

zero field from $t=0$ to $t=\Delta t$ is obtained analytically from the classical Smoluchowski equation. For a given time delay, the quantum efficiency is then obtained by quadrature from Eq. (1). Typical curves for the quantum efficiency at various field strengths and thermalization distances r_0 are shown in Ref. 8, where the evolution from $\eta(E)$ to $\eta(0)$ is shown as a function of the time delay.

Fitting the PVK data by this theoretical model gives the solid lines shown in Fig. 2, with $D \sim 10^{-16}$ cm²/sec for $T=293$ K and $D \sim 10^{-14}$ cm²/sec for $T=373$ K. These small values of the diffusion constants mean that in zero applied field the charge carriers are essentially immobile, and we are close to the "Anderson limit,"⁹ where the disorder in the system precludes any diffusion at all. The small values of the mobilities we deduce from this experiment are perhaps not inconsistent with the known fact that hole drift mobilities in PVK are strongly field dependent, ranging from 10^{-7} cm²/V sec at 10^5 V/cm to 10^{-9} cm²/V sec at 10^4 V/cm,¹⁰ although the actual value at zero field is not known. Nevertheless, it is difficult to understand why the carriers do not have a larger diffusion constant in the presence of their mutual Coulomb field. A possible answer is that the number of paths available for geminate recombination to take place at rather small values of r_0 (25 Å) is severely reduced by the local disorder, whereas the number of paths available for dissociation by the external electric field is

not affected to the same extent.

In conclusion, we believe that it is an exciting development to be able to resolve the photogeneration process in some systems by a relatively simple experimental technique, and that these preliminary results should stimulate further experimental and theoretical work in this area.

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Instability of the Electron-Hole Plasma in Silicon

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It is shown that the electron-phonon interaction in covalent semiconductors drives an instability in the electron-hole plasma at high temperature. The instability might be the reason for melting of tetrahedrally bound semiconductors. If this is true, the intrinsic carrier concentration of silicon at the melting temperature would be of the order of 10^{21} cm⁻³ instead of the commonly accepted value of 2×10^{19} cm⁻³.

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In the last few years, there has been a large amount of work¹⁻⁹ induced by the discovery of laser annealing for ion-implanted semiconductors, which is a promising technique in microelectronics. However, the actual mechanism responsible for annealing is still rather controversial.⁶⁻⁸ The

problem is to know if the laser pulse is essentially heating the sample which simply melts or if the electron-hole (e-h) pairs created by the laser generate a new fluidlike state.⁸

Previous work^{9,10} on the electron-phonon interaction has shown that if a certain fraction α of the

total number n_0 of valence-band electrons are excited into the conduction band, then the frequency of the TA phonon, responsible for the stability of the crystal, goes to zero and the crystal should become fluid. This softening of the TA phonon mode has been used to explain the observed band-gap variation with temperature.

In this Letter, we want to show that the softening of the TA phonon mode produces an instability leading to a first-order phase transition which can be the one observed in the melting.¹⁰ The instability temperature T^* depends essentially on two parameters, the electron and hole (e-h) masses and the electron-phonon coupling, the last one being related to the decrease of the gap with temperature. Unfortunately, these quantities are unknown at temperatures close to the melting one, and seem difficult to obtain. With their values at room temperature, T^* is of order 2000 K.

One of the most striking consequences of this theory is the value of the intrinsic carrier density which, up to now, has been believed to be of order $2 \times 10^{19} \text{ cm}^{-3}$ at the melting point by extrapolation of a well-known formula true only in the classical limit. If the e-h plasma instability is the reason for melting, we predict at the melting point an intrinsic carrier density as high as 10^{21} cm^{-3} .

One can calculate the variation of T^* when an extra amount of e-h pairs is introduced in the system. One finds that the radiation beams usually used in annealing do not create enough e-h pairs to produce a sizable modification of the instability temperature. This theory also shows that a tetracoordinated solid with a high plasma density (say above 10^{21} cm^{-3}) is unstable and therefore cannot exist.

In order to show that the softening of the TA phonon modes by the e-h pairs leads to a phase transition, one can consider the free energy F of a crystal having N_a atoms in a volume V , at temperature T , in the presence of N e-h pairs. The phonon contribution to the free energy has the form

$$\sum kT \ln(1 - e^{-\hbar\omega/kT}) \sim \sum kT \ln(\hbar\omega/kT) \quad (1)$$

for $\hbar\omega \ll kT$, which is true at large T . The ω are the phonon frequencies. For the TA mode, their variation with the e-h density $n = N/V$ can be written as⁹

$$\omega(q, n) = \omega_0(q)(1 - \alpha n/n_0), \quad (2)$$

where $n_0 = N_a/V = 5 \times 10^{22} \text{ cm}^{-3}$ is the density of Si atoms. As $4n_0$ is the density of valence-band electrons, $(4\alpha)^{-1}$ is the fraction of those electrons

necessary to soften the TA mode. Using (2) in Eq. (1), one finds that the phonon free energy contains an n -dependent part

$$\Delta F_{e-ph} = N_a kT \ln(1 - \alpha n/n_0), \quad (3)$$

which will contribute to the e-h pair chemical potential, giving an additional term

$$\frac{\partial(\Delta F_{e-ph})}{\partial N} = - \frac{\alpha kT}{1 - \alpha n/n_0}. \quad (4)$$

If one neglects the Coulomb interaction, negligible compared to the kinetic part at densities higher than 10^{19} cm^{-3} , then the e-h pair chemical potential $\mu = \partial F / \partial N$ is

$$\mu(n, T) = E_{G0} - \frac{\alpha kT}{1 - \alpha n/n_0} + \mu_e + \mu_h, \quad (5)$$

where E_{G0} is the band gap (1.17 eV for Si) and μ_e and μ_h are the chemical potentials of a free electron and hole gas of density n at temperature T . They are related to n by

$$\begin{aligned} \frac{n}{n_G} &= g_e m_e^{*3/2} \left(\frac{kT}{E_{G0}} \right)^{3/2} F \left(\frac{\mu_e}{kT} \right) \\ &= g_h m_h^{*3/2} \left(\frac{kT}{E_{G0}} \right)^{3/2} F \left(\frac{\mu_h}{kT} \right), \end{aligned} \quad (6)$$

with

$$F(y) = \int_0^\infty dx \sqrt{x} / (e^{x-y} + 1) \quad (7)$$

and

$$n_G = 2\pi (2mE_{G0}/h^2)^{3/2} = 4.5 \times 10^{21} \text{ cm}^{-3}, \quad (8)$$

m_e^* and m_h^* being the electron and hole effective masses and $g_{e,h}$ their degeneracies.

At thermal equilibrium, the e-h pair density adjusts itself such that the free energy is minimum, i.e., $\partial F / \partial N = \mu = 0$. μ is negative for low n as usual but also, because of the softening of the TA phonon modes, for $n \lesssim n_0/\alpha$; so that, at low T , $\mu = 0$ for two densities as shown in Fig. 1. The lowest one, associated with a minimum of F , corresponds to the well-known intrinsic carrier density

$$\begin{aligned} n(T) &= n_G (g_e g_h m_h^{*3/2} m_e^{*3/2})^{1/2} \\ &\quad \times \exp[-E_G(T)/2kT], \end{aligned} \quad (9)$$

with

$$E_G(T) \simeq E_{G0} - \alpha kT. \quad (10)$$

The second zero of μ corresponds to a maximum of F and leads to an unstable state.

When T increases, this oscillation of F is smoothed and finally disappears above a certain

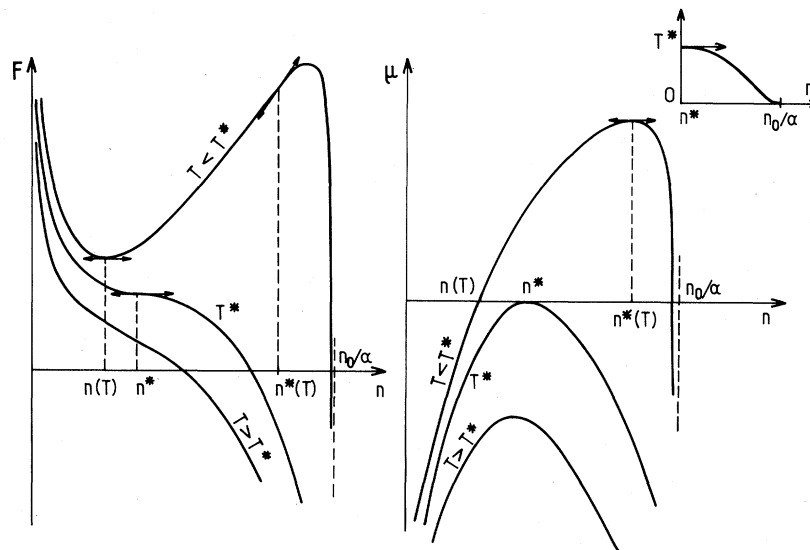


FIG. 1. The variation of the free energy F and the e-h pair chemical potential $\mu = \partial F / \partial N$ as a function of the e-h pair density, above and below the instability temperature T^* . Inset: the variation of this instability temperature when an extra amount of e-h pairs is created by laser radiation.

temperature T^* , the equilibrium carrier density $n(T)$ increasing up to n^* such that

$$\mu(n^*, T^*) = 0 = \partial \mu / \partial n |_{n^*, T^*}. \quad (11)$$

At higher T , there is no longer a stable equilibrium density, and the system undergoes a first-order phase transition at T^* . That effect is due to the decrease of the TA phonon frequency and n^* has to be a sizable fraction of n_0/α . α can be related to the variation of the gap via Eq. (10). Measurements of the temperature variation $E_G(T)$ have been made up to 400 K,¹¹ which is low compared to the Debye temperature of 645 K. The fit of $E_G(T)$, made at low T , would give $\alpha \sim 6.5$ for the linear term, but the linear regime is not yet reached at 400 K, and in the range 1500–1700 K, α could be modified by the expansion of the crystal. The electron and hole effective masses are also expected to vary with T , but they have not been measured at high temperature. A solution for Eq. (11) is obtained for $T^* = 1700$ K by taking $\alpha = 9.5$ and the masses as for $T = 0$ or by taking $\alpha = 7$ with the masses having twice their values at $T = 0$ ¹²; the equilibrium carrier density is found in all cases to be between $(1 \text{ and } 2) \times 10^{21} \text{ cm}^{-3}$, i.e., outside the classical limit where Eq. (10) is valid (one has $\mu/kT \sim 1$).

If the crystal is linked to an e-h source, which can be a laser or an electron beam, the system is no longer isolated and the equilibrium density is different from the value $n(T)$ given by $\mu = 0$. With an e-h generation rate¹³ G , the carrier den-

sity will be larger than $n(T)$ and is such that

$$dn/dt = 0 = G - n/\tau(n) + n/\tau(n(T)). \quad (12)$$

$\tau(n)$ is the e-h lifetime, which depends on the plasma density¹⁴; the last term of Eq. (12) describes the thermal dissociation. Since the e-h source is a kind of reservoir with a chemical potential μ_{ext} , the appropriate free energy one has to consider is now $\bar{F} = F - \mu_{\text{ext}}N$, leading to the equilibrium condition $\mu(n, T) - \mu_{\text{ext}} = 0$. The new instability temperature $T^*(G)$, for a generation rate G , is obtained when the solution $n(G, T)$ of Eq. (12) corresponds to the density $n^*(T)$ of the inflection point of F (see Fig. 1). As $\Delta n = n^*(T) - n(T)$ increases when T decreases, the instability temperature decreases when G increases as expected. At very low T , the inflection point and the maximum of F are very close to n_0/α , so that the instability temperature goes to zero for a generation rate leading to a carrier density equal to n_0/α . More generally, one expects a sizable decrease of the instability temperature if the laser can add to the preexisting plasma a comparable amount of e-h pairs, i.e., a few n^* more.¹⁵ By an expansion of the free energy around (T^*, n^*) , one finds that the instability temperature as a function the extra amount of e-h pairs created by the laser has a horizontal tangent around T^* (see Fig. 1), in contradiction with what one gets from the Lindemann criterion.⁷ This is due to the fact that the Lindemann criterion applies to a transition temperature, which corresponds to

a minimum of the free energy, while at the instability temperature the first and second derivatives of F cancel.

In summary, we have shown that, because of electron-phonon coupling, the tetrahedrally coordinated semiconductors undergo a plasma instability at high temperature which could be the cause of melting. For the case of silicon, we find that the electron-hole pair density near melting is much higher than the one predicted by the classical formula $n = (N_c N_v)^{1/2} \exp[-E_G(T)/2kT]$. The creation of a high-density electron-hole plasma by an external source decreases the instability temperature so that the crystal will melt at lower T .

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¹²The masses would decrease with T for a direct gap, which is not the case for Si.

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¹⁴The Auger effect gives $1/\tau(n) = Cn^2$ with $C = 4 \times 10^{-38} \text{ cm}^6 \text{ s}^{-1}$. But, at very high density, one can even expect a four-particle process.

¹⁵With the Auger lifetime, G would be of the order of $10^{33} \text{ cm}^{-3} \text{ s}^{-1}$.

Solitons in Charge- and Spin-Density-Wave Systems

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A unified description of solitons in both charge-density-wave (CDW) and spin-density-wave (SDW) systems is presented within Hartree-Fock theory. Spin-carrying solitons correspond to a localized SDW region within a CDW ground state or vice versa. Solitons can have a fractional spin component when the CDW and SDW coexist in the ground state. In particular, a SDW in an odd-order commensurate system must coexist with a CDW and solitons have an irrational spin component.

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The ground state of most quasi-one-dimensional (1D) conductors is either a charge-density wave (CDW) or a spin-density wave (SDW).¹ The CDW system has been extensively studied and a variety of nonlinear soliton-type excitations were found.²⁻¹⁰ The present work extends these theories to include also a SDW order parameter. In this scheme the previously known solitons are naturally manifest and the counting rule^{9,11} for charge or spin is derived by use of derivative expansions. A table of all possible solitons is presented; new solitons with an irrational or fractional spin component are found to exist when the

CDW and SDW coexist in the ground state. This is indeed the case for a SDW with odd-order commensurability.

The system under consideration is that of a quasi-1D electron gas with nonretarded coupling constants¹² g_1 for backward scattering, g_2 for forward scattering, and g_3 for umklapp scattering when the electron band is half filled. The system is studied in the Hartree-Fock scheme^{13,14} which is a reasonable approximation to the SDW compounds of the (tetramethyl tetraselenafulvalene)₂X family.¹⁵

Consider the electron spinor $\psi^\dagger(x) = (u_\dagger^\dagger(x),$