Disorder-order structural transition in highly excited semiconductor plasma

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It is shown that a symmetry-breaking dissipative structure, consisting of a self-organized carrier superlattice, may appear in an otherwise homogeneous steady nonequilibrium semiconductor plasma with inverted electron populations. This macroscopic ordered structure occurs beyond a critical deviation from equilibrium, and can be maintained while the open carrier system remains in a dissipative regime governed by nonlinear kinetic laws.

Recently there has been mounting evidence of the existence of numerous open physico-chemical systems where well-organized structures arise out of chaotic states. Such ordering should occur necessarily in far from equilibrium conditions, and has led in the last decade to new and unexpected developments.[1] When physico-chemical systems are driven away from equilibrium beyond a critical point, a macroscopic structure may spontaneously build up from fluctuations. These dissipative structures can be maintained in such steady low-entropy states by a flow of energy, and possibly matter from the outside.[2] The conditions for stability of these systems have been given by Glansdorff and Prigogine,[2] who propose an extended formulation of classical thermodynamics encompassing a large variety of situations, near and far away from equilibrium. Although it is of special interest to apply these results to biological problems, it is also a practical question to ask if, in a quite less complex level of description, processes of self-organization may be found in much simpler physical systems, susceptible to reproducible experimental studies. For this purpose semiconductors under high levels of excitation appear to be appropriate systems. These hot semiconductors are of great interest because of the variety of observed phenomena associated with them, their technological applications, and mainly for constituting an attractive problem since they form an excellent testing ground for theoretical ideas concerning systems far from equilibrium. Possible occurrence of disorder-order transformations in the hot semiconductor plasma have been considered by several authors: (a) Using a quasihydrodynamical approximation, Bonch-Bruevich studied the formation of a hot-electron-temperature superlattice in a doped semiconductor under nonuniform heating[3]; (b) Kerner and Osipov considered stratification of a hot-electron-hole semiconductor plasma in the presence of charge scattering centers[4]; (c) Degtyarenko, Elesin, and Furmanov[5] analyzed the possibility of space and time oscillations of the density and temperature of nonequilibrium photoexcited carriers under triple recombination conditions; (d) Van Vechten and Compaan suggested order formation in laser annealing of semiconductors.[6] In previous articles we have considered the question of relaxation phenomena in ultrafast transient optical properties of semiconductors,[7] and in this Brief Report we address the question of instability of steady-state macroscopic states in these systems. We demonstrate that, under high levels of excitation, a steady-state dissipative structure in the form of a stationary charge-density wave (SCDW) may arise in the semiconductor plasma. A possible connection between our results with the observed filamentation effect in semiconductor lasers,[8] and also with the possible cooperative morphological transformation in laser annealing of semiconductors,[6] is briefly discussed at the end of this report.

We consider an intrinsic direct-gap semiconductor sample illuminated by a cw-laser beam, with power flux P and frequency Ω_1. The photogenerated electron-hole pairs, created in photon absorption processes, come into internal equilibrium in a fraction of picosecond as a result of the strong long-range Coulomb interaction.[7,9] These carriers relax energy to the lattice, while their total number changes with the rates of the photon absorption and recombination processes. We assume a constant laser light intensity throughout the volume of laser light focalization, and diffusion effects out of this region will not be considered. The system Hamiltonian describes electrons and holes in the effective-mass approximation, photons, phonons, and their interaction with carriers. Stimulated emission and self-absorption are neglected, and we assume that the phonon system is constantly kept in thermal equilibrium with a large reservoir at temperature T_0. These approximations allow us to consider the carriers as an *open nonequilibrium system* macroscopically characterized by a basis set of macrovariables consisting of the band carrier energy and carrier density, $E(t)$ and $n(t)$, respectively. The evolution equations for these variables are

$$\frac{dE(t)}{dt}=\frac{d}{dt}\mathrm{Tr}[H_c\rho(t)]=\mathrm{Tr}\{(i\hbar)^{-1}[H_c,H]\rho(t)\}\ , \tag{1a}$$

$$\frac{dn(t)}{dt}=\frac{d}{dt}\mathrm{Tr}[N\rho(t)]=\mathrm{Tr}\{(i\hbar)^{-1}[N,H]\rho(t)\}\ , \tag{1b}$$

where H_c is the carrier Hamiltonian, N the operator for the pairs number, H the total Hamiltonian of the semiconductor, and $\rho(t)$ the nonequilibrium statistical operator (NSO) appropriate for the description of the system under the given experimental conditions. This NSO is built as a functional of a coarse-grained statistical operator (CGSO), and belongs to a class of solutions of Liouville equations which, for isolated systems, insures irreversible behavior according to the second law of thermodynamics.[10] The CGSO can be constructed by application of Jaynes's maximum entropy formalism (MEF).[11] In recent years several schemes based on the MEF have been developed, and among them Robertson's[12] and Zubarev's[13] are closed methods of quite general application. The latter makes explicit allowance for initial conditions for the determination of the nonequilibri-

um statistical operator, eliminating transient effects. We resort here to Zubarev's scheme which provides simpler mathematical manipulations; its restrictions are unimportant for the steady-state solution we are looking for.

A practical way to solve Eqs. (1) is to expand the last member in a series of collision operators of increasing order in the interaction strengths, obtained by means of a perturbationlike expansion around the state characterized by the CGSO.[14] This is a kind of generalization of the classic Chapman-Enskog method.[15] The advantages of the method reside in the fact that it allows for the description of a large class of experimental situations where the system is arbitrarily away from equilibrium, and where nonlinear, nonlocal, and memory effects are incorporated from the onset. In a low-order approximation, when the expansion in series of collision operators is truncated, keeping only contributions up to second order in the coupling strengths, and for a uniform system, thermomechanical and cross-relaxation terms vanish. Then the collision integrals reduce to contributions corresponding to a Born-type approximation for the scattering processes taking place at time t. The detailed form of these approximated collision operators is given elsewhere.[7] The calculation is performed using a Debye model for the lattice vibrations and the dipole approximation for the electron-radiation interaction. Further, we restrict the analysis to the case of experimental conditions that produce a nondegenerate carrier gas. Then, because of the very rapid internal thermalization of carriers,[9] the electron and hole distribution functions become instantaneous Maxwell-Boltzmann distributions corresponding to a classical plasma characterized by an effective temperature $T^*(t)$ and concentration $n(t)$. Under these conditions $E(t) = 3k_B n(t) T^*(t)$ holds at any given time t, and Eqs. (1) can be transformed into a set of equations for $n(t)$ and $T^*(t)$.

The steady-state solutions correspond to $dn/dt = 0$, meaning optical saturation since the rate of pair production equals the recombination rate, and $dT^*/dt = 0$ which is just the equalization of the rates of incoming (from the laser source) and outgoing (relaxation to the lattice and luminescence) energy flows. These results simply follow by putting expressions (1) equal to zero. The solutions n and T^*, for any given value of the laser power, can be obtained solving this coupled system of equations once the parameters involved (effective masses, coupling constants, etc.) are given.[7] To obtain numerical results we use a set of physical parameters corresponding to GaAs.[16] Further, we consider illumination by a yttrium aluminum garnet laser with frequency doubling, $2\Omega_L = 2.4$ eV.

The steady-state solutions are parametrically dependent on the laser power per unit area P, and they are shown in Fig. 1. The effective temperature of the carrier system is a monotonic increasing function of the cw-laser power, acquiring values not larger than 40% above lattice temperature. The pair concentration also grows monotonically with laser power; it should be recalled that diffusion from the active region has been neglected, i.e., we have assumed confinement of this plasma. Clearly, the steady-state solutions should occur after a transient period has elapsed; we have estimated, through approximate solution of Eqs. (1), that it has a duration of roughly 100 μ sec for a laser power of near 0.5 MW/cm^2.

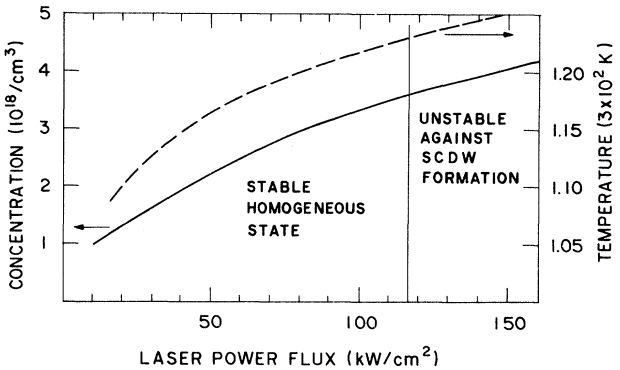

FIG. 1. Stationary values of the concentration of photoinjected carriers (full line), and carrier effective temperature (dashed line). The regions of stability of the uniform state and of instability against carrier superlattice formation are indicated.

However, if the constraints force the system further and further away from equilibrium a transition from the homogeneous steady state to a new structure with a higher degree of organization may follow at a certain "distance" from equilibrium. We show here that a transition from the homogeneous to a patterned structure of the highly excited Coulomb gas follows after the cw-laser power has reached a critical value. For this purpose we test the stability of the steady uniform carrier plasma against formation of a stationary charge-density wave. The instability onset occurs when the static ($\omega = 0$) wave-vector–dependent dielectric response function diverges, or its inverse, the dielectric constant $\tilde{\epsilon}(\omega = 0, \vec{Q})$ becomes zero. The dielectric function $\tilde{\epsilon}(\omega = 0, \vec{Q})$ depends on the thermodynamic state and on the incident laser power in a nonlinear way. Equivalently, one can show that at the instability threshold an arbitrary fluctuation in the form of a static, thermodynamically stationary, charge-density wave of small Fourier amplitude $\rho(\vec{Q})$ remains nonvanishing in the absence of any nonuniform electrostatic external field. Now consider $\rho(\vec{Q}) = \sum_{\vec{k}\alpha} \rho^{\alpha}_{\vec{k}\vec{Q}}$, where $\rho^{e}_{\vec{k}\vec{Q}} = \langle c^{\dagger}_{\vec{k},\vec{Q}} c_{\vec{k}} \rangle$ and $\rho^{h}_{\vec{k}\vec{Q}} = \langle h^{\dagger}_{-\vec{k}-\vec{Q}} h_{-\vec{k}} \rangle$, where $c(c^{\dagger})$ and $h(h^{\dagger})$ are annihilation (creation) operators for electrons and holes in plane-wave states, and the angle brackets enclose the average over the nonequilibrium steady-state statistical ensemble. The static steady-state fluctuation satisfies that $\partial \rho^{\alpha}_{\vec{k}\vec{Q}}/\partial t = 0$ ($\alpha = e,h$), which is equivalent to Eqs. (2):

$$(\epsilon^{e}_{\vec{k}+\vec{Q}} - \epsilon^{e}_{\vec{k}} + i B^{ee}_{\vec{k}\vec{Q}}) \rho^{e}_{\vec{k}\vec{Q}} - (n^{e}_{\vec{k}+\vec{Q}} - n^{e}_{\vec{k}}) \frac{4\pi e^2}{Q^2 \epsilon_0} \rho(\vec{Q}) + i B^{eh}_{\vec{k}\vec{Q}} \rho^{h}_{\vec{k}\vec{Q}} = 0 \ , \quad (2a)$$

and a similar one [(2b)] for holes exchanging $e \rightleftarrows h$ in (2a). The second term is due to the Coulomb interaction which has been treated in the random-phase approximation (RPA). Coefficients B appear as a result of the interactions of the electrons with phonons and photons contained in the Hamiltonian H. They have been obtained through a decoupling of the equations of motions up to second order in these interactions to find

$$B^{e(h)}_{\vec{k}\vec{Q}} = -\pi |V_L|^2 [\delta(E_G + \epsilon^{x}_{\vec{k}} - \hbar\Omega_L) + \delta(E_G + \epsilon^{x}_{\vec{k}+\vec{Q}} - \hbar\Omega_L)] + \pi \sum_{\vec{q}} |V_{\vec{q}}|^2 [n^{h(e)}_{\vec{k}} \delta(E_G + \epsilon^{x}_{\vec{k}} - \hbar\Omega_{\vec{q}}) + n^{h(e)}_{\vec{k}+\vec{Q}} \delta(E_G + \epsilon^{x}_{\vec{k}+\vec{Q}} - \hbar\Omega_{\vec{q}})] \ . \quad (3)$$

The first term on the right-hand side is due to photon absorption from the laser light and the second is a result of spontaneous recombination; we find that intraband carrier scattering by phonons produces no relevant contribution near the instability and has been neglected in Eqs. (3). E_G is the gap energy, $\epsilon_k^x=\hbar^2k^2/2\mu$, where μ is the reduced effective mass, Ω are the photon frequencies, and the matrix element V_L is proportional to the laser field power.[7] Further, let us recall that Eqs. (2) depend on the stationary values of n and T^*, already determined and shown in Fig. 1.

Adding up both Eqs. (2) and summing over $\vec{k}$ we obtain the characteristic equation, i.e., the one that ensures a nontrivial (nonvanishing) solution for $\rho(\vec{Q})$. This condition is

$$\tilde{\epsilon}(\vec{Q};\omega=0)=1-\frac{4\pi e^2}{\epsilon_0 Q^2}\sum_{\vec{k}}(N^{e}_{\vec{k},\vec{Q}}+N^{h}_{\vec{k},\vec{Q}})D^{-1}_{\vec{k},\vec{Q}}=0\ , \tag{4}$$

$$N^{e,h}_{\vec{k},\vec{Q}}=(n^{e,h}_{\vec{k}}-n^{e,h}_{\vec{k}+\vec{Q}})(E^{h,e}_{\vec{k},\vec{Q}}+iB^{h,e}_{\vec{k},\vec{Q}}) -i(n^{h,e}_{\vec{k}}-n^{h,e}_{\vec{k}+\vec{Q}})B^{e,h}_{\vec{k},\vec{Q}}\ , \tag{5a}$$

$$D_{\vec{k},\vec{Q}}=(E^{e}_{\vec{k},\vec{Q}}+iB^{e}_{\vec{k},\vec{Q}})(E^{h}_{\vec{k},\vec{Q}}+iB^{h}_{\vec{k},\vec{Q}}) +B^{e}_{\vec{k},\vec{Q}}B^{h}_{\vec{k},\vec{Q}}\ , \tag{5b}$$

and $E^{e,h}_{\vec{k},\vec{Q}}=\epsilon^{e,h}_{\vec{k}+\vec{Q}}-\epsilon^{e,h}_{\vec{k}}$, and $n^{e,h}_{\vec{k}}$ are the distribution functions for electrons and holes in band state $\vec{k}$. This generalized dielectric function, when putting all coefficients B equal to zero, goes over the Lindhart RPA-static dielectric constant as it should. The latter does not cancel for any value of Q; $\tilde{\epsilon}=0$ is only possible for the presence of the coefficients B, arising from nonlinear effects in far from equilibrium thermodynamic states. This stationary and static generalized dielectric constant always has a zero value for large enough values of the laser power, except for the symmetric case when both effective masses, for electrons and holes, are equal. Clearly, dependent on the values of the different parameters associated with the particular system, the instability may occur for nonaccessible experimental conditions.

The zeros of $\tilde{\epsilon}$ (obtained by making null the real and imaginary parts of ϵ) determine the power threshold for the onset of the instability (and then the critical values of pair concentration and effective temperature) and the SCDW wavelength. We solve numerically these equations using the ansatz of taking Q small to find that there exists the expected instability against a SCDW with wave number Q of roughly 0.4 cm^{-1} at a cw-laser threshold power of nearly 0.6 MW/cm^2. The instability should occur when the steady uniform state of the carrier plasma has a concentration $n\sim 4\times 10^{18}$ cm^3 and an effective temperature $T^*\sim 1.2$ times the bath temperature of 300 K (see Fig. 1).

This shows that in a direct-gap semiconductor with steady inverted population of electrons, collective effects (arising out of the Coulomb interaction) in conjunction with far from equilibrium constraints may lead the carrier system to be unstable against the formation of the symmetry-breaking dissipative structure. The dissipative structure occurs beyond a critical deviation from equilibrium when a fluctuation drives the system to a macroscopic ordered state, presently a self-organized carrier plasma superlattice. Thus, as expected,[2] creation of order may follow spontaneously in far from equilibrium open systems obeying nonlinear kinetic laws, as those of Eqs. (1).

Here we have established only the conditions for the onset of the instability; the complete characteristics of the SCDW should be determined after the quantity $\rho(\vec{Q})$ is added to the basis set of variables used for the MEF-macroscopic description of the system. Then, for instance, the dynamic dielectric constant $\tilde{\epsilon}(\omega,q)$ can be calculated and from it the optical spectra of the antiferroelectriclike new structure. If experimentally feasible, comparing these theoretical spectra with measured data would provide confirmation and information on the SCDW. Two kinds of situations may correspond to conditions like those discussed here. One is the case of semiconductor lasers which develop a homogeneous density of electrons and holes along the junction parallel to the mirrors.[17] In these devices has been observed a filamentation effect in the recombination region along the diode junction.[8] This confinement of the emitted light has been ascribed to a spatial variation of the refraction index of material in the active region.[18] Existing theories do not properly account for the effect.[8] The conclusions of the present work suggest that a possible mechanism to look for is the formation of a SCDW in the homogeneous plasma along the diode junction. Note that the large value we have obtained for the SCDW wavelength is a result of the model, free carriers in plane-wave states, and it should be much smaller for localized states. Another quite interesting case is the morphological transition that takes place during laser annealing of semiconductors. It has been interpreted by some authors as a process of melting, followed by rapid crystallization and quenching,[19] while others suggest a nonthermal transition.[17,20] Our results here point to a large-scale orgaization of the semiconductor plasma much in the direction proposed and discussed by Van Vechten[20] except that we are dealing with itinerant carriers in plane-wave Bloch-like states instead of the chemical-band approach he uses. It must be stressed that this kind of transition does not exclude that a normal thermal transition may take place during laser irradiation of the ion implanted semiconductor surface prior to the disorder-order dissipative structural transition.[21]

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