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HOT-CARRIER DYNAMICS IN Ge ON SINGLE PICOSECOND TIMESCALES: COMPARING RAMAN AND REFLECTIVITY EXPERIMENTS WITH A SELF-CONSISTENT KINETIC MODEL

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ABSTRACT

Through comparisons of picosecond Raman and transient reflection experiments with a comprehensive kinetic model of photo-excited carrier and lattice dynamics in Ge, we demonstrate the ability of these techniques to probe subtle aspects of non-equilibrium carrier dynamics in group IV materials at moderate injected carrier densities. Using material parameters taken from the literature, the temporal evolution of the non-equilibrium optical phonon population generated by the relaxation of photo-excited electrons and holes is obtained by solving a coupled set of Boltzmann equations for the electron and hole particle and thermal currents. The results of the calculation agree, in absolute terms, with the experimentally observed evolution of the non-equilibrium optical phonon population. The calculation also predicts that the hot plasma initially diffuses rapidly away from the sample surface, on a 5 picosecond timescale, and subsequently diffuses much slower as the carrier temperature decays to the lattice temperature, and the density gradient diminishes due to the hot carriers which have already migrated into the material. This prediction is verified by comparison of the calculated change in reflectivity due to the plasma, and picosecond reflectivity measurements performed at room temperature with 575 nm pulses.

KEYWORDS

Picosecond Raman scattering, Non-equilibrium phonons, Germanium, Boltzmann equations, Time-resolved reflectivity.

INTRODUCTION

Progress in understanding the microscopic details of hot carrier relaxation in group IV semiconductors has not advanced at the same pace as in group III-V materials due largely to the indirect bandgaps of Si and Ge. Experimental techniques such as time-resolved photoluminescence and differential absorption spectroscopies that have proven so powerful in the III-V materials are limited in their utility when the fundamental gap is indirect. Transient transmission, reflection and diffraction measurements have been performed, but most of this work was concerned with high excitation levels where non-linear absorption and recombination processes often obscure the more subtle carrier-lattice interactions. However, the motivation for developing techniques to address these issues in group IV materials continues to increase as sophisticated, high-speed electronic devices such as double-barrier resonant tunneling structures are now being studied in the Si/SiGe material system (Houghton 1988).

The purpose of the present paper is to demonstrate the utility of picosecond Raman scattering and visible reflectivity measurements for investigating non-equilibrium carrier and lattice dynamics in the group IV semiconductor Ge, at moderate excitation levels for which minimal lattice heating occurs. The experimental conditions are such that non-linear absorption and recombination processes, which complicate the analysis of high-excitation experiments in Ge, are also absent. This allows a detailed analysis of the results using a kinetic model which focuses on the microscopic energy relaxation processes, in much the same way as is commonly done in the group III-V hot-carrier field.

One important result from this study is the quantitative agreement between theory and experiment for the absolute non-equilibrium optical phonon population generated ($\sim$0.1) at an injected carrier density of $\sim 1\text{x}10^{18}\text{cm}^{-3}$. This demonstrates that even with a wavevector independent carrier-phonon matrix element, as is appropriate for the deformation potential interactions in Ge, pure kinematic constraints of energy and momentum conservation severely limit the range of wavevectors through which energy may be transferred to the lattice from the hot carriers.

Another interesting effect, predicted by the model and verified by a time-resolved reflectivity experiment, is the very significant role which non-linear carrier diffusion plays, even on picosecond timescales, when using visible excitation in Ge. The non-linearity stems from the carrier temperature dependence of the ambipolar diffusion coefficient, and leads to enhanced diffusion at short times and retarded diffusion at times long after the excitation pulse.

EXPERIMENT

The experimental setup used to time-resolve the anti-Stokes component of the Raman signal from non-equilibrium optical phonons in Ge has been described in detail elsewhere (Young 1988). Briefly, pump and perpendicularly polarized probe beams were derived from a train of 4 ps (FWHM) synchronously mode locked pulses at 575 nm. The pump pulses were focused to yield a fluence of $\sim 0.1mJ/cm^2$ on the Ge surface while the probe pulses were focused to the same spot size, with $\sim 30\%$ of the pump beam's fluence. Scattered light due to the probe beam was collected in a back-scattering geometry and the anti-Stokes component was monitored on a Si charge coupled array detector at the output of a triple spectrograph.

The time-resolved reflectivity measurements were performed using two different experimental arrangements, and similar results were obtained from both. In the first experiment pulses from the synchronously pumped dye laser were amplified with a 4 stage dye cell system, pumped at 20 Hz by an eximer laser (Corkum 1987). The amplified pulses were split into orthogonally polarized pump and probe beams and then superimposed on the Ge sample with a 10^o angle between them and with the probe beam focussed to one fifth of the pump beam diameter. In the second experiment the pump and probe beams were derived from a synchronously pumped dye laser with a cavity dumper operating at 3.8MHz. The high repetition rate enabled a lock-in detection scheme which yielded improved signal to noise over that obtained from the boxcar detection scheme used with the amplified pulses. The fluence of the incident pump beam on the Ge sample was $\sim 3mJ/cm^2$, with a pulse duration of $2ps$ (FWHM).

THE MODEL

The fundamental interactions which occur during and following the application of a short, above-bandgap laser pulse on a semiconductor surface have been described by many (van Driel 1986, Elci 1976). Here we give a brief summary of the processes that are relevant to our work. Germanium is an indirect-gap semiconductor whose band structure is well known (Neuberger 1971). To make the calculations tractable, we make similar simplifying assumptions about the band structure as those described by Elci (1976). In particular, in the conduction band we assume that the band-edge energies of the 4 L and 6 X valleys are the same, but assign each their respective effective masses. In the valence band, only heavy holes are considered since at the elevated temperatures of interest here, the curvatures of the two valence bands are identical, and there is very little difference in their energies.

The model allows for one and two photon interband absorption and single photon free carrier absorption. For the excitation levels used in the Raman experiments, the only important mechanism is single photon interband absorption near the Γ point of the Brillouin zone. This results in the creation of electron-hole pairs with total kinetic energy $\hbar\omega$-E_g. The electrons initially created in the Γ valley quickly scatter into the side valleys, where they are assumed to thermalize through electron-electron scattering with an initial temperature of $\sim 6800K$ (at an ambient temperature of $77K$). Once in the side valleys the hot electrons thermalize with the lattice via electron-phonon deformation potential interactions, and with the cooler holes (initial hole temperature $\sim 3000K$ at an ambient temperature of $77K$) via the Coulomb interaction. The optical phonon mediated relaxation of L valley electrons and heavy holes generates non-equilibrium populations of optical phonons with relatively small wavevector which can be monitored via Raman scattering. Energy relaxation via acoustic mode phonons and via inter-valley optical phonon processes acts to cool the carriers without generating any Raman-active optical phonons.

To model the dynamics of hot electrons, holes and optical phonons we use the formalism of van Driel (1986) which deals with coupled Boltzmann's equations, in the relaxation time approximation, for particle number, particle energy and lattice energy. Three coupled continuity equations are solved numerically for the depth and time dependent density N, carrier temperature T_c and lattice temperature T_L. To specifically model the Raman and reflectivity experiments in Ge, the above formalism was generalized to include different electron and hole temperatures, and to include detailed microscopic expressions for energy exchange processes. This therefore involves the solution of four coupled differential equations:

$$\frac{\partial N}{\partial t} = -\nabla \cdot \mathbf{J} + N_{gen} + N_{rec}, \qquad C_L \frac{\partial T_L}{\partial t} = -\nabla \cdot \mathbf{W}_{lat} + L_e + L_h$$
$$\frac{\partial U_e}{\partial t} = -\nabla \cdot \mathbf{W}_e + S_e - L_e - L_{e-h}, \qquad \frac{\partial U_h}{\partial t} = -\nabla \cdot \mathbf{W}_h + S_h - L_h + L_{e-h} \tag{1}$$

where N_{gen} is the carrier generation rate, and N_{rec} is the net recombination rate given by $\delta N - \gamma N^3$, where δ and γ are the impact ionization and Auger recombination coefficients. In the above equations $\mathbf{J}$, $\mathbf{W}_e$, and $\mathbf{W}_h$ refer to the particle current, and energy current flow for electrons and holes, U_e and U_h represent the total energy density of the electron and hole systems, S_e and S_h are the source terms for the electrons and holes, while L_e, L_h, and L_{e-h} are the kinetic energy transfer terms. In the continuity equation for the lattice temperature, C_L is the specific heat and $\mathbf{W}_{lat}$ is the lattice heat flow.

Due to the very large initial kinetic energy of the free carriers, it is important to allow for the carrier temperature dependence of the ambipolar diffusion coefficient D. In the Maxwell-Boltzmann limit, the expression for the diffusion coefficient is given by

$$D = D_e^0 D_h^0 \left\{ \frac{T_e + T_h}{D_h^0 T_e + D_e^0 T_h} \right\} \tag{2}$$

where D_e^0, D_h^0 are the Maxwell-Boltzmann electron and hole diffusion constants appropriate for the ambient temperature.

For a direct comparison with the Raman experiments, we also calculate the spatial and temporal evolution of the optical phonon population generated due to intra L valley and intra heavy hole valence band relaxation processes. This involves solving a partial differential equation for the phonon occupation number n_q

$$\frac{dn_q}{dt} = \left(\frac{dn_q}{dt}\right)_{gen} + \left(\frac{n_q^{eq} - n_q}{\tau}\right) \tag{3}$$

where τ is the non-equilibrium phonon decay time determined experimentally(Young 1988), n_q^{eq} is the equilibrium phonon occupation, and $\left(\frac{dn_q}{dt}\right)_{gen}$ is the optical phonon generation rate (Young 1988) given by

$$\left(\frac{dn_q}{dt}\right)_{gen} = \sqrt{\frac{\pi}{2}} \frac{\mathcal{D}_c^2}{\rho \varepsilon_{ph} q} \sqrt{\frac{m^*}{k_B T_c}} \frac{\exp\left[\frac{\varepsilon_{ph}}{k_B}\left(\frac{1}{T_L} - \frac{1}{2T_c}\right)\right] - \exp\left(\frac{\varepsilon_{ph}}{2k_B T_c}\right)}{\exp\left(\frac{\varepsilon_{ph}}{k_B T_L}\right) - 1}$$
$$\times \exp\left[\frac{-\hbar^2}{2m^* k_B T_c}\left(\frac{m^{*2}\varepsilon_{ph}^2}{\hbar^4 q^2} + \frac{q^2}{4}\right)\right] \tag{4}$$

where $\mathcal{D}_c$ is the optical deformation potential constant, and ε_{ph} is the optical phonon energy. For the total energy loss rate of the carriers we use analytic expressions for the various scattering mechanisms (Conwell 1967, Nag 1972, Jacoboni and Reggiani 1983, Young 1987). These include:

(1) Intravalley acoustic phonons and optical phonons.
(2) Intervalley acoustic and optical phonons.
(3) Electron-hole scattering.

The average rate of energy loss of a carrier to the acoustic modes is given by the following equation:

$$\left(\frac{dE}{dt}\right)_{ac} = -\frac{8\sqrt{2}}{\pi^{3/2}} \frac{\varepsilon_{ac}^2 m^{*5/2}}{\hbar^4 \rho} (k_B T_c)^{3/2} \left(1 - \frac{T_L}{T_c}\right) \tag{5}$$

where ε_{ac} is the acoustic deformation constant, and ρ is the density of the semiconductor. The

energy loss rate for hot carriers due to intra-L valley and intra-valence band optical phonon processes is obtained by integrating Eqn. 4 over all wavevectors, which gives,

$$\left(\frac{dE}{dt}\right)_{op} = -\sqrt{\frac{2}{\pi}}\frac{\mathcal{D}_c^2 m^{*3/2}}{\pi\hbar^2\rho}(k_B T_c)^{1/2}\frac{\exp\left[\frac{\varepsilon_{ph}}{k_B}\left(\frac{1}{T_L}-\frac{1}{T_c}\right)\right]-1}{\exp\left(\frac{\varepsilon_{ph}}{k_B T_L}\right)-1}\frac{\varepsilon_{ph}}{2k_B T_c}$$

$$\times \exp\left(\frac{\varepsilon_{ph}}{2k_B T_c}\right)\mathcal{K}_1\left(\frac{\varepsilon_{ph}}{2k_B T_c}\right) \qquad (6)$$

where $\mathcal{K}_1$ is the modified Bessel function. Electron intervalley scattering may be treated much like the intravalley scattering by optical phonons. The average rate of energy loss of a carrier due to intervalley scattering form valley i to valley j may be calculated using Eqn. 6 with $\mathcal{D}_c$ replaced by $\mathcal{D}_{ij}$, $\hbar\omega_0$ with $\hbar\omega_{ij}$ and finally m^* with the density of state mass of the j valley, $m_j{}^*$ (Conwell 1967). Electron-hole energy exchange was treated in the static screening limit, including intra-heavy hole transitions, as described elsewhere (Young 1987).

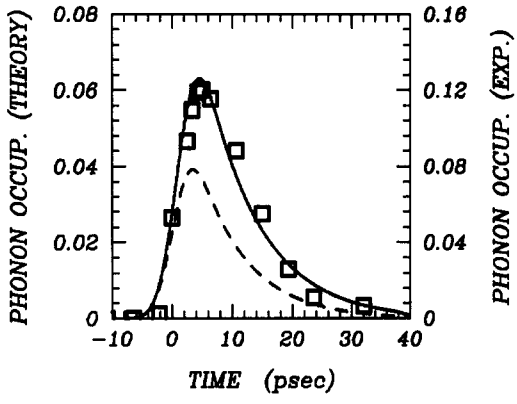

Fig. 1. Temporal profiles of the non-equilibrium optical phonon occupation number at $77K$. The squares represent experimental data, the solid and dashed curves are calculated using the model with $\mathcal{D}_h/\mathcal{D}_e = 2.2$ and $\mathcal{D}_h/\mathcal{D}_e = 3.3$ respectively.

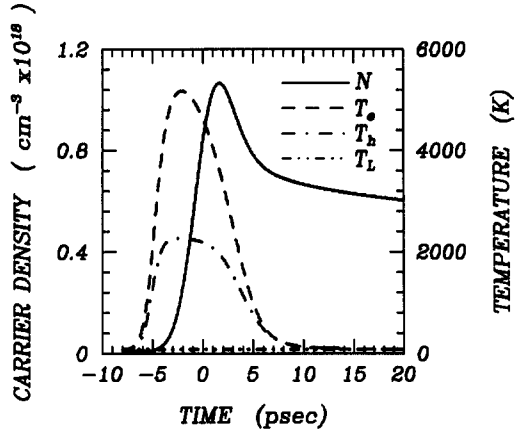

Fig. 2. Temporal profiles of the carrier density(N), electron(T_e), hole(T_h) and lattice(T_L) temperatures in Ge at $77K$.

RESULTS AND DISCUSSION

The model described above was solved using the material parameters listed in Jacoboni (1983), with an excitation term corresponding to a 4 ps (FWHM), 575 nm laser pulse of energy $0.7nJ$, focused to a spot of diameter $30\mu m$. The skin depth of the pump and probe pulses is $0.2\mu m$ at $77K$. The calculated non-equilibrium optical phonon population at this temperature is shown together with the experimental Raman scattering data in Fig. 1. Note that the delay between the peak of the pump pulse ($t = 0$) and the maximum non-equilibrium phonon occupation agree well, while the absolute value of the excess population agrees within a factor of 2. This agreement between experimental Raman data and a calculation with no variable fit parameters is satisfying in two respects. First, the delay is a function of material parameters only, and is therefore insensitive to errors in estimating the precise excitation conditions. Second, the error in the absolute scale for the experimental non-equilibrium phonon population shown in Fig. 1 is $\sim \pm 50\%$, due mainly to uncertainties in the precise sizes and the overlap of the pump and probe beams. Therefore, even the absolute value of the excess occupation number is basically in agreement within the experimental error.

We note that the ratio of optical phonon deformation potentials for holes to electrons used in the calculation (Jacoboni 1983) is 2.2. If the value of 3.3, suggested by Conwell (1969) is used instead, with the same electron deformation potential, the calculation yields the dashed curve in Fig. 1. Clearly the agreement is not as good.

Perhaps the single most important component of the model is the carrier diffusion process. With

the full temperature-dependent ambipolar diffusion coefficient included (Eqn.2), the maximum carrier density achieved in the Raman experiments is $\sim 10^{18} cm^{-3}$ (see Fig. 2). At this density, Auger recombination, impact ionization, non-linear absorption, and lattice heating are all negligible effects, thus confirming the claim above concerning the moderate level of excitation used in these experiments. However, if diffusion is ignored altogether, the peak carrier density and the non-equilibrium optical phonon occupation numbers are a full order of magnitude larger, which is clearly inconsistent with the Raman data. If a constant (equilibrium) ambipolar diffusion coefficient is used, the error is not so large, nevertheless there is still a significant difference compared to the temperature-dependent result. To verify that non-linear, hot-carrier diffusion effects are in fact playing a role, we used a simple Drude model to estimate the carrier density induced change in the reflectivity of the Ge at $300K$, in response to a $2ps$ excitation pulse as described above, for both constant and temperature-dependent diffusion. The results of these two calculations are shown in Fig. 3 along with the experimentally determined change in reflectivity. It is clear that the full temperature-dependent calculation yields a much better fit to the experimental results then does the calculation with a constant diffusion term. We note that the fluence of the pump pulse used in the reflectivity experiments was more than an order of magnitude higher than in the Raman experiments. As a consequence, the peak carrier density achieved in the reflectivity experiment is $\sim 8 \times 10^{19} cm^{-3}$, which is still below the value at which Auger recombination and lattice heating effects occur. The only deficiency of the model at these densities might be the assumption of Maxwell-Boltzmann carrier distributions, however, the inclusion of Fermi-Dirac distributions is not expected to make a significant difference to the calculated reflectivity at these densities.

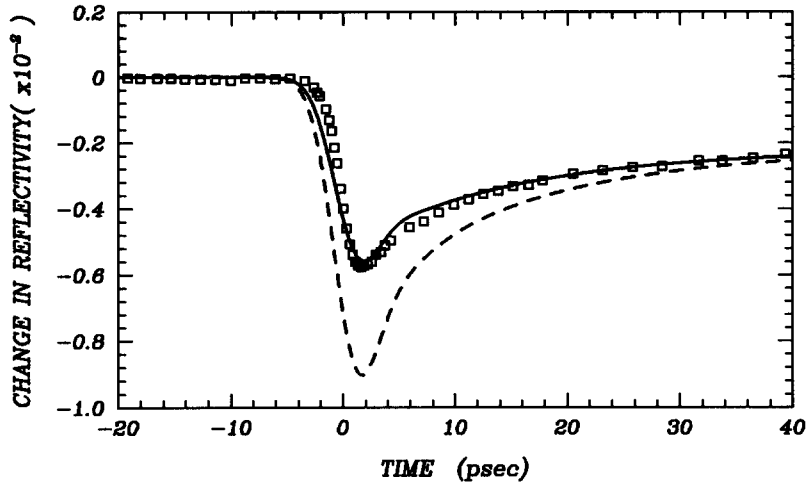

Fig. 3. Time resolved reflectivity at 575nm. The squares are experimental data, the solid and dashed curves are calculated reflectivity changes for the ambipolar diffusion coefficient assumed temperature dependent and constant respectively.

Through comparisons of picosecond Raman scattering and time-resolved reflectivity experiments with a kinetic model, we have demonstrated the ability of these techniques to probe subtle aspects of non-equilibrium carrier dynamics in Ge at moderate injected carrier densities. In particular, non-equilibrium optical phonon generation and hot carrier diffusion processes can be quantitatively understood.

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