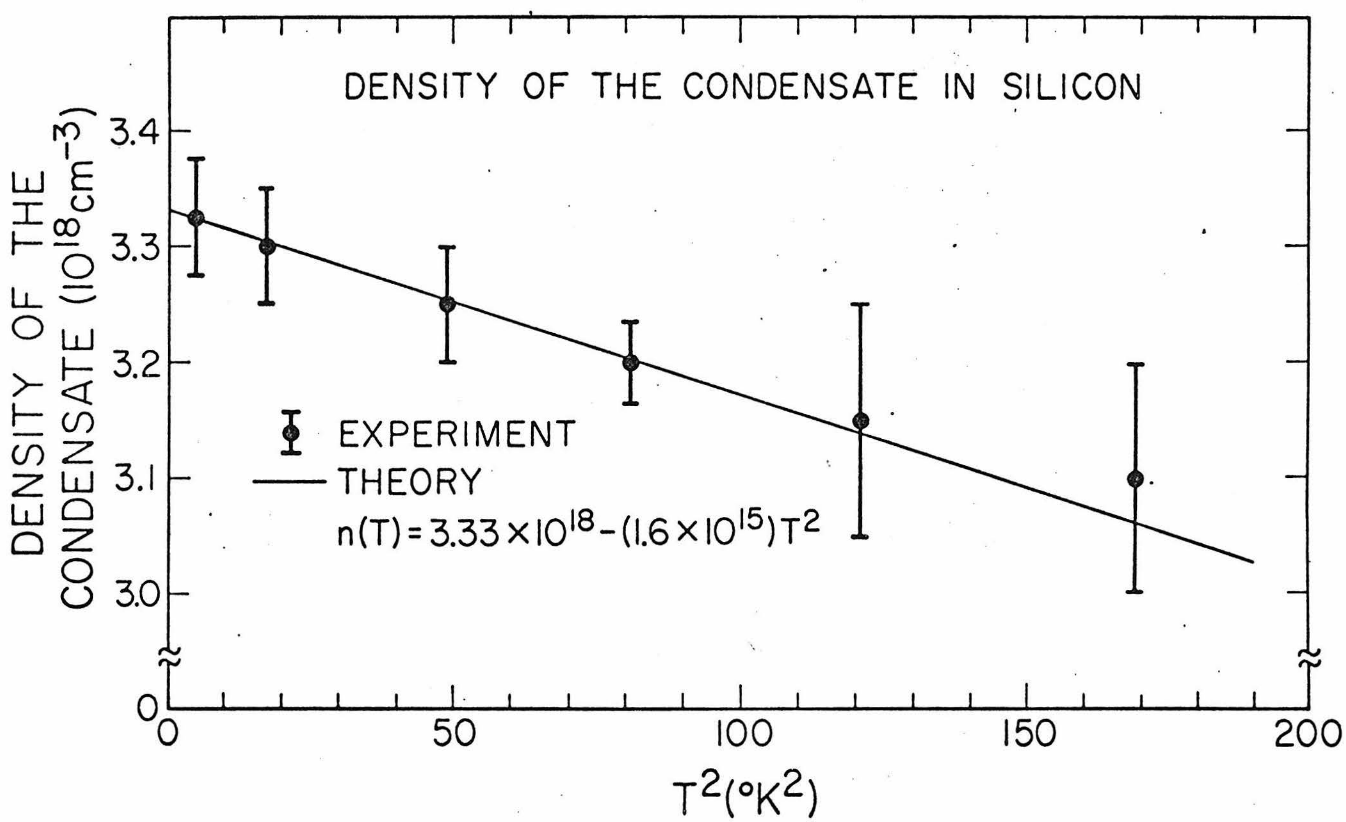


Figure 13. Results of lineshape fits to the LO- and TO-phonon assisted condensate luminescence for the density of the electron-hole liquid in laser excited, high purity Si.

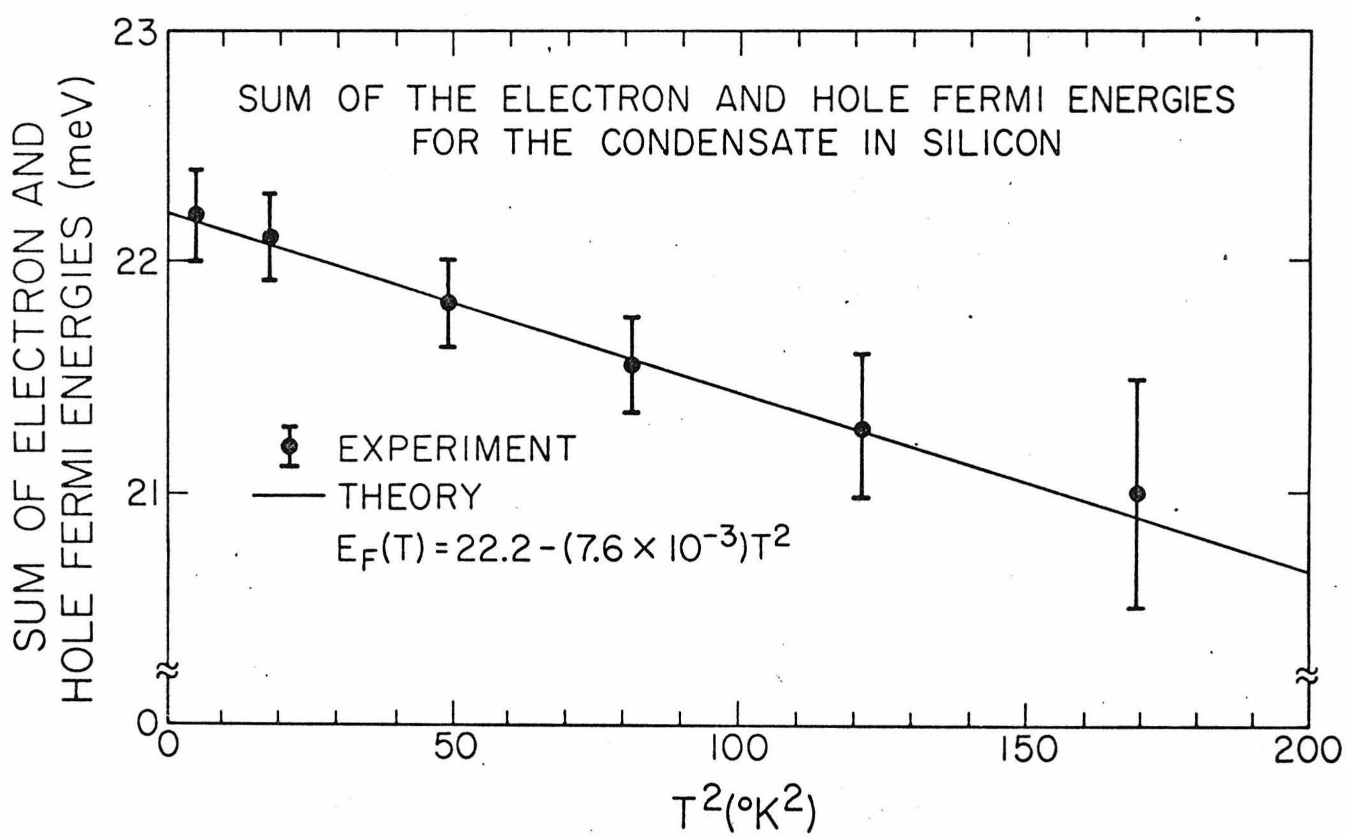


Figure 14. Results of the lineshape fits to the LO- and TO-phonon assisted condensate luminescence for the Fermi energy of the electron-hole liquid in laser excited, high purity Si.

TABLE II

Silicon Electron-hole Liquid at 0°K

ϕ	n_o	E_F	$\mu-\hbar w_{ph}^{TO}$
8.2±.1meV	$3.33\pm.05\times10^{18}cm^{-3}$	22.2±.2meV	1.0887±.0001eV

VI. Discussion and Summary

Theoretical calculations giving 3.1[16], 3.2[17], and 3.4[18] x 10^{18} cm^{-3} for the zero temperature condensate density are comparable to our measured value, 3.33 ± .05 x $10^{(18)}$ cm^{-3}. The measured zero temperature work function, 8.2meV, is slightly higher than theoretical estimates of 5.7meV[16], 6.3meV[17], and 7.3meV[18].

Although we were unable to fit the condensate lineshape above 13°K due to interference from the free exciton, we were able to observe it at temperatures up to 17°K. This then is a lower bound on the critical temperature for the exciton-condensate phase transition, T_c. We expect the critical temperature to be significantly higher than this since our laser was able to produce exciton densities of at most 10^{17} cm^{-3}. By extrapolating the measured T^2 dependence of the condensate density and using the measured work function, 8.2meV, in the law of mass action[10], it is possible to make a crude estimate of T_c. If we write:

$$n(T) = n_o - \beta T^2$$

$$n_{ex}(T) = 32 \left(\frac{M^*kT}{2\pi h^2}\right)^{3/2} e^{-\phi/kT}$$

and set these condensate and exciton densities equal, we get $T_c \sim 25°K$ and the critical density, $\rho_c \sim 1.5 \times 10^{18}$ cm^{-3}. An analogous procedure for Ge using the measured values for the electron-hole condensate by Thomas _et al._[2] yields $T_c \sim 7.8°K$ and $\rho_c \sim 1.2 \times 10^{17}$ cm^{-3}. These over-estimate the measured[20] values of $T_c = 6.5°K$ and $\rho_c = .8 \times 10^{17} cm^{-3}$ as we might expect. Since the work function goes to zero at the critical temperature, we would expect this procedure to always give an over-estimate of T_c. Putting our two bounds together for the phase transition in Si we get:

$$17°K < T_c < 25°K$$

Calculated values for T_c are 20.8°K[17], and 28°K[19]. 20.8°K is within the range of our bounds, but 28°K is probably too large an estimate.

Vashishta et.al.[18] have calculated several of the thermodynamic properties of the electron-hole condensate in Si. Their calculations are comparable to the results reported here. They predict: $\alpha = 3.8\text{x}10^{-3}$ meV-°K^{-2}, lower than the measured value $5.9\pm1.0\text{x}10^{-3}$meV-°K^{-2}; $\beta = 2.46\text{x}10^{15}$ cm^{-3}-°K^{-2} in agreement with the measured value $1.6\pm1.0\text{x}10^{15}$; and δ - $12.3\text{x}10^{-3}$meV-°K^{-2}, consistent with the measured value $8\pm4\text{x}10^{-3}$meV-°K^{-2}. All the calculated values for the condensate properties which we have measured spectrscopically are summarized in Table III along with our measured values.

It is important to note that the lack of temperature gradients in the experiment is crucial to the validity of the results reported here. Heating in photoluminescence experiments has been reported and also suggested as being important by several investigators in both Ge and Si. In studying the condensate luminescence in Si, the possibility of heating is greatly increased compared to Ge due to several factors. Since the condensate density is more than an order of magnitude higher in Si than in Ge and the lifetime is more than two orders of magnitude smaller, the heat produced by condensate recombination (mostly non-radiative) is more than three orders of magnitude higher in Si for the same condensate volume. In this work, for the reasons outlined

TABLE III

Measured and Calculated Properties of the

Electron-hole Liquid in Si

	ϕ_ℓ (meV)	n_o (cm^{-3})	α ($meV\text{-}°K^{-2}$)	β ($meV\text{-}°K^{-2}$)	δ ($meV\text{-}cm^6$)
Experimental (this paper)	8.2±.1	3.33±.05	5.9±1.0	1.6±1.0	8.7±4.0
Vashishta Das, Singwi	7.3	3.2	3.8	2.46	12.3
Brinkman Rice	5.7	3.4			
Combescot Nozieres	6.3	3.1			

in Section V, temperature control has been adequate.

As pointed out in Section V, the discrepancy region C in Fig. 9 of the condensate line fits has been attributed to electrons and holes recombining from the condensate and simultaneously producing excitations not described in the standard band model. Carriers which recombine in this manner will probably tend to distort the lineshape in some way depending on which states are favored for this process. Thus, these processes may also account for the discrepancy regions A and B in the line fits (see Fig. 9). That these three discrepancy regions are related is indicated also by the fact that they decrease continuously in the line fits at increasing temperatures. Although we have no understanding of the mechanism involved, it is surely significant that the differences between the calculated lineshape and the experimental spectra diminish monotonically with increasing temperature.

Although not directly related to our study of the electron-hole condensate in Si, our observation of luminescence lines due to excitons bound to impurity sites in very high purity Si suggests the possibility of using photoluminescence as a very sensitive measure of the presence of dopant impurities in Si.

There are several important results of the electron-hole condensate line fits which substantiate the degenerate electron-hole plasma model for the condensate in Si. First, the model gives a qualitative fit to the lineshape at each temperature and excitation level. Second, the lineshape displays the correct temperature dependence. That is, the high energy side of the line is fit well at each temperature. Finally, the density, chemical potential, work function, and Fermi level each show a variation with temperature which is consistent with the T^2 dependence expected from Fermi liquid theory.

In summary, we find that the simple luminescence model for the electron-hole condensate in Si fits the experimental lineshapes with only slight discrepancies. Despite these small discrepancies, it is possible to extract parameters from these line fits which lend support to the electron-hole plasma model for Si and also give several properties of the condensate.

APPENDIX

In Fig. 15 is shown a Si electron-hole condensate luminescence lineshape calculation for LO-TO phonon assisted recombination. Three parameters, the full width at half maximum (FWHM), the position of the low energy threshold of the line relative to the peak position, and the sum of the electron and hole Fermi levels are shown. The calculation has not been modified for experimental distortion, resolution or sensitivity but is a direct evaluation of Eq. (1). The results of similar lineshape calculations for these three parameters are given in the graphs of Figs. 16-18 for various temperatures and densities.

Knowing the temperature, FWHM, and peak position of the condensate luminescence in Si, it is possible to determine the condensate density, Fermi level, and low energy threshold from Figs. 16-18. If one includes a knowledge of the free exciton threshold, one can also determine the work function.

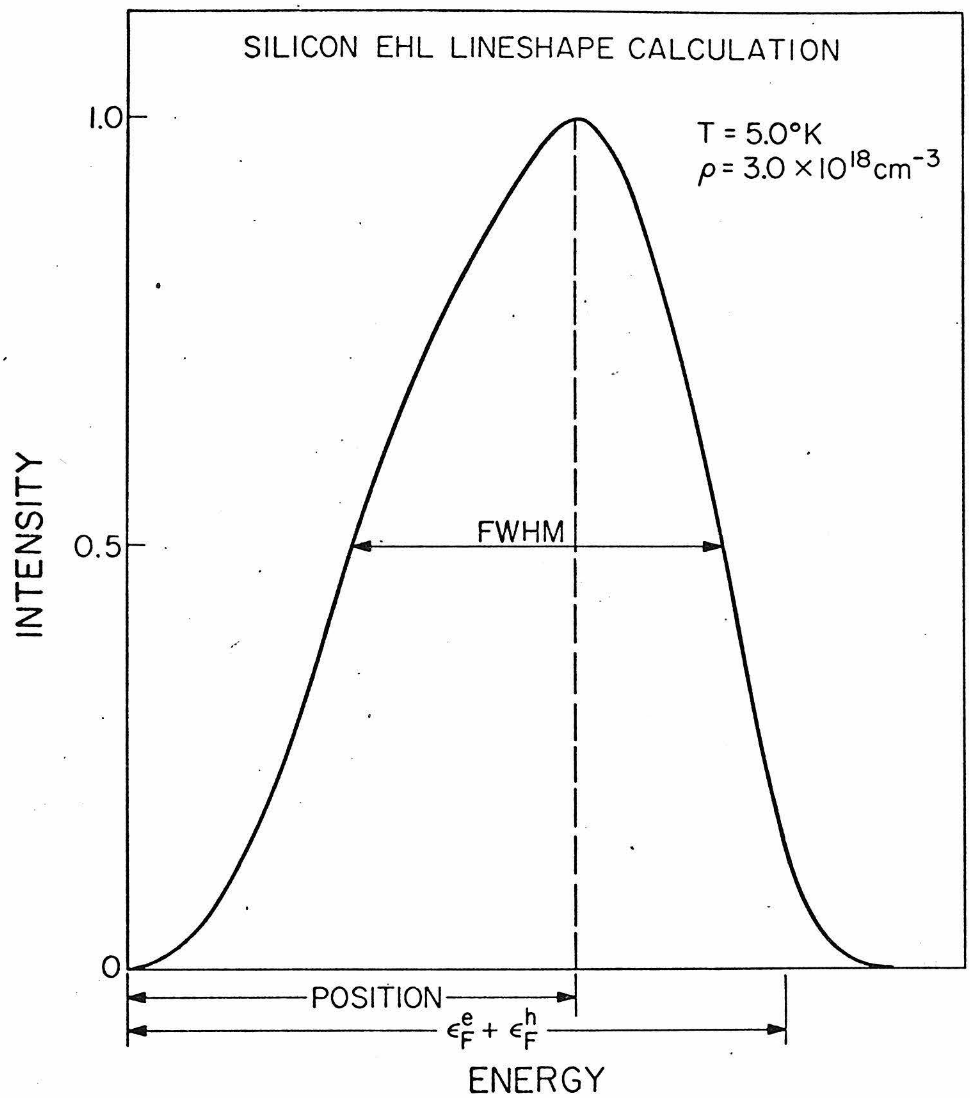


Figure 15. A Si electron-hole liquid lineshape calculation for 5°K and a density of 3.0 x 10^{18} cm^{-3}.

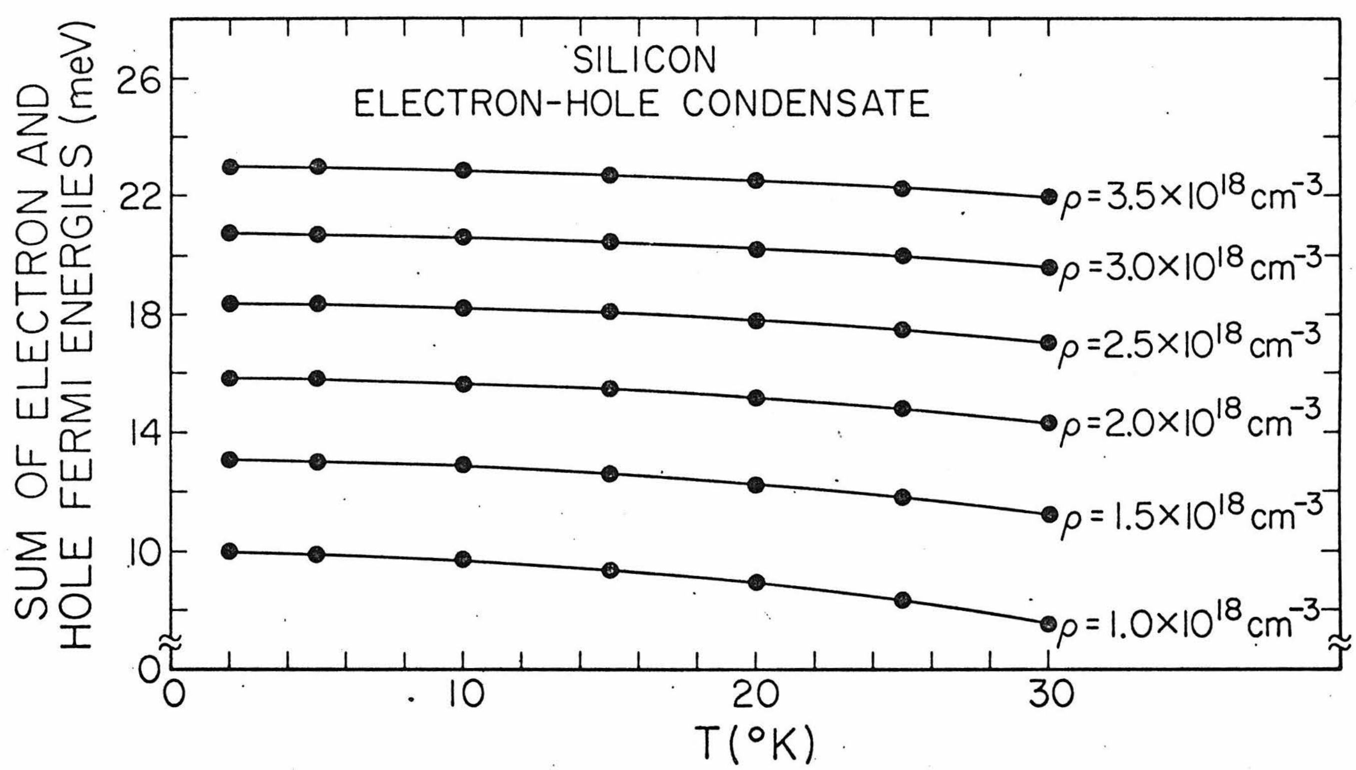


Figure 16. The Fermi energy for the electron-hole condensate in Si at various densities as a function of temperature.

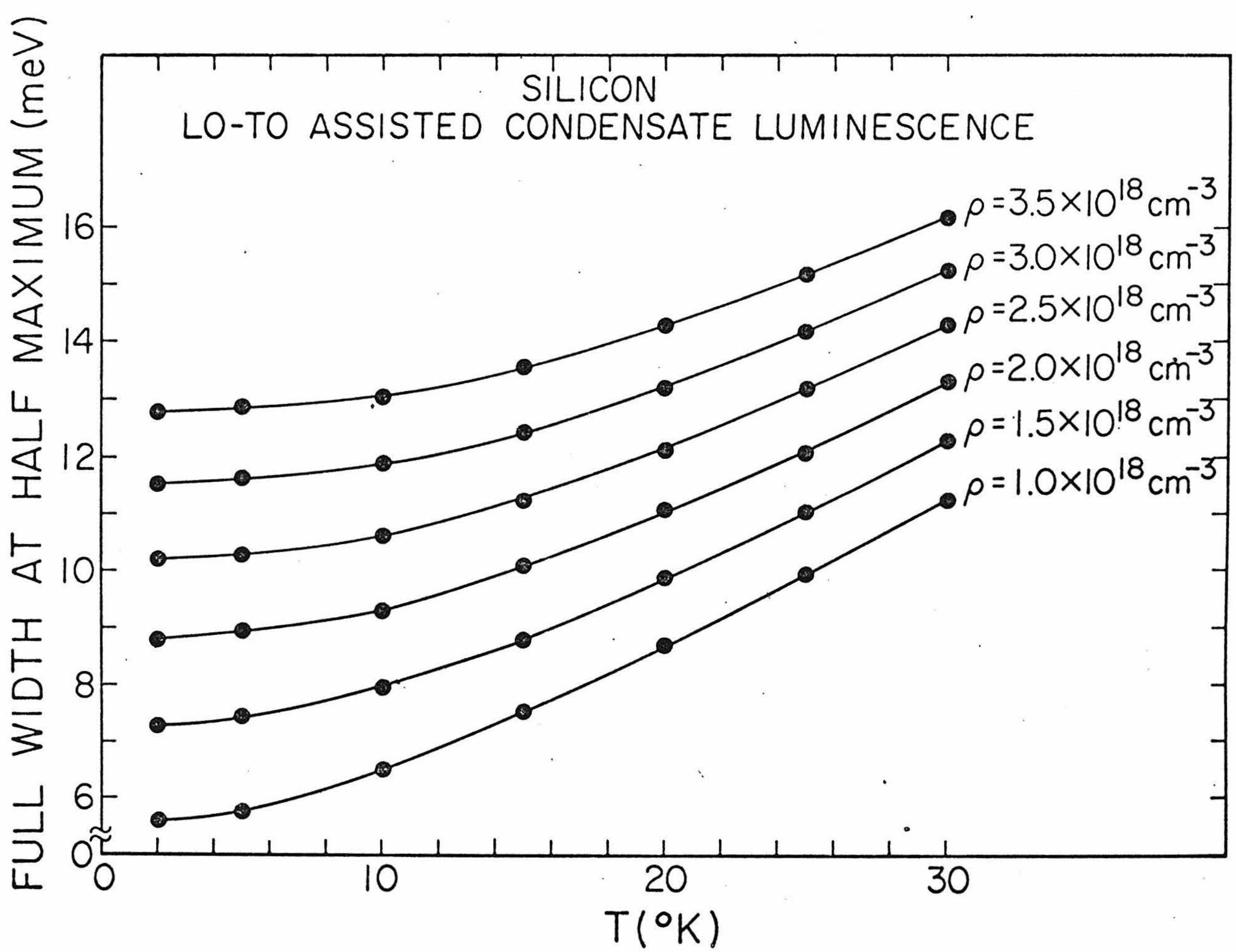


Figure 17. Results of LO- and TO-phonon assisted condensate luminescence lineshape calculations for the full width at half maximum (FWHM) of the luminescence line.

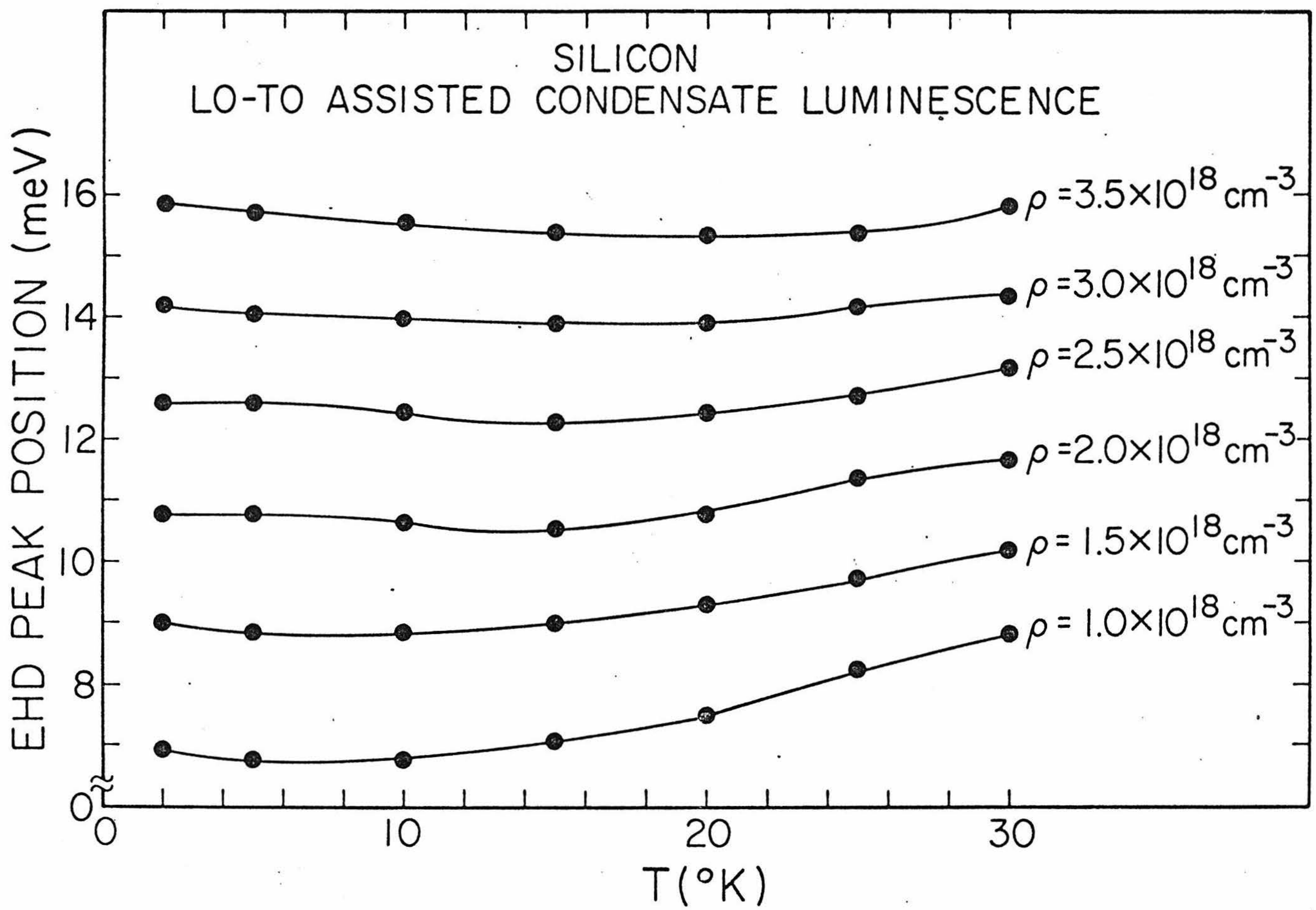


Figure 18. Results of LO- and TO-phonon assisted condensate luminescence lineshape calculations for the peak position of this luminescence relative to the low energy threshold of the line.

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CHAPTER 4

PROPERTIES OF THE ELECTRON-HOLE LIQUID LUMINESCENCE IN SILICON DOUBLE INJECTION DIODES

INTRODUCTION

Several experiments have shown that a high density, metallic phase of nonequilibrium electrons and holes can be produced in Ge at temperatures < 6°K by optical excitation.[1,2] This electron-hole condensate has also been produced by this same excitation method in Si at temperatures < 20°K.[1,3] A second method of excitation, current injection from p^+ and n^+ doped contacts, has been used to produce this high density phase in Ge.[4] From a comparison of the shapes of recombination spectra from laser excitation and double injection, Chen et.al.[14] concluded that the line positions and shapes of spectra do not depend on the type of excitation in Ge.

Preliminary reports of the observation of electron-hole condensate in Si double injection devices have been given by Hammond _et_. _al_.[5] and Collet _et_. _al_.[6] Collet _et_. _al_ interpret a luminescence line at 1.086 eV as being due to TO-phonon assisted recombination from the electron-hole condensate. However, this line position is not in agreement with the line position of 1.082 eV previously observed in optical excitation experiments.[1] In addition, their spectral resolution was not sufficient to make any comment on line width or lineshape. Due to impurity effects, it is necessary to obtain high resolution spectral data to distinguish the condensate luminescence from other lines. Lines due to bound excitons and bound multi-exciton complexes may appear on the high energy side of the condensate luminescence in Si in the vicinity of 1.086 eV.

Impurity effects in luminescence have been observed by several investigators. In Ge double injection studies, Chen et. al.[14] have observed the influence of dopant impurities in the luminescence spectra. They reported a bound exciton line and a narrow condensate line from some of their double injection devices. They attributed both of these effects in luminescence to the presence of dopant impurities introduced into the double injection device during fabrication. In laser excitation of Si, the influence of impurities on luminescence has been observed by Sauer,[7,8] Martin and Sauer,[9] and Kosai and Gershenzon.[10] They all observed luminescence lines which appeared in energy between the free exciton and condensate luminescence. They attributed these lines to excitons bound at impurity atoms. Martin and Sauer found that impurities in general caused a narrowing of the electron-hole condensate luminescence lineshape and sometimes small shifts (< 2 meV) in the peak position of this line.

In this paper, we report on a study of the luminescence properties of Si double injection devices. The primary purpose of this study was to determine if any major changes in the luminescence occurred by this method of excitation as compared to luminescence in laser excitation. We also sought to investigate the influence of impurities introduced into the Si during device fabrication. Previously reported difficulties with joule heating[5] of the double injection devices have been solved by fabricating the devices on large area Si slices.

Section II of this paper contains a description of the device fabrication procedure and experimental techniques. Section III presents the experimental spectra from electrically excited double injection structures, and spectra from pure silicon and Li doped silicon excited by a laser. The transient response of the luminescence from the condensate is also reported. Finally, Section IV contains the conclusions that we can draw from the reported results.

II. EXPERIMENTAL

Double injection diodes for the luminescence study were fabricated from p-type, high-purity, single crystal Si with net doping concentration $N_A - N_D = 10^{11} - 10^{12}$ cm^{-3}. To improve heat dissipation, the double injection diodes were made on slices of Si. These slices were 300 mm^2 in area and 0.8 mm thick. One face of the Si slices was lapped and etched and had an Al film, 5000Å thick, evaporated onto it. The slices were then heated at 630°C for 30 min. and then slowly cooled to room temperature (~ 2°C/min.). This procedure produces an Al-alloyed p-contact. The opposite sides of the slices were then lapped and painted with a suspension of Li in mineral oil. They were heated at 460°C for 4 min. and then immediately cooled to room temperature. The Li-diffused faces were then lightly lapped. This procedure produces a Li-diffused n-contact. After these contact forming steps, the Si slices were etched to isolate mesa-type Al contact areas, 2. - 10. mm^2 in area. After etching, each

Al contact and the Li contact on the reverse side were In soldered. A typical mesa double injection diode is shown in Fig. 19. Samples for the photoluminescence studies were prepared from slices of Si similar to those used for the double injection diodes. These samples were laser excited in the middle of a 15 mm x 20 mm face which was mechanically polished and chemically etched.

The sample temperature during the luminescence experiments was controlled in a Janis variable temperature He Dewar and measured with a Ge resistance thermometer in contact with the Si sample. For laser excitation, a GaAs laser mounted inside the Dewar 4 mm above the sample surface produced a circular excitation spot on the sample of ~ 0.5 mm in diameter. To minimize heating, the laser was pulsed with 2 μs pulses at a repetition rate of 10 kHz. Instantaneous optical powers of 0.3 - 3.0 watts were used. The Si luminescence was analyzed with a Spex 1400-II double grating spectrometer, detected with a RCA 7102 S-1 photomultiplier tube operated at 195°K, and the electrical signal processed with a lock-in amplifier or box-car integrator and recorded on a strip-chart recorder.

For the double injection luminescence experiment, a systematic investigation using both time-resolved spectroscopy with a box-car integrator and time-averaged spectroscopy with a lock-in amplifier was made to determine the effect of joule heating in the devices. In the time-resolved analysis, the luminescence spectrum was observed to change during a single

SILICON DOUBLE INJECTION MESA STRUCTURE

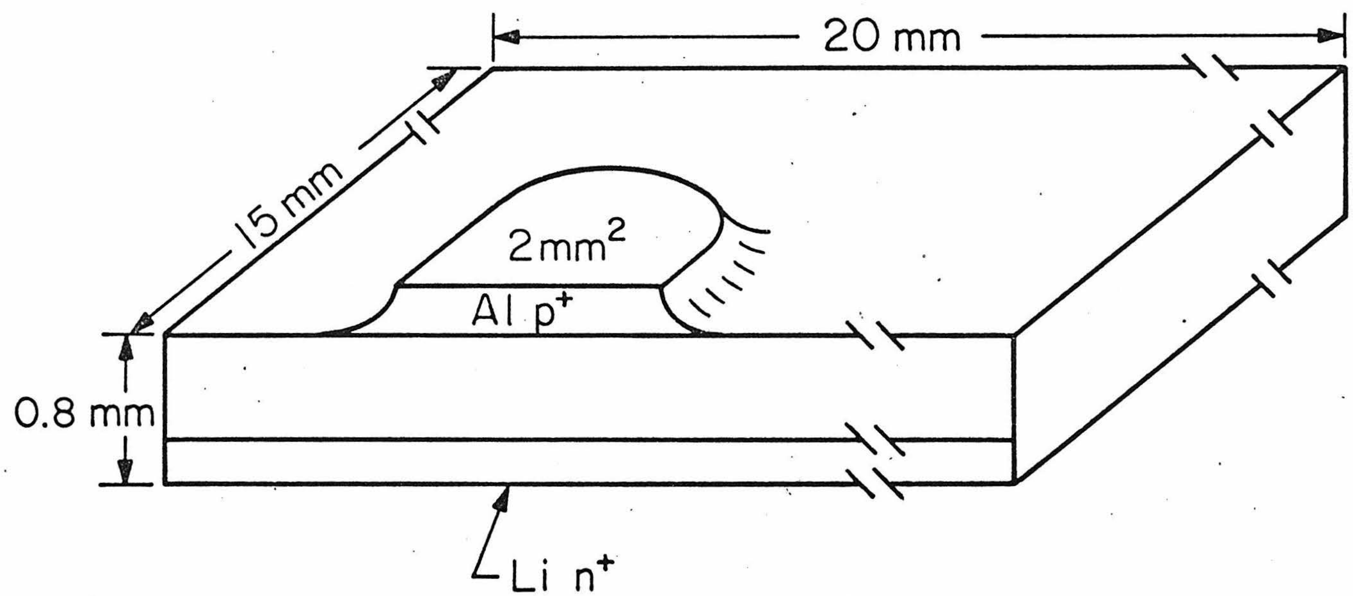


Figure 19 Typical double injection diode of the mesa type.

current pulse. It showed the characteristics of luminescence at higher temperatures at later times in the pulse. In the time-averaged analysis the luminescence spectrum was observed to change with increased repetition rates using fixed pulse length. The spectrum showed the characteristics of spectra at higher temperatures when the repetition rate was increased. These results imply the presence of temperature gradients between the luminescing region of the double injection device and the Ge resistance thermometer.

In the present work, the pulse duration and repetition rate were reduced to avoid device heating. At each temperature a pulse length of 2 μs was found to produce no change in the luminescence spectrum during a current pulse at the highest current levels. Also repetition rates up to 5 kHz produced no change in the spectra. For longer pulse lengths with the same duty cycle and for higher repetition rates, changes in the spectra, e.g. changes in the relative intensity of free exciton and electron-hole condensate emission, were observed. Thus, for the double injection luminescence studies, we chose current pulses of 2 μs duration and a repetition rate of 5 kHz to avoid heating.

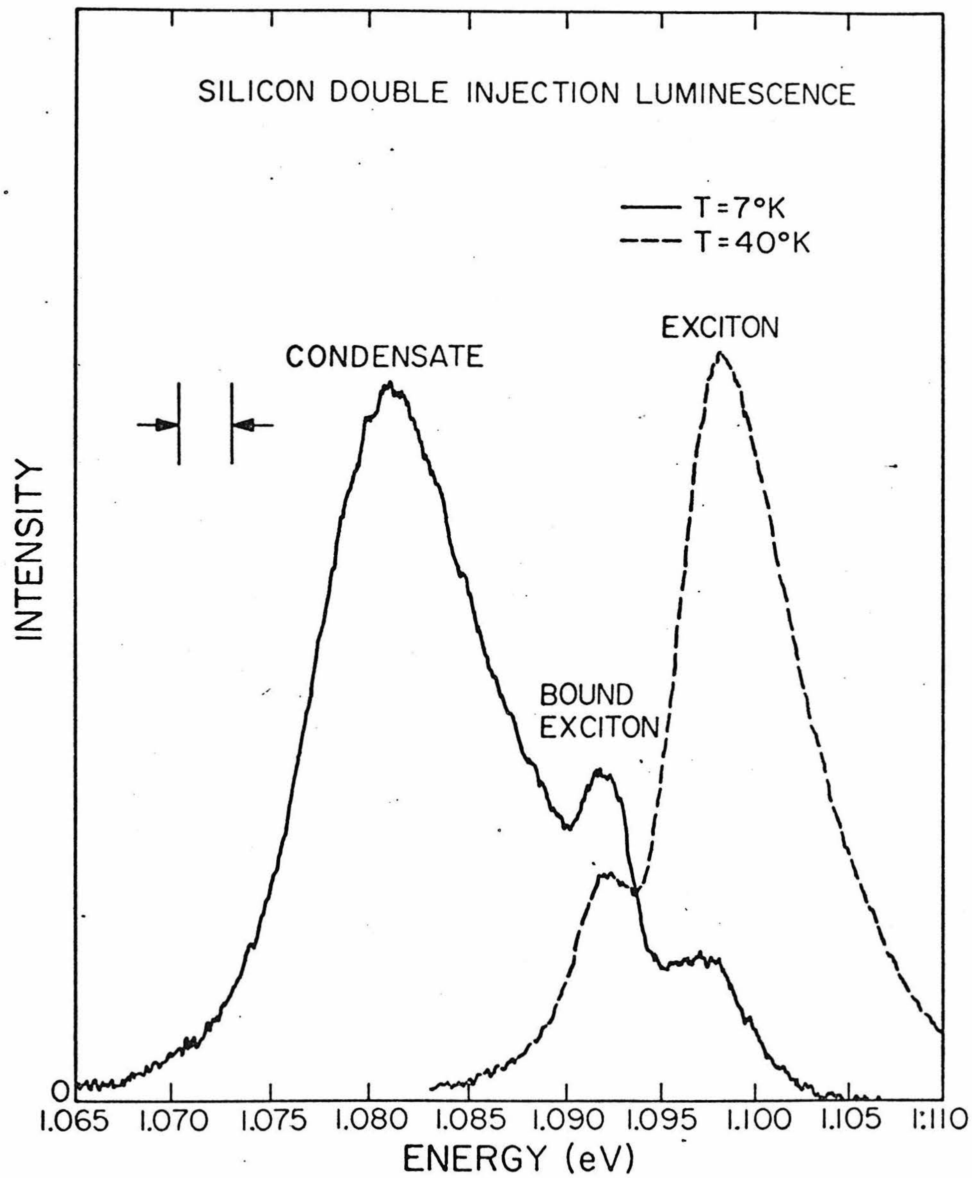
III. RESULTS

Spectral data was taken for the double injection studies at temperatures between 5 and 16°K, and at current densities of 0.2 - 40.0 A/cm^2. The strong LO-TO phonon assisted recombination radiation contained lines due to recombination of electrons and holes from several states: free excitons (FE), bound excitons (BE), bound multi-exciton complexes (MEC), and electron-hole condensate (EHD). Before discussing the results of the condensate luminescence study, it is appropriate to illustrate the main features of the low temperature recombination radiation spectra. Figure 20 shows double injection spectra taken at 7°K and at 40°K. The low temperature spectrum is taken at 10 A/cm^2 which is above the current threshold for electron-hole condensate formation. It shows three prominent lines due to LO-TO phonon assisted recombination from condensate (at 1.082 eV), bound exciton (at 1.092 eV), and free exciton (at 1.097 eV) states. At higher temperatures, as seen in the 40°K spectrum taken at 2 A/cm^2, the free exciton luminescence broadens and becomes more intense, the condensate luminescence disappears, and the bound exciton luminescence is diminished. The bound exciton was not observed above 60°K while the free exciton was observed at temperatures up to 120°K.

Using the luminescence model for the radiative recombination of electrons and holes in the electron-hole condensate in Si, it is possible to calculate the luminescence lineshape for LO-TO phonon assisted recombination from this state. Since the electron-hole liquid lineshape is a function of temperature and density, the pair density of the condensate may be determined by fitting the calculated lineshape to the experimental spectrum. We have used this technique, which is described in detail in reference 11, to

Figure 20. LO- and TO-phonon assisted recombination radiation spectra from a Si double injection device at 7°K (solid line) for a device current of 1 amp and at 40°K (dashed line) for a device current of 200 ma. The vertical scales are not the same for these spectra. Luminescence due to electron-hole droplet (EHD), bound excitons (BE), and free excitons (FE) are observed.

FIGURE 20


SILICON DOUBLE INJECTION LUMINESCENCE
T=7°K
T=40°K
CONDENSATE
EXCITON
BOUND EXCITON
INTENSITY
0
1.065 1.070 1.075 1.080 1.085 1.090 1.095 1.100 1.105 1.110
ENERGY (eV)

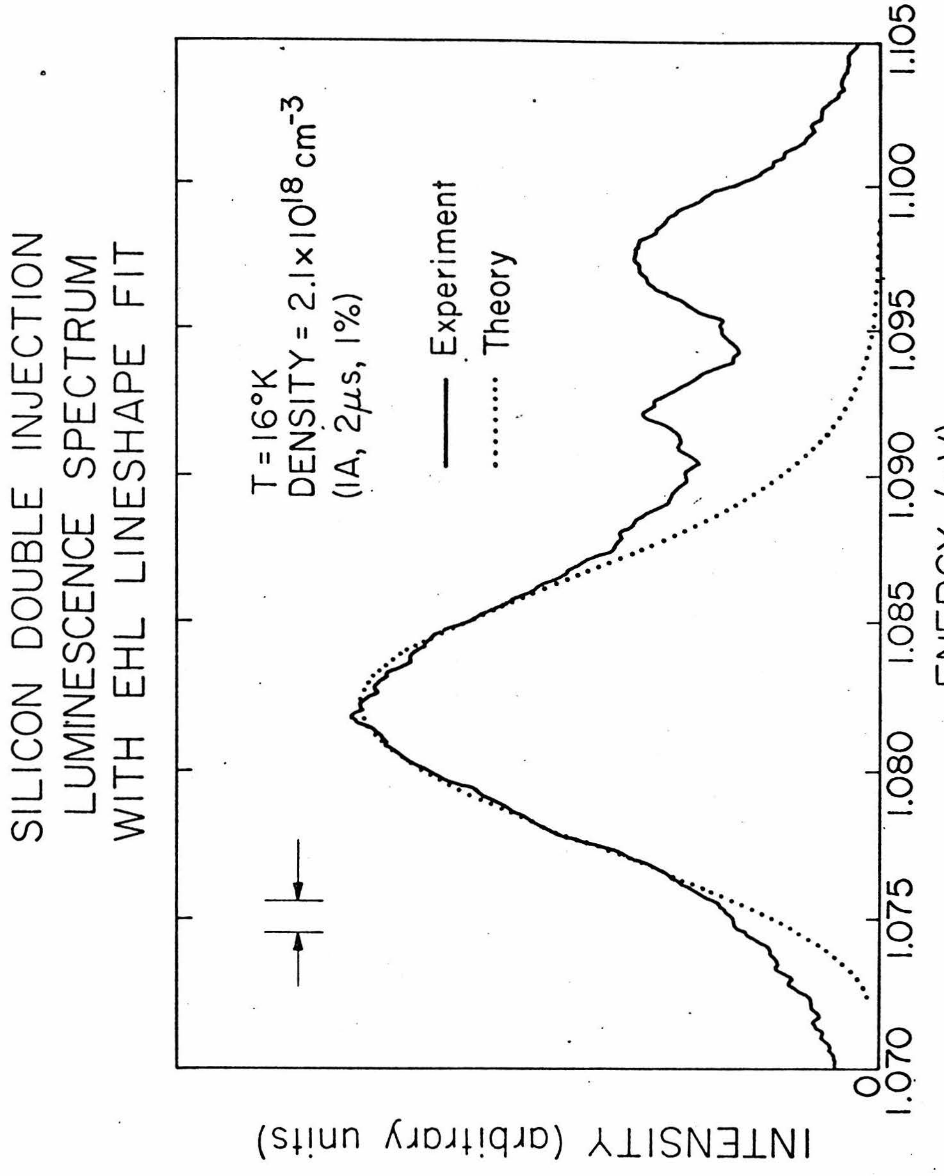
determine the density of the electron-hole liquid in Si double injection devices, laser excited pure Si, and laser excited Li doped Si.

Figure 21 shows a condensate line fit to a double injection spectrum at 16°K. The fit yields a condensate density of 2.1 x 10^{18} cm^{-3}. This value is significantly smaller than the density obtained from fitting condensate lineshapes from laser excited high-purity Si, ~ 3 x 10^{18} cm^{-3}.(11) Figure 22 shows a double injection luminescence spectrum at 7°K taken below the current threshold for electron-hole condensate formation. The specturm has three lines: a weak free exciton line at 1.097 eV, a strong bound exciton line at 1.092 eV, and a line at 1.088 eV. This third line corresponds closely to a line observed by Sauer(8) at low temperature and low excitation levels in the photoluminescence of doped Si. He attributed it ot recombination from bound multi-exciton complexes. The presence of bound exciton lines and bound multi-exciton complex lines in the double injection spectra suggest the influence of dopant impurities. Dopants may also account for the discrepancy in the double injection condensate density compared with the density observed in photoluminescence experiments on high purity Si.(9)

Dopant impurities are introduced into the contact regions of the double injection device during device fabrication as explained in Section II. The Al alloy only dopes to a depth of ~ .2 μ whereas we can expect from simple diffusion theory that the Li diffusion will dope as high as 10^{16} cm^{-3} at a

Figure 21. LO- and TO-phonon assisted recombination radiation from a Si double injection device at 16°K. The condensate luminescence is fit with a lineshape calculation (dotted line) giving a density of 2.1×10^{18} cm^{-3}.

FIGURE 21


SILICON DOUBLE INJECTION
LUMINESCENCE SPECTRUM
WITH EHL LINESHAPE FIT
T = 16°K
DENSITY = 2.1×10^18 cm^-3
(IA, 2μs, 1%)
Experiment
Theory
INTENSITY (arbitrary units)
0
1.070
1.075
1.080
1.085
1.090
1.095
1.100
1.105
ENERGY (eV)

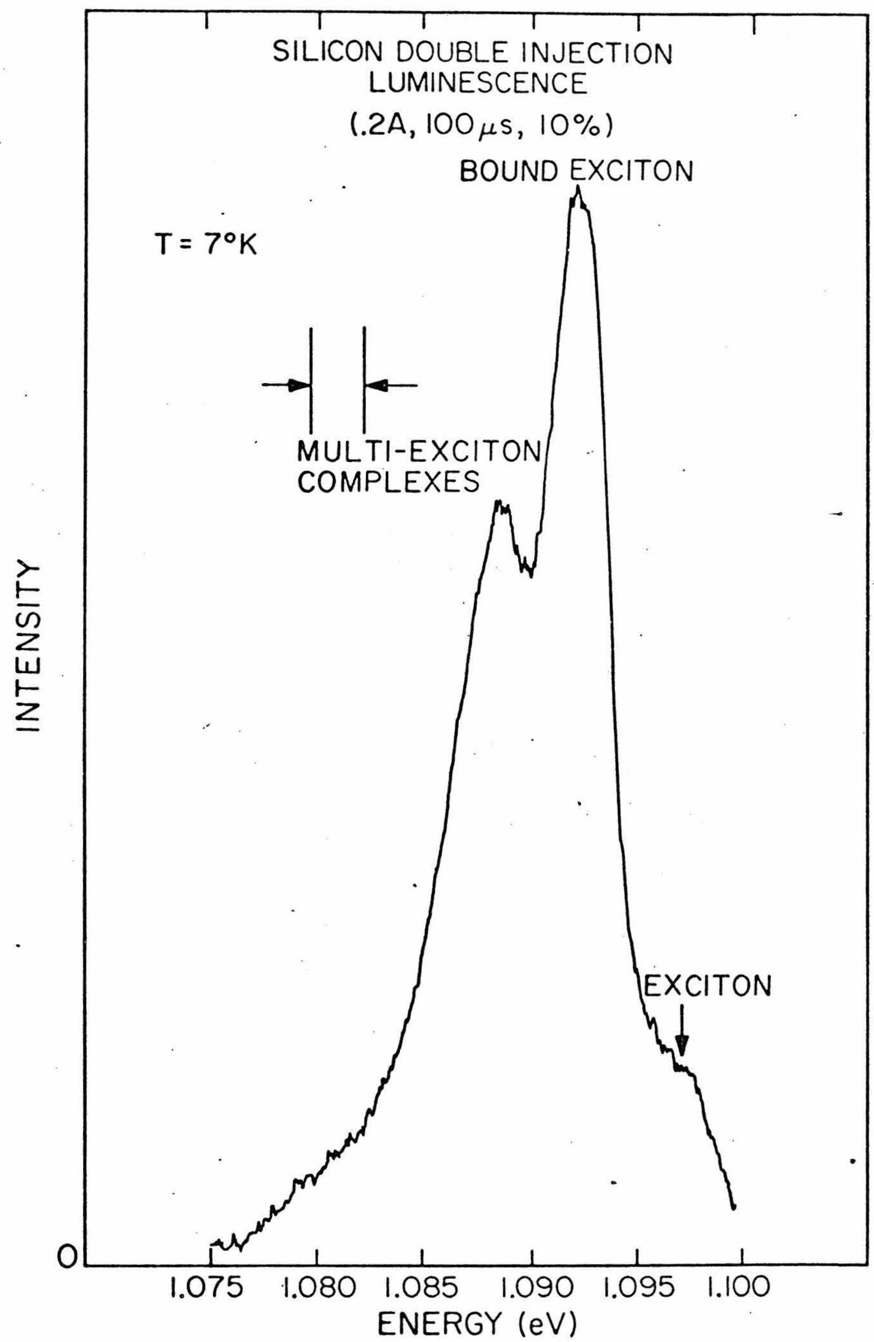


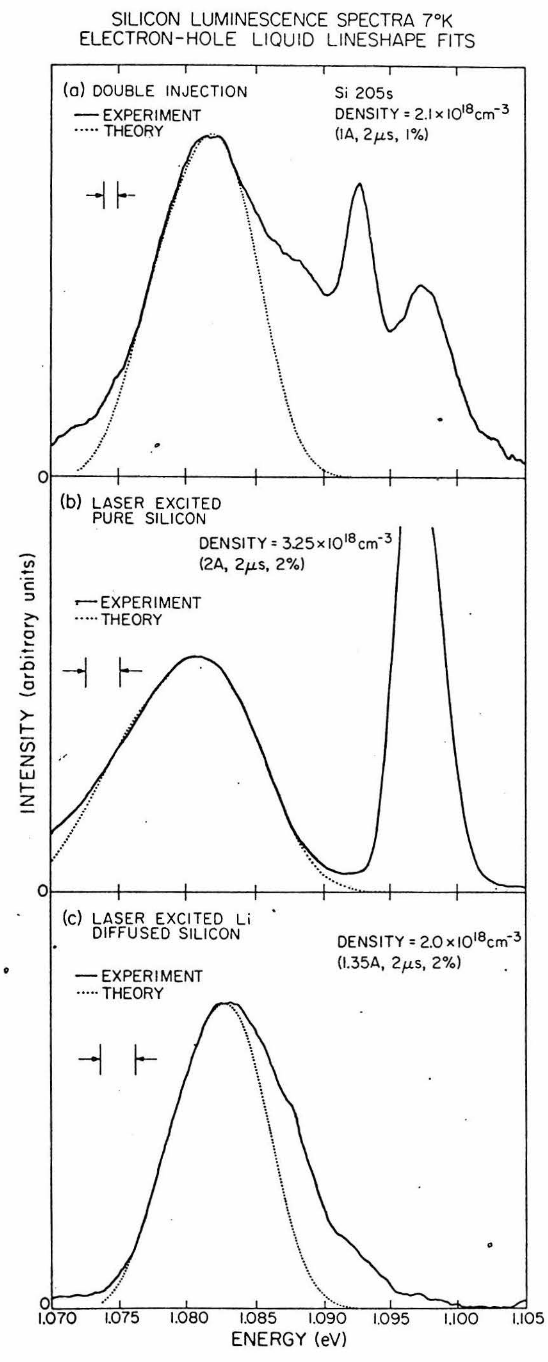
Figure 22 LO- and TO-phonon assisted luminescence from a SI double injection device showing lines due to recombination from free excitons (FE), bound excitons (BE), and bound multi-exciton complexes (MEC). The device current is 200 ma.

depth of 200 μ into the Si crystal.[12] Because of this relatively large amount of Li, we might expect to see some effect from it in the luminescence. To investigate the effects of Li in the low temperature Si recombination radiation, we performed laser excitation experiemnts on a Si crystal with a Li diffusion identical to that used to form the n-contact in the double injection diodes. We compared spectra from these experiments with double injection spectra and laser excited high-purity Si spectra.

Figure 23 shows three representative spectra: one from double injection, one from laser excited high purity Si, and one from laser excited Li diffused Si. Each spectrum is taken at 7°K. The double injection spectrum (top curve) shows an electron-hole liquid line with some structure on the high energy side due to bound multi-exciton complex recombination. (This is the same luminescence seen at 1.088 eV at lower excitation in Fig. 22.) In addition, there is a bound exciton line, and a free exciton line. In contrast with this double injection spectrum, the laser excited high purity Si spectrum (middle curve) shows a broader electron-hole liquid line and a very strong free exciton line. The laser excited Li diffused Si spectrum (lower curve) has many features in common with the double injection spectrum. In the spectrum taken on Li diffused Si, there is a narrow electron-hole liquid line with some structure on the high energy side due to multi-exciton complex recombination. Also, the exciton luminescence, both bound and free, is weak.

Figure 23. LO- and TO-phonon assisted recombination radiation from (a) Si double injection device, (b) laser excited, high-purity Si, and (c) laser excited, Li doped Si. The intensity scales are not the same for the three spectra. The dotted lines are calculations of the condensate lineshapes.

FIGURE 23



SILICON LUMINESCENCE SPECTRA 7°K
ELECTRON-HOLE LIQUID LINESHAPE FITS
(a) DOUBLE INJECTION
— EXPERIMENT
····· THEORY
Si 205s
DENSITY = 2.1×10^18 cm^-3
(1A, 2μs, 1%)
(b) LASER EXCITED
PURE SILICON
DENSITY = 3.25×10^18 cm^-3
(2A, 2μs, 2%)
— EXPERIMENT
····· THEORY
(c) LASER EXCITED Li
DIFFUSED SILICON
DENSITY = 2.0×10^18 cm^-3
(1.35A, 2μs, 2%)
— EXPERIMENT
····· THEORY
INTENSITY (arbitrary units)
0
0
0
1.070
1.075
1.080
1.085
1.090
1.095
1.100
1.105
ENERGY (eV)

We note five important qualitative differences between the laser-excited high purity Si spectrum, and the other two spectra in Fig. 23. The double injection and Li doped spectra each show (1) the low energy threshold of the electron-hole liquid line at a higher energy than in the high purity Si case, and (2) a narrower electron-hole liquid line. In addition, (3) the free exciton luminescence is weak and (4) a bound exciton line is present along with (5) luminescence due to bound multi-exciton complexes.

Comparison can be made of the condensate luminescence in these spectra by fitting the experimental lineshapes and thus, determine the condensate densities produced in these experiments. This line fitting analysis was performed and the results are summarized in Fig. 24. This graph also includes the results of high purity Si laser excitation luminescence lineshape fits from reference 11, along with the results of condensate lineshape fitting to spectra at temperatures other than 7°K. The densities obtained from double injection spectra are in agreement with the densities obtained from the laser excitation of Li diffused Si and are very different from condensate densities in laser excited, high purity Si.

Since it is possible to introduce impurities into the Si crystal merely by the heat treatments used during contact formation in the double injection devices, we put a Si crystal through these heating steps without introducing either Li or Al. During laser excitation this crystal produced

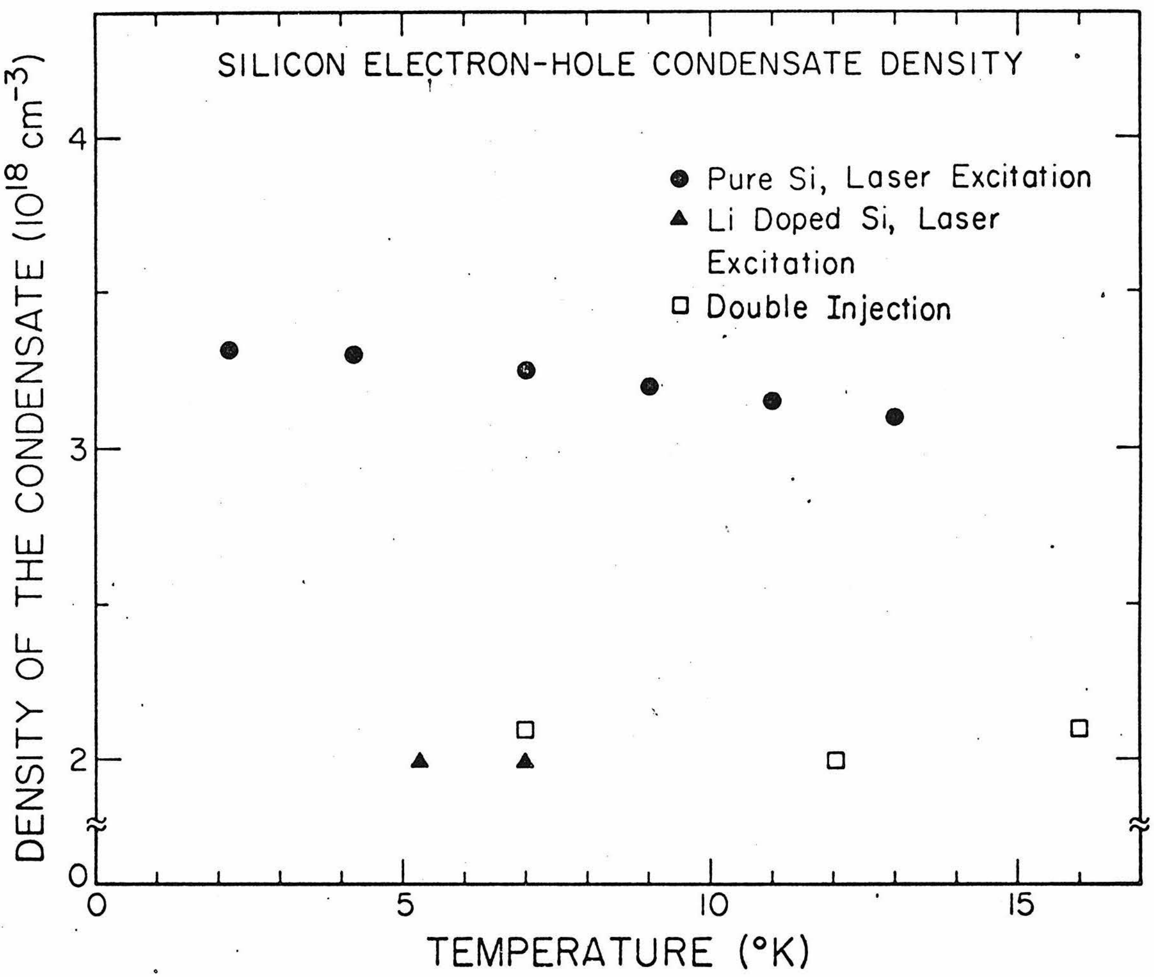
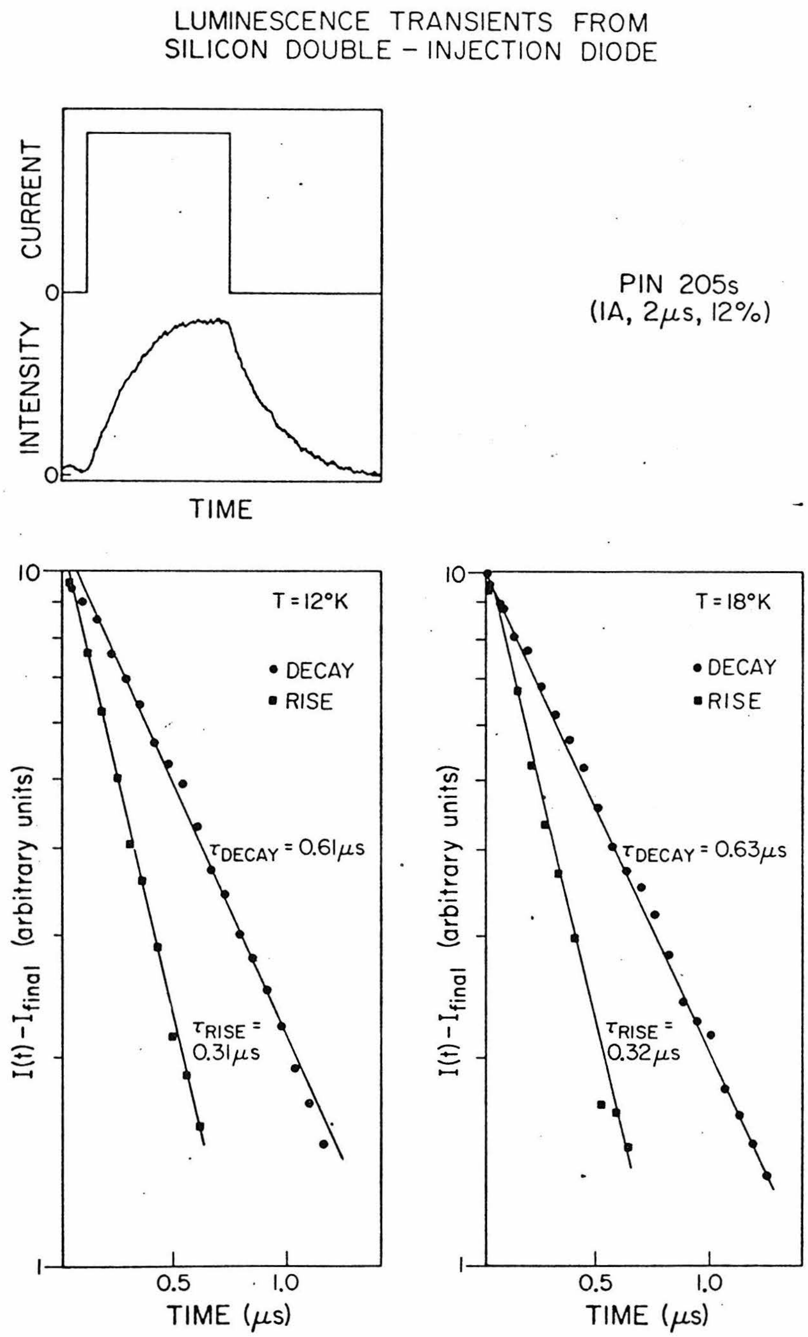


Figure 24. Condensate densities from luminescence lineshape fits of LO- and TO-phonon assisted condensate recombination radiation in Si.

Figure 25. LO- and TO-phonon assisted condensate luminescence transients from a Si double injection device. The device was pulsed with a square current pulse as shown in the top of the figure. The condensate luminescence shows an exponential rise during the pulse and an exponential fall after the pulse. The rise and decay transients of the condensate luminescence are plotted on log-linear plots for 12°K and 18°K. The vertical axis in each case is a log scale.

FIGURE 25



LUMINESCENCE TRANSIENTS FROM
SILICON DOUBLE - INJECTION DIODE
CURRENT
INTENSITY
0
0
TIME
PIN 205s
(1A, 2μs, 12%)
10
1
I(t) - I_final (arbitrary units)
T = 12°K
• DECAY
▪ RISE
τDECAY = 0.61μs
τRISE = 0.31μs
0.5
1.0
TIME (μs)
10
1
I(t) - I_final (arbitrary units)
T = 18°K
• DECAY
▪ RISE
τDECAY = 0.63μs
τRISE = 0.32μs
0.5
1.0
TIME (μs)

luminescence spectra identical with those from unheated, high purity Si.

Finally, the transient rise and fall of electron-hole condensate luminescence from Si double injection devices was measured. The condensate luminescence decay from Si double injection diodes shows a pure exponential character with a characteristic lifetime of ~ 0.6 μs as shown in Fig. 25. The rise in the condensate luminescence also follows an exponential. The 0.6 μs decay lifetime is significantly longer than condensate lifetimes observed in laser excitation experiments on high purity Si. These lifetimes are < 0.2μs.[1,15] Measurements of condensate luminescence decays from laser excited Li diffused Si also show lifetimes ~0.6 μs in agreement with the double injection results.[16]

IV. CONCLUSIONS

We have shown that the electron-hole condensate can be produced in Si by current injection from p^+ and n^+ doped contacts. The environment of the excited region of a double injection device differs from that in a laser excitation experiment in several ways. Double injection is a bulk excitation method whereas, laser excitation generally occurs at or near a crystal surface. Also, there is current flow and electric field in a double injection device although there may also be fields in a region of laser excitation due to the presence of a nearby surface. Finally, there are dopant impurities introduced into the semi-conductor to form the p^+ and n^+ contacts in a double injection device. We might expect that any of these differences would alter the luminescence properties of Si excited by double injection compared to the luminescence properties of laser-excited Si. Effects due to all of these differences may be present in our spectral data.

Although our results do not permit us to comment on the effects of current flow, electric field, and bulk excitation in double injection; we have strong evidence of the influence in the luminescence of Li introduced into the devices during the formation of the n^+ contact. Luminescence spectra in double injection and in laser excitation of Li doped Si show all the same qualitative features and also indicate that similar electron-hole condensate densities are produced in these two experiments. Also, the condensate luminescence decays show the same long characteristic lifetime in these two cases. Despite these similarities, however, it is apparent that there are some differences between double injection spectra and laser excitation spectra of Li doped Si. These differences are in the intensities of the observed luminescence lines. Although these differences may be due to the presence of current flow and electric field in the double injection device, they may also be simply due to differences in excitation level. Also, the region of excitation in the Si is different in these two cases and may account for the observed differences. The GaAs laser only excites a region ~ 50 μ deep into the Li-diffused Si, whereas double injection excited the entire region between the contacts.

In summary, although we have demonstrated that double injection can be used to produce the electron-hole condensate in Si, impurities introduced during our device fabrication have important effects in the spectra.

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APPENDIX

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CONDENSATION OF INJECTED ELECTRONS AND HOLES IN SILICON*†

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(*Received* 5 *February* 1974 *by H. Suhl*)

We report that the condensed electron–hole phase in silicon has been produced by electrical carrier injection. The condensed phase recombination radiation occurred at 1.082 ± 0.001 eV with a linewidth of 0.012 eV. Hence the line position and linewidth appear to be independent of whether the semiconductor is excited by optical or electrical injection. Joule heating is shown to be important by analyses of time resolved recombination radiation spectra and double pulse experiments.

IT IS well established that at low temperatures non-equilibrium electrons and holes in silicon and germanium undergo a phase transition from an exciton gas to a metallic liquid.[1–4] Whereas other experimental groups have employed optical excitation to study these phenomena, in a previous letter we reported that the condensed phase of electrons and holes had been produced in germanium by electrical injection of the holes and electrons from *p* and *n* doped contacts.[5] While the condensate in silicon is in some ways analogous to that in germanium,[2] there are significant differences. The density of electron–hole pairs is more than an order of magnitude higher and the lifetime of electrons and holes in the condensate is much shorter in silicon than in germanium.[2] These differences suggest that higher injection efficiencies would be required to produce the condensate in silicon. In this letter we report that by injection techniques the condensed electron–hole phase has been produced in silicon. We also report the results of time resolved luminescence and double pulse experiments on silicon which show the importance of device heating.[6]

The silicon devices, fabricated from ~ 10 kΩ cm material, were typically 2 mm × 1 mm × 1.2 mm long, with injecting aluminium alloyed *p* contacts and lithium diffused *n* contacts on opposing faces. Similar devices have been used to study double injection phenomena in silicon at higher temperatures.[7] The recombination radiation was analyzed using a Spex 1400–II spectrometer, S-1 photo-multiplier at dry ice temperature, lock-in amplifier and signal averager.

Figure 1 shows the phonon assisted recombination radiation spectra due to free excitons, and electrons and holes in the condensed phase produced by current injection. The spectrum labeled 23°K was obtained while the device was in an ambient atmosphere at 23°K; current pulses with an amplitude of 180 mA and a duration of 50 μsec were passed through the sample with a repetition rate of 750 Hz. The applied voltage was approximately 19 V. The spectrum labeled 1.8°K was obtained while the device was in a bath at 1.8°K; and current pulses with an amplitude of 210 mA and a width of 50 μsec were passed through the sample with a repetition rate of 400 Hz. The applied voltage was approximately 40 V. The spectra were obtained by integrating throughout the current pulse.

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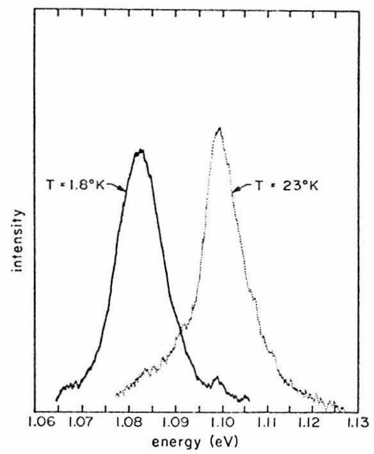

FIG. 1. Recombination radiation spectra from a silicon device in an ambient atmosphere at 23°K (dotted line) and in a bath at 1.8°K (solid line). The peaks at 1.098 ± 0.001 eV and 1.082 ± 0.001 eV are due to the LO–TO phonon assisted recombination of free excitons and condensed electron–hole phase, respectively.

The 23°K spectrum exhibits a peak at 1.098 ± 0.001 eV which is due to the LO–TO phonon assisted recombination radiation of the free exciton. The 1.8°K spectrum also shows a small peak at this energy but, more importantly, exhibits a peak at 1.082 ± 0.001 eV with a width of 0.012 eV. A peak at this energy with the same width has been observed previously in experiments in which the silicon was excited optically,[2] and has been identified with the LO–TO phonon assisted recombination of electrons and holes in the condensed phase with a carrier concentration of approximately 3×10^{18} cm^{-3}. The agreement between optical excitation and carrier injection experiments are consistent with the formation of a condensed phase whose properties are independent of the method of excitation.

The linewidth and peak position of the condensed phase radiation for short duration pulses also appear to be independent of the level of injection. They were the same over a two orders of magnitude change in current level in experimental situations in which little sample heating is observable. An increase in current is found to cause only an increase in the intensity of recombination radiation. If the density and other properties of the condensed phase are fixed

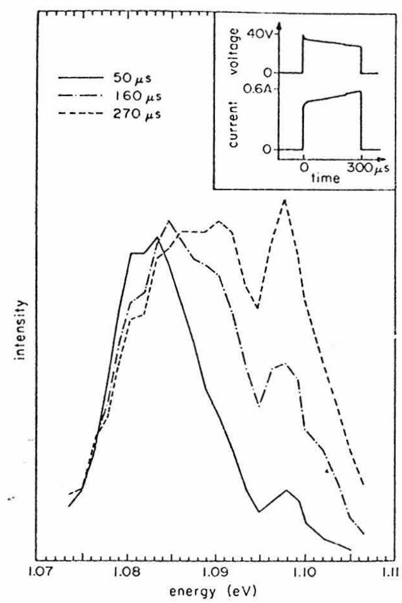

FIG. 2. Time resolved recombination radiation from a silicon device in a helium bath at 2.0°K pulsed with a 300 μsec, 600 mA current pulse at a repetition rate of 100 Hz. The recombination radiation spectra is shown for (a) 50 μsec, (b) 160 μsec and (c) 270 μsec after the beginning of the current pulse. Insert shows the current through the device and the voltage across the device. See discussion in text.

by the temperature, an increase in current corresponds to an increased amount of condensate.

Heating of the device during a single injection pulse was explored by measuring the recombination radiation spectrum as a function of time. The time resolved spectra shown in Fig. 2 were obtained by monitoring the radiation as a function of time at a fixed wavelength. The signal was sampled at a wavelength interval of 10 Å. The optical signal from the spectrometer was detected with the photo-multiplier set at a rise time of 40 μsec and processed by a signal averager using a 10 μsec gate. The silicon devices were pulsed with 600 mA, 300 μsec current pulse repeated at 100 Hz. The insert shows the current and voltage. Similar spectra were obtained at several other combinations of currents, pulse widths, and repetition rates.

One observes three distinct changes in the spectra with increasing time after the onset of the current pulse: (a) an increase in the exciton line intensity; (b) a shift of the condensed phase line to higher energies; and (c) a broadening of the condensed phase line. All three features can be explained in terms of device heating given the generally accepted model of a first order phase transition between an exciton gas and a metallic electron–hole liquid. The exciton line intensity is proportional to the number of excitons in the sample, and in a first order transition the number of excitons in equilibrium with the condensate increases with increasing temperature. The energy of the condensed phase recombination line is correlated with its binding energy, and in a first order transition the magnitude of the binding energy decreases with increasing temperature resulting in a lineshift to higher energies as observed. The lineshape of the condensed phase radiation is determined by the energy distribution of the carriers in the condensate, and in a Fermi liquid this distribution should spread with increasing temperature resulting in the observed broadening. Such temperature dependent line positions[8] and linewidths[9] have already been reported for optically excited germanium.

Further evidence for device heating during a single current pulse was obtained from double pulse experiments. An initial current pulse was followed at a later time with a second pulse. With the two pulses close together we observed an increase in the exciton recombination radiation intensity in the second pulse compared to the first. With the two pulses widely separated the radiation spectra were the same in each pulse. The increase in exciton intensity in the second pulse cannot be explained by carriers left in the device after the initial pulse since the pulse separation was always much larger than any characteristic decay times of either excitons or condensed phase.[2]

We conclude that the electron–hole condensate in silicon can be produced by electrical injection and that the condensed phase recombination radiation is the same as obtained when the condensed phase is produced by optical excitation. In light of similar results for germanium[5,6] we conclude that electrical injection offers a viable method for studying the collective properties of electrons and holes in semiconductors at low temperatures. Device heating must be taken into account in interpreting the spectra, but this also offers the opportunity to explore the kinetics associated with the phase transition.

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Nous reportons la production d'une phase condensée electron–trou par injection de porteurs électriques. La radiation de recombinaison de la phase condensée apparait à 1.082 ± 0.001 eV avec une largeur de raie de 0.22 eV. Ainsi la position et la largeur de la raie semblent être indépendantes d'une exitation du semi-conducteur par injection optique ou électrique. L'importance de l'effet joule est montré par analyses de la résolution temporelle du spectre de radiation de recombinaison et par des expériences à double impulsion.