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Thermodiffusion of High-Density Electron-Hole Plasmas in Semiconductors

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The spatial distributions of temperature and density in electron-hole plasmas in surface-excited semiconductors are investigated with use of linear irreversible thermodynamics and a microscopic plasma theory. Above a certain threshold the density distribution is dominated by a characteristic density, which increases with temperature. Experimental results for Ge, unstressed Si, and Si under high uniaxial stress are in agreement with the theory.

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Contrary to the well understood phenomenon of electron-hole liquid (EHL) condensation,[1] the properties of the charge-carrier system above the critical point for liquid formation are discussed rather controversely to date: In Ge the luminescence band has been assigned to the overlapping emissions of a low-density electron-hole plasma (EHP), free excitons (FE), and of various higher-order bound states.[2] In GaAs the emission band was ascribed to a high-density EHP and was observed up to temperatures of 70 K.[3] A surprisingly weak dependence of the plasma density n_{EHP} on the excitation intensity and an increase of n_{EHP} with temperature were reported.[3] Recent experiments on Si reported similar results as obtained for GaAs and displayed no indication of noticeable densities of higher-order complexes.[4] Furthermore it was demonstrated that the band structure influenced the plasma via the density of states masses,[4] which ruled out earlier speculations on a correlation of the plasma density and the density of the metal-insulator transition.[3]

In spite of the contradicting conclusions drawn from the individual experiments, a direct comparison of the high excitation spectra obtained from the very different semiconductors Ge,[2] Si,[4] GaP,[5] CdS,[6] and GaAs[3] displays striking resemblances: At temperatures above the critical point for liquid formation a broad "liquidlike" emission is observed in the energy range just below the FE. Equilibrium thermodynamics, however, gives no indication for the occurrence of distinguished states above the critical temperature. Nonequilibrium phenomena, on the other hand, have been discussed so far mainly in the context of EHL nucleation and under isothermal conditions.[6,7]

In this Letter we present the basic features of a new approach to describe the properties of high-density electron-hole plasmas in semiconductors. Using linear transport equations[8-10] and a microscopic plasma theory, plasma thermodiffusion is studied in a stationary nonequilibrium model. The most unexpected prediction of our model is this: If the excitation level exceeds a temperature- and band-structure dependent threshold the effective diffusion constant of the EHP reaches negative values. Then the plasma density as a function of the distance from the excited surface goes through a temperature-dependent maximum which in turn should dominate the optical response.

In order to test our model, new experimental results for the plasma density n_{EHP} as a function of temperature are used from Ge, unstressed Si, and Si under high uniaxial stress, as well as previously reported data for CdS[6] and GaAs.[3] From the satisfying agreement of experiment and theory for the present systems with widely varying band structure we conclude that this distinguished EHP state should be observable in semiconductors in general, being perhaps the most universal collective excitation effect observed in these materials.

For our theoretical treatment, the experimental situation is pictured by a semiconductor half-space ($x>0$), which is homogeneously excited at the surface by a strong light source. We assume that the plasma current j_m into the bulk is controlled exclusively by boundary conditions at $x=0$, where the absorption process and the relaxation to a local thermal equilibrium[11] $T(0), n(0)$ have already been completed. Neglecting in a first approximation any lifetime effect,[12] j_m remains constant over the whole spatial range of interest.[13] The substantial current density of internal energy is the heat-current density j_q.[9] We assume that the temperature is not fixed externally[14] and hence conclude from the principle of minimum entropy production[9] $j_q(x)=0$. The linear transport equations for the heat and particle fluxes then read

$$j_q = L_{qq}X_q + L_{qm}X_m = 0, \tag{1}$$

$$j_m = L_{mq}X_q + L_{mm}X_m, \tag{2}$$

where $X_m = \mathrm{grad}(-\mu/T)$, $X_q = \mathrm{grad}(1/T)$, and $\mu(n,T)$ is the chemical potential. With $N = L_{qq}L_{mm} - L_{qm}{}^2 > 0$, and $L_{qm} = L_{mq}$ (Ref. 9) we obtain from Eqs. (1) and (2) in our one-dimensional geometry

$$\frac{dn}{dx} = \frac{-T}{(\partial\mu/\partial n)_T N}\left\{L_{qq} + \left[T\left(\frac{\partial\mu}{\partial T}\right)_n - \mu\right]L_{qm}\right\} j_m, \tag{3}$$

$$\frac{dT}{dx} = T^2 L_{qm} N^{-1} j_m. \tag{4}$$

The Onsager coefficients[8,9] L_{ik} can approximately be related to phenomenological parameters and thermodynamic response functions[10]:

$$L_{qq} = DT^2 n(\partial U/\partial T)_n > 0,$$

$$L_{mm} = DT/(\partial\mu/\partial n)_T > 0, \quad L_{qm} = L_{mm}Q.$$

Here $U(n,T) = E_{\mathrm{kin}}(n,T) + E_{\mathrm{xc}}(n,T)$ is the internal energy of the electron-hole plasma per pair (with E_{kin} the kinetic energy, E_{xc} the exchange-correlation energy) and D is the plasma diffusion constant for $\nabla T = 0$. For the heat of transport[10] $Q = j_q/j_m$ for $\nabla T = 0$ we obtain from a simple kinetic approach $Q = n(\partial U/\partial n)_T$.

To date no detailed model is available for the calculation of $U(n,T)$ in the wide range of densities and temperatures considered here. For example, standard plasma theories[1] do not approach the exciton limit at low densities. First, we therefore consider the EHP in a simple Fermi gas model. Second, we include an average E_{xc} from $T=0$ K calculations which overestimates E_{xc} in the temperature range considered.[15]

Spatial profiles of the density $n(x)$ have been derived from Eqs. (3) and (4) using a diffusion constant $D = 100\ \mathrm{cm}^2/\mathrm{s}$ (Ref. 16) and $j_m = 10^{23}/\mathrm{cm}^2\ \mathrm{s}$ (Ref. 17). Figure 1 shows $n(x)$ in the Fermi gas model for unstressed Si. The curves have been calculated for two different initial densities $n(x=0)$ of $3\times10^{18}\ \mathrm{cm}^{-3}$ and $1\times10^{18}\ \mathrm{cm}^{-3}$ at the

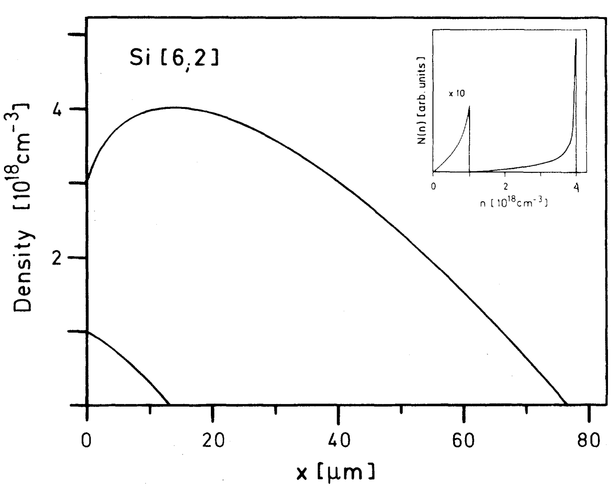

FIG. 1. Density profiles (Ref. 13) for $n(0) = 1\times10^{18}$ cm^{-3} (lower trace), 3×10^{18} cm^{-3} (upper trace) at $T(0) = 30$ K. The inset depicts the number of electron-hole pairs $N(n)$ to be found in the density range $[n, n+dn]$ of each profile.

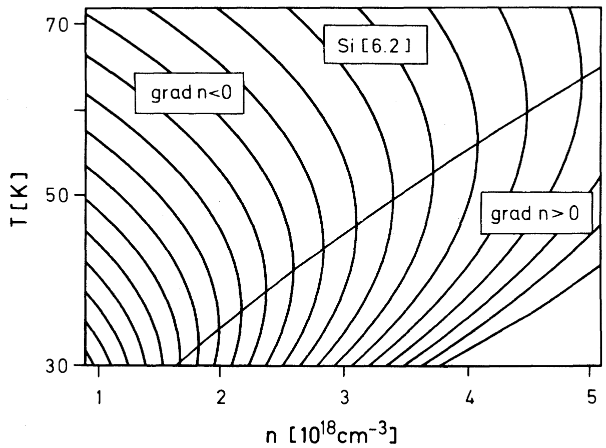

FIG. 2. Trajectories of the plasma in the density-temperature plane. The spatial development is along increasing temperature. The relation grad$n(n, T) = 0$ is included.

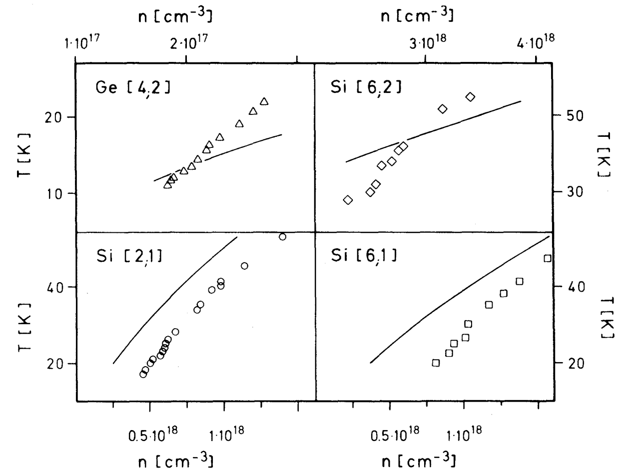

FIG. 3. Experimental data for the plasma density as a function of the temperature (points) for unstressed Ge [4;2], unstressed Si [6;2], and Si under high uniaxial stress along the [100] and the [111] axes (Si[2;1] and Si[6;1]). The full lines depict the theoretical results for $n_{max}(T)$.

same $T(x=0)$ of 30 K. Two different types of density profiles result: At low initial densities a monotonous decrease of $n(x)$ with increasing x is found. Raising $n(0)$ beyond a "critical" density $n(0) \cong 1.7 \times 10^{18}$ cm^{-3} at $T = 30$ K surprisingly leads to the formation of a rather flat maximum in the density profiles at n_{max}, where $\nabla n(n, T) = 0$. This behavior of $n(x)$ is due to the thermodiffusion of the EHP; the prefactor of $-j_m$ in Eq. (3) may be interpreted as an inverse effective diffusion constant D_{eff}. Depending on the EHP density and temperature D_{eff} can be either positive or negative.

The inset in Fig. 1 displays the distribution of the relative number of electron-hole pairs $N(n)$ versus density. $N(n)$ is dominated by a sharp maximum at n_{max} in the case of high $n(0)$. For a comparison with experimental data this leads to an important conclusion: Any spatially averaging experiment will be dominated by features of a plasma with n_{max}. For the lower $n(0)$ the sharp peak vanishes and $N(n)$ is roughly proportional to n.

Figure 2 depicts typical trajectories of the EHP in the n-T plane. Depending on the initial values of n and T the plasma density either decreases monotonously or first increases up to a value n_{max} [at the intersection with grad$n(n, T) = 0$] and then decreases. The temperature gradient is always positive in the Fermi gas model and a monotonous increase of T is observed along the trajectories. Including E_{xc} leads to a negative grad T at low densities. Both approaches for $U(n, T)$, however, predict the existence of a function $n_{max}(T)$ defined by grad$n(n, T) = 0$ which should be observed in experiments.

In order to test this prediction we have performed luminescence measurements using surface excited Ge and Si.[18] In the case of Si the electronic band configuration was varied through the application of high uniaxial stress. In terms of the numbers of occupied extrema of the conduction and valence bands the systems denoted Ge[4; 2], Si[6; 2], Si[6; 1], and Si[2; 1] were studied. For the experiments luminescence spectra were recorded in the temperature range between the critical temperatures[4] for EHL and $T \cong 50$ K. The plasma density and temperature were determined by line shape fits of the emission spectra using calculated line shapes of EHP and FE.[18]

In Fig. 3 the resulting plasma densities n_{EHP} are plotted versus temperature. For all band configurations the experimental n_{EHP} is found to increase with T. The full lines in Fig. 3 show the corresponding $n_{max}(T)$. The theoretical results are calculated using the density of states masses for the different band structures, which are the only input data in the Fermi gas model. As shown in Fig. 3 the overall agreement between experimental data and the results of the theory is rather good, considering the fact that there is no fit parameter.

The experimental density values are mostly somewhat higher than the theoretical results, which we attribute to the neglect of exchange-correlation effects and dissipative processes (phonons). Including the zero temperature E_{xc} gives consistently higher values of n_{max} than found in the experiments. For example in Si[2; 1] the experimental $n_{EHP}(45\text{ K}) = 1.1\times10^{18}\text{ cm}^{-3}$ is larger than $n_{max} = 8.3\times10^{17}\text{ cm}^{-3}$ calculated in the Fermi gas model and smaller than $n_{max} = 3\times10^{18}\text{ cm}^{-3}$ including E_{xc}.

The plasma densities in both experiment and theory vary according to changes of the density of states mass between the different band structures. For a further test we have applied our theory to the cases of GaAs[3] and CdS,[6] where a plasma density increasing with temperature has also been reported. For GaAs at 10 K $n_{EHP} = 4.5\times10^{16}\text{ cm}^{-3}$ was found experimentally, which compares reasonably well with $n_{max} = 2\times10^{16}\text{ cm}^{-3}$ ($E_{xc} = 0$). CdS experiments at 65 K give a density of $3.8\times10^{18}\text{ cm}^{-3}$ and from the Fermi gas model we obtain $n_{max} = 1.5\times10^{18}\text{ cm}^{-3}$.

In summary we have presented a linear nonequilibrium model to describe the stationary plasma thermodiffusion in highly excited semiconductors. Similar cross phenomena in transport properties are known in multicomponent classical systems as Soret-Dufour effects.[9,10] In the present case of a one component ambipolar diffusion we predict a correlation between a characteristic density and the temperature which is indeed found in experiment.

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[11] Local equilibrium requires that variations in temperature and velocity within a typical mean free path of the particles are small with respect to the average temperature and the sound velocity, respectively. In the parameter space considered here these conditions are satisfied.

[12] Experiments on the time evolution of the EHP show that the characteristic time constant is given by the transit time τ_{tr} through the high-density part of the profile. Since τ_{tr} is much smaller than the appropriate recombination times (e.g., τ_{Auger}) the neglect of recombination is a good approximation; A. Forchel, B. Laurich, W. Schmid, G. Maier, G. Mahler, and J. Lum, in Proceedings of the International Conference on Luminescence, Berlin, 1981, edited by I. Broser (to be published).

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