Probing ultrafast carrier and phonon dynamics in semiconductors

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(Received 28 October 1996; accepted for publication 29 September 1997)

Over the past 2 decades there has been tremendous advancements in the field of ultrafast carrier dynamics in semiconductors. The driving force behind this movement other than the basic fundamental interest is the direct application of semiconductor devices and the endless need for faster response and faster processing of information. To improve and develop microelectronics devices and address these needs, there must be a basic understanding of the various dynamical processes in the semiconductors which have to be studied in detail. Therefore, the excitation of semiconductors out of their equilibrium and the subsequent relaxation processes with various rates has become a key area of semiconductor research. With the development of lasers that can generate pulses as short as a few femtoseconds the excitation and subsequent probing of semiconductors on an ultrashort timescale have become routine. Processes such as carrier momentum randomization, carrier thermalization, and energy relaxation have been studied in detail using excite-and-probe novel techniques. This article reviews the status of ultrafast carrier and phonon dynamics in semiconductors. Experimental techniques such as excite-and-probe transmission, time-resolved up-conversion luminescence, and pump-probe Raman scattering along with some of the significant experimental findings from probing semiconductors are discussed. Finally, a selfconsistent theoretical model, which correlates the carrier and phonon dynamics in germanium on an ultrashort time scale, is described in detail. © 1998 American Institute of Physics.

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I. INTRODUCTION

Much of the information technology is based on the fast response of small and high-speed microelectronics devices. In the last 20 years there has been considerable interest in exploring the limitations of semiconductors used in this technology by investigating at a fundamental level the underlying fast microscopic processes which occur on a picosecond or even a femtosecond time scale. Fundamental processes like momentum and energy relaxation, as well as mechanisms such as carrier–carrier scattering, intervalley and intravalley scattering, optical phonon scattering, and carrier diffusion, have been investigated thoroughly. This article will review some of the advances made over the past 2 decades in the field of ultrafast carrier dynamics in semiconductors. This review will cover primarily the experimental aspects of the field.

In semiconductor microelectronics devices high speeds and small distances are closely related. Transistors with effective lengths of only few tens of nanometers have electrons transit time that can be as short as a picosecond and some times as short as a few hundreds of femtoseconds. This very fact has motivated a great deal of interest in very small-scale electronic devices. In other words making semiconductor devices smaller allows a faster response. The development of such high-speed devices requires a clear understanding of the various dynamical properties of carriers as well as phonons in semiconductors on an ultrashort time scale. For example, the maximum attainable speed of gallium arsenide field effect and heterojunction bipolar transistors is limited by the rate at which electrons transfer between high-mobility and low-mobility regions in the conduction band of this material. Another interesting example is the rate at which energy relaxation occurs in a semiconductor material, the rate for this process may be limited by relaxation of the nonequilibrium phonons generated during carrier equilibration.

One of the first challenges facing researchers in the early days of photoexcitation of semiconductors by laser pulses was to achieve high temporal resolution. The shorter the duration of the pulse used in the excitation of the material the better the temporal resolution of the various dynamical processes. The motivation was to generate very short optical pulses that would allow researchers to probe faster processes. By the early 1980s this challenge was met with the availability of subpicosecond laser pulses allowing researchers to use time-resolved ultrafast processes. However, time-resolved measurements with ultrashort resolution is a formidable task.

The traditional approach, which uses high-speed electronic instruments, failed since the response time of such instrumentation is several orders of magnitude slower than the ultrashort optical pulses themselves. Novel and precise optical techniques are now being used to explore the properties of semiconductors on a time scale much shorter than those previously believed to be attainable. The development of excite-and-probe techniques has shown how to probe extremely short lived processes with resolution limited only by the laser pulse itself.1

Over the past decade there have been many experiments using excite-and-probe techniques to investigate the temporal behavior of semiconductors. Most of these experiments have separately probed various aspects of nonequilibrium (hot) carrier and phonon dynamics on a picosecond or subpicosecond time scale. Although much of the emphasis has been placed on understanding nonequilibrium carrier kinetics alone, nonequilibrium phonons can influence hot carrier relaxation and transport.2,3 In fact, observations of nonequilibrium phonon populations through transient Raman scattering have directly provided evidence for the existence and decay of nonequilibrium phonon populations generated by hot carrier relaxation.4–6 However, there has been virtually no effort to simultaneously investigate the correlated kinetics of both carriers and phonons under similar experimental conditions and relate these to a single, selfconsistent theoretical model. The last section of this article reviews some of this work.

To set the stage for the work covered in this review it is helpful to consider how ultrafast optical techniques have allowed the investigation of fundamental transient semiconductor properties. First of all, there have been astonishing advances in the generation of laser pulses, with widths as short as 6 fs.7–9 Second, the specific application of a variety of optical techniques allows the investigation of microscopic processes in semiconductors. In view of the importance of laser pulses in investigating transient processes in semiconductors, and for the benefit of a reader who is a newcomer in the field of ultrafast laser technology, a brief overview on the generation of ultrashort laser pulses will be given in Section III of this review.

II. SEMICONDUCTOR INTERACTIONS
A. Semiconductor dynamics

A brief overview of some of the relevant microscopic processes will follow in order to allow the reader to develop a perspective on some of the important processes which occur in a semiconductor following pulsed laser excitation. Illumination of a semiconductor with above band gap energy photons results in the generation of large nonequilibrium carrier densities and elevated carrier temperatures.10 Depending on the incident fluence and the photon energy of the laser radiation, particle densities several orders of magnitude above the equilibrium value may be reached and carrier temperatures of several thousands degrees may be obtained. This in turn will affect various macroscopic parameters such as those governing the optical properties of the system.

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Part of the light radiation incident on a semiconductor is reflected and part of it enters the solid where some of it is absorbed and the rest transmitted. Linear absorption takes place when the photon energy is larger than the fundamental energy gap of the semiconductor (Fig. 1). In a direct optical absorption a quantum of light from the laser pulse is absorbed by an electron, thus making a transition from the valence to the conduction band. This produces a hole in the valence band.

Following optical excitation, electrons and holes undergo spatial and temporal evolution with characteristic times which depend on the various relaxation processes (see Table I and Fig. 2). Initially the excitation energy is transferred entirely to the carriers, leading to the creation of nonequilibrium carrier densities with specific momentum states and elevated carrier temperatures. As the system evolves towards equilibrium there is momentum and energy relaxation. Momentum relaxation occurs on a femtosecond time scale via elastic and inelastic scattering. On the same time scale carrier–carrier scattering of the electrons (holes) results in Coulomb thermalization and allows the electron (hole) system to be described by a Fermi–Dirac distribution with temperature \( T_e \) (Fig. 4). Similarly, electron-hole scattering eventually brings the two distributions into thermal equilibrium.

Energy relaxation of carriers occurs primarily via the emission of optical phonons. For the holes this interaction involves optical phonons generated near the center of the Brillouin zone. However, in addition to small wave-vector phonon emission, conduction band electrons can interact with large wave-vector phonons (Fig. 3). This involves the scattering of electrons from the central valley of the Brillouin zone to the various side valleys (intervalley scattering) resulting in large wave-vector phonon emission. All optical phonons generated eventually decay into two or more lower energy photons (LA+LA or LA+LO, etc.) via multiphonon processes associated with lattice anharmonicity (Fig. 4). The decay time depends on the lattice temperature, which for the zone center optical phonons varies from \( \sim 10 \) ps at cryogenic temperatures to \( \sim 4 \) ps or less at room temperature. Because this time can be longer than the carrier–optical phonon thermalization time, large nonequilibrium optical phonon populations can occur during carrier energy relaxation. These “hot phonons” can inhibit energy relaxation of the carriers (hot phonon re-absorption).

On a time scale greater than 100 ps (depending on the carrier density) electron–hole recombination occurs at high carrier densities via the three-body Auger process. Other re-

### Table I. Fundamental processes in semiconductors.

<table>
<thead>
<tr>
<th>Microscopic process</th>
<th>Characteristic time(s)</th>
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<tbody>
<tr>
<td>Carrier–carrier scattering</td>
<td>( 10^{-15} )–( 10^{-12} )</td>
</tr>
<tr>
<td>Interv alley scattering</td>
<td>( 10^{-14} )</td>
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<td>Intr valley scattering</td>
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<tr>
<td>Carrier–optical phonon thermalization</td>
<td>( 10^{-12} )</td>
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<tr>
<td>Optical phonon–acoustic phonon interaction</td>
<td>( 10^{-11} )</td>
</tr>
<tr>
<td>Carrier diffusion (0.1 ( \mu m ))</td>
<td>( 10^{-10} )</td>
</tr>
<tr>
<td>Auger recombination (carrier density ( 10^{16} ) ( cm^{-3} ))</td>
<td>( 10^{-9} )</td>
</tr>
<tr>
<td>Radiative recombination</td>
<td>( 10^{-12} )</td>
</tr>
<tr>
<td>Lattice heat diffusion (1 ( \mu m ))</td>
<td>( 10^{-13} )</td>
</tr>
</tbody>
</table>
combination processes take place on even longer time scales and therefore are considered negligible for the ultrashort time domain.

Due to the spatial inhomogeneous absorption of light, one has to also consider the spatial behavior of the various microscopic processes in addition to the temporal aspect of laser pulse excitation.\textsuperscript{17,18} The absorption of visible laser light in semiconductor material like germanium occurs over a depth of $\sim 0.1 \mu m$. Most of the carriers are generated within this small region of the semiconductor. This in turn leads to carrier diffusion causing the system to return to equilibrium. However, this ambipolar diffusion (the combined electron–hole diffusion) depends on the carrier temperature. Therefore the initial rise in the carrier temperature due to the excess kinetic energy received during laser excitation causes a substantial increase in the diffusion coefficient.\textsuperscript{17,19} This results in a rapid diffusion of carriers out of the interactive region (see Section V). In most semiconductors this enhanced diffusion occurs over the initial period of photoexcitation lasting a few picoseconds until the carriers lose their kinetic energy. As the carriers lose their kinetic energy and the system returns to thermal equilibrium the diffusion coefficient also returns to its ambient value. However, the diffusion of carriers persists over a period of nanoseconds until the spatial inhomogeneity returns to equilibrium.

Above band gap excitation of a semiconductor with an intense ultrashort laser pulse produces a large number of nonequilibrium carriers. The presence of such a large number of carriers within a small interacting region results in many body effects\textsuperscript{20} that are not noticeable at low carrier densities. Some of these effects are exciton screening\textsuperscript{21,22} and band gap renormalization.\textsuperscript{23} Exciton screening refers to the process where increasing carrier concentration makes the resonant exciton absorption broaden and eventually disappear (screened). At high densities the presence of free carriers not only leads to screening of excitons, but also leads to band gap renormalization due to exchange and correlation effects between carriers. Experimental work\textsuperscript{24} resulted in a simple expression for band gap renormalization in GaAs $\Delta E_G(eV) = 2.15 \times 10^{-8} \rho^{1/3}$ ($\rho$ is the carrier density in $cm^{-3}$).

It is clear from the above introduction that a detailed knowledge of how, when, and where the laser radiation is initially deposited and how it is redistributed in time and space is a very complicated problem. Nevertheless this is a problem that has to be addressed in order to obtain a better understanding of ultrafast semiconductor dynamics.

B. Ultrashort laser pulse excitation: “The first few picoseconds”

In a semiconductor under equilibrium conditions free electrons and holes are distributed according to Fermi–Dirac statistics, whereas phonons characterizing lattice excitations follow Bose–Einstein statistics. In the absence of an external force, energy and momentum interchanged through carrier–carrier and carrier–phonon interactions keep the three distributions at a common temperature. Under this condition the average momentum of the carrier and phonon systems is zero, with their average energies corresponding to their common temperature. When electromagnetic radiation is absorbed by a semiconductor the equilibrium is disturbed and under such a condition the two systems may have different thermal states. However, the carriers return to equilibrium as soon as the external disturbance is removed. The average momentum relaxes to zero, while the average carrier temperature relaxes to the lattice temperature value as carriers lose momentum and energy to phonons through various scattering processes. The relaxation rate of the momentum and energy of the carriers to the equilibrium value is determined by the nature of the scattering, and the number of the processes involved.

Figure 5 shows a schematic representation of the major processes following photoexcitation of a semiconductor with a monochromatic polarized laser light that is a delta function in time (ultrashort pulse excitation). Absorption of optical electromagnetic radiation by a semiconductor where the energy quanta $\hbar \omega_0$ is higher than the band gap energy $E_g$ results in the creation of electron–hole pairs with excess kinetic energy corresponding to the residual energy $\hbar \omega_0 - E_g$. This initial excitation by a monochromatic and polarized radiation produces distributions of electrons and holes that are narrow in energy and peaked in particular directions of momentum space [Fig. 5(a)]. However, elastic as well as inelastic scattering events randomize momentum within tens of femtoseconds [Fig. 5(a)–5(b)].

Following photoexcitation the electrons will possess most of the excess kinetic energy since their effective mass is much lighter than that of the holes. This means that initially electrons and holes have to be considered as separate systems each with their individual thermal distributions. Electron–electron and hole–hole collisions are density dependent. For carrier densities greater than $10^9 \text{cm}^{-3}$ these collisions occur on $\sim 10^{-13}$ s time scale which thermalizes the carriers (time required to establish a carrier temperature)
into a Fermi–Dirac distribution [Figs. 5(b)–5(c)]. The distribution functions for electrons and holes possess different temperatures which may be higher or lower than the lattice temperature depending on $\hbar \omega_0$. As time evolves the hot carriers lose their excess kinetic energy while attempting to reach thermal equilibrium with the lattice through optical phonon scattering (d).

C. Techniques for probing ultrafast dynamics in semiconductors

In order to observe extremely fast phenomena such as the various carrier dynamics in semiconductors, several ultrafast interrogation techniques have been developed. Some of these are the excite-and-probe technique, the streak camera, optical Kerr gate, and up-conversion gate. In this section a brief description of some of the most popular techniques is given.

1. Pump-and-probe technique

In the pump-and-probe (excite-and-probe) technique an ultrashort laser pulse is separated into two pulses, the pump and the probe, with a variable optical delay between them ($\Delta t$). The two incident ultrashort laser pulses are made to overlap spatially on the sample under investigation (ideally the probe beam has to be covered completely by the excitation beam). The intense pump pulse excites the sample, causing a change in its properties. A weaker probe pulse monitors these changes initiated in the sample by the pump pulse. The time evolution of the excited state is investigated by varying the time delay ($\Delta t$) between the pump and the probe pulses. The pump-and-probe technique may be used to investigate such properties as reflectivity, transmission, Raman scattering, and induced absorption. Figure 6 shows a schematic diagram of a typical pump-and-probe technique.

2. Streak camera

Streak cameras are devices that convert time information from luminous events into spatial information. Streak camera technology was pioneered more than 2 decades ago by Bradley and Schele. Modern streak cameras can measure optical pulses with subpicosecond resolution. A typical streak camera consists of a streak tube, fast-sweeping electronics, input optics, and output optics (Fig. 7). The streak camera is mostly used for ultrafast luminescence measurements. In this technique light emitted from the sample that is photoexcited by an ultrashort laser pulse is focused onto the photocathode of the streak camera. The flux of the photoelectrons released by the photocathode is proportional to the light intensity incident on the system. These electrons are accelerated and then deflected by an applied voltage that sweeps the electrons across a phosphor screen. Clearly the electrons released at different time from the photocathode will strike the phosphor screen at different positions. This will cause a track, or streak, with a spatial intensity profile directly proportional to the incident temporal intensity profile.
of the photoluminescence. The temporal resolution of streak cameras commercially available approaches 0.5 ps with spectra sensitivity in the ultraviolet (UV) to infrared (IR) range.

3. Optical Kerr gate

Early studies in ultrafast luminescence utilized the optical Kerr gate, which consists of a Kerr active liquid, such as carbon disulfide. This liquid is situated between two crossed polarizers as shown in Fig. 8. Normally, due to these crossed polarizers the gate is closed. However under an intense electric field (synchronized with the ultrafast laser pulse) the molecules of the liquid experience a short-lived induced birefringence. This birefringence makes the Kerr gate transparent, thus in effect it acts like a mechanical shutter that allows the light in for only a short period of time. Therefore an intense laser pulse can be used to carve out successive portions of the temporal profile of the emitted photoluminescence by simply varying the delay time of the gating pulse. This can be achieved by incorporating a moveable retroreflector in an optical delay line. The resolution of the optical Kerr gate depends upon the reorientation time of the molecules of the active Kerr medium assuming the laser pulse is a delta function in time. For example, the reorientation time of CS$_2$ is approximately 2 ps.

4. Up-conversion gate

The process of parametric up-conversion (frequency sum generation) has been used as a mechanism for ultrafast optical shutters. A schematic diagram of the basic principle of the parametric up-conversion technique is shown in Fig. 9. After an ultrashort pulse excites the sample, the luminescence from the sample is collected, collimated, and combined with part of the excitation pulse in a nonlinear crystal such as LiNbO$_3$. The angle of the crystal is set in order to phase match the frequency of the gating pulse with a selected frequency of luminescence. A signal whose frequency is the sum of the laser and luminescence frequencies is generated by the crystal and detected by a photomultiplier tube. By varying the delay of the gating pulse and measuring the sum frequency signal, the temporal profile of the luminescence is obtained with no background signal. Since up-conversion involves virtual electronic transitions, this gate has a response time on a femtosecond time scale.

D. Specific examples of pump-probe techniques

In this section a detailed description of some of the most popular pump-probe techniques for measuring the ultrafast process in semiconductors will be given.

1. Transmission and reflection

A schematic diagram of a typical setup for time-resolved reflection and transmission experiments is shown in Fig. 10. An ultrashort laser pulse is divided into two parts: the pump, which is the more intense of the two and the probe pulse, which is much weaker in order to produce the minimum perturbation on the sample. The separated beams follow different optical paths with one having a variable path length. Varying the path length will in effect vary the time delay between the pump and probe pulses. The delay is typically done with a precise motorized transitional stage due to
the extreme accurate requirements for temporal resolution (light travels 0.33 μm in a single femtosecond). Following the different optical paths the pump-and-probe beams are then directed and focused on the same spatial area on the sample, always taking care such that the probe beam is completely within the excitation beam. The reflection (transmission) beam is then detected with a photodiode or a photomultiplier (depending of the wavelength of probing). To improve the sensitivity of the experiment in many cases a lock-in amplifier is utilized along with an optical chopper. The chopper is normally placed in the path of the pump beam, which modulates the excitation, thus giving a synchronization signal to the lock-in amplifier. In some cases where wavelength selectivity is required one may use supercontinuum generation. This can be accomplished by focusing an intense ultrashort laser pulse in certain material like water, ethylene glycol, or a glass fiber. The white light source generated this way (a continuum of wavelengths) provides a selection of any wavelength desired for the pump and probe. Typically, part of the fundamental intense laser pulse is used as the pump, whereas the weak probe is chosen from the white light continuum. This will allow the selection of the excitation states being probed.

2. Raman scattering

The generation of nonequilibrium phonons after photoexcitation by an ultrashort pulse can be monitored using time-resolved Raman scattering. In semiconductors the time scales of interest for the decay of optical phonons is of the order of a single picosecond. This temporal resolution can be achieved by an excite-and-probe technique. The basic idea is to use the pump beam to excite the sample and then use the probe beam to monitor the nonequilibrium phonon population generated. A schematic of a typical collinear time-resolved Raman scattering is shown in Fig. 11. An ultrashort laser pulse is separated into a pump and a probe beam using a cube polarizer (note, a cube polarizer may not be an ideal element due to dispersion effects for femtosecond pulses, in which case an alternative optical element has to be used). The ratio of the two beams (pump and probe) is controlled with a λ/2 waveplate placed just before the polarizer. Since the incoming laser beam is polarized, a rotation of the λ/2 waveplate will result in changing the ratio of the pump-and-probe beams. After passing through a variable delay line the two pulses are recombined and collimated with another cube polarizer. At this point the collimated pump-probe beam is focused on the sample which is normally in a cryostat. The semiconductor under investigation is normally cooled at 77 K in order to eliminate the background phonon population. The Raman signal is collected and collimated with a system of lenses. The collimated signal is then passed through another cube polarizer that acts as a means of separating the Raman signal coming from the probe as opposed to the one coming from the pump beam. The signal from the probe beam is then directed into a double spectrometer to reject the fundamental light and spectrally resolve the Raman signal. The amplitude of the Raman signal in this experimental configuration is an indication of the nonequilibrium phonon population generated during carrier relaxation in the semiconductor. The detection of the signal is typically done with a two-dimensional charge-coupled device (CCD) array over a specific accumulation time interval (typically a few minutes depending on the signal present). The Raman signal is measured as a function of time delay between the pump and probe. This gives a temporal evolution of the nonequilibrium phonons generated from the pump beam.

3. Photoluminescence

The dynamics of photoexcited carriers in a semiconductor can be probed by monitoring its photoluminescence. The most widely accepted technique for monitoring luminescence with ultrafast resolution is the excite-and-probe method. In this technique the laser pulse itself acts as a switching gate and relates the photoluminescence signal with the time domain. A typical time-resolved photoluminescence experimental setup is shown in Fig. 12. The photoluminescence signal from the semiconductor is collected and focused on a nonlinear crystal (see up-conversion gate in Section II.C.4). Part of the incident laser beam is directed and focused on the same spot on the nonlinear crystal after

FIG. 11. A schematic diagram for typical time resolved Raman scattering experiment in a collinear backscattering geometry. Cube polarizers are utilized to separate and recombine the incoming laser pulse into a pump and probe beam with a variable optical delay between them.

FIG. 12. An arrangement for time-resolved photoluminescence experiment. An excite-and-probe unconversion technique is utilized to time resolve luminescence with ultrafast temporal resolution. The laser pulse itself acts as a switching gate in order to relate the photoluminescence signal to the time domain.
passing through a variable delay line. The up-conversion signal from the photoluminescence and the pump beam is directed through filters and a spectrometer to eliminate the background light from the signal. The signal is normally detected with a single photon counting unit giving it an extremely high sensitivity.

### III. GENERATION OF ULTRASHORT LASER PULSES

The availability of short laser pulses provides a natural probe for investigating ultrafast phenomena in semiconductors. In recent years, the technology of generating and detecting short optical pulses has advanced substantially. In this section a brief outline on the technology of generating ultrashort laser pulses will be given (an expert in the field may skip this section).

#### A. Historical background

The development of mode-locking techniques in laser systems has triggered a new era in short pulse generation. Following the development and improvement of these techniques over the past 2 decades, picosecond and femtosecond pulses are now relatively easy to obtain. In mode-locking, the phases of the different axial modes of the laser cavity are locked together to obtain a pulse width which is limited by the inverse of the frequency bandwidth. This can be accomplished by techniques such as: active mode-locking with modulation of the laser intracavity losses or the laser gain or by passive mode-locking with the use of a saturable absorber. The first demonstration of laser mode-locking involved passive mode-locking of the ruby laser by Mocker and Collins over 30 years ago. Shortly after, the generation of the first optical pulses in the picosecond range with a Nd:glass laser was reported by DeMaria. Since that time there has been enormous advancement in the technology of pulse generation. As shown schematically in Fig. 13 the width of optical pulses has fallen by more than 3 orders of magnitude since 1966. Optical pulse widths of a few femtoseconds, approaching the fundamental limits of what is possible in the visible region of the spectrum, are now being generated. In addition, ultrashort pulse lasers have become more useful as advances and improvements in pulse energy, tunability, repetition rate, and reliability have taken place.

With the development of the mode-locked Nd:glass laser, typically producing pulses a few tens of picoseconds in duration with energy in excess of 100 μJ/pulse at a repetition rate of 1 Hz, experiments investigating ultrafast electronic processes in semiconductors were made possible. For the first time, nonequilibrium carrier densities up to $10^{20}$ cm$^{-3}$ could be generated in a sample, where the dynamics and kinetics of carrier transport and relaxation following this excitation may be resolved on a picosecond time scale. However, the low repetition rate made data acquisition tedious and often impossible when small signals were involved. Also, several processes of interest in semiconductors occurring on subpicosecond and even femtosecond time scales could not be time resolved. These shortcomings have been surpassed in the last 15 years with the development of mode-locked continuous-wave sources. In the early 1970s techniques were developed for passively mode-locking such lasers. The first such report, made in 1972, involved a cw rhodamine-6G dye laser with DODCI as the saturable absorber, where pulses as short as 1.5 ps with peak powers of 100 W were obtained. In 1974 Shank and Ippen reported the generation of the first optical pulses less than a picosecond in duration; the peak power was in the kilowatt range. This was done in a cavity dumped and passively modelocked rhodamine-6G dye laser. Since this version of mode-locked dye laser several advances have made possible the generation of even shorter pulses. Systems such as the colliding pulse mode-locked (CPM) laser developed by Fork and Shank have made possible ultrafast semiconductor measurements with femtosecond resolution.

#### B. Methods of mode-locking

Ultrashort light pulses are generated by locking the phases of a large number of modes sustained by the laser gain bandwidth. A typical mode-locked laser consists of the resonator with an intracavity modulator. This modulator, whether it is a saturable absorber, an acousto-optic, or an electro-optic modulator, or a self-phase modulating component, modulates the amplitude or the phase of the field inside the cavity to generate short pulses. There are two broad categories of mode-locking mechanisms: passive and active.

In a laser, many modes are allowed along the resonator axis with frequency separation of $c/2L$, where $L$ is the optical length of the cavity and $c$ is the speed of light. These modes usually oscillate with random phase and irregular amplitudes, resulting in a randomly time-varying amplitude within the round trip period $T = 2L/c$. However, if these modes have the same phase they will constructively interfere at the same instant $T_0 = (\phi/2\pi)T$ of the round trip time. The output will thus consist of a series of pulses centered at $T_0, T_0 + T, T_0 + 2T, \ldots$ (Fig. 14) and the laser is said to be mode-locked. The element that fixes these relative phases is...

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**FIG. 13.** Schematic diagram of the shortest pulses reported versus year. Optical pulse widths of a few femtoseconds (6.5 fs) are now possible directly from a mode-locked Ti:sapphire laser.
referred to as the mode-locker. The width $\Delta t$ of each of the successive pulses is approximately equal to the inverse of the frequency range spanned by the modes being locked in phase. In the laser resonator, modelocking in the time domain corresponds to a single pulse traveling back and forth between mirrors with loss on the output mirror being compensated by the gain from pumping at each round trip.

C. Systems for generating ultrashort pulses

1. Synchronous pump dye lasers

Synchronous pumping can be classified under active mode-locking. The principle behind this mode-locking scheme is a periodic modulation of the gain in the laser cavity. Synchronously pumping of dye lasers is usually accomplished by actively mode-locking the pump source and matching the cavity lengths of the two lasers (Fig. 15). An acousto-optic crystal may be used to actively modelock a laser system such as a Nd:YAG laser or an argon ion laser. These lasers can be use to pump and modulate the gain of a linear or ring dye laser, thereby causing mode-locking. This type of pumping is referred to as synchronous pumping and yields pulses as short as a few picoseconds over the full range of available dyes (visible $\leq \lambda$ near infrared) with a typical energy of 1 nJ/pulse at a repetition rate of the pump source. The addition of a saturable absorber jet further shapes and reduces the pulse width of the laser to approximately 500 fs. Generation of 29 fs pulses from a synchronously pumped dye laser using dispersion compensation prisms has been reported at the 6th International Conference of Ultrafast Phenomena. The nanojoule energies obtainable from laser oscillators are not sufficient for many applications, especially those probing nonlinear optical effects where peak power is very important. One can achieve higher energies at the expense of repetition rate by employing cavity-dumping techniques. This can be done with the introduction of an acousto-optic modulator in the cavity acting as an output coupler. This repetitive cavity dumping results in energies per pulse which are approximately 20 times larger than those of noncavity dumping at the cost of lower repetition rate (at least a 20 times reduction). To obtain higher energies, optical amplifiers have been developed which amplify the nanosecond pulses to energies as large as tens of millijoules.

2. Colliding pulse mode (CPM) locked laser

The CPM system is a continuous-wave argon ion pumped ring laser which utilizes the interaction, or “collision,” of two pulses in the saturable absorber in order to enhance its effectiveness. In a cw mode-locked dye laser, significantly shorter pulses can be obtained if the mode-locked cavity is arranged as a ring cavity, with the pulses traveling in both direction around the ring, rather than as a linear or standing wave cavity. The CPM laser cavity is arranged as shown in Fig. 17, with the dye jets for the gain medium and the saturable absorber separated by one quarter of the round trip path length. The stable mode of operation consists of two equal-amplitude pulses circulating in opposite direction around the ring such that these pulses collide in the saturable absorber cell and “anti-collide” in the active gain medium. This type of colliding pulse mode-locking in a cw pumped dye laser has produced extremely short laser pulses. Typically a CPM laser generates an average power of...
10 mW in the visible region of the spectrum ($\lambda = 0.61 \mu m$) with a repetition rate of 100 MHz and pulse widths <100 fs.

3. Ti:Sapphire laser

The CPM dye lasers were the "workhorses" for ultrafast studies in all branches of science and in particular semiconductor studies during the 1980s. However, due to the difficulty of operating and maintaining such systems, people were looking for an alternative. At that time a series of broad-bandwidth solid-state laser materials were developed, with the most notable of these been the titanium-doped sapphire (Ti:Al$_2$O$_3$), which lased over a continuous band stretching from 680 nm to 1100 nm. In late 1989, a group at MIT reported 200 fs pulses generated from a Ti:sapphire laser. They used a novel mode-locking technique called additive pulse mode-locking (APM). The APM is accomplished by feeding back into the laser part of its output after it has been nonlinearly modulated in an external cavity. In 1991 a very exciting result was reported by Spence et al. at the University of St. Andrews. They observed self-mode-locking or Kerr lens mode-locking of a Ti:sapphire laser. This type of mode-locking is induced in a solid-state laser because of the nonlinearity present in the laser crystal. The nonlinear index of refraction $n_{nl}$ introduces an intensity dependent index given by $n = n_0 + n_{nl}I$, where $n_0$ is the linear index of the crystal, and I is the instantaneous laser pulse intensity. The nonlinear phase delay of the beam will be highest at the center of the beam when it focuses into the crystal, causing self-focusing. Therefore, there is an additional lens in the cavity with an intense pulse, which is not there for low-intensity light. The cavity alignment can be adjusted so that the pulse spatial mode suffers less loss than the cw spatial mode. When self-focusing is induced the mode-locked profile will match the pump mode, and will favor pulse operation. Because this mode-locking is induced by the pulse itself, the laser is said to self-mode-locked, and the effect is the same as if a fast saturable absorber were present in the cavity. Today Ti:sapphire lasers (Fig. 18) can generate 25 fs pulses with not much difficulty allowing researchers to explore semiconductor dynamics at very short time scales. Recently, Jung and co-workers have demonstrated 6.5 fs pulses from a Ti:sapphire laser using a combination of a prism pair and a doublechirped mirror for dispersion compensation.

4. Ultrafast super-continuum pulses

Ultrafast super-continuum refers to an ultrashort burst of white light. This burst of white light is usually generated by passing an intense ultrafast laser pulse through certain material media. The input ultrashort laser pulse undergoes extreme frequency broadening through nonlinear interaction in the material medium, generating a super-continuum pulse. The physical mechanism responsible for the white light generation is self-phase modulation. This ultrafast super-continuum white light source is a versatile tool for time-resolved absorption spectroscopy, and most excite-and-probe measurements. Its broad spectral range allows time-resolved measurements over many different wavelengths.

5. Pulse compression

Pulse compression reduces the pulse width of ultrashort lasers down to the bandwidth-limited region. In addition it increases the attainable pulse peak power as it narrows down the pulse. The ultimate duration of a laser pulse is determined by the pulse width–bandwidth uncertainty product $\Delta t \Delta f > 1$ ($\Delta t$ is the temporal pulse width, and $\Delta f$ is the frequency bandwidth). Generation of increasingly shorter pulses requires the corresponding spectral broadening. However, the bandwidth of the laser is determined by the gain bandwidth of the lasing medium and the design of the optical cavity. This clearly sets a limit on the shortest attainable pulse width from a laser. Pulse compression, on the other hand, depends on nonlinear optical properties of the materials used and operates from ultraviolet to infrared. This has a significant advantage over the direct pulse generation in a laser oscillator, especially for the generation of pulses in the femtosecond time domain. In a typical pulse compression technique an optical fiber is used to spectrally broaden an input pulse due to self-phase modulation, and then reduce the pulse to a value shorter than the value of the input pulse using a grating pair (Fig. 19).
IV. PROBING ULTRAFAST PROCESSES IN SEMICONDUCTORS

This chapter reviews some of the experimental results obtained in probing ultrafast processes in semiconductors. Specific experiments utilizing time-resolved reflectivity, optical absorption, Raman scattering, luminescence, and other excite-and-probe techniques are discussed. Section IV A reviews work in group III-V semiconductors and mainly work on GaAs. Section IV B covers low-temperature grown GaAs. Section IV C gives a brief report on II-VI material, and Section IV D a summary on group IV semiconductors and in particular Ge and GeSi alloys (a more detailed work in these and other semiconductors is beyond the scope of this article since each one may be a review article itself).

A. GaAs and related semiconductors

Since the realization that ultrashort optical techniques allow the direct observation of carrier and phonon dynamics in semiconductors there has been an enormous amount of research performed in group III-V materials. The direct band gap characteristics of GaAs along with the availability of good quality samples had made GaAs the material of choice in studying ultrafast carrier and phonon dynamics. Another reason for choosing group III-V as opposed to group IV materials is that type III-V materials were thought simpler to understand and model due to their direct absorption and emission. Furthermore, photoluminescence, which is considered a key experimental technique for investigating carrier distributions and carrier dynamics, yields results only in direct gap material. A brief description of the GaAs band structure will be given next allowing the reader to obtain a better understanding of the experimental results that will follow in this section. Figure 3 shows a schematic of the band structure of GaAs. The top of the valence band, at \( k = 0 \) (\( \Gamma \) point), is fourfold degenerate. Away from the \( \Gamma \) point, the degeneracy is lifted and there are two twofold degenerate bands: the upper termed the heavy-hole and lower called the light-hole band. About 340 meV (\( T \approx 300 \) K) below the top of the valence band lies a twofold degenerate band termed the spin-orbit split-off band. The minimum of the conduction band in GaAs also lies at \( k = 0 \), thus making it a direct-gap semiconductor. The energy gap is approximately 1.43 eV at 300 K. There are two sets of satellite conduction-band valleys in GaAs: the L valleys and the X valleys. The L valleys have minima at the boundary of the Brillouin zone in the \( (111) \) direction at an energy about 290 meV above the central valley. The X valleys have minima at the zone edges in the \( (100) \) directions at an energy about 480 meV above the central valley.

1. Early pump-and-probe experiments

Time-resolved reflectivity measurements with picosecond pulses were carried out by Auston et al.\(^{54,55}\) in GaAs. The experiment consisted of two optical pulses (pump-probe), one which was used to generated free carriers by direct band-to-band absorption, and the other to measure the changes in reflectivity from the surface of the sample. A variable time delay between the excitation and probe pulse enabled the measurement of the complete dynamics of the reflectivity with a time precision of a picosecond. The source of optical pulses used in their experiments was a mode-locked cw cavity dumped dye laser. The pulses from the laser were typically 5 nJ and approximately 0.5 ps in duration. The pump beam was set at 307.5 nm and the reflectivity was measured at the fundamental wavelength of the dye laser which was at 615 nm. Figure 20 shows some of the experimental results for GaAs. Initially a decrease in reflectivity was observed followed 2 ps later by an increase and leveling off at a value of approximately \( 10^{-3} \). These results can be interpreted by considering the effect of the nonequilibrium carriers on the real and imaginary parts of the optical dielectric function. Immediately after photoexcitation the carrier distribution is very hot and for short time delays, numerous high-energy conduction band states are occupied and the corresponding valence band states are vacant. As a result the imaginary part of the dielectric function reduces at frequencies which are high compared to the probing frequency. From the dispersion theory, this reduces the real part of the dielectric function at the probing frequency, and hence the reflectivity decreases. When the carrier distribution has relaxed to the band edge the imaginary part of the dielectric function decreases at frequencies near the band edge (which is below the probing frequency) and hence the real part of the dielectric function increases at the probe frequency, causing the reflectivity to increase. The zero crossing time (which occurs at 2 ps as seen in Fig. 20) is a measure of the rate of...
energy loss of the hot electron distribution. From these ex-
periments Auston et al. deduced the energy relaxation rate of
hot electron distribution in GaAs to be approximately 0.4
eV/ps.

A short time after Auston's experiments, Shank et al.\(^5\) carried out some interesting absorption measurement in
GaAs. They reported on time-resolved absorption measure-
ments in GaAs at 80 K, following an ultrashort laser pulse
excitation. This experiment provided the means of directly
monitoring the hot carrier distribution as it cooled to the
lattice temperature with a time constant of approximately 4
ps. Exciton screening and band gap renormalization were
observed to occur in less than 0.5 ps. As mentioned earlier
absorption of photons with energy much greater than the
band gap will generate carriers with significant excess en-
ergy, which relax to the band edge primarily by optical pho-
non emission which is an extremely rapid process for GaAs.
Photoexcited carriers generated a few tenths of an eV above
the band edge are expected to relax within an LO phonon
energy of the band edge in less than a picosecond. Simultaneously, carrier–carrier scattering redistributes en-
ergy among the carriers and leads to a carrier distribution
described by an effective temperature higher than the lattice
temperature for sufficient high carrier density. By observing
the time evolution of the transmission spectrum, the cooling
rate for these carriers can be determined. In these experi-
ments Shank et al. had used 0.5 ps pulses generated by a
passively mode-locked dye laser, which was cavity dump-
at 10 Hz. The laser beam was then amplified and divided to
form two separate beams. The first beam was used to gen-
erate a Raman shifted pulse at 750 nm. This pulse was used as
the means of exciting the sample. The second beam was
focused into a cell containing water, generating a broadband
subpicosecond continuum, which was used to probe the
sample. The probe pulses were imaged through the region of
the sample excited by the pump pulses and onto a spectrom-
eter. The sample consisted of a molecular beam grown layer
of GaAs (1.5 \(\mu\)m thick), and it was mounted on a cold finger
which was maintained at approximately 80 K. In Fig. 21 one
of the traces shows the transmission spectra of the GaAs
sample prior to optical pumping (see trace for \(\tau<0\)). The
sharp dip in transmission near 820 nm was due to the free
exciton absorption. Spectra at different delays following the
excitation pulse are also seen in Fig. 21. There are some
interesting features regarding these results. For example, one
notices that the exciton resonance absorption has disappeared
for a probe delayed 1 ps with respect to the pump. This is
attributed to screening of the exciton by the photoexcited
carriers. In addition, the absorption edge is shifted to an
energy just below the unperturbed free-exciton energy consist-
tent with renormalization of the band gap.

A complementary picture of the above dynamical pro-
cesses was obtained by simply measuring transmission as a
function of time delay for a fixed wavelength. At the free-
exciton energy the transmission trace exhibits an initial rapid
increase as the exciton is screened within the time resolution
of the experiment (0.5 ps), and a more gradual increase as
the carriers came into equilibrium with the lattice. Transmis-
sion measurements at the long wavelength side of the free
exciton revealed an initial fast decrease followed by a slow
increase. This was attributed to the band gap renormalization
followed by band filling as the carriers relax.

It become obvious from the description of the above
experiments that indeed probing carrier dynamics in semi-
conductors, even in simple systems like GaAs, is a very
complicated and formidable task. Innovating new probing
techniques were constructed to investigate such ultrafast
properties like carrier energy and momentum relaxation. In
what follows in this section some of the most interesting
experimental results along with experimental techniques uti-
ilized in probing ultrafast dynamics in semiconductors will be
discussed. I will begin with the technique of optically in-
duced transient gratings. It perhaps encompasses some of the
oldest picosecond resolution experiments utilized in investi-
gating semiconductor dynamics.

2. Optically induced transient gratings

When two excitation pulses are superimposed in a
sample, whereby a standing wave develops, it can lead to

FIG. 21. Transmission spectra corrected for wavelength variation of probe
beam and OMA detector response. Spectra were recorded over a range of
delay time between the pump and probe beams (from Ref. 56).
time. The plasma grating kinetics following laser excitation are described by the following simple differential equation:

\[
\frac{\partial N(x,z,t)}{\partial t} = \nabla[D \nabla N(x,z,t)] - \frac{N(x,z,t)}{\tau_r},
\]

where \(N(x,z,t)\) is the electron–hole pair density, \(z\) is the direction of the grating normal, \(D\) is the ambipolar diffusion coefficient, and \(\tau_r\) is the bulk recombination lifetime. Assuming a surface recombination velocity \(S\), then we have the following boundary conditions:

\[
\frac{\partial N(x,z,t)}{\partial z} \bigg|_{z=0} = \frac{S}{D} N(x,0,t), \quad \text{and} \quad N(x,\infty,t) = 0.
\]

Taking the excitation pulse as a delta function in time, the initial condition is simply \(N(x,z,0) = g(x)h(z)\), where \(g(x)h(z) = N_0 \left[1 + \cos(2\pi x/\Lambda)\right] \exp(-\alpha z)\) is the spatial generation function and \(N_0\) the initial excess carrier density at the surface. \(\Lambda = \pi K \sin(\theta/2)\) is the grating period, \(K\) and \(\alpha\) are the wave vector and absorption coefficient for the excitation laser pulse, and finally \(\theta\) is the angle between the two excitation beams. Assuming density independent diffusion coefficient and recombination lifetime the solution to Eq. (1) is given by:

\[
N(x,z,t) \equiv \left\{1 + \cos \left(\frac{2\pi x}{\Lambda}\right) \exp \left[-\left(\frac{4\pi^2 D}{\Lambda^2}\right)t\right]\right\} \Psi(z,t),
\]

where \(\Psi(z,t)\) is

\[
\Psi(z,t) = \frac{N_0}{2} \exp \left[-\left(\frac{1}{\tau_r}\right)\right] \exp \left[-\left(\frac{z^2}{4Dt}\right)\right] \\
\times \left\{E \left(\alpha \sqrt{D} - \frac{z}{2\sqrt{D}t}\right) + E \left(\alpha \sqrt{D} + \frac{z}{2\sqrt{D}t}\right)\right\} - \frac{2S/D}{(S/D) - \alpha} E \left(\alpha \sqrt{D} + \frac{z}{2\sqrt{D}t}\right) - E \left(\frac{S}{D} \sqrt{D} + \frac{z}{2\sqrt{D}t}\right)
\]

with \(E(x) = \exp(x^2)\text{erfc}(x)\). Using the Drude model for a free-carrier plasma which acts as a thin periodic phase grating, the first order diffraction intensity from such a grating is

\[
I_1(t) = \frac{\pi}{\lambda} \frac{e^2}{2\pi m_e^* \omega^2 \epsilon_0} \int_0^\infty \left[N(\Lambda z, t) - N \left(\frac{\Lambda}{2}, \z, t\right)\right] dz,
\]

where \(I_1\) is the first-order Bessel function and its argument is one half the full phase modulation depth of the grating. In the above equation \(n\) is the refractive index, \(\omega\) is the probe frequency, and \(m_e^*\) is the reduced mass.

The integration of the plasma modulation over \(z\) makes the diffraction intensity dependent on the total number of electron–hole pairs in the sample and not on a specific density profile. Bulk diffusion therefore has little effect on the diffraction intensity. Diffusion also affects \(N(x,z,t)\) as seen in Eq. (2) through the term \(\exp[-(4\pi^2 D/\Lambda^2)t]\). This corresponds to the decay of the grating contrast as the electron–hole pairs diffuse parallel to the sample surface and this decay is faster for larger \(D\). In addition, larger \(D\) will also decrease surface recombination because of increased diffusion current into the bulk away from the surface and possible recombination. This is clearly seen from the \(S/D\) coefficient in Eq. (3).

Next let us consider the contributions from Auger, bimolecular, and linear processes on the recombination rate. The linear term corresponds typically to a carrier lifetime of 5–10 ns. For picosecond time scales considered here (ultrafast measurements) this lifetime will therefore have negligible effect. Bimolecular recombination for GaAs contributes to the recombination rate for \(N > 5 \times 10^{18} \text{ cm}^{-3}\) and reaches a limit at 300 ps for \(N = 3 \times 10^{19} \text{ cm}^{-3}\). Auger recombination is comparable to the other two processes for \(N > 5 \times 10^{18} \text{ cm}^{-3}\). Bimolecular and Auger recombination would deplete the plasma on a time scale of hundreds of picoseconds. On the other hand diffusion and surface recombination rapidly dilute the plasma in tens of picoseconds.

While techniques, which are based on transport measurements or luminescence, must extract a value for \(S\) from information which also depends on \(D\) and \(\tau_r\) and other parameters, the transient grating method is largely independent of diffusion and bulk recombination processes and provides a much more direct means of measuring surface recombination velocity.

**b. Experimental work utilizing transient grating technique**: Hoffman et al. have used the transient grating technique to measure surface recombination in \(n\)-InP, \(p\)-InP and \(n\)-GaAs. They used laser pulses (\(\lambda = 0.53 \mu\text{m}\)) two picoseconds in duration interfering at the surface of the semiconductors. Direct one photon interband absorption of the 0.53 \(\mu\text{m}\) radiation (\(a_{\lambda = 0.53} = 7 \times 10^4 \text{ cm}^{-1}\), \(a_{\lambda = 0.53} = 1.05 \times 10^5 \text{ cm}^{-1}\)) generated a thin free-carrier grating at the semiconductor surfaces under study. Some of the experimental results are shown in Fig. 22. They found that \(S = 2 \times 10^4 \pm 1 \times 10^4 \text{ cm/s for } n\)-InP (Sn, 1 \(\times 10^{17} \text{ cm}^{-3}\) and \(S = 1.5 \times 10^5 \pm 0.5 \times 10^5 \text{ cm/s for } p\)-InP (Cdx, 1 \(\times 10^{17} \text{ cm}^{-3}\). Both samples were grown by the liquid-encapsulated Czochralski method and had (111) surface chemomechanically polished. They also measured \(S\) on a similarly prepared \((100) n\)-GaAs (Te, 6 \(\times 10^{16} \text{ cm}^{-3}\) surface). They found the surface recombination velocity to be \(S = 5 \times 10^5 \pm 1 \times 10^5 \text{ cm/s, which is in excellent agreement
with the results from previous work using electron micro-probe techniques. Optically induced picosecond transient gratings have also been used to measure diffusion coefficient and recombination effects in germanium. These experiments will be discussed later in Section IV.D.

3. Saturation of optical absorption

Time-resolved saturation of the optical absorption could reveal many important relaxation mechanisms. The physical basis for saturation occurs due to the occupancy of electronic states by nonequilibrium carriers. When a photon is absorbed, an electron makes a transition from the valence to conduction band, leaving an unoccupied state in the valence band and an occupied state in the conduction band. Full saturation occurs when the occupations of the excited and ground states are equal. However, a small population of the excited state is sufficient to produce a measurable change in the absorption. Saturation effects in semiconductors can be measured with an excite-and-probe technique providing a time resolution comparable to the pulse duration itself. A variation of this method for measuring saturation effects is the equal pulse correlation technique.

a. Saturation optical absorption pump-and-probe technique: One of the pulses in an excite-and-probe experiment usually is at least an order of magnitude more intense than the second pulse and it is known as the pump. The pump is used to induce the saturation of the optical absorption in the material under study. The other pulse which is normally much weaker is known as the probe and it is used to measure the change in the absorption. If the carriers remain in the excited nonequilibrium states long enough, the absorption of the probe is reduced. However, as the excited carriers are scattered out of their initial states by phonon emission or carrier–carrier scattering, the absorption recovers. The delay time between the pump and probe pulses can be varied in such a way as to map out the time evolution of the saturation. Thus timeresolved saturation measurements will give an accurate measure of the rate at which the electrons and holes scatter out of the excited states.

Pump-and-probe transient absorption saturation measurements were performed at room temperature using photon energies of $\sim 2$ eV. The laser source for the experiments was a colliding pulse mode-locked ring dye laser incorporating internal prisms for dispersion compensation which allowed the laser to produce transform-limited pulses of 35 fs full width at half maximum. Experimental measurements were performed on 0.5-μm-thick samples of GaAs and Al$_x$Ga$_{1-x}$As ($x = 0, 0.1, 0.2, 0.3, $ and 0.4). Transient absorption saturation was measured by detecting the differential between the transmitted probe beam and a reference beam, so that absorption changes as small as several times $10^{-6}$ could be detected.

Absorption saturation recovery measurements for GaAs shown in Fig. 23 correspond to excitation carrier densities of $10^{17}$, $3 \times 10^{17}$, and $10^{18}$ cm$^{-3}$. All traces were normalized to the amplitude of the slow component (from Ref. 63).
excited carriers out of their optically excited states prior to the formation of a quasithermal distribution. A significant increase in the initial carrier relaxation time was observed for increasing Al mole fraction. Some of these results are shown in Figs. 24(a) and 24(b). This decrease in carrier relaxation rate may be attributed to the following reasons:

(i) A decrease in the number of allowed scattering states: with increasing $x$ the band gap increases, thus the carriers are generated with less excess energy resulting in a decrease in the number of allowed scattering states.

(ii) A change in intervalley scattering rates: the $G \rightarrow X$ scattering becomes energetically less favorable due to the decrease in excess carrier energy resulting from the increase in the band gap as $x$ increases.

In 1988 Schoenlein et al. investigated hot carrier dynamics in GaAs and Al$_{x}$Ga$_{1-x}$As using the femtosecond pump and continuum probe technique. They observed spectral hole burning due to a transient nonthermal carrier distribution and a rapid energy thermalization on a time scale of several tens of femtoseconds. In their experiments they utilized $\sim 60$ fs pulses to excite the sample and a broadband femtosecond continuum to probe the carrier relaxation. Time-resolved measurements of absorption saturation were performed in 0.5-$\mu$m-thick GaAs and Al$_{x}$Ga$_{1-x}$As samples at room temperature. Figure 25 shows the band structure of GaAs near $k=0$ and the allowed optical transition for 1.99 eV photon pump energy.

Some of the time-resolved measurements for GaAs are shown in Fig. 26(a). An excited carrier density of $10^{18}$ cm$^{-3}$ was generated by a pump pulse of 60 fs at 625 nm (1.99 eV). The magnitude of the absorption saturation $\Delta T/T$, at each of the probe photon energy is seen on the plots. At probing energy of 1.99 eV the behavior of the curve is very similar to that observed by Lin et al. with the following three characteristics:

(i) an initial saturation (corresponding to the presence of photoexcited carriers from the heavy and light hole bands),

(ii) a fast recovery (which is comparable to the pulse width and is set by the fast scattering of the carriers out of their initial excited state), and

(iii) a slow recovery (resulting from the cooling of the hot carrier distribution to the lattice temperature).

The same group (Lin et al.) investigated in more detail the time evolution of saturation of the optical absorption in GaAs for energies of probe close to the pump photon energy. They attributed the same fast recovery of the saturation to a transfer of the hot electrons from the central valley to the X and L satellite valleys.

In Fig. 26(a) the traces correspond to the absorption measurements in GaAs for photon energies ranging from 1.88 eV to 2.14 eV. These curves display an initial saturation.
and a partial recovery within the first 100 fs. This behavior indicates a spectral absorption hole resulting from an initial nonthermal carrier distribution. The ~200 meV width of the hole is an indication of the initial scattering time. The carrier distribution excited from the split-off band was probed with photon energies ranging between 1.68 and 1.73 eV. The curves display a similar ultrafast partial recovery corresponding to the nonthermal electronic distribution excited from the split-off band. The experimental measurements for all the photon energies under investigation show a rapid onset of absorption saturation. This indicated that excited carriers scatter out of their initial states and assume a broad energy distribution within the first several tens of femtoseconds. The interesting feature of rising absorption saturation observed at 1.55 eV, which is near the band edge, may be explained by an increase in electronic occupancy below the Fermi energy as the thermalized hot electron distribution cools to the lattice temperature.

To eliminate the effect of split-off band, similar measurements have been performed by the same group for Al$_{0.2}$Ga$_{0.8}$As with a band gap of 1.68 eV. Measurements near the pump energy from 1.88 eV to 2.0 eV display an initial absorption saturation and ultrafast partial recovery characteristic of a transient spectral hole. This behavior is the result from an initial nonthermal carrier distribution due to optical excitation from the heavy and light hole bands. Furthermore, the rapid onset of absorption saturation is present at all probe energies, which indicated that the carriers scatter from the initial nonthermal distribution and assume a broad energy distribution within the first ~100 fs. The picosecond response behavior is consistent with a cooling of the thermalized hot electron distribution cools to the lattice temperature.

At approximately the same time Becker et al. at Bell Labs performed a related experiment to study the absorption saturation of GaAs using 6 fs optical pulses with a photon energy at 2.0 eV. Figure 27 shows a plot of the induced transmittance measured with 6 fs optical pulses. Figure 27(a) shows a rapid decay followed by a slow decay with a time constant of 1.5 ps, which is consistent with the results from other measurements. The long time constant has been interpreted as being due to the thermalization of the carrier distribution to the lattice temperature via carrier–phonon interactions with in the central valley. The fast time constant was revealed by subtracting the 1.5 ps time response from the data. They observed a clear single fast decay with a time constant of 

![Figure 26](image_url)

**FIG. 26.** Transient transmission changes of femtosecond pump and continuum probe measurements performed in: (a) GaAs using a pump photon energy of 1.99 eV and probe energies $E_{\text{pro}}$, ranging from 1.55 to 2.14 eV at carrier density of $10^{18}$ cm$^{-3}$, (b) Al$_{0.2}$Ga$_{0.8}$As at probe photon energies ranging from 1.78 to 2.07 eV (from Ref. 65).

![Figure 27](image_url)

**FIG. 27.** (a) Excite-and-probe induced transmittance of a 0.1-mm-thick sample of GaAs at temperature of 295 K, with 6 fs optical pulses. (b) Convolution of the 1.5 ps decay of the signal with the intensity autocorrelation of the pulse. (c) Curve (a) minus curve (b) (from Ref. 67).
constant of 33 fs. No noticeable variation in this time decay was observed for densities in the range of $3 \times 10^{18} - 6 \times 10^{18}$ cm$^{-3}$. The decay can be attributed to a rapid transfer of electrons to both the X and L valleys. The same team repeated the experiment at lower temperatures namely at 35 K, where the band gap of the GaAs sample permits transfer to the L valley, but not the X valley. This allowed them to determine separately the rates of transfer to each valley. These rates were 55 fs for the X valley and 80 fs for the L valley. For the energy densities used in their experiments ($5 \times 10^{18}$ cm$^{-2}$) it is believed that carrier–carrier scattering was the dominant mechanism for this rapid thermalization. Optical phonon emission produces a much slower relaxation—on a time scale of a few picoseconds, and accounts for the slow return of the electrons to the bottom of the $\Gamma$ valley.

b. Equal pulse correlation technique: The equal pulse correlation technique is based on the study of the saturation effects on the transmission characteristics of a thin sample using two short pulses of equal intensity. Two pulses of equal intensity $I$ and orthogonal polarization derived from the same laser but with a variable delay $\Delta t$ between them are utilized to perform time-resolved studies of fast energy relaxation due to carrier–carrier and optical phonon scattering. Let $h_1(t)$ represent the shape of the first laser pulse, and $h_2(t) = h_1(t + \Delta t)$ the shape of the second pulse which is identical to the first, except that there is a variable delay, $\Delta t$, between them. Therefore, the two incoming pulses will be represented by $h_1(t)$ and $h_2(t)$.

If there is a non-negligible number of electrons created in the conduction band by the pulses then there is a mutual saturation effect of one beam on the other while the carriers are in the photoexcited states. As a result of the saturation effect, the total absorption of both beams will decrease when the two pulses overlap within a lifetime $\tau_c$ of each other and the measured time averaged total transmitted power of both beams as a function of delay will show a transmission correlation peak ($T_{cp}$). The change in the transmitted power of both beams through an optically thin sample due to the saturation effect is:

$$\Delta T_{trm} \propto \int_{-\infty}^{\infty} \eta(t) I[h_1(t) + h_2(t)] dt,$$

where $\eta(t)$ is the electron occupation density in the photoexcited conduction band states:

$$\eta(t) \propto \int_{-\infty}^{t} I[h_1(t') + h_2(t')] \exp[-(t-t') / \tau_c] dt'$$

$$\propto \int_{0}^{\infty} I[h_1(t-x) + h_2(t-x)] \exp[x / \tau_c] dx$$

(6)

since the transmission correlation peak corresponds to the cross term in (5), using Equation (6) the $T_{cp}$ is proportional to

$$I^2 \int_{-\infty}^{\infty} \int_{0}^{\infty} [h_1(t)h_2(t-x) + h_2(t)h_1(t-x)]$$

$$\times \exp[-x / \tau_c] dx \ dt.$$

(7)

Changing the order of integration and substituting $h_2(t)=h_1(t+\Delta t)$, it can be shown that the $T_{cp}$ is proportional to the convolution of the intensity autocorrelation $A(\Delta t)$ of the pulse with a two sided exponential decay factor. Therefore the $T_{cp}$ as a function of $\Delta t$ is proportional to

$$I^2 \int_{0}^{\infty} \int_{-\infty}^{\infty} [h_1(t)h_1(t+\Delta t-x) + h_1(t+\Delta t)h_1(t-x)] dt$$

$$\times \exp[-x / \tau_c] dx = I^2 \int_{-\infty}^{\infty} A(\Delta t-x) \exp[-|x| / \tau_c] dx.$$

(8)

In 1983 Tang and Erskine$^{71}$ used this technique to measure lifetimes of highly excited carriers in Al$_x$Ga$_{1-x}$As with $x = 0.34$. They used 80 fs pulsed at 615 nm with a repetition rate of $10^8$ Hz. The pulses were divided into two beams of orthogonal polarizations by a polarizing beam splitter. The beams were recombined collinearly at the beam splitter with the path length of one arm held fixed and that of the other dithering at $\omega$ about the position of zero path length difference (see Fig. 28). The combined pulses were focused onto the sample with a spot diameter of approximately 2 $\mu$m. The transmitted light through the sample was detected by a photodiode. Figure 29 summarizes the results on the measured relaxation time as a function of incident power. The relaxation time was determined from the best fit with the mea-

![FIG. 28. A schematic of an experimental setup of the equal-pulse correlation technique used in Reference 71.](image)

![FIG. 29. Measured relaxation time for Al$_x$Ga$_{1-x}$As $x = 0.34$ vs total input power of both beams: 1 mW corresponds to a carrier density of $7 \times 10^{18}$ cm$^{-3}$ (from Ref. 71).](image)
sured $T_m$ according to Eq. (8). The measured lifetimes for states 160 meV above the band edge in Al$_{0.34}$Ga$_{0.66}$As were in the range of 80–30 fs depending on the photoexcited carrier density.

Later on in 1986, Rosker et al. used the equal pulse correlation technique to study ultrafast relaxation of photoexcited GaAs, AlGaAs, and GaAs/AlGaAs quantum well structures. They have found the initial exponential decay for each of these materials to be dominated by a 40 fs component.

**c. Summary of saturation absorption results:** It appears that ultrafast pulse excitation with above band gap photon energy in GaAs and related semiconductors results in absorption saturation curves with the following three characteristics:

(i) **Initial saturation:** this corresponds to the initial excitation of carriers from the valence to the conduction band.

(ii) **Fast recovery:** this recovery of the saturation is set by the fast scattering of the carriers out of their initial excited state. The time constant for this process in GaAs was measured to be a few tens of femtoseconds. The actual value depends on the band gap characteristics of the material, carrier density, as well as the probing spectral state (for example if the transfer of electrons to the side valleys is energetically permissible).

(iii) **Slow recovery:** this slow recovery is on the order of a picosecond resulting from cooling of the hot carrier distribution to the lattice temperature.

### 4. Ultrafast luminescence spectroscopy

Luminescence spectroscopy, and in particular time-resolved luminescence spectroscopy with picosecond and subpicosecond resolution, has played a crucial role in understanding ultrafast carrier dynamics in semiconductors. In this section some of the critical luminescence experiments and experimental results which played a key role in understanding carrier dynamics in III-V semiconductors and in particular GaAs will be described.

Radiative recombination of nonequilibrium electrons and holes produces a luminescent spectrum that measures the energy distribution of electrons and holes. Conservation of energy dictates that the energy of each luminescent photon is equal to the sum of the kinetic energies of the electron, hole and band gap. The relative energies of the electron and hole cannot be determined unambiguously in luminescence spectroscopy. When transitions between sets of bands are involved (as in the case with III-V semiconductors) the interpretation of the spectra becomes complicated and it is not possible to make a unique determination of the energies of both the electron and hole. Nevertheless, because holes have a much greater effective mass than electrons in these materials, nearly all of the excess energy can usually be attributed to the electrons.

Various scattering processes play an important role in determining high field transport in semiconductors. Luminescence spectroscopy of nonequilibrium carriers in semiconductors has proved to be a powerful technique for obtaining valuable information on the nature of these processes. The early work in this field was performed with steady-state excitations. However, with the development of ultrashort optical pulses the emphasis has shifted towards time-resolved spectroscopy. Methods used in time-resolving luminescence include Streak cameras, Optical Kerr cells and upconversion technique. Streak cameras have been very successful. However, their use is limited to the visible and near infrared spectral regions and their temporal resolution is not as good as that encountered in the up-conversion technique. Optical Kerr cells can provide subpicosecond time resolution but their low efficiency limits the technique to strong signals, a luxury not shared in most semiconductor studies. The most widely used technique with the highest temporal resolution in luminescence spectroscopy is the optical sum frequency generation. This technique has been used as early as 1978 for time-resolving luminescence from CdSe and for picosecond studies of emission from semiconductor lasers.

One of the early experiments in time-resolving luminescence using the up-conversion technique is the work by Kash and Shah. In their work they measured the temporal evolution of luminescence with picosecond resolution in In$_{0.53}$Ga$_{0.47}$As. The measurements were made on a 0.5-μm-thick layer of In$_{0.53}$Ga$_{0.47}$As grown lattice matched to InP by liquid phase epitaxy. The sample was mounted on a cold finger and maintained at 10 K. The laser pulse (8 ps) was generated from a synchronously pumped dye laser operating at 610 nm. The experimental setup was similar to the one shown in Fig. 12. The luminescence spectra at three different times after an excitation pulse of 2 nJ energy is shown in Fig. 30. At the shortest time the spectrum is broad, extending over 200 meV above the band gap energy. The long high energy tail is exponentially decaying with energy. At longer time delays the spectra becomes narrower, the exponential tails steeper and the intensity of the luminescence near the band gap increases. A qualitative explanation of these data is as follows; the laser pulse excites electrons from the light, capturing their energy, and then these excited electrons relax to the ground state, emitting photons with energy equal to the energy difference between the ground and excited states.
heavy, and split-off valence bands into the conduction band with an initial kinetic energy of about 1 eV. The photoexcited carriers rapidly relax out of these initial states and carrier–carrier collision thermalize this electron–hole plasma to a temperature $T_L$, which is far above the temperature of the lattice $T_L$. The plasma will then cool off by losing energy to the lattice through polar and nonpolar optical phonon emission. The luminescence spectrum would be relatively flat for energies between the band gap $E_g$ and $E_g + E_F$, where $E_F$ is the quasi-Fermi energy for the electrons at $T_F$. For energies sufficiently greater than $E_g + E_F$ one would expect the spectrum to decay exponentially as $\exp[-E/KT_L]$, reflecting the exponentially decaying electron and hole distribution function. As seen in the Fig. 30 all the curves have this qualitative behavior.

Up-conversion photoluminescence were also used by Kash et al. to measure carrier cooling rates in $p$-type modulation doped GaAs–AlGaAs quantum wells. These results included the first picosecond measurement of the cooling rate of a single-component semiconductor plasma.

In 1987 Shah and co-workers reported on subpicosecond luminescence using the up-conversion technique. Their time resolution was better than 500 fs, which was limited by the laser pulse itself. They used nonlinear optical sum-frequency generation to gate the luminescence signal. By mixing the luminescence signal with a short pulse from the laser in a nonlinear optical crystal, they produced a pulse whose frequency was the sum of the two inputs and whose intensity was proportional to the product of the intensities of the luminescence signal and the gating pulse. Since the gating pulse was only 500 fs long, they were able to make a spectroscopic measurement of the time evolution of the luminescence by delaying the gating pulse by a variable amount and recording the variation of the intensity of the sum-frequency pulse. Using the same experimental apparatus, Shah and his colleagues applied this technique to study the temporal evolution of the luminescence from GaAs and InP following subpicosecond excitation and estimated intervalley scattering rates. Limited by the resolution of their experimental apparatus they were able to provide results in the range of 0.5–15 ps, which were still unexplored during that period. They found that the electron energy distribution became Boltzmann-like almost immediately after excitation and had a characteristic temperature greater than 600 K (even at low carrier densities such as those in their experiments; $5 \times 10^{16}$ cm$^{-3}$). Their most important finding was that following excitation by a 0.5 ps pulse, the luminescence signal increased in GaAs much more slowly than in InP. In GaAs the signal reached 90% of its maximum in approximately 10 ps, whereas in InP this rise occurred in 2 ps. In GaAs the L valley is only 0.29 eV above the $\Gamma$ minimum; however in InP the L valley is located 0.6 eV above the $\Gamma$ minimum. Thus intervalley transfer will occur in GaAs but not in InP. Because electrons in the satellite valley do not contribute to the luminescence, Shah and co-workers attributed the slowly rising signal in GaAs to the return of electrons from the L to the $\Gamma$ valley. From observations of the luminescence spectrum over a broad range of wavelengths, they were able to estimate the time evolution of the electron temperature. They found that the rapid initial transfer of electrons to the L valley in GaAs produced a lower initial electron temperature than would be found if the electrons remained in the $\Gamma$ valley. A substantial fraction of the kinetic energy of hot electrons in the $\Gamma$ valley is converted to potential energy in the higher energy satellite valleys. The slower return of electrons from the L to the $\Gamma$ valley acted as a source of heating of the electrons in the $\Gamma$ valley by converting this potential energy back into kinetic energy. This temporary storage of electron energy in the satellite valley resulted in a much slower overall cooling of the electron distribution that would have occurred if intervalley transfer were not allowed. In their work they have also determined the $\Gamma$–$L$ deformation potential $D_{\Gamma L}$, by comparing their experimental results with an ensemble Monte Carlo calculation. This was an important finding since at the time the deformation potential which governs the intervalley scattering rate had values ranging from $1 \times 10^6$ eV/cm$^{-1}$ to $7 \times 10^6$ eV/cm$^{-1}$. They have determined the deformation potential to be $6.5 \pm 1.5 \times 10^6$ eV/cm.

Later in 1988, Damen and Shah improved the resolution of the up-conversion luminescence spectroscopy to 65 fs by utilizing 60 fs compressed pulses. A schematic of their experimental setup is similar to the one shown in Fig. 12. The substantial improvement of the previous 500 fs temporal resolution, besides the improvement on the shorter excitation pulses utilized, may be attributed to the following two factors:

(i) all dispersive elements have been eliminated or reduced to an absolute minimum so that they do not degrade the performance;

(ii) thinner nonlinear crystal has been utilized, to reduce the effect of group velocity mismatch between the pump and luminescence wavelength.

For 0.3 mm LiIO$_3$ crystal, it was estimated that the effects were smaller than 50 fs for the spectral range of interest. The nonlinear crystal was cut and oriented such that the phase-matched sum frequency generation for the luminescence and laser wavelength were obtained at near normal incidence. The angular position of the crystal was controlled by a motor for automation of spectral measurements. The unconverted signal was dispersed by a spectrometer and then detected by a photomultiplier followed by photon-counting electronics. The spectrometer allows for better spectral resolution and rejection of unwanted light. Temporal evolution of the luminescence was obtained by setting the angle of the crystal and the spectrometer wavelength to the appropriate value and simply scanning the delay stage.

In 1989 Wise and Tang reported their work on subpicosecond luminescence in GaAs quantum wells. The time-resolved luminescence spectra were obtained by sum-frequency generation (up-conversion) technique, which was an arrangement similar to the luminescence experiment of Damen and Shah. Measurements were made in a quantum well sample grown by molecular beam epitaxy. The sample consisted of 40 periods of 5-nm-thick GaAs wells and 50-nm-thick Al$_{0.7}$Ga$_{0.3}$As barriers. The barriers were transparent to the 1.95 eV excitation beam. Time-resolved luminescence was recorded with the sample at room temperature and at a
single carrier density of $3 \times 10^{18}$ cm$^{-3}$. The time evolution of some of the luminescence data at photon energies of 1.55 eV and 1.75 eV are shown in Fig. 31. The luminescence intensity at 1.55 eV reaches its peak value by about 5 ps, compared to 10 ps in bulk GaAs.\textsuperscript{82} This result was further evidence that indeed fewer carriers scatter to the satellite valleys in narrow quantum well than in bulk material. At 1.75 eV, which is just above the L-valley minimum, the luminescence rises very rapidly, reaching a peak at about 300 fs and decaying in a picoseconds time scale. Cooling curves from the photoluminescence data were compared to theoretical predictions for times an order of magnitude smaller than was possible in previous studies of semiconductors.\textsuperscript{88,89} They found that a calculation of the cooling of an unscreened electron–hole plasma, which assumes a thermal phonon distribution, agrees well with the experimental result for times below 500 fs. At longer times, the measured cooling was much slower than that predicted by the simple theory. The difference between calculated and measured cooling was qualitatively consistent with the generation of a hot phonon population in the experiment.

Excitation of bulk GaAs with 2 eV photons, results in an initial electron distribution consisting of three narrow peaks created by transition from heavy-hole, light-hole and split-off valence bands with relative electron densities of 0.4, 0.4 and 0.2, respectively. Clearly there is a difficulty in interpreting pump–probe transmission experiment data, where transitions from heavy-hole, light-hole, and split-off valence bands contribute to the observed transmission changes (the sum of the electron and hole distribution function $f_e + f_h$ is measured). Both carriers, electrons and holes, can cause bleaching, and carriers in different regions of the valence and conduction bands are monitored simultaneously at the specific probe wavelength. Therefore, unambiguous information on the electron distribution is difficult to extract from absorption data. In contrast, the luminescence spectrum at energies below 1.7 eV is dominated by recombination with heavy holes. The intensity of the luminescence is a product of $f_e f_h$ at the same wave vector. Thus luminescence can give new information on the carrier distribution. In 1991 Elsaesser \textit{et al.}\textsuperscript{90} presented a luminescence study of carrier thermalization in GaAs with temporal resolution of approximately 100 fs. Temporal and spectral evolution of luminescence within the first picosecond after excitation at 1.93 eV was measured for plasma densities of $1.7 \times 10^{17}$ and $7 \times 10^{17}$ cm$^{-3}$. The experiments were based on a femtosecond luminescence up-conversion technique. Some of the results are shown in Fig. 32, for a number of fixed energies. As evident from the curves in Fig. 32 all luminescence data exhibit the same instantaneous onset between 200 and 200 fs. There is an initial ultrafast transient, which is related to carrier relaxation. This initial response is followed by a slower picosecond increase in intensity, which is due to the backscattering of electrons from the L and X to the Γ valley and to carrier cooling. Heavy hole recombination dominates the luminescence signal in the observed spectral region because of the larger density of states and the larger occupation of the heavy hole band. At ultrashort times (<200 fs) the electrons in the Γ valley come from two sources: (a) electrons excited from the split-off band and (b) a small fraction of electrons excited from the heavy and light bands that have not transferred to the subsidiary valleys. These electrons and holes are created with narrow (15 meV) distributions and thermalize by interaction with other carriers. The large spectral width, the absence of any narrow structures in their spectra and the rapid initial rise of luminescence at all energies demonstrate that for excitation densities of $1.7 \times 10^{17}$ and $7 \times 10^{17}$ cm$^{-3}$, the electrons in the Γ valley as well as the holes in the heavy-hole band equilibrate within the time resolution of their experiment which was 100 fs.

Time relaxation of hot holes is not well understood, at
least much less than relaxation of hot electrons. A quantitative understanding of the energy relaxation of holes is a challenge due to the complicated multivalence band nature of the material. Experimental information about the dynamics of hole relaxation is difficult to obtain for the following two reasons:

(i) Larger energy relaxation rate is expected for holes than that for electrons because of the large effective hole mass. Clearly an investigation of hole relaxation will require better temporal resolution.

(ii) Suitable measurement techniques for direct investigation of hole relaxation are lacking. Most ultrafast optical techniques such as luminescence spectroscopy and pump–probe spectroscopy interrogate a combination of electron and hole distribution. A separation of the carrier distributions in intrinsic samples is virtually impossible.

In 1992 Zhou et al. used femtosecond luminescence to study ultrafast photoexcited holes in n-doped III-V compounds. In their work Zhou and co-workers have presented subpicosecond measurements of the initial hole relaxation in GaAs and InP epilayers. The dynamics of electrons and holes were studied separately using n-doped samples, and setting the excitation density much lower than the doping density. Therefore to a first approximation, the band-edge luminescence signal I was controlled by the hole dynamics:

\[
I(t) \propto [f_e(E_g, t) + f_d] f_h(E_g, t)
\]

\[
\propto f_e \int [f_e(E_g, t)] f_h(E_g, t) dz f_h(E_g, t),
\]

where \(f_e\) and \(f_h\) represent the photoexcited electron and hole distribution, respectively, and \(f_d\) the doping electron distribution. In their experiment they used 50 fs laser pulses generated by a colliding pulse mode-locked laser. The emitted luminescence was collected and focused onto a nonlinear BBO crystal. A second pulse from the CPM laser was sent through a variable delay and focused on the BBO crystal to gate the luminescence signal by means of sum-frequency generation. They concluded that thermal equilibrium between the excited holes and the lattice was established at approximately 700 fs in GaAs at room temperature. At low carrier densities, electron–phonon interactions were less important than relaxation of hot electrons. A quantification of this relaxation was achieved primarily through the screened Coulomb interaction which occurs between carriers. Elastic as well as inelastic carrier–carrier collisions contribute to dephasing of momentum. At low carrier densities, electron–phonon interactions begin to dominate in the intrinsic material. The density dependence of the polarization dephasing can provide important information concerning carrier–carrier interaction.

5. Femtosecond photon echoes

The photon-echo technique has become an important tool for investigating dephasing processes in gases and solids. The use of coherent optical transients to study processes for band-to-band transitions in semiconductors has been suppressed due to the ultrafast time scale on which such processes occur. Developments however, in ultrashort pulse techniques—which have led to the generation of optical pulses as short as a few femtoseconds in duration—have made photon-echo experiments possible. Polarization dephasing rate measurements will provide a direct measure of the process of momentum dephasing. At high carrier densities the carrier momentum loses phase coherence primarily through the screened Coulomb interaction which occurs between carriers. Elastic as well as inelastic carrier–carrier collisions contribute to dephasing of momentum. At low carrier densities, electron–phonon interactions begin to dominate in the intrinsic material. The density dependence of the polarization dephasing can provide important information concerning carrier–carrier interaction.

In 1988 Becker et al. (Bell Labs) have reported on the first observation of femtosecond photon echoes from the band-to-band transition in bulk semiconductor. In their experiment they observed photon echoes using a two-pulse sequence. Two pulses, with wave vectors \(k_1\) and \(k_2\), generated an echo in the momentum matched direction \(2k_3 - k_1\), where the angle between \(k_1\) and \(k_2\) was small. The echo was then separated spatially from the excitation pulses. Due to the short duration of the pulses there was a large frequency spread in each pulse, therefore there was an angular spread of \(k\) vectors that made up the echo signal, which was well separated spatially from the incident beams. The energy of the generated echo was measured as a function of the relative time delay between the excitation pulses.

One can simply model the band-to-band absorption in a direct semiconductor such as GaAs as a set of Lorentzian two-level transitions having a half-width of \(2T_2\). The band-to-band absorption coefficient \(\alpha(E)\) can be written as:

\[
\alpha(E) = \int \frac{\rho(E')}{(E-E')^2 + (2\hbar/T_2)^2} dE',
\]

where \(\rho(E')\) is the density of states at energy \(E'\).
Thus the polarization dephasing time $T_D$ where $m_3$ is the density of states at energy $E'$ and $T_2$ is the polarization dephasing time. Using this model for the absorption, the energy of the photon echo can be determined to vary exponentially as follows:

$$E(\Delta t) \propto \exp\left(-\frac{\Delta t}{T_2/4}\right),$$

where $\Delta t$ is the relative time delay between the two pulses. Thus the polarization dephasing time $T_2$ can be directly determined by simply measuring the echo energy as a function of time.

Becker and his co-worker performed the photon echoes with 6 fs pulses at repetition rate of 8 kHz and pulse energy of the order of 1 nJ. The sample was 0.1-μm-thick GaAs grown by molecular beam epitaxy and both faces were antireflection coated. The excitation energy at the focus was measured to be $30 \mu$m in diameter. Figure 33 shows the photon-echo signal from GaAs at room temperature as a function of relative time delay between the 6 fs excitation pulses. The time constant of the exponential decay $T_{\text{echo}}$ is indicated for each carrier density (from Ref. 93).

These data indicate a dephasing time ranging from 14 to 44 fs with the density ranging from $7 \times 10^{17}$ to $1.5 \times 10^{18}$ cm$^{-3}$. The dephasing times obtained from these experiments are significantly shorter than those measured by Oudar et al.,$^92$ in their experiments on the relaxation of induced anisotropy in GaAs for band-edge carriers. It is interesting to note that the dephasing rate dependence on the density, which suggests that the dephasing process is dominated by carrier–carrier interaction.

6. Time-resolved Raman scattering

If the kinetic energy of the photoexcited carriers is much larger than the thermal energy ($k_B T_L$, where $k_B$ is the Boltzmann constant and $T_L$ is the lattice temperature) the carriers are known as hot carriers. Hot carriers typically relax to the band extrema by emission of optical phonons. In GaAs, this relaxation proceeds via emission of longitudinal optical (LO) phonons in a very short time, typically a few picoseconds. After excitation of hot carriers with an ultrashort laser pulse, the optical phonon population will rise temporarily above the thermal equilibrium value. This transient nonthermal population of phonons has been referred to as “hot phonons.”

Time-resolved Raman scattering is an experiment based on the variant of the excite-and-probe scheme, which is utilized to measure the temporal evolution of nonequilibrium optical phonons. It is important to point out that this technique is also suitable for studying the dynamics of other nonequilibrium excitations not just optical phonons. In time-resolved Raman experiments, two short light pulses with the same frequency and approximately the same intensity (normally one takes the excited beam to be a few times more intense than the probe beam) are used in a pump-and-probe configuration. The strength of the excitations is measured by detecting the Raman light scattered off these excitations. In the case where the excitations are optical phonons, a measure of the anti-Stokes intensity is proportional to the number of phonons generated. The scattered light produced by the first pulse (the pump pulse) is eliminated by a suitable oriented analyzer in front of the detector such that only scattering due to the second pulse (the probe pulse) is detected (Fig. 11). The total signal of the probe pulse consists of two parts. First, there is light scattered off phonons left behind by the pump pulse. The variation of this contribution with the time delay $\Delta t$ will reveal the rise and decay of the phonons under study. Second, there is a signal caused by phonons generated by the probe pulse itself. This contribution is independent of $\Delta t$ and therefore it leads to a constant background signal.

Time-resolved Raman scattering determines the relaxation time ($\tau_p$) of the incoherent phonon population at the probing wave vector. This in general may be different from

![FIG. 33. The photon-echo signal in GaAs at room temperature is plotted as a function of relative time delay between the two 6 fs exciting pulses. The time constant of the exponential decay $T_{\text{echo}}$ is indicated for each carrier density (from Ref. 93).](image1)

![FIG. 34. Echo decay time constant as a function of the carrier density for GaAs at room temperature (from Ref. 93).](image2)
the phonon lifetime $\tau$. The phonon lifetime $\tau$ characterizes the decay of a single coherent lattice mode of specific frequency and wave vector. This phonon lifetime can be determined by measuring the decay of such a mode using coherent Raman scattering.\(^{95}\) The phonon lifetime $\tau$ and the population relaxation time $\tau_p$ correspond to the dephasing time and lifetime, respectively, of molecular vibration encounter in liquids and gases.

The first experiment, which I wish to refer to, was performed in GaAs by Von Der Linde et al.\(^{4}\) who used time-resolved Raman scattering to study the dynamics of nonequilibrium incoherent optical phonons and their interaction with photoexcited hot electrons and holes. In the experiment photoexcited carriers were generated with light from pulses of synchronously mode-locked dye lasers with autocorrelation duration of 2.5 ps. The electron–hole pairs generated by 575 nm (2.16 eV) laser light had excess energy that was 17 times the LO phonon energy ($\sim 37$ meV). The phonons generated occupy a volume of the Brillouin zone, which is determined by the conservation of energy and momentum for the carrier–phonon scattering. The upper and the lower limit of the range of phonon wave vectors is $q(\text{min}) = 3.2 \times 10^{5}$ cm$^{-1}$, and $q(\text{max}) = 10^{7}$ cm$^{-1}$. In a backscattering Raman configuration the wave vector of phonons probed assuming the above wavelength is $7.7 \times 10^{5}$ cm$^{-1}$ [this corresponds to a fraction of the LO phonons near $q(\text{min})$]. The GaAs crystal they investigated had a (100) surface and the laser pump and probe pulses were polarized along (010) and (001) directions, respectively. A polarizer with (010) orientation blocked LO scattering due to the pump pulse. The anti-Stokes Raman signal as a function of delay time between the pump and probe is shown in Fig. 35. The time independent background signal is the result of carrier excitation by the probe pulse. The observed variation of the anti-Stokes signal with time delay between the pump and probe pulses is a clear indication of the generation and relaxation of nonequilibrium phonons. The rise of the signal signifies the growth of the phonon population due to energy relaxation of the photoexcited carriers. However, the temporal resolution in this experiment was only 2.5 ps, thus no further attempt was made to use this information to determine the electron–phonon interaction time. The observed decrease in the anti-Stokes signal is a function of the decay of the LO phonons into acoustic phonons. As seen in the Fig. 35 the decay of the LO phonons follows an exponential function with a decay time of $7 \pm 1$ ps when the sample was kept at 77 K.

The above experiments was repeated by Kash et al.\(^{96}\) using subpicosecond laser pulses. In this experiment the carriers in GaAs were photoexcited with compressed 600 fs pulses from synchronously pumped rhodamine-6G dye laser operating at 588 nm. The nonequilibrium LO phonon population versus probe delay is displayed in Fig. 36 for low temperature (less than 80 K) and room temperature. The phonon decay time at low temperatures was found to be 7.5 ps and 4.0 ps at room temperature. This decrease in the phonon decay at low temperatures is expected since the LO phonons decay into acoustic phonons through anharmonic terms in the Hamiltonian which become less important at low temperatures. Given the energy of the excitation photon (2.11 eV) and the energy of the band gap, each photoexcited electron created about 14 (16 at room temperature) LO phonons before reaching the band edge. In a Raman backscattering geometry, the probe detected only phonons with wave vectors $8.4 \times 10^{5}$ cm$^{-1}$. Thus for parabolic conduction band with effective mass 0.067$m_e$, it was estimated that they detect approximately 12 cascade phonons at room temperature at which time the anti-Stokes Raman signal reaches a maximum. Using the amount of time for the Raman signal to reach maximum ($\sim 2$ ps) and the above reasoning of the 12 cascade phonons they were able to deduce that the electron–phonon scattering time was approximately 165 fs. Kash et al. have also noted that for higher injected carrier densities (carrier concentration approaching $10^{19}$ cm$^{-3}$), substantial time dependent changes were observed in the spontaneous Raman spectra which result from screening of the LO phonons by

FIG. 35. Semilog representation of the anti-Stokes signal showing the decay of the LO-phonon population. The dashed curve is the measured autocorrelation function of the pulses. The solid curve is calculated (from Ref. 4).

FIG. 36. Anti-Stokes Raman signal as a function of delay between pump and probe for GaAs 77 K and room temperature (from Ref. 96).
the free carriers and the relaxation of the free carriers to the band edges.

Tseng and Morkoc have used sub-picosecond time-resolved Raman spectroscopy to study LO phonons in GaAs–Al$_x$Ga$_{1-x}$As multiple-quantum-well structures. The ultrashort pulses used in their experiment were generated from a DCM double-jet dye laser synchronously pumped by the second harmonic of a continuous wave mode-locked yttrium-aluminum-garnet (YAG) laser. The dye laser was operating at 1.81 eV which was very close to the $E_0 + \Delta_0$ energy gap of GaAs in order to take advantage of the resonance enhancement. The GaAs–Al$_x$Ga$_{1-x}$As multiple-quantum-well structures investigated in this work were grown by molecular beam epitaxy on a (001) oriented undoped GaAs substrate. They consist of 30 periods of 10-nm-thick Al$_x$Ga$_{1-x}$As ($x=0.05$ and 0.1) and different thickness of GaAs layers (ranging from 5 to 30 nm). The average photoexcited carrier density was estimated to be about $2 \times 10^{15}$ cm$^{-3}$ and the occupation number of the excited non-equilibrium LO phonons $\sim 0.005$.

The number of LO phonon (probed by Raman scattering) emitted by the photoexcited carriers was estimated to be approximately five after considering the fact that once the carriers were trapped inside the wells, they were unable to emit LO phonons that were active under the experimental conditions. Using this information along with the experimental data they were able to estimate the average electron-LO-phonon scattering time for electrons occupying the continuum states to be approximately $170 \pm 40$ fs. They also found that this scattering time was insensitive to the well thickness.

a. Summary of time-resolved Raman scattering results: The temporal evolution of nonequilibrium phonons in a semiconductor generated after photoexcitation with an ultrashort laser pulse provides direct evidence of the energy relaxation of carriers. Time-resolved Raman scattering may be used to determine the time evolution of the nonequilibrium optical phonons near the center of the Brillouin zone. The typical temporal evolution of the anti-Stokes Raman signal which corresponds to the temporal evolution of the nonequilibrium phonon population has the following two characteristics:

(i) Initial rise: This initial rise in the signal signifies the growth of the phonon population due to energy relaxation of the photoexcited carriers. Using the amount of time for the signal to reach maximum and the total number of phonons expected to decay from a single photoexcited carrier the electron–phonon scattering time may be estimated (assuming the laser pulse duration is short compared to the time measured). For GaAs this time was measured to be approximately 165 fs.

(ii) Slower decay: This slow decay corresponds to the decay of the LO phonons into acoustic phonons. This decay of optical phonons in GaAs was determined to be approximately 4 ps at room temperature and 7.5 ps at 77 K. Similar results with approximately the same values have also been demonstrated in other III-V materials.

B. Low-temperature-grown GaAs

Low temperature grown GaAs has recently attracted interest due to its application in electronic and optoelectronic devices. This material is grown via molecular beam epitaxy on a GaAs substrate whose temperature is approximately 200 °C, well below the normal growth temperature for high quality GaAs. This results in an excess arsenic concentration of 1%–2%. Post-growth annealing of LT (low temperature grown) GaAs at temperatures above 600 °C leads to the nucleation of excess arsenic in As precipitates. The influence of As precipitates on the high resistivity of annealed low temperature GaAs is related to As clusters, which act as buried Schottky barriers responsible for trapping of electrons and holes. The recombination time of photoinjected carriers can be as short as a few hundreds of femtoseconds. The semi-insulating nature, high mobility and subpicosecond response time make low temperature grown GaAs an attractive material for ultrafast, laser activated high voltage switches and photodetectors.

Subpicosecond carrier lifetimes in GaAs grown by molecular beam epitaxy at low temperatures was reported at the end of 1991 by Gupta et al. They used an ultrashort laser pulse from a colliding pulse mode-locked dye laser ($\lambda = 620$ nm) in a pump-and-probe configuration and measured the transient reflectivity with a resolution of 100 fs. From their results they demonstrated that molecular beam epitaxy (MBE) grown GaAs exhibits a subpicosecond carrier lifetime for growth temperatures near 200 °C. After annealing this material had significantly better responsivity when used as a photoconductive material for the generation of subpicosecond electrical pulses.

Photoluminescence from hot carriers in low temperature grown gallium arsenide have been reported by van Driel et al. in 1992. A LT GaAs grown by molecular beam epitaxy on a GaAs substrate at a temperature of 200 °C and annealed at 600 °C was used to obtain photoluminescence spectra. The spectra were obtained using 5 ps pulses from an 80 MHz repetition rate dye laser, which could be tuned between 610 and 765 nm (2.03–1.62 eV). The luminescence was collected with a two-dimensional synchronscan streak camera, with overall system time resolution of less than 10 ps. Although these experiments do not time resolve the light emission and carrier kinetics, the very short recombination time effectively acted as a “gate in time,” permitting the observation of highly nonequilibrium carriers under quasi-steady state conditions without the need for subpicosecond sources. Figure 37 shows typical spectra obtained from LT GaAs at 10 K with excitation of 680 nm at average intensities of 50 and 0.5 kW/cm$^2$. The luminescence efficiency decreases slightly with increasing temperature and has a value at least four orders of magnitude below that of normal GaAs.

The photoexcited carrier lifetimes as a function of annealing temperature for low temperature grown GaAs was measured with a femtosecond transient absorption experiment. The work by Harmon et al. included the study of two low temperature grown GaAs films with approxi-
These results dramatically differ from the results of Gupta et al. 

The excess carrier lifetime was more than an order of magnitude longer than that for unannealed material. 

The 125 fs laser pulses were obtained from a titanium sapphire laser tuned to 866 nm. The wavelength was chosen approximately 10 meV above the band gap of normal GaAs in order to probe the states near the conduction and valence band edges. The excess carrier lifetime was more than an order of magnitude longer than that for unannealed material. These results dramatically differ from the results of Gupta et al., which was attributed to relatively weak annealing temperatures used in their studies. 

Zhou et al. have reported on direct observation of a reduced cooling rate of hot carriers in the presence of nonequilibrium LO phonons in low temperature grown GaAs. They used a prepump–pump pulse technique whereby one can independently vary the carrier and nonequilibrium phonon densities (since the carrier lifetime is short compared to the phonon lifetime) to examine the effects of phonons alone on the carrier cooling rate. The cooling rate was determined from femtosecond, time-resolved luminescence spectroscopy. The GaAs used in their study was grown at 200 °C by MBE on a GaAs substrate, and subsequently annealed at 600 °C for 10 min. The principle of the method is illustrated in Fig. 38. A laser pulse with photon energy larger than the band gap of LT GaAs (called the pre-pump) created carriers with density of about \( n_{pp} = 10^{18} \text{ cm}^{-3} \). The hot phonons generated during the cooling process will remain for a long time compared to the carriers, which essentially disappeared after a few picoseconds. The sample was then excited with a second pump pulse that injected a carrier density of approximately \( n_p = 10^{17} \text{ cm}^{-3} \), sufficiently low that the many body effects such as screening do not influence the carrier phonon interaction. Changing the intensity of the pre-pump pulse or the separation between pre-pump and pump pulses it was possible to produce a variable density of phonons that can interact with the carriers generated by the pump pulse. This way the influence of hot phonons alone on carrier energy relaxation can be determined. This influence was deduced from the characteristic temperature, extracted from the high-energy tail of the carrier luminescence. It is interesting to point out that unlike Raman scattering experiments this technique is sensitive to optical phonons with a wide range of wave vectors. Figure 38(b) shows two different luminescence spectra at \( \tau' = 0.5 \text{ ps} \). In one case the pump pulse is delayed by \( \tau = 5 \text{ ps} \) to the pre-pump (injecting \( n_{pp} = 2 \times 10^{18} \text{ cm}^{-3} \) carriers), and in the other case the pre-pump is absent. The fitted characteristic temperature had a value of 650 K when the pre-pump was on and 510 K without the pre-pump. This directly shows the influence of the nonequilibrium phonons induced by the pre-pump pulse. Carrier temperature data as a function of time delay between pre-pump and pump pulses yield a decay time of \( 3.9 \pm 0.4 \text{ ps} \). This value correlated well with the phonon lifetime of 5 ps obtained from Raman scattering experiments. 

Recently the author and co-workers have developed a rate equation formalism to model the carrier dynamics in low temperature grown GaAs. The processes incorporated in this model are included in Fig. 39 which shows a band diagram with additional mid-gap states created by the excess arsenic. These mid-gap states (EL2-like defects) with concentration as high as \( 10^{20} \text{ cm}^{-3} \) rapidly trap excited carriers. The three main assumptions in the rate-equation model are:

![Image](62x565 to 286x739)

**FIG. 37.** Luminescence spectra of low temperature grown GaAs at 10 K for \( \lambda = 680 \text{ nm} \) excitation at 50 and 0.50 kW/cm². The cutoff at high energies is set by a low-pass filter designed to reject stray light from the laser (from Ref. 102).

![Image](333x490 to 542x739)

**FIG. 38.** (a) A schematic diagram of the two pulse experiment with a prepump and pump pulse. (b) Luminescence energy spectra obtained at \( \tau' = 0.5 \text{ ps} \) from the pump pulse. The upper data set (squares) was obtained when the pump pulse was delayed from the prepump pulse by \( \tau = 5 \text{ ps} \), while the lower data set (circles) was obtained without a prepump pulse (from Ref. 104).
(1) The population of carriers, \( N \), at the bottom of the conduction band contribute to absorption saturation.

(2) Both \( N \) and \( n \) (the population of carriers in excited states within the conduction band) contribute to the refractive index change.

(3) The population of carriers in the traps, \( N_T \), contributes to the absorption but not to the index changes.

The equations of the model are as follows:

\[
\frac{dN}{dt} = \alpha I_0(h\omega)^{-1} - N\tau_1^{-1} + n\tau_3^{-1},
\]

where \( \alpha \) is the band-to-band absorption coefficient.

\[
\frac{dN_T}{dt} = -\alpha_T I_0(h\omega)^{-1} - N_T\tau_2^{-1} + N\tau_1^{-1} + n\tau_4^{-1},
\]

\[
\frac{dn}{dt} = -\alpha_T I_0(h\omega)^{-1} + I_0^2\beta(h\omega)^{-1} - n\tau_3^{-1} - n\tau_4^{-1},
\]

where \( \alpha_T \) is the absorption coefficient from the traps to excited states in the conduction band, and \( \beta \) is the two photon absorption coefficient. In all the cases the decay time, \( \tau \), refers to the relaxation processes indicated in Fig. 39. The total absorption is thus given by \( \alpha + \alpha_T + \beta I_0 \).

After photo-excitation of electrons at the bottom of the conduction band, these carriers will be trapped in mid-gap states (\( N_T \)) from where they can be optically excited to upper states (\( n \)) in the conduction band. This process gives rise to an additional absorption mechanism in LT grown GaAs. This can produce a much larger carrier concentration in the conduction band than is possible with just band-to-band absorption. Experiments were performed using 150 fs pulse from a mode-locked Ti:sapphire laser tunable around the band edge of the sample material. The absorption was probed with a variable delay after an intense saturating pulse.

Initial experiments with a relatively weak excitation pulse exhibit a fast rise followed by a single exponential decay of absorption saturation (due to band filling). This provided a direct measure of the trapping time \( \tau_1 \). Figure 40 shows some of our experimental pump-and-probe measurements at \( \lambda = 0.870 \mu m \) of absorption dynamics of LT:GaAs at high pump intensities. The absorption saturation due to band filling is present, however, it is offset early on by an increase in absorption that decays away on a time \( \tau_2 \) and causes the negative dips seen in Figs. 40(a) and 40(b). This additional absorption process is optical excitation of carriers from the trap levels back into the conduction band. The dynamics of this additional absorption can be described as follows. Two photon absorption of the pump pulse placed carriers high in the conduction band where they rapidly fell (\( \tau_4 \) comparable to the resolution of our experiments) in the midgap states. This lead to a rapid increase in the trap related absorption as evidenced by the rapid decrease in transmission near zero delay. The related increase in absorption due to carriers in the traps then decays away as the traps empty with a time \( \tau_2 \). The experimental data of two samples with different growth conditions were fitted with the rate equation model (see Fig. 40). These samples were chosen to illustrate the absorption dynamics for the cases \( \tau_1 < \tau_2 \) and \( \tau_1 > \tau_2 \).

The two photon absorption coefficient \( \beta \) was measured and found to be 35 cm²/GW. The rate equations were fitted to the experimental measurements which determined \( \tau_1 \), \( \tau_2 \), \( \tau_3 \), and \( \tau_4 \). For the 250 °C grown sample, it was estimated that \( \tau_1 = 3.0 \) ps; \( \tau_2 = 3.8 \) ps; \( \tau_3 = 100 \) ps, and \( \tau_4 = 0.6 \) ps. For the 300 °C grown sample, it was found that \( \tau_1 = 1.4 \) ps; \( \tau_2 = 3.0 \) ps, \( \tau_3 = 100 \) ps, and \( \tau_4 = 0.31 \) ps.
1. Summary of low-temperature-grown GaAs results

Low temperature grown GaAs appears to be a very promising semiconductor material for application in electronic and optoelectronic devices. Of particular interest for ultrafast photonic applications is the fact that this material exhibits an enhanced light-induced refractive index change as large as 0.1 for light resonant with the band gap, and that the carrier lifetime can be reduced from tens of nanoseconds in standard growth temperature GaAs to picoseconds or even subpicoseconds in annealed low temperature grown material.

In view of the great deal of research conducted in this material, clarification of the dependence of key parameters on material growth and annealing conditions will be offered in the near future and even more important, an indication of how this material (and possible related material to LT GaAs) can be optimized for ultrafast photonic switching and other optoelectronic applications.

C. Group II–VI semiconductors

In semiconductors much interest has focused on materials in which below band gap radiation is utilized and nonlinear absorption processes such as two photon absorption are the dominant sources of beam attenuation. For optical sources in the visible and near infrared region of the spectrum, the materials, which have drawn considerable interest because of their large nonlinear susceptibilities, are the group II–VI semiconductors. In this section some work in this area is presented.

The dynamics of the optical nonlinearity have been studied on CdS$_{0.75}$Se$_{0.25}$ mixed crystal, pure CdSe, and CdS using picosecond excite-and-probe techniques. However in those experiments the temporal resolution (a few picoseconds) was not good enough to resolve the nonlinear switching of the material. Puls et al. used pulses generated from a CPM ring laser in an excite-and-probe configuration to study the nonlinearity on these material with femtosecond resolution. The pulses were approximately 115 fs centered at 0.618 μm and amplified with a four stage amplifier that was pumped with an excimer laser. In this work they have studied three different situations: (a) above band gap excitation of CdSe, (b) below band gap, exciton resonant excitation of CdS$_{1-m}$Se$_m$ mixed crystal, and (c) above edge excitation of a color filter made from CdS$_{1-m}$Se$_m$ microcrystallites embedded in glass. These data directly demonstrated that these semiconductors can be used for optical switching and logic operation on the subpicosecond time scale. This is particularly true for the exciton resonant nonlinearity, where they observed a maximum around zero delay, followed by a plateau and subsequently, partial recovery with a characteristic time of 300 fs.

Time-resolved probe beam deflection was used by Fox et al. to determine the temporal evolution of the refractive index changes induced in CdS$_{0.75}$Se$_{0.25}$ single crystal at 300 K. The source of optical pulses was an amplified colliding pulsed mode-locked laser which provided 620 nm, 120 fs pulses, with energies up to 20 μJ at a repetition rate of 20 Hz. The band gaps in CdS$_{0.75}$Se$_{0.25}$ were 125 meV higher than the photon energy of the optical pulses, thus two photon absorption was the dominant absorption mechanism. In their deflection experiments, the pump-and-probe beams were orthogonal polarized and each was incident at a small angle (less than 10°) from the surface normal. The transmitted probe beam was imaged onto a two-dimensional array and the angle deflection was recorded as a function of probe delay. Experimental result for CdS$_{0.75}$Se$_{0.25}$ are shown in Fig. 41, where positive deflection angles correspond to a Δn<0.

As seen in the graph, at low incident irradiance, the deflection follows the temporal profile of the pulse. For irradiances greater than 3 GW/cm$^2$ and with increasing probe pulse delay, a larger contribution to Δn is seen to completely dominate the zero-delay contribution.

The change in index of refraction observed in these deflection experiments was attributed to virtual excitation of the electronic system for which Δn=2n$_2$I (n$_2$ is the nonlinear refractive index). The observed delay, strong negative contribution to Δn with a risetime of 1.5 ps for CdS$_{0.75}$Se$_{0.25}$, was attributed to changes induced by optically generated free carriers. Initially the carriers generated were very hot and hence contributed little to the change in the index of refraction because the blocked oscillators were associated with optically coupled states far removed from the probe frequency. As the carrier relaxed near the band edge the magnitude of Δn increased. Therefore this initial rise time of the deflection was a direct measure of the carrier cooling time. Once the
CdSe at various carriers excitation densities, the energy relaxation rates in hot-carrier energy loss rates in CdSe obtained using up-tic phonon interactions. In their work they present result on determined by the less stronger nonpolar–optical and acoustic phonons, a nonequilibrium population of LO phonons builds up, leading to their reabsorption by the carriers. In effect, the carrier energy loss rates slow down considerably, being now determined by the less stronger nonpolar–optical and acoustic phonon interactions. In their work they present result on hot-carrier energy loss rates in CdSe obtained using up-conversion luminescence. The energy relaxation rates in CdSe at various carriers excitation densities \((2 \times 10^{17}, 4 \times 10^{17}, 8 \times 10^{17} \text{ cm}^{-3})\) were measured. These cooling rates were found to be very sensitive to the carrier density. A comparison of these results with theoretical calculations was performed with and without the effect of hot-phonon dynamics. While the theory without the hot-phonon effects gives cooling rates much faster than the experimental rates, a satisfactory explanation of the data was obtained in the framework of hot-phonon theory, which leads to a prediction of the optical phonon lifetime in CdSe (at 8 K) of 6–9 ps. They also found that as carriers cool, the carrier energy loss is in effect dominated by optical phonon emission by hole via the nonpolar optical deformation potential interaction, and not by LO emission due to the Frohlich mechanism.

### D. Group IV semiconductors

The understanding of carriers and phonon dynamics in group IV semiconductors has not advanced at the same pace as in group III-V materials due to the indirect band gaps of silicon and germanium. Experimental techniques such as differential absorption spectroscopies and time-resolved photoluminescence are limited in their utility when the fundamental gap is indirect. Nevertheless, there has been some interesting work in this area which I will describe in this section.\(^{116-120}\)

In 1981 Moss et al.\(^{121}\) used the optical transient grating technique to measure the diffusion coefficient and recombination effect in germanium. In their experiments they used 35 ps pulses at 1.06 \(\mu\)m separated by an angle 2\(\theta\). These pulses were focused onto the germanium sample such that they were both spatially and temporally coincident. Absorption of these pulses produced a spatially modulated carrier density which decays by bulk recombination and by diffusion (in their experiments surface recombination was negligible). The grating decay was monitored by measuring the first order diffraction from a third pulse (probe) at 1.55 \(\mu\)m as a function of time delay between pump pulses and probe pulses. The probe wavelength was chosen purposely less than the direct band gap in Ge, so that the probe beam interrogated primarily an index or phase grating.

Temporal evolution measurements by Moss and coworkers of the diffraction efficiencies of these optically induced gratings were performed for four different grating spacings, 22.7, 15.7, 11.5, and 6.8 \(\mu\)m at room temperature. Some of the results are shown in Fig. 42. Note that the grating lifetime decreases with decreasing grating spacing, indicating the increasing importance of diffusion for smaller grating spacing. Using the results from the different grating spacings they were able to determine the ambipolar diffusion coefficient for Ge at 295 K to be of 53 \(\text{cm}^2/\text{s}\), a value slightly smaller than the accepted value of 65 \(\text{cm}^2/\text{s}\). The lower value for the diffusion coefficient extracted is suspected to be due to a local increase in sample temperature from the excess energy during interband absorption.

Smirl et al.\(^{122}\) used transient orientation gratings produced in germanium and reported the direct observation of anisotropic state filling in semiconductors. It should be made clear that one can distinguish two transient grating source namely; (a) concentration grating and (b) orientation grating. As mentioned earlier gratings are formed when two (or more) noncollinear pulses interfere. The type of grating depends on the relative polarization of the pulses. If they have identical polarizations the intensity will vary periodically in space. In this case if the excitation is resonant, the population of excited states will be spatially periodic and we say that a concentration grating has been produced. Conversely, if the two pulses are orthogonally polarized, the intensity is everywhere uniform but the direction of polarization of the resultant field will be modulated periodically in space. If the strength of the resonant excitation depends on this polarization, then the population of excited states will have a preferred orientation that is modulated periodically. In this case one speaks of orientation grating. In Smirls experiments an orientational grating was produced by anisotropic state filling. They have demonstrated that anisotropic state filling in germanium can be achieved at excitation intensities in excess of 1 GW/cm\(^2\). They have also established that the lifetime associated with anisotropic state filling is considerably less than a picosecond (this is no surprise since momen-
tum randomization is expected to be on the order of a femtosecond, as seen in GaAs from the photon-echo experiments).

The dynamics of high density, and high temperature plasma, generated in silicon by single 1.06 and 0.53 μm picosecond laser pulses were studied by van Driel. The laser pulse excitation was simulated with a model based on the Boltzmann transport equation. Balance equations, which included possible plasma degeneracy effects, were used to obtain the spatial and temporal evolution of the lattice temperature as well as the carrier density and temperature. The model was able to account quantitatively for the weak dependence of the melt threshold on pulse width at 0.53 μm as well as the strong dependence at 1.06 μm.

This model was later generalized by Othonos et al. to include different electron and hole temperatures, and to include detailed microscopic expressions for energy exchange processes between carriers and phonons. More detail and a description of this model will be given in the next section (Section V).

Subpicosecond infrared pulses were used to study the cooling of carrier plasma in germanium by Roskos and his co-workers. In their experiments a typical pump–probe configuration was utilized to excite the germanium sample and then probe the subsequent changes in the carrier dynamics via the changes in the transmission of the probe beam. The laser source was a synchronously mode-locked dye laser which generated approximately 1 ps duration pulses at 1.25 μm. The sample was intrinsic germanium [ρ ~ 40 Ω cm, (111) plane] which was polished to a thickness of 1.3 μm. In these experiments the pump photons at 1.0 eV induce transition from the heavy and light hole bands to the Γ valley. The electrons in the Γ valley are rapidly scattered to the four L valleys either directly or via transient population of the X valleys. Since intervalley scattering occurs on tens of femtoseconds the Γ valleys states were not populated substantially on the time scale of the experiment. Figure 43 shows time-resolved transmission at 300 K for excited carrier density of approximately 7 x 10^17 cm^-3. A coherent artifact due to non-linear coupling of the excite-and-probe beams appears at a time delay of zero. Subsequently, the transmission rises for 7 ps, indicating the cooling of the photoexcited carriers. An increase in transmission is observed since hole states close to the band edge are monitored. Cooling of carriers leads to depopulation of high-energy hole states and to an increase of population of the probed low-lying states. At later delay between the pump and probe pulses, the transmission signal decreases with a time constant of approximately 100 ps due to surface recombination of carriers.

Picosecond Raman scattering from nonequilibrium optical phonons in germanium was first reported by Young et al. The temporal evolution of nonequilibrium TO and LO phonon populations in photoexcited germanium was monitored at 300 K and 77 K using a picosecond Raman scattering technique. Similar nonequilibrium TO and LO phonon populations were observed, indicating that the carrier–LO phonon and carrier–TO phonon interaction strengths are similar, at least at the particular wave vector probe by the dye laser pulses (575 nm). Analysis of their data indicated that the lifetime of the LO and TO phonons were the same, and equal to 8 ± 1 ps at 77 K and 4 ± 1 ps at 300 K.

Ge_{1-x}Si_x alloys are becoming increasingly important for integrated optoelectronic devices. In addition to their technological potential, GeSi alloys grown on Ge substrates offer an interesting system in which to study the effect of binary alloying on the phonon dynamics of an elemental semiconductor such as Ge. Phonon dynamics studies of LO modes in the AlGaAs ternary alloy system by Kash et al. revealed that although the steady-state line shape broadened substantially as Al was introduced, the phonon lifetime determined in the time domain was unaffected.

Three, single-layer Ge_{1-x}Si_x alloy samples were investigated with x = 0.045, 0.10, and 0.25. These layers were grown on (100) Ge wafers to thicknesses of greater than 0.2 μm. The anti-Stokes Raman spectra from all three alloy samples exhibit well defined optical vibration modes near 300 cm^-1, 395 cm^-1, and 450 cm^-1, corresponding to vibrations of Ge–Ge, Ge–Si and Si–Si nearest neighbor pairs. This work by the author deals primarily with the Ge–Ge vibrational mode, mainly because it corresponds to the longitudinal optical phonon mode seen in pure germanium. Time-resolved Raman scattering experiments were carried out at liquid nitrogen temperature for all three alloy samples, with a 4 ps laser pulse and a fluence of approximately 0.1 mJ/cm^2. The experimental arrangement was similar to the one described in Sec. II.D.2. Figure 44 show the Raman scattering data for all the alloys. All the data reveal a fast rise time (this is a characteristic of the ultrashort laser pulse), as in the case of pure Ge or GaAs. However, the decay time of the Raman probed nonequilibrium optical phonons appear to be different from the decay time observed in pure crystalline...
germanium. The phonon lifetime increases with increasing silicon concentration up to $x=0.10$ and decreases for the $x=0.25$ sample (see Fig. 45). The reason for this influence of alloy composition on the phonon lifetime is not well understood. However, there is evidence from steady-state Raman spectra and phonon density of states calculation that the increase in lifetime could be associated with an alloy-induced shift of a sharp feature that join the two phonon density of states with respect to the first order Ge–Ge optic frequency.

The short lifetime measured in the 25% Si sample is correlated with an abrupt increase in the strength of nonallowed first-order Raman scattering below 300 cm$^{-1}$. This suggests that in the 25% sample the random potential fluctuation in the alloy might become very strong, leading to a complete breakdown of selection rules for the optical decay process and hence increasing the available density of states.

Time-resolved reflectivity measurements were also obtained for the same Ge$_{1-x}$Si$_x$ alloys. The optical source for these experiments was a mode-locked cavity-dump dye laser, which produced pulses at 0.575 μm and a width of 2 ps at a repetition rate of 3.8 MHz. Table II gives a summary of the linearly interpolated band gap energies, $E_g$, densities $\rho$, specific heat $C_L$, absorption coefficient $\alpha$, diffusion coefficient $D_0$ (all taken from the literature) and the refractive index temperature coefficients $dR/dT_L$ deduced from this work. Figure 46 shows the time-resolved reflectivity for the different alloys for a pulse fluence of 1 mJ/cm$^2$. For comparison, results are also shown for pure germanium. All data sets show a rapid drop in the reflectivity which is characteristic of the rise time of the pulse. This is followed by a rise, initially rapid and then more gradual with increasing delay. With increasing Si fraction one observes that the minimum reflectivity becomes less negative while the long term reflectivity increases and actually becomes positive at $x=0.25$.

In order to interpret the data Othonos’ kinetic model (described in detail in Section V) for Ge was extended for the GeSi alloys. The reflectivity characteristics were modeled by carrier density and lattice temperature induced changes to the dielectric constant ($\varepsilon$)

$$\Delta \varepsilon = \Delta \varepsilon_N + \Delta \varepsilon_{T_L},$$

where $\Delta \varepsilon_N$ and $\Delta \varepsilon_{T_L}$ is the change in the dielectric constant due to carriers of density $N$, and an increase in lattice temperature $T_L$. Expression for the free carrier contributions of

<table>
<thead>
<tr>
<th>$x$</th>
<th>$E_g$ (eV)</th>
<th>$dR/dT_L$ ($\times 10^{-5}$)</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>$D_0^c$ (cm$^2$/s)</th>
<th>$D_0^e$ (cm$^2$/s)</th>
<th>$C_L$ (J/cm$^3$/K)</th>
<th>$\alpha$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.66</td>
<td>&lt;1</td>
<td>5.32</td>
<td>103</td>
<td>54</td>
<td>1.70</td>
<td>3.0x10$^5$</td>
</tr>
<tr>
<td>0.05</td>
<td>0.68</td>
<td>1.1</td>
<td>5.17</td>
<td>100</td>
<td>52</td>
<td>1.71</td>
<td>2.8x10$^5$</td>
</tr>
<tr>
<td>0.1</td>
<td>0.70</td>
<td>2.3</td>
<td>5.02</td>
<td>96</td>
<td>50</td>
<td>1.73</td>
<td>2.7x10$^5$</td>
</tr>
<tr>
<td>0.25</td>
<td>0.77</td>
<td>6.4</td>
<td>4.57</td>
<td>86</td>
<td>44</td>
<td>1.77</td>
<td>2.3x10$^5$</td>
</tr>
</tbody>
</table>
The minimum reflectivity and the long term increase in reflectivity results is the uniform increase in the reflectivity with increasing silicon content. This increased sensitivity of the alloys to lattice heating is largely due to a temperature coefficient $dR/dT_L$, which increases with increasing silicon content.

Recently Choo et al. investigated nonequilibrium carrier dynamics in Ge and GeSi alloys using femtosecond ellipsometric technique. Using this technique they were able to distinguish the real and imaginary part of the time-varying Drude–Lorentz dielectric function $\varepsilon_i(t) + i\varepsilon_2(t)$. These results were modeled microscopically in terms of the Drude contribution from diffusing hot-carrier plasma.

V. CORRELATION OF HOT-CARRIER AND HOT-PHONON KINETICS IN GERMANIUM

A. Introduction

Over the last decade many experiments in semiconductors have separately probed aspects of hot-carrier and phonon dynamics on a picosecond and subpicosecond time scale using ultrashort laser pulses. At very high peak intensities the electron and hole sub-systems can be driven far out of equilibrium, as can certain phonon modes. Although most of the emphasis has been directed toward understanding the nonequilibrium carrier kinetics alone, it is generally realized that nonequilibrium phonon effects can influence hot carrier relaxation. In fact, observations of nonequilibrium phonon populations through transient Raman scattering have directly provided evidence for the existence and decay of nonequilibrium phonon populations generated by hot-carrier relaxation. However, there has been little work directed toward studying both the carrier and phonon dynamics under experimental conditions that can be related to a single, self-consistent theoretical model. Clearly, we will improve our understanding of the subtle aspects of coupled system dynamics if we can correlate the behavior of carrier and phonon systems. This section of this article, reviews some of the effort to achieve this correlation for intrinsic crystalline germanium.

Germanium might seem an unlikely candidate for such a study given the fact that relatively little research has been performed on group IV materials, as compared to group III-V materials, with respect to aspects of hot-carrier and phonon dynamics. Progress in understanding the 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 fact that silicon and germanium are indirect band gap material. Experimental techniques such as time-resolved photoluminescence and differential absorption spectroscopies, that have proved 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 carried out for germanium and silicon but most of this work was concerned with high excitation levels where nonlinear absorption and recombination processes often obscure the more subtle carrier–lattice interactions. It is only recently that transient Raman scattering experiments have been done at sufficiently low injected-carrier densities to make use of detailed microscopic models of the energy relaxation processes.

Despite the relative lack of work on group IV materials the fact remains that they are centrosymmetric, which gives them a tremendous advantage over their noncentrosymmetric group III-V counterparts, if one explicitly wishes to study both carrier and lattice dynamics under comparable experimental conditions. This is so because the longitudinal optic phonon modes in centrosymmetric material generate no mac-
roscopic electric field and hence they do not couple with long range electric fields associated with free carrier density fluctuations. This has the practical consequence that the Raman-active optical phonons in germanium do not become renormalized in the presence of free carriers due to plasmon–phonon coupling so that they may be observed unaltered up to densities of \( \sim 10^{20} \text{ cm}^{-3} \). The lack of long range coupling between optical phonons and free carriers also simplifies tremendously the microscopic modeling of carrier–phonon dynamics since many-body effects can be ignored to first order. Although many models of hot-carrier dynamics in group III-V materials also ignore many-body effects, the problem is manifestly many-body in nature. Any truly complete understanding of these processes in group III-V materials will eventually have to treat the many-body-related issues. In addition to these technical reasons for studying germanium there is also a practical motivation for developing techniques to address these issues in group IV materials since sophisticated, high-speed electronic devices such as double-barrier resonant tunneling structures are now being studied in the Si/SiGe material system.\(^{134}\)

Time-resolved Raman scattering, as mentioned earlier, is usually employed to study transient phonon kinetics in semiconductors. This technique allows one to obtain information about optical phonon relaxation on an ultrashort time scale. Such scattering directly monitors the population of phonons near the center of the Brillouin zone as dictated from conservation of energy and momentum. In 1980 von der Linde et al.\(^{4}\) demonstrated the use of this tool for studying the dynamics of nonequilibrium phonons on this short time scale (see Section V).

In compound semiconductors like GaAs vibrations of oppositely charged atoms (longitudinal optical phonon modes) give rise to long range macroscopic electric fields. These electric fields associated with the longitudinal optical (LO) phonons interact (Frohlich interaction) with the carriers producing the dominant scattering mechanism in compound semiconductors. The scattering rates of the Frohlich interaction have a \( 1/q^2 \) dependence, where \( q \) is the wave vector of the LO phonon (Fig. 47). As shown by Collins and Yu,\(^{135}\) a distribution of hot electrons in GaAs will emit energy through a range of LO phonon modes while cooling off. However, due to the \( 1/q^2 \) of the scattering rate most of the energy is routed through relatively small wave vector phonons. In fact, it is somewhat fortuitous that the wave vector probed by typical phonon Raman experiments\(^{4}\) lies very close to the peak of the distribution of hot phonons. Based on this information it may seem unlikely that for germanium, comparable nonequilibrium populations could be observed where the optical nonpolar scattering (optical deformation potential scattering) is independent of \( |q| \). However, it was demonstrated\(^{119}\) that even with a wave vector independent carrier–phonon matrix element, as is appropriate for the deformation potential interactions in germanium, pure kinetic constraints of energy and momentum conservation severely limit the range of wave vectors through which energy may be transferred to the lattice from the hot carriers.

Othonos et al.\(^{117}\) have carried out time-resolved Raman scattering and reflectivity experiments in germanium, in conjunction with a self-consistent kinetic model for investigating nonequilibrium phonon and carrier dynamics. In the experiments moderate excitation levels are used for which minimal lattice heating occurs and for which nonlinear absorption and recombination processes, which complicate the analysis of high-excitation experiments in germanium or silicon, are also absent. This allows a detailed analysis of the results using a model, which focuses on the microscopic energy relaxation processes, in much the same way as is commonly done for III-V materials. One important result obtained from this study is the achievement of quantitative agreement between theory and experiment for the absolute nonequilibrium optical phonon population (\( \sim 0.1 \)) generated at an injected carrier density of \( \sim 10^{18} \text{ cm}^{-3} \). Such a large nonequilibrium population demonstrates that even with a wave vector independent carrier–phonon matrix element, as is appropriate for the deformation potential interactions in germanium, pure kinematic constraints of energy and momentum conservation severely limit the range of wave vectors 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 played by the carrier temperature dependence of the carrier diffusion coefficient even on picosecond time scales. The larger value of the ambipolar diffusion coefficient at higher temperatures leads to enhanced diffusion at short times. At times long after the excitation pulse where the coefficient returns to its ambient value normal diffusion resumes.

B. Carrier dynamics in germanium

To allow the reader to obtain a better understanding of carrier kinetics in germanium following photoexcitation the various relevant characteristics will be discussed here. This section begins with a summary of the band gap structure of germanium followed by the absorption characteristics of 2.15 eV laser radiation (which is the laser radiation used by the author and co-workers in their experiments). The various
The band minimum at the X point is; energy gap is at the center of the Brillouin zone at G the one in the minimum at the L point. There are five other valleys like Brillouin zone and along the @minima there are upper minima located at the G taken to be 0.34 ligible. The heavy-hole density of state effective mass is valence bands and its energy is 28 meV lower, therefore its of the split-off band is very small compared to the other very little difference in their energies. The density of states curvatures of the two valence bands are identical and there is considered since at the elevated temperatures of interest here the heavy-hole and the split-off band. Only heavy-holes are con-

300 K.
The separation of the direct conduction-band valley from the gap separation between the valence band maximum, located at the center of the Brillouin zone. In germanium first-order optical phonon scattering occurs through the deformation potential interaction. This type of scattering as mentioned earlier, unlike the Frohlich scattering in polar semiconductors, is inde-

The relevant features are shown in Fig. 48 for a lattice temperature of 77 K.

The conduction minimum is located at the edge of the Brillouin zone in the [111] direction at the L point. The band gap separation between the valence band maximum, located at the center of the Brillouin zone, and the L point minimum is approximately 0.734 eV at 77 K and 0.664 eV at 300 K. There are four equivalent valleys like the one shown in Fig. 48 for the entire set of [111] directions. Besides the L point minima there are upper minima located at the @ point of the Brillouin zone and along the [100] direction at the X point. The band minimum at the X point is ~0.18 eV higher than the minimum at the L point. There are five other valleys like the one in the [100] direction. The location of the direct energy gap is at the center of the Brillouin zone at @ point. The separation of the direct conduction-band valley from the top of the valence band is 0.889 eV at 77 K and 0.804 eV at 300 K.

The valence bands consist of three bands, light-hole, heavy-hole and the split-off band. Only heavy-holes are con-
sidered 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 density of states of the split-off band is very small compared to the other valence bands and its energy is 28 meV lower, therefore its contribution to the carrier dynamic may be considered neglig-
ible. The heavy-hole density of state effective mass is taken to be 0.34m0.139

Next, the various microscopic processes in germanium following ultrashort laser pulse excitation will be described in detail allowing the reader to obtain a better understanding of photoexcited germanium. The absorption of laser light of wavelength 0.575 μm by germanium near the central point of the Brillouin zone (see Fig. 49) results in the creation of electron–hole pairs with excess kinetic energy over 1.4 eV. In particular at 77 K the holes receive approximately 0.4 eV of the excess kinetic energy, whereas the electrons receive ~1 eV in kinetic energy. These excess kinetic energies cor-
respond to initial temperature distribution of 7000 K for the electron system and about 3000 K for the hole system. This suggests that initially the electrons and holes have to be treated as separate systems with their own thermal distribu-
tion. However, electron–hole scattering, which occurs on the order of 10−13 s allows for the two systems to reach thermal equilibrium.

The electrons created from the initial absorption of the laser pulse at the central valley of the conduction band rapidly scatter to the side valleys (L,X) of the conduction band by long wave vector phonons. This intervalley scattering mechanism is over within tens of femtoseconds. Once the electrons are in the side valleys they scatter within the four L and the six X valleys. This type of scattering persists until the electrons lose all their excess kinetic energy. Intervalley scattering between the L and X valleys is also allowed. How-
ever, intervalley scattering from the L to the X valleys is only possible if the electrons have kinetic energy higher than the energy separation of the two valleys (~0.2 eV). In ad-
dition to intervalley scattering highly excited carriers may lose energy through emission of optical phonons within the same valley (intravalley scattering) for the electrons, and within the same band (intraband scattering) for the holes.

In nonpolar material such as germanium and silicon, phonon scattering occurs through the deformation potential interaction. This type of scattering as mentioned earlier, un-
like the Frohlich scattering in polar semiconductors, is inde-
pendent to first order of the phonon wave vector. However, in the case of intravally and intraband scattering conserva-
tion of energy and momentum results in the emission of optical phonons restricted to a narrow region near the center of the Brillouin zone. In germanium first-order optical pho-
non deformation potential scattering is nonzero at the L val-
leys of the conduction band and at the zone center of the valence bands. On the other hand first-order optical phonon deformation potential scattering is forbidden at the X valley because of symmetry restrictions.140 To make the calcula-
tions of carrier and phonon kinetics tractable simplified assumptions about the band structure are made. In particular, the complex energy band structure of germanium is replaced with the appropriate parabolic valleys at the respective minima of the Brillouin zone (L, Γ, and X). The band-edge energies of the four L and six X valleys are assumed to be the same, with each of these valleys assigned their respective effective masses. The experimental work was performed with picosecond laser pulses in the visible region of the spectrum 0.575 μm. Although the repetition rate of these laser pulses is very high, with separation of the pulses as short as 13 ns, it is still long enough for most of the induced processes in the semiconductor to reach equilibrium. This suggests that it is sufficient to consider a single laser pulse in calculating the various carrier and phonon dynamics rather than a train of pulses.

C. A model for transport dynamics in germanium

Next I will describe in detail the transport model developed to simulate the temporal and spatial evolution of plasmas generated by short laser pulses. To model the dynamics of hot electrons, holes, and optical phonons a formalism is used which deals with coupled Boltzmann’s equations in the relaxation time approximation for particle number, particle energy and lattice energy. In his model four coupled continuity equations are solved numerically for the depth and time dependent density N, carrier temperature T, (the subscript ‘c’ will signify carriers = e, h) and lattice temperature T. To specifically model the Raman and reflectivity experiments in germanium, the formalism include different electron and hole temperatures and also include detailed microscopic expressions for energy exchange processes.

The model therefore involves the solution of four coupled differential equation for the spatial and temporal dependence of N, T, T, and T. From these parameters and the microscopic model of the carrier–phonon interaction one can also obtain the time evolution of the population (N) of the appropriate Raman-active phonons with wave vector q. One can proceed from the microscopic Boltzmann equation to a macroscopic description by integrating the microscopic transport quantities over the appropriate carrier or phonon distribution functions. In the relaxation time approximation of Boltzmann’s equation one obtains relations for the electrical (j) and energy current (W) of the carriers

\[ j_c = \frac{e}{q} \sigma_c \nabla \xi - \sigma_c Q \nabla T_c \]

\[ W_c = \left( \Pi_c - \frac{1}{e} \xi_c \right) j_c - \kappa \nabla T_c, \]

where \( \sigma_c \) is the electrical conductivity, \( Q_c \) is the Seebeck coefficient, \( \Pi_c \) is Peltier coefficient, \( \kappa \) is the thermal conductivity, \( -e \) is the charge of an electron, and \( \xi_c \) is the chemical potential of the carriers. For an intrinsic semiconductor under laser excitation, phonon scattering is expected to be the most important mechanism involving free carriers. This implies that the energy dependence of the momentum relaxation is proportional to \( (E - E_c)^{-1/2} \). Under these assumption the coefficients in Eqs. (17) and (18) are simply given by

\[ \sigma_c = eN \mu c MB H^0_{1/2}(\xi_c) \]

\[ Q_c = -\frac{k_B}{e_c} \eta_c - 2H^0_0(\eta_c) \]

\[ \Pi_c = -T_c \frac{k_B}{e_c} \eta_c - 2H^0_0(\eta_c) \]

\[ \kappa_c = -\frac{k_B^2 \sigma_c T_c}{e_c} \{ 6H^0_0(\eta_c) - 4[H^1_0(\eta_c)]^2 \}, \]

where \( H^i_j(\eta_c) \) is the ratio of the Fermi–Dirac integrals \( F_i(\eta_c)/F_j(\eta_c) \) for reduced Fermi level \( \eta_c \), and \( \mu c MB \) is the mobility of carriers in a Maxwell–Boltzmann distribution and, \( e_c \) equals \(-e \) for electrons and \(+e \) for holes. For a laser induced plasma the Dember field which develops due to charge separation prohibits the carrier charge and current density from becoming significantly different so that

\[ j_e = -j_h, \quad N = N_e = N_h. \]

Given the above equations we can write the particle current J as follows:

\[ J = -D \left( \nabla N + \frac{N}{k_B T_c} \nabla E_g \right) \]

\[ + \frac{N}{k_B T_c} \left[ H(\eta_c) \nabla T_c + H(\eta_h) \nabla T_h \right] \],

where \( J = -j/e, \quad T_c = T_H^{1/2}(\eta_c) + T_H^{1/2}(\eta_c), \quad H(\eta_c) = 2H_0^1(\eta_c) - \frac{1}{2}H_0^2(\eta_c), \quad E_g = E_c - E_v \) is the band gap energy. The symbol D in the above equation represents the ambipolar diffusion coefficient and is given by

\[ D = D_0^c D_h^0 \frac{T_H^{1/2}(\eta_c) + T_H^{1/2}(\eta_h)}{D_H^0 T_H^{1/2}(\eta_c) + D_H^0 T_H^{1/2}(\eta_h)}, \]

where \( D_0^c \sim T_h^{1/2}, \quad D_0^c \sim T_h^{1/2} \) are the low density electron and hole diffusion constants appropriate for the ambient lattice temperature. The electron and hole energy current can be rewritten in the following form:

\[ W_c = J [E_c + 2k_B T_H^{1/2}(\eta_c)] - \kappa_c \nabla T_c \]

\[ W_h = J [-E_v + 2k_B T_H^{1/2}(\eta_h)] - \kappa_h \nabla T_h \]

Similarly the lattice current for the lattice system the is given by

\[ W_{lat} = -\kappa_{lat} \nabla T_L, \]

where \( \kappa_{lat} \) is the lattice thermal conductivity. After photoexcitation, electrons and holes possess kinetic as well as band gap energy. Therefore, one may express the total energy density for the electron (\( \Phi_e \)) and hole (\( \Phi_h \)) system of N carriers in the following way:

\[ \Phi_e = NE_c + \frac{1}{2}N k_B T_H^{1/2}(\eta_c) \]

\[ \Phi_h = -NE_v + \frac{1}{2}N k_B T_H^{1/2}(\eta_h) \]
This completes the set of equations which governs carrier and thermal transport, assuming that the particles are in local thermodynamic equilibrium, and can be represented by spatially and temporally varying macroscopic parameters.

The four continuity equations, which dictate the dynamics of the macroscopic variables, \( N, T_e, T_h, \) and \( T_L \) are given by:

\[
\frac{dN}{dt} = - \nabla \times J + \mathcal{S} + \mathcal{R},
\]

\[
\frac{d\Phi_e}{dt} = - \nabla \times W_e + S_e - L_e - L_{e\to h},
\]

\[
\frac{d\Phi_h}{dt} = - \nabla \times W_h + S_h - L_h + L_{e\to h},
\]

\[
C_L \frac{dT_L}{dt} = - \nabla \times W_{lat} + L_e + L_h,
\]

where \( L_e, \) \( L_h, \) and \( L_{e\to h}, \) are the energy transfer terms (between electrons and phonons, holes and phonons, and electrons and holes, respectively), \( S_e \) and \( S_h \) represent the energy source terms for electrons and holes, \( C_L \) is the lattice thermal conductivity, \( \mathcal{R} \) is the net recombination rate, and \( \mathcal{S} \) is the carrier generation rate. The net recombination rate is given by \( -\gamma N^3, \) where \( \gamma \) is the Auger recombination coefficient.

The generation rate is taken as the following expression

\[
\mathcal{S}(z,t) = \frac{a I_0(t)(1-R) \exp(-a z)}{\hbar \omega_0},
\]

\( R \) is the reflectivity of the optical excitation, \( I_0(t) \) is the intensity, \( \hbar \omega_0 \) is the photon energy, and \( a \) is the one photon absorption coefficient.

The quantities \( S_e \) and \( S_h, \) which are the energy generation ratio for electrons and holes, respectively, can be calculated using conservation of energy and momentum in the absorption process from \( \mathcal{S}. \)

In order to simplify the computational solution of the equations when the microscopic energy transfer terms are included below, the distribution functions are now simplified to be of a Maxwell–Boltzmann form. One simply replaces the factor \( H^i_j(\eta_k) \) by unity in the above equations. This approximation to the Fermi–Dirac distribution function is valid for the carrier densities and temperature considered here. The total energy-loss rate of the carriers is incorporated in the model through the use of analytic expressions for the various scattering mechanisms.\(^{15,16,72,141}\) These include

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

The average energy-loss rate of a Maxwellian distribution of carriers of effective mass \( m^* \) to acoustic modes is given by

\[
\left\langle \frac{dE}{dt} \right\rangle_{ac} = -\frac{8 \pi \hbar^2 e_{ac}^2 m^*} {\pi^2 \hbar^4 \rho} \left( k_B T_c^2 \right)^{3/2} \left( 1 - \frac{T_L}{T_c} \right),
\]

where \( e_{ac} \) is the appropriate acoustic deformation constant (see Table III), and \( \rho \) is the density of the semiconductor.

### Table III. Material parameters of germanium.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
<th>Units</th>
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<tr>
<td>( \rho )</td>
<td>3.52</td>
<td>g/cm(^3)</td>
</tr>
<tr>
<td>( m_e^* )</td>
<td>0.04</td>
<td>( m_0 )</td>
</tr>
<tr>
<td>( m_h^* )</td>
<td>0.22</td>
<td>( m_0 )</td>
</tr>
<tr>
<td>( m_e^* )</td>
<td>0.32</td>
<td>( m_0 )</td>
</tr>
<tr>
<td>( m_h^* )</td>
<td>0.34</td>
<td>( m_0 )</td>
</tr>
<tr>
<td>( m_0 )</td>
<td>9.108</td>
<td>( 10^{-28} ) g</td>
</tr>
<tr>
<td>( D_e^* ) (77 K)</td>
<td>583</td>
<td>cm(^2)/s</td>
</tr>
<tr>
<td>( D_h^* ) (77 K)</td>
<td>232</td>
<td>cm(^2)/s</td>
</tr>
<tr>
<td>( D_e^* ) (300 K)</td>
<td>103</td>
<td>cm(^2)/s</td>
</tr>
<tr>
<td>( D_h^* ) (300 K)</td>
<td>54</td>
<td>cm(^2)/s</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>0.2</td>
<td>( 10^{-31} ) cm(^6)/s</td>
</tr>
<tr>
<td>( C_L )</td>
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<td>J K(^{-1}) cm(^{-1})</td>
</tr>
<tr>
<td>( \nu_{ac} (\Gamma) )</td>
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<td>eV</td>
</tr>
<tr>
<td>( \nu_{ac} (X) )</td>
<td>9.0</td>
<td>eV</td>
</tr>
<tr>
<td>( \nu_{ac} (L) )</td>
<td>11.0</td>
<td>eV</td>
</tr>
<tr>
<td>( \nu_{ph} (hole) )</td>
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<td>eV</td>
</tr>
<tr>
<td>( \nu_{ph} (\Gamma) )</td>
<td>4.0</td>
<td>( 10^6 ) eV/cm</td>
</tr>
<tr>
<td>( \nu_{ph} (X) )</td>
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<td>( 10^6 ) eV/cm</td>
</tr>
<tr>
<td>( \nu_{ph} (L) )</td>
<td>9.5</td>
<td>( 10^6 ) eV/cm</td>
</tr>
<tr>
<td>( \nu_{ph} (LO) )</td>
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<td>( 10^6 ) eV/cm</td>
</tr>
<tr>
<td>( \nu_{ph} (LA) )</td>
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<td>( 10^6 ) eV/cm</td>
</tr>
<tr>
<td>( \nu_{ph} (LA) )</td>
<td>4.1</td>
<td>( 10^6 ) eV/cm</td>
</tr>
</tbody>
</table>

Energy loss by hot carriers to acoustic modes is generally small compared with the loss due to optical phonons.

The energy-loss rate for a Maxwellian distribution of free carriers is given by

\[
\left\langle \frac{dE}{dt} \right\rangle_{gen} = \frac{\pi m^* \nu_{ph}^2 \nu_{ph}^2}{2 k_B T_c \rho} \left[ \exp(x_0) - 1 \right] \exp(x_1),
\]

where \( x_0 = \nu_{ph} (k_B T_c), \) \( x = \nu_{ph} / k_B T_c, \) \( x_1 = -(h^2 x / 2 m^* \nu_{ph}^2), \) \( \nu_{ph} \) is the optical deformation potential constant, and \( \nu_{ph} \) is the optical phonon energy. Multiplying this equation by \( \nu_{ph} \) and integrating it over all wave vectors give for the energy relaxation rate due to a particular phonon branch,

\[
\left\langle \frac{dE}{dt} \right\rangle_{op} = -\pi \nu_{ph} \nu_{ph} \frac{m^*}{k_B T_c} \left( \frac{x}{2} \right)^{3/2} \exp(x_0) \left[ \exp(x) - 1 \right] \frac{1}{2} \nu_{ph} \nu_{ph} \left( \frac{x}{2} \right),
\]

where \( \nu_{1/2} \) is the modified Bessel function. Electron intervalley scattering may be treated much like the intravalley scattering by optical phonon.\(^{72,141}\) The average rate of energy loss by a carrier due to intervalley scattering from valley \( i \) to valley \( j \) may be calculated using Equation (29) with \( \mathcal{S}_i \) replaced \( \mathcal{S}_{ij}, \) \( \mathcal{S}_{ph} \) with \( h \omega_{ij}, \) and finally \( m^* \) with the density-of-state mass of the \( j \) valley, \( m_j^*. \) Here \( \mathcal{S}_{ij} \) and \( h \omega_{ij} \) are the intervalley deformation-potential constant and phonon ener-
gies associated with intervalley scattering, respectively. The terms $L_e$ or $L_h$ are found by summing the energy relaxation rates over the various phonon modes.

The electron–hole energy exchange, $L_{e\rightarrow h}$, was treated in the static screening limit, including only intra-heavy-hole transitions, to be consistent with the simplifying band structure assumption made above. Details of the computational technique used to evaluate the electron–hole energy exchange rate can be found elsewhere.\textsuperscript{142}

For a direct comparison with the time-resolved Raman scattering experiments the temporal evolution of the optical phonon population generated due to the intra-L-valley and intra-heavy-hole valence-band relaxation processes will be calculated. This involves solving a partial differential equation for the Raman active phonon occupation number $n_q$ at 0.575 $\mu$m

\[
\frac{\partial n_q}{\partial t} = \left( \frac{\partial n_q}{\partial t} \right)_T \left( \frac{n_q - n_q^{eq}}{\tau} \right),
\]

where $n_q^{eq}$ is the equilibrium phonon occupation, $T$ indicates the total contribution from relaxing electrons and holes, and $\tau$ is the nonequilibrium phonon decay time determined experimentally.

D. Results and discussion

This section is devoted in comparing and discussing the theoretical results obtained from the above model with experimental data. The equations of the preceding section which describe the evolution of electron temperature, hole temperature, carrier density and optical phonon population were solved using the material parameters listed in Table III. The excitation term in these simulations was assumed to be a Gaussian 4 ps full width half maximum (FWHM) laser pulse, $\lambda = 0.575 \mu$m with fluence of 0.1 $\text{mJ/cm}^2$. The sample temperature is taken to be 77 K and the steady-state carrier density is assumed to be $10^{16}$ $\text{cm}^{-3}$. The absorption depth of laser pulses at this wavelength is 0.1 $\mu$m at 77 K and 0.04 $\mu$m at 300 K while the reflectivity $R$ is 0.5. Appropriate boundary condition were used to solve the equations, assuming negligible surface recombination and a sample thickness of 5 $\mu$m, a thickness which is large compared to carrier diffusion depths for time scales of interest.

1. Temporal dependence

Figure 50 shows some of the simulation results for the temporal evolution of $N$, $T_e$, $T_h$, and $T_L$ at the surface of the sample. The simulations start at $-10$ ps and end at 20 ps with peak of the pump pulse taken at $t=0$ (this is shown in Fig. 50 as the Gaussian curve). The main features of the carrier density evolution are the fast rise time, which simply reflects the integrated profile of the incident Gaussian pulse, and the two distinct regions in which the carrier density drops at different rates. After the carrier density reaches its peak value there is an initial rapid reduction which occurs only for a few picoseconds. This is followed by a much slower rate of density drop which persists for tens of picoseconds. The reduction of surface density is due to diffusion along, since Auger recombination is the dominant recombination mechanisms is still negligibly slow (lifetime $\sim 10 \mu$s at carrier density of $10^{18}$ $\text{cm}^{-3}$) at these densities and time scales. The fact that the rapid diffusion takes place only while the carrier temperatures remain well above the ambient temperature give a clue as to the origin of the two regimes of diffusion. From the model it is understood that the increase of carrier temperature causes the ambipolar diffusivity to increase above the value corresponding to $T_e = T_L = 77$ K, thereby forcing carriers to move out of the excitation region faster. When the temperature of the carriers reaches that of the lattice the diffusivity decreases to its equilibrium value and the carrier density decay rate is reduced. The density is in fact reduced below what it would be at the same time if a constant diffusion coefficient had been used, since by the time the diffusion coefficient drops to its ambient value the carrier density gradient is reduced.

The electron and hole temperatures start increasing before the peak of the Gaussian and reach maximum values at $t = -2.5$ ps. This initial rise in temperature occurs because at very low densities the rate, at which the optical pulse is increasing the kinetic energy of the carrier system, is larger than the rate at which the heat capacity is increasing. The surface carrier temperatures peak at 5200 K for the electron system and at 2400 K for the hole system with both maximum occurring at approximately $\tau = -2.5$ ps. The maximum values are consistent with $\sim 1$ eV of energy is provided to each optically excited electron and $-0.4$ eV to each hole. The temperature curve for the holes has a plateau once it reaches a maximum value; this is due to the energy drawn from the electron system under $e$–$h$ scattering.

To obtain a better understanding of the effect of carrier–carrier scattering on semiconductor dynamics calculations are carried out with the two extreme scattering relaxation times. Simulations are carried where the carrier–carrier scattering relaxation time $\tau_{e\rightarrow h}$ was set equal to $\infty$ and 0 (Figs. 51(a) and 51(b)). In the case where electrons and holes are viewed as decoupled systems ($\tau_{e\rightarrow h} = \infty$) the simulation curves appear similar to those seen in Fig. 50. The most noticeable difference is observed in the time dependence of $T_h$. Under these conditions no plateau is observed and once the peak value is reached the hole temperature drops and...
reaches the lattice temperature at a time different from the time at which the electron temperature reaches the lattice temperature. In the opposite extreme where electrons and holes are strongly coupled ($t_{e\rightarrow h} \rightarrow 0$) they are forced to share a common temperature as shown in Fig. 51. The calculation of statically screened electron–hole energy transfer therefore suggests that under the present experimental conditions the two carrier subsystems are essentially decoupled. Although the model calculation of the time resolved reflectivity are not sensitive to details of the electrons–hole energy exchange, the calculated nonequilibrium optical–phonon dynamics are. In particular, the good agreement between experiment and theory described below for the delay and absolute magnitudes of nonequilibrium phonon populations is obtained only if the electron–hole energy exchange is calculated explicitly, or if the two systems are assumed decoupled. A significant, 25% error in both the delay and peak magnitudes of the phonon population is made if the carriers are assumed to maintain a common temperature at all times.

Another interesting point to be made about the strong coupled and decoupled systems is the actual carrier density behavior. The peak temperature of the strong-coupled system occurs at approximately 3500 K, which is less than that of the decoupled system. This lower overall carrier temperature results in a slight decrease of the temperature enhanced diffusion coefficient which allows the carrier density to build up to higher peak values before diffusing away from the surface. This carrier diffusion effect may be seen in Fig. 51(b) where the carrier density is slightly (10%) larger than that shown Fig. 51(a).

2. Spatial dependence

Figure 52 shows the temporal evolution at a depth of 0.5 μm inside the sample under the same conditions as those of Fig. 50. The main difference from the profile at the surface is the evolution of the carrier density. At this depth the carrier density reaches a maximum value of $0.8 \times 10^{19} \text{ cm}^{-3}$, which is less than the peak density at the surface but surprisingly large for a distance in the sample which is several times the penetration depth. This value of the carrier density so far inside the sample is purely due to the rapid diffusion of the carriers from the surface toward the bulk. Once the carrier density reaches its peak value there is an initial rapid reduction due to the carrier temperature enhanced diffusion; this is followed by a slower rate of density reduction.

The variation of $N$, $T_e$, $T_h$ and $T_L$ along the depth of the sample at a particular instant with respect to the laser pulse, whose peak occurs at $t=0$, is considered. Figure 53 shows the spatial profile of $N$, $T_e$, $T_h$ and $T_L$ at the carrier temperature maximum, which occurs at $t=-2 \text{ ps}$. The spatial decay depths reflect the diffusion dynamics. A significant result is the lack of variation of the carrier density over the absorption depth (0.1 μm). It appears that to a good approximation one may consider the carrier density to be homoge-
neous over the absorption depth under the conditions employed in the model. The decay depth associated with the carrier temperatures is larger than that of the carrier density since heat can be transported not only through carrier diffusion but also through carrier collisions.

3. Nonequilibrium phonon population

The calculated temporal evolution of the nonequilibrium optical phonon population of wave vector $1.2 	imes 10^6 \text{ cm}^{-1}$, at 77 and 300 K, is shown by the solid curves in Figs. 54 and 55. There is a fast rise time associated with phonon generation by cooling carriers and a slower decay due the decay of the zone-center phonons into acoustic phonons. Also shown are the time-dependent optical-phonon populations deduced from the anti-Stokes Raman scattering intensity. The absolute values were obtained from calibrated Stokes/anti-Stokes ratios in the case of 77 K data, and from the ratio of nonequilibrium to equilibrium anti-Stokes scattering intensities for the 300 K data. The phonon lifetimes used to obtain the calculated curves were 8 and 4 ps for 77 and 300 K, respectively.

Note that the delay between the peak of the pump pulse at $t = 0$ and the maximum nonequilibrium phonon occupation agree, while the absolute value of the nonequilibrium population agree within a factor of 1.4 (note this is a much better agreement that previously reported by the author and co-worker, mainly because in the new Raman scattering experiments, the parameters, were more accurately controlled, in particular the overlap of the pump and probe beams). This agreement between experimental Raman data and the calculated result, with no variable fit parameters, is considered 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.

We note that the ratio of optical phonon deformation potentials for hole to electrons used in the calculation is 2.1. If the value of 3.2 suggested by Conwell (1969) is used instead, with the same electron deformation potential, the calculation yields the dashed curve in Fig. 54. Clearly the agreement isn’t as good.

It is interesting that one is able to measure a significant nonequilibrium population of optical phonons in Ge using time-resolved Raman scattering in the visible region of the spectrum. The success of the same technique in III-V materials, such as GaAs, has been attributed to the polar nature of the electron–LO–phonon interaction in these materials. It has been argued that the $1/q$ dependence of the interaction matrix element in polar materials forces all of the electron’s kinetic energy to flow to the lattice through a very restricted range of LO phonon mode near the zone center, close to the wave vector probed by visible beams. In nonpolar materials such as Ge and Si, the carrier–phonon matrix element is wave vector independent and it is not clear, a priori, why significant nonequilibrium phonon populations may be observed. Using the equation for phonon generation the contribution from both relaxing hole and electrons to the population of different optical–phonon modes in the Brillouin zone is calculated at 77 K (Fig. 56). The first notable feature in this figure is that most of the optical phonons are generated by the hot hole, as one would expect from the values of the deformation potential constant (see Table III). It is also clear that most of the deformation potential interaction takes place at small wave vectors, close to that sample by the Raman probe, despite the fact that the matrix element is wave vector independent. The restriction of energy flow preferentially...
through relatively small wave vector phonons is due to the
kinematics restriction required by energy and momentum
conservation imposed by the band structure. These purely
kinematic constraints, together with the ability to maintain a
well defined LO phonon mode at carrier densities in excess
of $1 \times 10^{17}$ cm$^{-3}$ (due to the lack of polar electron–phonon
interactions), explains why significant nonequilibrium
optical–phonon populations can be observed in Ge.

4. Importance of carrier diffusion

Perhaps the most sensitive and important component of
the model is the carrier diffusion process. With the full tem-
perature dependent ambipolar diffusion coefficient included,
the maximum carrier density achieved in the Raman exper-
iments is estimated to be $\sim 10^{18}$ cm$^{-3}$ (see Fig. 50). At this
density, Auger recombination, impact ionization, nonlinear
absorption, and lattice heating are all negligible effects, thus
confirming the claim above concerning the moderate level of
excitation used in these experiments and justifying the use of
Maxwell–Boltzmann statistics. However, if diffusion is ig-
ored altogether (Fig. 57), the peak surface carrier density
and the nonequilibrium optical–phonon occupation numbers
are a full order of magnitude larger, which is clearly incon-
sistent with the Raman data. If a constant ambipolar diffusion
coefficient is used, the difference between experimental and
theoretical results is not as large; nevertheless there is still a significant difference compared to the result obtained
using a temperature-dependent diffusion coefficient.

5. Time-resolved reflectivity

Experimental data for the time-resolved reflectivity are
shown in Fig. 58. The data reveal an initially fast decay in
the reflectivity, followed by a much slower recovery towards
the equilibrium value. The carrier density temporal profiles
obtained from the simulations have features similar to those
of the time-resolved reflectivity measurements. This sug-
gested that a simple model of the optical properties with only
carrier density dependence, such as the Drude model, might
be used to estimate the change in reflectivity. However, a
comparison of the reflectivity data and simulation using only
the Drude model show that the small ($< 5$ K) change in lat-
tice temperature $T_L$ might also be contribution to the reflec-
tivity change. This effect was therefore also included in the
reflectivity calculation using the time dependent $T_L$ from
the simulation.

At normal incidence the change in reflectivity due to
changes in $N$ and $T_L$ is given by

$$\Delta R = \frac{1 - \sqrt{\Delta \varepsilon}}{1 + \sqrt{\Delta \varepsilon}} \frac{1 - \sqrt{\varepsilon}}{1 + \sqrt{\varepsilon}}$$

(31)

where $\Delta \varepsilon = \Delta \varepsilon_N + \Delta \varepsilon_{T_L}$, and $\varepsilon = 34 + 13i$ is the equilibrium
dielectric constant at $\lambda = 0.575 \mu$m. In the Drude model we have

$$\Delta \varepsilon_N = -\frac{4 \pi e^2 N}{\varepsilon_0} \left( \frac{1}{m_{op}^e} + \frac{1}{m_{op}^h} \frac{1}{\omega^2 + i\omega \tau_m} \right)$$

(32)

where $m_{op}^e$ and $m_{op}^h$ are the optical effective masses for the
electrons and holes, respectively, $\varepsilon_0$ is the permittivity of
the vacuum, and $\tau_m$ is the momentum relaxation time. For vis-
ible light $\omega \gg \tau_m^{-1}$ and we can neglect the imaginary contri-
bution to $\Delta \varepsilon_N$. The term $\Delta \varepsilon_{T_L}$ is given by $\Delta \varepsilon_{T_L} = (\partial \varepsilon / \partial T_L)(T_L - 300 \text{ K})$, where $\partial \varepsilon / \partial T_L \sim 0.75 
\times 10^{-5}$ K$^{-1}$ at $\lambda = 0.575 \mu$m was estimated by extrapolation
of the temperature dependence of the reflectivity at nearby
wavelengths. Note that without inclusion of $\Delta \varepsilon_{T_L}$ the calcu-
lated value of $\Delta R/R$ agrees with the data for short times but
is 25% lower than the data for delay times longer than 10 ps.
The above model was use to estimate the carrier density
induced change in the reflectivity of the Ge at 300 K, in
response to a 2 ps excitation pulse for both constant and
temperature dependent diffusion. The results of these calcu-
lations are shown in Fig. 58 along with the experimentally
determined change in reflectivity. It is clear that the full tem-
perature dependent calculation yields a much better fit to the
experimental result than does the calculation with a constant
diffusion term. As with the phonon data, although more sig-
nificance should be placed in the agreement with respect to
shape than to the absolute magnitudes, both shapes and magni-
tudes are well accounted for by the model. To obtain an
acceptable signal to noise ratio the fluence of the pump pulse
used in the reflectivity experiments was approximately three
times higher than in the Raman experiments. As a conse-

FIG. 57. Temporal evolution of the surface carrier density for different
diffusion coefficients. The solid, dashed, and dash-dotted curves correspond
to temperature-dependent, constant and zero ambipolar diffusion coeffi-
cients, respectively.

FIG. 58. Time-resolved reflectivity at 0.575 $\mu$m for fluence of 0.3 mJ/cm$^2$
and $T_L = 300$ K. The triangles are experimental data, the solid and dashed
curves are calculated reflectivity changes from the ambipolar diffusion co-
efficient assumed temperature dependent and constant, respectively.
VI. CONCLUSIONS

With the age of information and technology there comes a great need and requirements on our existing technological resources. The transfer and, in particular, the processing of information is limited in its speed by the performance of semiconductor devices, which are the fundamental building blocks of our technology. In view of this, over the past decade there has been a great deal of research spent in studying the temporal behavior of semiconductors. This article covers a certain fraction of this field; namely, it reviews the dynamics of semiconductors following ultrashort pulse excitation.

With the development of ultrashort pulse processes such as momentum randomization, carrier thermalization and energy relaxation have been studied extensively in GaAs and, to a lesser extent, in other semiconductors. Excite-and-probe techniques utilized to study extreme rapid processes in semiconductors were reviewed along with some key experiments. Experiments such as the measurement of photon echoes in GaAs have truly given insight into some of the most fundamental processes in photoexcited carriers; namely, carrier momentum randomization. Pump-and-probe transmission experiments using super-continuum generation allows the probing of almost all excitation states. This impressive tool has improved our understanding of semiconductor behavior tremendously. In addition, up-conversion luminescence has offered complementary information as well as new information regarding carrier relaxation in semiconductors.

Modeling the dynamics of various processes in semiconductors has also played a key role in the understanding these systems. The last section of this article presents a self-consistent model for correlating the various processes after ultrashort pulse excitation in germanium. This model may be easily extended to other semiconductors for predicting their behavior.

It is expected that, in the next few years, improvements in ultrashort techniques for generating laser pulses will result in the generation of extremely short duration pulses (atosecond timescale). This will allow research to probe semiconductors with even higher temporal resolution. In addition, the absorption of so much energy over such an extremely short period of time will result in the generation of highly nonlinear effects that have to be explored.

Probing of semiconductors over a very broad spectrum from UV to far infrared will also be pursued with the help of newly developed crystal material for optical parametric oscillators generating ultrashort pulses.

A great deal of information has been learned over that past few years concerning the behavior of semiconductors following short pulse excitation. This information eventually will be transferred to the semiconductor industry which will result in faster response and more efficient devices.

1 The Hot Carriers in Semiconductors, Proceedings of the Fifth International Conference [Solid-State Electron. 31 (1988)].
133 H. R. Choo, Ph.D. dissertation, University of Texas of Austin, 1992.