Quantum kinetics regime during and immediately after laser excitation of semiconductors

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Abstract

We investigated carrier dynamics in the semiconductor GaAs, during and just after creation by \( \approx 30 \) fs laser pulses, much shorter than the phonon and plasma time scales. We observed a quasi-instantaneous spread of the carrier population in momentum-energy space, that is not even qualitatively consistent with Boltzmann kinetics. The observations are, however, in qualitative agreement with quantum kinetic theories of carrier–carrier and carrier–phonon scattering. © 1997 Elsevier Science S.A.

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1. Introduction

Carrier populations excited by laser pulses form an ideal model system for studying fundamental aspects of thermodynamics [1]. In the optical excitation of a semiconductor one can distinguish several time scales. Initially, during the first few optical cycles, e-h pairs oscillate coherently between the valence and conduction bands. In the next few tens of femtoseconds (fs) dynamic many-body interactions start to take place destroying the e-h quantum mechanical phase coherence, and creating ‘real carriers’. This stage of the dynamics is highly non classical, because of the uncertainty principle the energy of each e-h pair is not well defined, polarization and populations are strongly coupled, and both the lattice and the photo-plasma are still immobile. Then a transient regime begins as e, h and nuclei start to move and screening and phonon interaction are ‘turned on.’ Although the carriers have started to lose their coherence, their populations can only be described by \( k \)-dependent occupation numbers and not by Fermi distributions, so that a ‘temperature’ cannot be defined. In that regime the dynamics of the polarization and \( k \)-dependent occupation numbers must be described by quantum kinetics (QK), with non-Markovian statistics and memory structure. After several tens of fs the scattering processes have completely destroyed the quantum coherence and the usual regime of validity of Boltzmann kinetics is reached. Then carrier populations gradually approach Fermi–Dirac statistics. In that regime there is still no equilibrium among different carrier species or between the carriers and the lattice, but carrier–phonon and carrier–carrier scattering recover their usual behavior.

The very early time regime of e-h dynamics is not well documented. Only limited theoretical work has been devoted to this complicated topic [2–7], and experimental work is very scarce [8]. Yet it is of fundamental and practical interest. Because of the recent advances in ultrafast laser technology it is now within reach of experimental investigations. In this contribution we present a study of carrier dynamics in the model semiconductor GaAs, during and just after creation by ultrashort laser pulses. We observe a quasi-instantaneous spread of the carrier population in momentum-energy space without the spectral hole-burning signature of the non-equilibrium carriers, and negative scattering rates just below the center of the pump spectra. We show that these two results are inconsistent with an analysis of the experiments based on the semiconductor Bloch equations (SBE) in the relaxation time approximation that originates from Boltzmann kinetics (BK). The experiments are, how-
ever, consistent with recent QK theories of carrier–carrier and carrier–phonon scattering [9].

2. Experimental procedure and results

The observables of any quantum mechanical system, and in particular the polarization that is measured in optical experiments, are determined by the density matrix, \( \hat{\rho}(t) \). It obeys the Liouville equation of motion

\[
\hat{\rho}(t) = [\hat{H}(t), \hat{\rho}(t)] + i\hbar \frac{\partial}{\partial t} \hat{\rho}(t),
\]

(1)

In the case of semiconductors, the populations in the conduction and valance bands and the interband polarization are associated with diagonal and off-diagonal matrix elements of \( \hat{\rho}(t) \). For example, in the simple case of a two-band dispersion relation, because the photon momentum is negligible the density matrix break in 2 \( \times \) 2 blocks. Then the \( k \)-space representation of \( \hat{\rho}(t) \) is:

\[
\hat{\rho}(t) = \sum_k \hat{n}_k(t) = \sum_k \left[ p_k \begin{pmatrix} n_k(k) & 0 \\ 0 & n_k^*(k) \end{pmatrix} \right].
\]

(2)

In Eq. (1) the first commutator describes the ‘coherent’ part of the time evolution, whereas the last term accounts for the effects of incoherent processes. These two terms are still poorly understood, and are the topic of much current research. The second one, however, is by far the least known, especially in the early time regime. It is often calculated in the framework of BK, and furthermore approximated by relaxation times.

Eq. (1) relates \( \hat{n} \) to \( \partial \hat{n}/\partial t \). The solution of this differential equation depends on the structure of the relaxation term, and cannot be generally solved. In particular there is no simple solution in the QK case. Therefore simultaneous study of both \( \hat{n} \) and \( \partial \hat{n}/\partial t \) is essential. In practice optical experiments measure the interband polarization of the medium, \( P = \Sigma n_k \). A powerful optical technique, often used to investigate the \( e\)-\( h \) in solids is that of frequency-resolved transient pump/probe technique [10]. It uses a strong ‘pump’ pulse to excite the sample, creating an \( e\)-\( h \) population that modifies the absorption. A weak ‘probe’ pulse delayed with respect to the pump by \( \Delta t \) monitors these changes as measured by the differential transmission spectra:

\[
\text{DTS}(\omega, \Delta t) = \frac{T(\omega, \Delta t) - T_d(\omega, \Delta t)}{T_d(\omega, \Delta t)},
\]

where \( T(\omega, \Delta t) \) and \( T_d(\omega, \Delta t) \) are the sample transmission with and without the pump. In the work presented here, consistently with the above discussion, we complement the conventional pump/probe measurement of the DTS(\( \omega \), \( \Delta t \)) by determining also the derivative of the DTS with respect to \( \Delta t \), \( \text{DTS-dot}(\omega, \Delta t) = \partial \text{DTS}(\omega, \Delta t) / \partial \Delta t \). The DTS and DTS-dot are not directly proportional to \( \hat{n} \) and \( \partial \hat{n}/\partial t \), but through Eq. (1) their evolutions are related. Thus, their simultaneous determination put very strict restriction on any theory invoked to explain our data: it must be able to adequately describe both the DTS and the DTS-dot.

Initial hole-burning by a non-equilibrium carrier distribution created by \( \tau \approx 100 \) fs pulses and thermalization within 200 fs have been observed in pump/probe experiments in GaAs [10–12]. Recently, very slow relaxation, dominated by emission of optical phonons, was reported in the low density limit, \( n_{eh} < 10^{16} \text{ cm}^{-3} \) [13]. The dynamics observed in the above experiments were analyzed within the framework of BK assuming, furthermore, a generation reflecting the pump spectrum and an independent measurement by the probe [14,15]. The BK treatments assume exact conservation of the kinetic energy, are local in time and only consider the evolution of populations. They become valid only for times much larger than the oscillation cycle of the elementary excitation responsible for the loss of coherence. In intrinsic semiconductors, carriers can experience two sorts of scattering mechanisms, carrier–carrier scattering (CCS) and carrier–phonon interactions (CPI). The natural time scale for CPI is \( \tau_{\text{CI}} = 2\pi/\Omega_{\text{CI}} = 113 \text{ fs} \) (in GaAs). That scale for CCS is \( \tau_{\text{CC}} = 2\pi/\omega_{\text{CC}} \approx 148 \text{ fs} \) for a plasma of density of \( n_{eh} = 5 \times 10^{17} \text{ cm}^{-3} \). Therefore for times much shorter that \( \approx 100 \) fs the full QK scattering integrals have to be taken into account, resulting in scattering rates significantly broadened in energy, and in memory effects in the evolution of the occupation numbers [2–7].

In order to focus on the very early time, during and immediately after the generation of \( e\)-\( h \) pairs, we use a modified frequency-resolved pump/probe technique, with pump and probe duration independently adjustable from 30 to 100 fs to measure the DTS(\( \omega \), \( \Delta t \)) in bulk GaAs at room temperature. The light source is a 30 fs self-mode locked Ti:Sapphire laser. The pump and probe beams are cross-polarized. The pump beam can be directed through a group-velocity-dispersion-compensated spectral filter with an adjustable slit to tune its duration \( \tau_p = 30 \text{ fs} \rightarrow 100 \text{ fs} \). \( \Delta t = 0 \) is determined with an accuracy of \( \approx 10 \) fs. Measurements were performed on two MBE-grown and anti-reflection coated GaAs samples, 0.25 \( \mu \text{m} \) (\( n_l \approx 0.4 \)), and 1 \( \mu \text{m} \) (\( n_l \approx 1.6 \)) thick, at densities \( 10^{16} \text{ cm}^{-3} < n_{eh} < 5 \times 10^{17} \text{ cm}^{-3} \). At these densities both CCS and CPI are significant.

Firstly, we have checked the consistency of our data with previous experiments by measuring the DTS(\( \omega \)) with long \( \approx 70 \) fs pulses at moderate density \( n_{eh} \approx 1.2 \times 10^{17} \) and with excess energy \( \Delta E = h\omega_{\text{pump}} - E_g \approx 38 \text{ meV} \) close to \( h\Omega_{\text{LO}} \) (\( h\omega_{\text{pump}} \) is the center frequency of the pump). In agreement with previous reports the DTS(\( \omega \)) exhibits a clear spectral hole slightly red shifted relative to the pump spectrum [12,16].

Fig. 1 shows DTS(\( \omega \)) and DTS-dot(\( \omega \), \( \Delta t \)) measured on the \( L = 0.25 \mu \text{m} \) sample, at high excess energy \( \Delta E = 73 \text{ meV} \approx h\Omega_{\text{LO}} \) with \( \tau_{\text{pump}} = 100 \) fs, \( \tau_{\text{probe}} = 30 \) fs and \( n_{eh} \approx 1.2 \times 10^{16} \text{ cm}^{-3} \). A weak spectral hole can be
distinguished at $\Delta t \leq 0$ below the pump spectrum and extending all the way to the band-edge. At the band-edge a strong excitonic contribution appears, with a lineshape characteristic of the broadening of a resonance. The red shift of the spectral hole can be attributed to dynamic Fermi edge singularity effects [17], but its breadth is difficult to explain. The light hole (lh) to conduction band (cb) contribution is expected to be weak and, in any case, it cannot explain the DTS$(\omega)$ profile. The DTS-dot$(\omega, \Delta t)$ spectrum for $\Delta t = -33$ fs is positive over a large range of energies above the exciton and exhibits a broad hump slightly below the pump spectrum indicative of a tendency for the transmission to increase below the energy where carriers are generated. However at $\Delta t = +100$ fs the DTS-dot$(\omega, \Delta t)$ becomes negative below the pump showing that this tendency reverses very quickly. The BK theory predicts LO-phonon emission rate ($\approx 5$ ps$^{-1}$) much slower than any of the changes seen experimentally, and a well defined phonon replica [15] which we do not observe. Any CCS broadening would result in a symmetric smearing of the spectral features, again inconsistently with the asymmetric spectral hole that extends only below the pump spectrum.

In Fig. 2 the DTS$(\omega)$ and DTS-dot$(\omega, \Delta t)$ measured with much shorter pump pulses, $T_{\text{pump}} = T_{\text{probe}} = 30$ fs, are shown. The excess energy is $\Delta E = 80$ meV and $n_{eh} \approx 4.4 \times 10^{16}$ cm$^{-3}$. There is absolutely no spectral hole around the pump spectrum but only a featureless signal extending below $h\omega_{\text{pump}}$, all the way to the exciton. The broadening of the exciton again results in a dip slightly above $E_{\text{exc}}$. The DTS-dot$(\omega, \Delta t)$ show a uniform positive growth shifted toward the exciton for $\Delta t = 0$ fs and $+26$ fs, that reverses and changes sign at $\Delta t = +53$ fs immediately at the end of the pump pulse. This is indicative of generation in the medium, during the pump pulse, of a polarization out of phase with the probe field, over a broad range of energy below the pump, and of a sudden change in phase when the pump pulse ends. These trends are typical of experiments performed with pump and probe pulses very short compared to the natural time scales of the system. Another example is shown in Fig. 3, where we present measurements performed with the $L = 1$ $\mu$m sample, $T_{\text{pump}} = T_{\text{probe}} = 30$ fs, and $n_{eh} \approx 4.4 \times 10^{16}$ cm$^{-3}$. In this case $\Delta E = 100$ meV, so that there is very little direct excitation at the band edge. Again the DTS$(\omega)$ has an instantaneous response at low energies very far from $h\omega_{\text{pump}}$. There is essentially no signal at the peak of the pump spectrum. Except for a complicated response around the exciton, the DTS-dot$(\omega, \Delta t)$ is positive and very strongly shifted toward the exciton for all $\Delta t \leq 26$ fs, and changes sign as soon as the pump pulse is over, $\Delta t \geq 40$ fs.

Finally, we have performed spectrally-integrated measurements over a much longer time scale. We found
that a steady state is reached in \( \approx 300 \text{ fs} \), in qualitative agreement with earlier experiments in GaAlAs [18]. A careful quantitative comparison of the peak magnitude of the DTS \( \approx 10^{-2} \) with the number of states in the laser bandwidth \( \approx 2 \times 10^{18} \text{ cm}^{-3} \) and excitation density \( \approx 1.4 \times 10^{17} \text{ cm}^{-3} \) shows a discrepancy of approximately one order of magnitude. The peak value is therefore inconsistent with Pauli blocking by a distribution which follows the pump spectrum, but must correspond to a carrier distribution which is immediately spread-out.

3. Interpretation

The DTS measures the change in the probe transmission and not directly the carrier distribution. We have therefore calculated the DTS using the SBE which have been shown to account correctly for the coherent processes in experimental conditions where pulses of duration \( \approx 100 \text{ fs} \) are used [19]. We have used a four-band version of the SBE in order to take into account the polarization selection rules in GaAs and the polarizations configuration of the experiments.

We have attempted to explain the results within the BK framework describing phenomenologically the irreversible processes in the relaxation time approximation [19]. Since we look for a major discrepancy, we try to reproduce qualitatively the data and restrict our discussion to the broad features of the calculated response. Firstly, consistently with the BK predictions we only consider dephasing and assume no population relaxation. We find that for reproducing qualitatively the lineshape of the DTS one has to assume a long \( T_2 \) (\( \approx 200 \text{ fs} \)) consistent with the time scale seen experimentally. The calculated DTS exhibits a red shift of the spectral hole and an instantaneous response at the band-edge. The comparison between the experimental and calculated DTS-dot is much more problematic. As shown in Fig. 4, for the case of a \( \tau_{\text{pump}} = \tau_{\text{probe}} = 30 \text{ fs} \) measurement on the \( L = 1 \mu\text{m} \) sample, the calculated DTS-dot, Fig. 4b, presents qualitative discrepancies with the experimental DTS-dot, Fig. 4a. The calculated response can reproduce neither the experimental shift towards the band-edge during the carrier generation, nor the negative sign of DTS-dot seen close to the laser center frequency immediately after the pump pulse is over. In order to pursue our attempt to explain the data within the BK we included a population relaxation towards a Maxwell-Boltzmann distribution with the same instantaneous number of carriers and total energy as that generated by the pump pulse.

![Fig. 3](image_url)

**Fig. 3.** DTS(\(\omega\)) and DTS-dot(\(\omega, \Delta\tau\)) measured on the \( L = 1 \mu\text{m} \) sample, with \( \tau_{\text{pump}} = \tau_{\text{probe}} = 30 \text{ fs} \). The excess energy is \( \Delta E = 100 \text{ meV} \), and \( n_{e-h} \approx 1.5 \times 10^{17} \text{ cm}^{-3} \).

![Fig. 4](image_url)

**Fig. 4.** A comparison between the experimental DTS-dot and the best simulations using the semiconductor Bloch equation within the relaxation time approximation. Fig. 4a, experimental results for \( \tau_{\text{pump}} = \tau_{\text{probe}} = 30 \text{ fs} \) and \( L = 1 \mu\text{m} \). Fig. 4b, theory with \( T_2 = 200 \text{ fs} \), and no population relaxation. Fig. 4b, theory with \( T_2 = 200 \text{ fs} \) and a population relaxation, \( T_1 \approx 36 \text{ fs} \), towards a Maxwell-Boltzmann distribution with the same instantaneous number of carriers and total energy as that generated by the pump pulse.
just after generation by ultrashort laser pulses. We found it is possible, using the population relaxation time \( T_1 \) as an adjustable parameter, to get a better qualitative agreement with the experiments, see Fig. 4c. However, this occurs only for population relaxation times too short to be compatible with any theory based on BK [15] and also much shorter than the polarization dephasing time, i.e. \( T_1 \sim 36 \text{ fs} \ll T_2 \). Our attempts to salvage BK by using more complicated models for dephasing, such as excitation-induced dephasing [20], failed to remove the unphysical results (i) \( T_2 \gg T_1 \) and (ii) \( T_1 \ll 2\pi/\Delta t_{\text{LO}} \) and \( \ll 2\pi/\omega_{\text{p}(\text{max})} \) of the BK model.

The features observed in the DTS are, however, consistent with the predictions of QK theories. At present, such theories have been developed to describe either CPI [2–6] or CCS [7]. They are not yet able to treat both effects on the same footing. In the case of CPI they predict broad and featureless scattering rates for times \( t < 1/\omega_{\text{LO}} \), due to the time-energy uncertainty. For times \( 1/\omega_{\text{LO}} < t < T_{\text{LO}} \), carrier transitions to the low-energy side become favored. Only for times \( t > T_{\text{LO}} \), the selection rules governed by the energy conservation are so well-defined that phonon replicas may form. In the experiments presented here, the additional QK CCS suppresses the build-up of the phonon replicas [7]. We have performed QK calculations of the occupation numbers in \( k \)-space that include only CCS. We find that, for excitation with \( \approx 30 \text{ fs} \) pulses well above the band edge, the carriers rapidly scatter out of the energy window in which they were created resulting almost instantaneously in a distribution much broader than that of the exciting pulse. These effects should be included in a future consistent calculation of the DTS signal.

4. Conclusion

We have investigated carrier dynamics, during and just after generation by ultrashort laser pulses. We measured the differential absorption spectra and their derivatives with respect to the time-delay, in a pump/probe experiment with independently adjustable pump and probe pulse durations. We observe a quasi-instantaneous spread of the carrier population in momentum-energy space, and negative scattering rates just below the pump spectra. Attempts to fit these two results, even qualitatively, with the Boltzmann kinetics yield unphysical results. The observations are, however, consistent with quantum kinetic theories of carrier–carrier and carrier–phonon scattering. It is important to realize that the processes discussed in this article apply to the very early phase of any laser pulse excitation, whatever the pulse duration is. Thus, our results show the need for a more comprehensive description of dissipation in the theoretical analysis of coherent phenomena in semiconductors, beyond the relaxation time approximation currently used.

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