Nonlinear Absorption and Ultrashort Carrier Relaxation Times in Germanium under Irradiation by Picosecond Pulses*

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The nonlinear optical properties of a high-purity germanium wafer have been measured at 1.06 μm using picosecond pulses from a mode-locked neodymium:glass laser. By using such pulses we are also able to probe the hot electron distribution in order to obtain information on the ultrafast carrier relaxation times.

The advent of high-power mode-locked pulse lasers makes possible the study of the nonlinear, nonequilibrium optical properties of semiconductors on a picosecond time scale. This paper is the first in a series concerning these properties in germanium.

The absorption coefficient α of germanium at 1.06 μm has been reported[1] as 1.2×10^4 cm^{-1}. This coefficient is valid only when the interband transitions remain unsaturated. Such a condition is always met at moderate light intensities. However, if an intense pulse of monochromatic light generates enough free carriers to fill the electron states that are resonant with the optical transition, a condition of enhanced transparency should result. This condition should persist for a time equal to the carrier relaxation time τ. A condition of transparency will also be observed if the incident light pulse generates enough free carriers to fill the band states up to and including those of the optical transition. This transparency should then exist for a time approximately equal to the recombination time T. In this regime, and neglecting free-carrier absorption, the absorption coefficient varies inversely with light intensity.[2] Recently, a third type of nonlinear optical absorption (due to the simultaneous absorption of two photons accompanied by the creation or annihilation of a phonon) in silicon has been observed with the aid of picosecond pulses at 1.06 μm.[3]

In this Letter we report measurements of the nonlinear optical absorption in Ge with picosecond pulses from a mode-locked Nd:glass laser. By using such pulses we are able to study carrier relaxation times on the picosecond time scale.

The experimental procedure used to measure the nonlinear absorption involves use of a mode-locked train of picosecond optical pulses (of wavelength 1.06 μm) generated in the conventional manner by a Q-switched Nd:glass laser with a saturable dye. A single pulse is switched out from the train of pulses with a laser-triggered spark gap and an electro-optical shutter. The single pulse is passed through a variable attenuator before it is focused onto the Ge sample to a spot diameter of ~1.0 mm. The sample is a high-purity germanium wafer (minimum resistivity of 40 Ω cm) cut along the (1, 1, 1) plane from a single crystal. The wafer is mechanically ground and polished to a thickness of ~20 μm. Final lapping of the polished sample[4] to a thickness of 8 μm is accomplished by bonding it to a glass substrate (Schott KZF-2). The glass is transparent to the 1.06-μm radiation and has the same coefficient of expansion as Ge. Thus, no strains are generated in the sample when it is cooled to liquid N_2 temperature. The incident and transmitted pulse intensities are monitored with p-i-n photodiodes with integrating circuits, hence the total energy of the pulse is measured rather than the intensity. The pulse widths are measured by the conventional two-photon fluorescence technique and are less than 5 psec.

Figure 1 shows the results of the single-pulse transmission as a function of the input energy. The lower limit on the incident pulse energy is determined by the detector sensitivity, whereas the upper limit is determined by the damage threshold of the sample which is ~3×10^{14} quanta/mm^2 (pulse duration). The low-intensity transmission is about 8×10^{-5} and agrees well with the

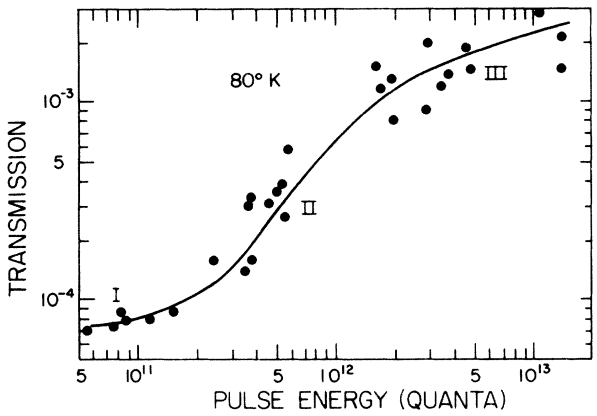

FIG. 1. Nonlinear single-pulse transmission of 8-μm-thick germanium wafer versus input energy in units of quanta ($\lambda = 1.06$ μm). The abscissa scale should be multiplied by 10.

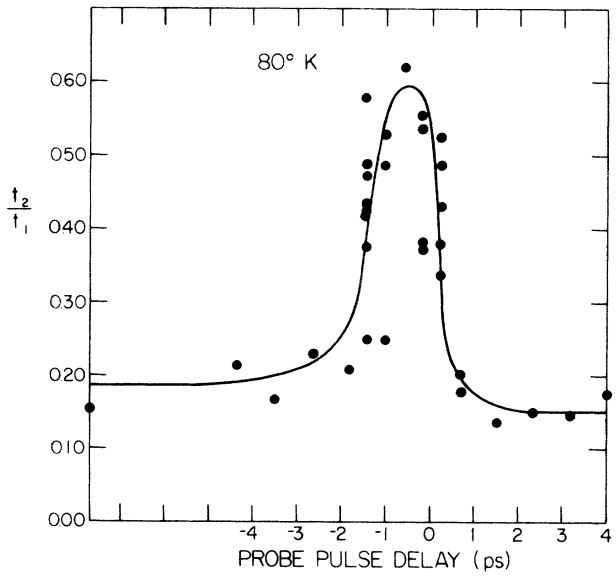

FIG. 2. Energy transmission ratio (t_2/t_1) versus delay time (in picoseconds) between the excitation pulse and the probe pulse.

Beer's-law transmission when surface reflectivity is taken into account.

The data indicate that there are three distinct regions (I, II, and III) in the transmission curve. The region identified by I is the linear (Beer's-law) region associated with direct transitions. In the transition region II the transmission increases with increase of the incident pulse energy indicating the beginning of saturation of direct optical transitions. This region begins at $\sim 3 \times 10^{12}$ quanta. The number of interacting electronic states in the sample volume illuminated by the beam is on the order of 10^{12}, and thus it is reasonable to expect the onset of saturation at this value of the incident energy. Finally, in region III other nonlinearities contribute to slow the monotonic increase of transmission with incident pulse intensity. A theoretical analysis of these effects will be published elsewhere.

In the remainder of this Letter we describe a measurement of the intraband relaxation time for nonequilibrium carriers. For an intrinsic semiconductor such as high-purity germanium this time is believed to be on the order of several picoseconds, and measurements of this time have been rather indirect.[5,6] However, with the advent of the mode-locked neodymium laser and the picosecond-duration pulses thereof, a convenient tool has become available by which such ultrashort times can be measured.[7] The technique is as follows: A powerful pulse ($\sim 5 \times 10^{13}$ quanta) of a few picoseconds duration prepares the system in a nonequilibrium carrier distribution via direct optical transitions from the valence band to the conduction band. The valence band in Ge is split, but the light holes interact only weakly (compared with the heavy holes) with the laser pulses. Information concerning the decay of this distribution is then measured with a less intense probe pulse ($\sim 3 \times 10^{11}$ quanta) selected to arrive at the sample a short time after the first. The delay time t_d between the pulses is selected by means of a variable optical delay line. Detector time-resolution problems are avoided by angularly separating ($\sim 20°$) the two beams and using separate detectors. By appropriate calibration and normalization procedures we obtain the ratio of the transmission of the probe pulse (t_2) to the transmission of the excitation pulse (t_1) as a function of delay time. The transmission ratio is plotted versus the delay time in Fig. 2. The relative transmission increases by a factor of 4 at its peak over the baseline of no coincidence between the two pulses. The time interval between onset and decline of increased relative transmission is of the order of the pulse with Δt (~ 5 psec). Since Δt is the minimum time that can be resolved, we are led to conclude that the relaxation time is less than this time.[8]

In conclusion, a saturation of the optical ($\lambda = 1.06$ μm) transmission of polished single-crystal germanium at 80°K is observed with onset at 3×10^{12} quanta/(picosecond pulse). In addition, the intraband relaxation time for hot electrons is determined to be < 5 psec.

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[8]There are at least two possible sources of error in our data. First, as in the single-pulse transmission experiment, there is no reliable measurement of the duration of the pulse switched out from the pulse train. The two-photon fluorescence measurement provides us with an averaged pulse duration due to the entire pulse train. Second, because of alignment difficulties and the angular separation of the beams the two beams do not perfectly overlap (in space) at the sample location. Furthermore, not all pulse trains are clear, i.e., sometimes weaker pulses are present between the regular pulses spaced $2L/c$ sec apart.

Surface and Bulk Contributions to Ultraviolet Photoemission Spectra of Silicon

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Photoemission measurements have been made on clean silicon surfaces having (111) 7×7, (111) 2×1, and (100) 2×1 low-energy electron diffraction patterns. An approximate separation of the data into surface and bulk components yields a bulk distribution which is in better agreement with the theoretical density of states than previous results. The surface distribution for the (111) 7×7 surface contains five distinct features.

Recently there has been a great deal of interest in the use of ultraviolet photoelectron spectroscopy (UPS) to obtain bulk valence-band density-of-states curves of several semiconductors.[1] Similar results[2] have also been obtained by x-ray photoelectron spectroscopy. We present UPS results for silicon which indicate that, in addition to bulk features, the experimental data contain significant contributions due to surface states over the entire ~12-eV width of the valence band. An approximate separation of the raw data into bulk and surface contributions results in a significantly improved bulk "density of states" as well as the identification by *photoemission* of additional surface states due to lattice relaxation of the (111) surface as predicted by the calculations of Appelbaum and Hamann.[3]

Previous UPS studies of silicon have been restricted to cleaved (111) surfaces and have identified both dangling-bond surface states and bulk band-structure features.[1,4,5] The use of higher photon energies, $\hbar\omega > 12$ eV, has the advantage of exposing the entire valence band but the complication that the escape depth[4] of photoelectrons is near its minimum (5–10 Å), resulting in both surface and bulk contributions. This weights the surface more heavily than lower photon energies corresponding to longer escape depths. In this paper we present UPS results for annealed (111) and (100) silicon surfaces as well as for cleaved