PART I

Plenary Overviews

FUNDAMENTALS OF PICOSECOND AND FEMTOSECOND LASER SOLID INTERACTIONS

H. Kurz
Institute of Semiconductor Electronics, Aachen University of Technology,
D-5100 Aachen, F.R. Germany

ABSTRACT

The current understanding of the interaction between ultrashort laser pulses and condensed matter is demonstrated on a few selected samples. Hot electronic carrier relaxation in GaAs, plasmon aided recombination in highly excited silicon and ultrafast energy transport in metals are discussed.

Introduction

In the last materials research society meetings the essential role of time resolved optical methods have been demonstrated convincingly as successful techniques to study fundamental processes of laser material interactions [1-9]. The power and range of optical methods has been remarkably enlarged by the rapid development of new laser sources delivering tunable and intense femtosecond pulses.

In this review most of the attention is paid to details of femtosecond pulse interactions in semiconductors and metals at high excitation levels. Three specific examples of systems driven far out of equilibrium are chosen. After a general survey of physical principles involved the relaxation of hot carriers in III-V compounds is adressed. The influence of collective plasma oscillations on energy relaxation and carrier dynamics is considered in a high excitation study of elemental semiconductors. New relaxation channels are opened as soon as the plasma energy becomes comparable to phonon- and bandgap energies. Finally the energy transport in metals by hot electrons is discussed. The high transport velocities observed in very recent experiments are of technical importance for laser processing of metals and alloys.

Mat. Res. Soc. Symp. Proc. Vol. 74, ©1987 Materials Research Society

II. PHYSICAL PRINCIPLES

The primary dissipative interaction step is the absorption photons by electrons. In a secondary step the energy is transferred from the excited state to other electrons or holes and lattice vibrational modes.

In metals the conduction electrons are excited by inelastic free-free transitions, well described by a high frequency conductivity. In semiconductors electron-hole pairs are created if the photon energy exceeds the bandgap. Photons below the bandgap may create electron-hole pairs via multiphoton absorption. Once the carrier density is sufficiently high, phonon assisted free carrier absorption and intervalence transitions between light and heavy holes increase the energy content of the electron-hole system without adding new carriers.

In semiconductors only narrow regions in the central valley of conduction band and valence band are coupled by the laser field. The lifetime of the optically coupled states is limited principally by inelastic intercarrier and phonon collisions. It requires femtosecond laser pulses to saturate the interband transition noticeable in most of the semiconductors.

At carrier densities above 10^{19} collective oscillations of electrons and holes have a major impact on the physics of relaxation. With increasing carrier densities the plasmon energy passes through resonances with phonon and bandgap energies. Coupled plasmon-phonon modes enlarge the carrier-phonon scattering rates significantly. Electrons can recombine with holes via emission of plasmons and finally particle-plasmon interactions enhance the rate of internal thermalization of the electron-hole plasmas.

Although there is no explicit treatment of carrier-plasmon scattering available in the case of monoenergetic carrier distributions the rate of carrier scattering can be estimated to be proportional to the density N. Energy relaxation by plasmon emission is possible when the kinetic energy of the carriers is larger than the plasmon energy. These plasmons decay subsequently into single particle excitations. At densities above 10^{19} cm^{-3} intercarrier collisions and plasmon production ensure an internal thermalization of the electron-hole system in times of order 10^{-14} sec. The thermal distribution can be characterized by temperatures $T_e=T_h=T_c$. Internal carrier thermalization occurs on a much faster time scale than energy transfer to the phonons. Large splittings between the carrier temperature T_c and lattice temperature T_l are expected on a subpicosecond time scale.

For femtosecond excitation in both, semiconductors and metals, the evolution of carrier temperature T_c can be described therefore adequately by:

$$C_c(T_c)\,\frac{\delta T_c}{\delta t} = K_c \nabla^2 T_c - g(T_c - T_l) + S(t) \qquad (1)$$

where C_c is the specific heat capacity of the excited carriers and K_c the thermal conductivity. $g(T_c-T_l)$ is the average energy loss rate due to phonon emission and g the coupling parameter. S(t) is the laser energy deposition rate. In metals the loss rate determined by deformation potential scattering is proportional to $(T_c-T_l)/T_l\,\tau_e$, where T_l is the lattice temperature and τ_e is the energy relaxation time.
The relaxation between loss term and temperature splitting (T_c-T_l) is strictly valid only after thermal equilibrium between phonons is established. Since $\tau_e \propto 1/T_l$ and $T_c \rightarrow T_l$ this equation can still be used for estimates in the femtosecond regimes. In the case of semiconductors in the coupling parameter g all relevant relaxation channels are taken into account.

In elemental semiconductors the carrier-phonon interaction process is based on deformation potential scattering for electron and holes. In polar compounds electron and holes may experience different scattering. Polar mode scattering is dominant for both types of carriers. The s-like conduction band prohibits, however, nonpolar phonon emission. The most effective energy loss mechanism for electrons located high in the conduction band is intervalley scattering, where large wave vector changes are involved. Intervalley scattering exceedspolar mode scattering by one order of magnitude in GaAs. It represents the most effective channels for the transfer of electron energies to phonons.

Free carrier scattering as well as carrier-phonon coupling are subject to screening, reducing the energy transfer at high carrrier densities. Critical densities at which screening begins to become important are in the order of 10^{19} cm^{-3} for intravalley processes, while intervalley scattering is effectively screened beyond 10^{21} cm^{-3} only. Although the hole transitions may be effectively screened rapid intercarrier collisions ensure that both types of carriers lose energy at the same rate.

When the plasmon energy becomes comparable to the energy of phonons involved new energy relaxation channels are opened. Especially in compound semiconductors the longitudinal optical phonons couple strongly with longitudinal plasma oscillations. Coupled plasmon-phonon modes increase in inelastic scattering rates of hot carriers significantly. The phonon

emission rate is increased by one order of magnitude in GaAs ($2x10^{13}$ s^{-1}).

Phonons emitted via different scattering mechanisms would occupy certain fractions of the Brillouin zone. They thermalize through anharmonic interactions relatively slowly at low densities (10-100 ps). In the presence of a highly dense electron-hole plasma, however, particular optical phonon lifetimes are shortened drastically speeding up phonon thermalization. As in the case of metals, phonons can decay into single electronic states, which decay into other phonons again. This multistep decay has been confirmed in Raman line widths measurements of heavily doped silicon. At a density of 10^{20} electrons /cm^{-3} the optic phonon lifetime is reduced to $\sim$ 200fs. Thus for time scales longer than one picosecond the energy transferred from electronic carriers can be treated as directly converted into lattice heat. Complementary to equation (1) the evolution of lattice temperature is given by:

$$C_l\ (T_c)\ \frac{\delta T_c}{\delta t} = g(T_c - T_l) \qquad (2)$$

where C_l is the specific heat capacity. Thermal diffusion can be neglected on the time scales considered here.

In semiconductors and metals the hot carrier distributions cool down to the equilibrium level, $T_c=T_l$, within picoseconds. During this cooling the semiconductor plasma changes from classical regime to the quantum limit. The cold carriers accumulate in the band extrema "waiting" in this quasi-equilibrium state for the possibility to recombine. As a consequence most of the semiconductors are driven far into degenerate conditions within picoseconds. For example in silicon the quasi-Fermi level are driven 400 mV into the conduction band minimum and 60 mV below the valence band maximum at a carrier density of 10^{20} cm^{-3} and temperatures below 1000K. This situation may be described by a temporary "quasi-metallic" state. The changes in the optical properties induced by the degenerate plasma resembles closely metallic behaviour.

The recombination kinetics of nonequilibrium carriers in highly excited semiconductors is mainly determined by nonradiative Auger-processes and radiative bimolecular recombination. In Si like semiconductors the main process is a phonon assisted Auger-process where the energy of an e-h-pair is transferred to a third particle, which can be either an electron or a hole. Due to combined effect of restriction to the Fermi sphere and of the wave vector and energy conservation the phonon free Auger-process is less probable in degenerate direct semiconductors. The main advantages of phonon assisted Auger recombination is the fact that the wave vector conservation must not be satisfied by carriers, but can be fulfilled by phonons, whereas

the energy conservation is hardly influenced by it. In silicon the recombination probability has been found to be weakly temperature dependent. In direct semiconductors, however, the recombination rates increase strongly with temperatures.

The rate at which carriers are transferred to high energetic states is defined by γN^3, where γ is the recombination coefficient. The extremely energetic Auger particles share rapidly their energy with other carriers and relax to the floor at the Fermi-level via phonon emission. Nonradiative Auger-recombination lowers the density of the electron-hole plasma, but increases the temperature. It causes a retarded heating of the plasma and lattice controlled by γN^3.

Principally the Auger process is balanced by impact ionization at the same rate if the average energy of the carriers exceeds the bandgap. The rate of this counter effect is determined by $\gamma(N_0^2-N^2)$ where N_0 is the equilibrium density of carriers at the temperature T_c. Because of the ultrafast energy relaxation, however, the carrier temperature drops too fast for impact ionization. Even in the case of femtosecond excitation, where phonon emission is too slow to cool the plasma significantly during the laser pulse, the still lower Auger rates exclude the possibility of impact ionization.

The most important effect of Auger recombination is the retarded heating of the carrier gas and the subsequent lattice heating. The splitting between carrier temperature and lattice temperature remains as long as the nonradiative Auger-process dominates radiative recombination processes. This secondary heating has to be taken into consideration when cooling rates on a psec time scale are analyzed in photoluminescence experiments.

III. HOT CARRIER RELAXATION IN III-V-COMPOUNDS

In III-V compounds large disparities between effective electron and hole masses lead to strong differences in excess energies. Thus the carriers lose energy via inelastic scattering of electrons mainly. The most important intravalley process is the emission (or absorption) of polar optical phonons. Scattering rates in the order of 6×10^{12} s^{-1} have been measured at low densities ($\leqslant 10^{17}$ cm^{-3}) in GaAs in close agreement with theoretical predictions. If the initial energy of electrons is greater than one optical phonon below the side valley conduction band minima, intervalley scattering becomes operative. The corresponding phonon emission rate exceeds

$3x10^{13}sec^{-1}$ in GaAs and increases with the density of states available. Thus intervalley scattering rates become comparable to the rate of inter-carrier collisions at high densities. Both processes limit effectively the lifetime of optically coupled states located high in the central valley.

The degree of absorption saturation of femtosecond laser pulses allows a qualitative estimate of the initial scattering rate. In transmission correlation experiments C.L. Tang and coworkers observed for the first time several relaxation times corresponding to different scattering processes [11]. Transmission correlation techniques allow principally the detection of relaxation phenomena which are faster than the duration of the laser pulse (80 fs). The fastest time constant has been found in GaAs with 40 fs, independent of carrier densities up to $10^{19}cm^{-3}$. This ultrafast scattering out from the optically coupled states has been attributed to intervalley transitions [11].

In AlGaAs and multiple quantum wells consisting of alternating layers of GaAS and AlGaAs, however, the scattering rate starts to depend on the density of carriers excited. The depopulation of optical coupled states becomes faster with the increasing carrier density.

Possible relevant carrier density dependent processes are screening of the carrier-phonon interaction and free carrier or plasmon scattering. If the plasmon energies are close to phonon energies, coupled plasmon-phonon modes contribute to the depopulation rate.

The principal restriction to a single probing wavelength in equal pulse correlation experiments is lifted in conventional pump and probe experiments. Here the interrogating pulse can cover the whole energy range between original excited levels and the minima of semiconductor bandstructure. In contrary to the equal pulse correlation technique the temporal resolution is limited by the convolution of pump and probe pulse.

Time resolved changes in the interband transmission correspond to the temporary occupation of intermediate electronic states. From time resolved transmission spectra using spectrally broadened (white light) fs-pulses the carrier cooling by phonon emission has been studied on a subpicosecond time scale. C.V. Shank et al. found that, for a comparable density, the cooling rates are the same for bulk GaAs and quasi-2D-systems (GaAs/AlGaAs). They did not find any effect of dimensionality. The cooling rate by phonon emission, however, seems to be reduced at densities of 2.10^{17} cm^{-3} [12]. Strong deviation in the cooling rate between bulk and 2D samples has been reported at even higher densities. In nonlinear hot luminescence correlation experiments this deviation has been found to start above 1017cm-3 and increases progessively at higher densities [13].

While the influence of dimensionality and carrier density on the carrier-phonon interaction in III-V compounds is under revision, the carrier-carrier interactions are documented quite clearly. In carefully designed experiments in both, bulk GaAs and in GaAs/AlGaAs quantum well structures, spectral hole burning in the valence to conduct band transition has been observed [14, 15]. The formation of an initial nonthermal distribution and the subsequent internal thermalization of the carrier gas could be resolved clearly. At an excitation density of $\backsim 10^{18} cm^{-3}$ the nonthermal distribution of electrons thermalizes in a time on the order of 200 fs, if the excess energy of the carriers is kept below the critical condition for LO-Phonon emission.

Based on the experimental facts reported up to now at medium density level ($< 10^{19} cm^{-3}$) following prediction for femtosecond laser pulse interaction at high excitation levels may be derived.

Scaling up to densities above 10^{20} cm^{-3} rapid internal thermalization of photoexcited electron-hole pairs can be anticipated in extremely short times ($\backsim$10fs), in which no energy transfer to the phonons can occur. Both, intercarrier collisions and plasmon production rate dominate the energy relaxation by phonon emission. Thus excitation with intense femtosecond pulses will result in the nearly instantaneous formation of an extremely hot classical carrier plasma during the excitation pulse, while the lattice temperature remains fairly unaffected. On a medium time scale ($<$1ps) the hot carrier distributions would experience strong intervalley scattering. Intercarrier collision ensure thermal equilibrium between holes and electrons. Holes lose their energy at the same rate via electron cooling. The intervalley scattering processes are barely screened.The total loss rate is expected to remain unchanged even at the highest carrier densities encountered. At a time scale of picoseconds thermal equilibrium is established between carrier and phonons. The carrier dynamics start to be controlled by Auger recombination.

All these predictions are still subject of future experiments with fs-pulses. They have to be consistent with several experimental facts already observed with picosecond pulses in GaAs and elemental semiconductors. Among them the most important result is the ultrafast phase transitions which occur within the picosecond excitation pulse. Using nonlinear optical detection techniques J.M. Liu et al. have shown that optical heating and subsequent melting of GaAs occurs within one picosecond [16]. The often cited screening of carrier-phonon interaction at high densities is not consistent with these experimental facts.

IV. HIGH EXCITATION PHENOMENA IN ELEMENTAL SEMICONDUCTORS

Previous optical time resolved investigations of phasetransitions at semiconductor surfaces irradiated with picosecond pulses provided surmounting experimental evidence for the validity of thermal model descriptions. Both the carrier- and the lattice temperature could be modelled in excellent agreement with experimental data. The thermal model assumes that thermal equilibrium is established between electrons and holes during the excitation pulse, characterized by a carrier temperature T_c as expressed in eqn. (1). Thermal equilibrium is also assumed to be established between phonons in this time too. The validity of this assumption is supported by Raman-line width measurements at high plasma densities and time resolved optical probing of lattice heating [17]. As in the case of metals, large disparities between carrier- and lattice temperatures are expected if the energy relaxation time τ_e is comparable to the duration of the exciatation pulse. From experimental data obtained in picosecond photoelectric experiments the maximum carrier temperature has been estimated to be less than 5000 K. From this upper limit an energy relaxation time in order of picoseconds has been derived [18]. Time resolved investigation of the optical absorption corresponding to interband transitions in silicon dedicated to monitor the temporal evolution of the lattice temperature have confirmed this conclusion [17]. Careful analysis of the optical data reveiled that lattice heating occurs in two steps. Direct heating is accomplished during the pulse due to the ultrarapid energy relaxation of hot carriers. There further energy transfer is blocked because of the lack of free energy states into which the electrons or holes can be scattered. This blockage lasts as long the quasi-Fermi levels remain unaffected by electron-hole recombination. As soon as the Fermi-level starts to move towards the band-gap center again with decreasing carrier density, the scattering channels into lower energy states are opened again. Thus a second heating phase follows controlled by the dynamics of recombination [17,18]. At extremely high excitation levels ($\backsim 5 \times 10^{20} cm^{-3}$ in silicon) the directed heating process vanishes due to strong band filling. The entire evolution of lattice temperature is defined by Auger recombination. The lattice heating rates in picosecond laser melting experiments are slower than anticipated up to now. The heating rate close to the melting point is slowed down remarkably. The exact knowledge about the final temperature evolution close to phasetransitions is important for the understanding of "superheating" the solid phase of semiconductors.

The two phases of lattice heating has been clearly resolved in previous