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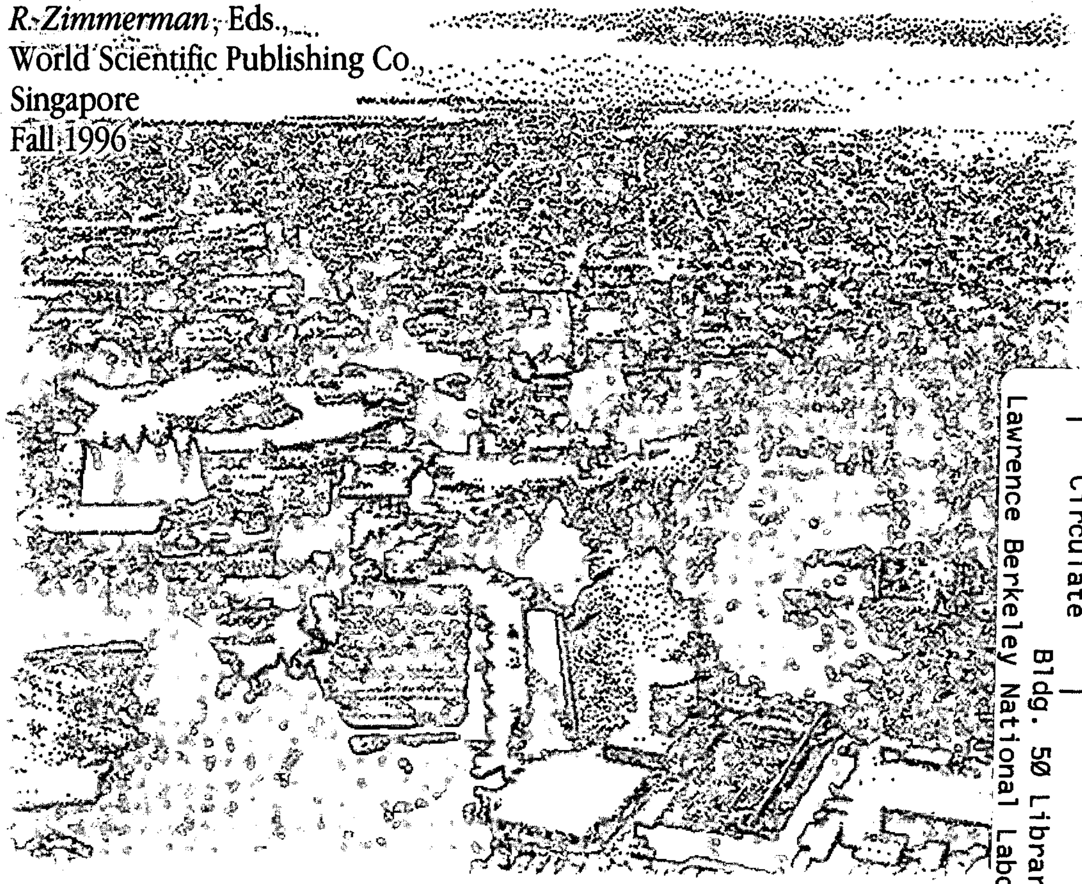

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PHOTOCARRIER DYNAMICS IN THE VERY EARLY TIME REGIME

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We present a study of carrier dynamics in the semiconductor GaAs, during and just after creation by ultrashort laser pulses. Using a pump-probe setup with independently adjustable characteristics for the pump and probe pulses we measure the differential absorption spectra and their time-delay derivative. We observe a quasi-instantaneous spread of the carrier population in momentum-energy space, and negative scattering rates just below the center of the pump spectra. Attempts to fit these two results, even qualitatively, with the Semiconductor Bloch Equations in the relaxation time approximation yield to unphysical results. We interpret this as a failure of Boltzmann Kinetics. The observations are, however, consistent with recent Quantum Kinetic theories of carrier-carrier and carrier-phonon scattering.

1 Introduction

In the excitation of a semiconductor by an ultrashort laser pulse, one can, intuitively, distinguish several times scales. Initially, during the first few optical cycles, $e-h$ pairs oscillate coherently between the valence and conduction bands. In the next stage, typically a few tens of femtoseconds (fs), dynamic many-body interactions occur, scatterings start to act destroying the quantum mechanical phase coherence of the system and "real carriers" are created. This stage, however, is highly non classical. First as required by the uncertainty principle each $e-h$ pair has no well defined energy, the polarization is strongly coupled to the populations and the lattice is still unable to move. Then a number of processes start to "turn on", the Coulomb potential, which is initially bare, starts to be screened and the lattice begins to reacts to the apparition of charges. During this transient period the dynamics of the "average" polarization and of the $k-$dependent occupation numbers can only be described by Quantum Kinetics (QK), with memory structure or non-Markovian statistics. Although the carriers start to relax their distribution cannot be described by a Fermi function and a "temperature" cannot be defined. As scattering processes become effective the coherence continues to decays, and is completely lost after a several tens of fs, when the quasi-particle scattering rates have reached a regime where the occupation numbers follow Fermi-Dirac statistics. In the final step of the dynamics the hot $e-h$ gas is completely phase incoherent.

Thus the very early time regime of true non-Markovian $e-h$ scattering and the first stages of the quasi-particle dynamics are of particular interest because they correspond to the initiation of fundamental mechanisms that are taken for granted in the conventional description of semiconductors. Owing to recent advances in laser technology they are now within reach of experimental investigations and one can start exploring this yet poorly understood regime. In this article 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).[1] Since theories based on BK predict very little relaxation in the sub-100 fs time frame of our experiments, we interpret the discrepancy as a failure of the BK. The experiments are, however, consistent with recent Quantum Kinetic (QK) theories of carrier-carrier and carrier-phonon scattering.

2 Experiments

A powerful technique, often used to investigate the $e-h$ thermalization process is that of frequency-resolved transient pump-probe[2] where a strong "pump" pulse excite the sample creating a $e-h$ population, that modifies the absorption. A weak "probe" pulse delayed with respect to the pump by Δt, monitors these changes as measured by the Differential Transmission Spectra: $DTS(\omega, \Delta t) = [T(\omega, \Delta t) - T_0(\omega, \Delta t)]/T_0(\omega, \Delta t)$, where $T(\omega, \Delta t)$ and $T_0(\omega, \Delta t)$ are the sample transmission with and without the pump. Initial hole-burning by a non-equilibrium carrier distribution created by $\tau \approx 100$fs pulses, and thermalization within 200fs, has been observed in such experiments in GaAs[2,3,4]. Recently, very slow relaxation, dominated by emission of optical phonons, was reported in the low density limit, $n_{eh} < 10^{16}\text{cm}^{-3}$.[5] The dynamics observed in the above experiments were analyzed within the framework of Boltzmann Kinetics (BK) assuming, furthermore, a generation reflecting the pump spectrum and an independent measurement by the probe.[6,7] The BK treatments, assume exact conservation of the kinetic energy, are local in time and only consider the evolution of populations. As mentioned above such treatments 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

$T_{LO} = 2\pi/\Omega_{LO} = 113$fs (in GaAs). That scale for CCS is $T_{pl} = 2\pi/\omega_{pl} \approx 148$fs for a plasma of density of $n_{eh} = 5\times10^{17}\text{cm}^{-3}$. Therefore for times much shorter that $\approx$ 100fs one expects qualitatively different results. In that case the full quantum kinetic 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 [8,9]. These effects have been studied theoretically, but only limited experimental work has been reported.[10]

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 30fs to 100fs to measure [2,11] the $DTS(\omega, \Delta t)$ in bulk GaAs at room temperature. Furthermore, since we are directly interested in the temporal evolution of the density matrix we determine also the derivative of the DTS with respect to Δt, $DTS\text{-}dot(\omega, \Delta t) = \partial/\partial\Delta t[DTS(\omega, \Delta t)]$. The *DTS* and *DTS-dot* are not directly proportional to the carrier population and scattering rate, but their simultaneous study is important, as they are related by the differential equations which describe the carrier dynamics. We require that any theory invoked to explain our data be able to adequately describe both. The light source is a 30fs 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. $\Delta t = 0$ is determined with an accuracy of $\approx$ 10fs. Measurements were performed on two MBE-grown and anti-reflection coated GaAs samples, $0.25\mu m$ ($\alpha l \approx 0.4$), and $1\mu m$ ($\alpha l \approx 1.6$) thick, at densities $10^{16}\text{cm}^{-3} < n_{eh} < 5\times10^{17}\text{cm}^{-3}$. At these densities both CCS and CPI are significant.

First we have checked the consistency of our procedure with previous experiments by measuring the $DTS(\omega)$ with long $\approx$ 70fs pulses at moderate density $n_{eh} \approx 1.2\times10^{17}$ and with excess energy $\Delta E = \hbar\omega_{pump} - E_g = 38meV$ close to $\hbar\Omega_{LO}$ ($\hbar\omega_{pump}$ is the center frequency of the pump). In agreement with previous reports the $DTS(\omega)$ exhibits a clear spectral hole slightly red shifted below the pump spectrum.[4,11]

Fig. 1 shows $DTS(\omega)$ and $DTS\text{-}dot(\omega, \Delta t)$ measured on the $L = 0.25\mu m$ sample, at high excess energy $\Delta E = 73\text{meV} >> \hbar\Omega_{LO}$ with $\tau_{pump} = 100$fs, $\tau_{probe} = 30$fs and $n_{eh} \approx 1.2\times10^{16}\text{cm}^{-3}$. 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 [12], but its breadth is difficult to explain. The $lh \rightarrow cb$ contribution is expected to be weak and in any case it cannot explain the $DTS(\omega)$ profile. The *DTS-*

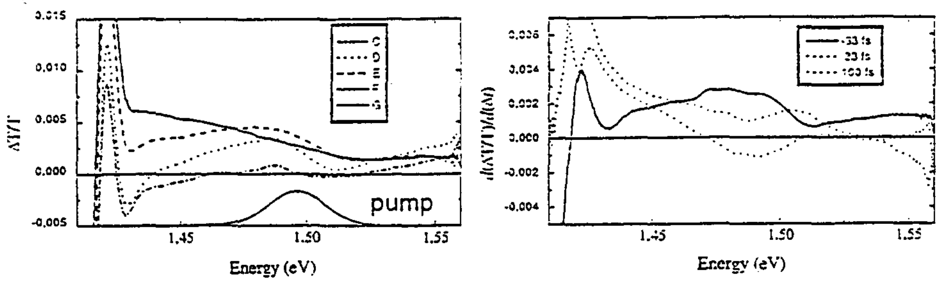

Figure 1: Differential Transmition Spectra and its Δt-derivative. Sample: $0.25\mu m$ GaAs, Probe 30fs, Pump 100fs $\Delta E = 73meV$, $n_{eh} \approx 1.2 \times 10^{16}\text{cm}^{-3}$.

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 ($\approx 5ps^{-1}$) much slower than any of the changes seen experimentally, and a well defined phonon replica[7] 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*(ω) and *DTS-dot*$(\omega, \Delta t)$ measured with much sorter pump pulses, $\tau_{pump} = \tau_{probe} = 30$fs, are shown. The excess energy is $\Delta E =$ 80meV and $n_{eh} \approx 4.4 \times 10^{16}\text{cm}^{-3}$. There is absolutely no spectral hole around the pump spectrum but only a featureless signal extending below $\hbar\omega_{pump}$ all the way to the exciton. The broadening of the exciton again results in a dip slightly above E_{ex}. The *DTS-dot*$(\omega, \Delta t)$ show a uniform positive growth shifted toward the exciton for $\Delta t = 0fs$ and +26fs, that reverses and changes sign at $\Delta t = +53$fs immediately at the end of the pump pulse. This indicative of the 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, which suddenly changes its phase when the pump puise ends. These trends are typical of experiments performed with pump and probe pulses very short as compared to the natural time scales of the system. An other example is shown in Fig. 3 where are presented the measurements performed with the $L = 1\mu m$ sample and also $\tau_{pump} = \tau_{probe} = 30$fs, but $n_{eh} \approx 1.5 \times 10^{17}$ cm^{-3} and $\Delta E = 100$meV, so that there is very little direct excitation at the

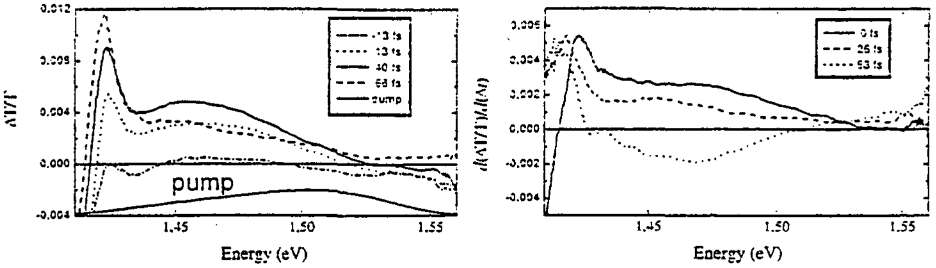

Figure 2: Differential Transmition Spectra and its Δt-derivative. Sample: $0.25\mu m$ GaAs, Probe 30fs, Pump 30fs $\Delta E = 80meV$, $n_{eh} \approx 4.4 \times 10^{16}\text{cm}^{-3}$.

band edge. Again the $DTS(\omega)$ has an instantaneous response at low energies very far from $\hbar\omega_{pump}$. There is essentially no signal at the peak of the pump spectrum. Similar observations were reported with probe tuned to the split-off band transitions that avoid excitonic effects by Alexandrou *et al.*[13] Except for a complicated response around the exciton, the $DTS\text{-}dot(\omega, \Delta t)$ is positive and very strongly shifted toward the exciton for all $\Delta t \leq$ 33fs and change sign as soon as the pump pulse is over $\Delta t \geq$ 47fs.

Finally we have performed spectrally-integrated measurements over a much longer time scale. We found that a steady state is reached in $\approx$ 300fs, in qualitative agreement with earlier experiments in $GaAlAs$.[14] A careful quantitative comparison of the magnitude of the $DTS \approx 10^{-2}$ with the number of states in the laser bandwidth, $\approx 2 \times 10^{-18} cm^{-3}$, and excitation density, $\approx 1.4 \times 10^{-17} cm^{-3}$ shows that this is inconsistent with an initial distribution following the pump spectrum and must corresponds to the "thermalization" of carrier distribution ***immediately spread-out*** by approximately one order of magnitude as compared to that spectrum.

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 our experimental conditions.[15] We have used a four-band version of the SBE in order to take into account the polarization selection rules in GaAs and the polarization's configuration of the experiments.

We have attempted to explain the results within the BK framework de-

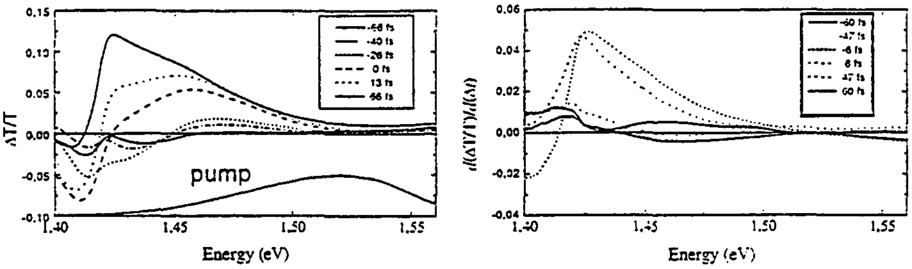

Figure 3: Differential Transmition Spectra and its Δt-derivative. Sample: $1\mu m$ GaAs, Probe 30fs, Pump 30fs $\Delta E = 100meV$, $n_{eh} \approx 1.5 \times 10^{17}\mathrm{cm}^{-3}$.

scribing phenomenologically the irreversible processes in the relaxation time approximation.[15] Since we look for major discrepancy, we try to reproduce qualitatively the data and restrict our discussion to the broad features of the calculated response. First 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 ($\sim$ 200 fs) consistent with the time scale of the experiment. The calculated *DTS* exhibits a red shift of the spectral hole and an instantaneous response at the band-edge. The calculated response shows, however, qualitative discrepancies with the experimental *DTS-dot.* It cannot reproduce neither its shift towards the band-edge *during carrier generation*, nor its *negative sign* close to the laser spectrum frequency immediately after 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: $\partial/\partial t f_k|_{relax} = \{f_k(t) - f_k^{MB}[n(t)]\}/\tilde{T}_1$. We found that is possible, using as adjustable parameter the population relaxation time $\tilde{T}_1$, to get a better qualitative agreement with the experiments. However this occurs only for population relaxation *much faster* than polarization dephasing $\tilde{T}_1 \sim 36$ fs $<< T_2$! Desperate attempts to salvage BK by using more complicated model for dephasing, such an energy-dependent T_2, or excitation-induced dephasing [16] failed to remove the unphysical results i) $T_2 >> \tilde{T}_1$ and ii) $\tilde{T}_1 << 2\pi/\Omega_{LO}$ and $<< 2\pi/\omega_{pl}(max)$ 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[8] or CCS[9]. 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 $t < 1/\omega_{LO}$, due to the time-energy uncertainty. For times $1/\omega_{LO} < t < T_{LO}$ carrier transitions to the low-energy side become favored. Only for times $t > T_{LO}$ 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.[9] We have performed QK calculations of the occupation numbers in k-space that include only CCS. We find that, for excitation with $\approx$ 30fs 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. Using a pump-probe experiment with independently adjustable pump and probe pulses duration we measured the differential absorption spectra and their time-delay derivative. 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.

Acknowledgments, Appendices, Footnotes and the Bibliography

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