tirely due to bulk resistance. No phase change could be observed in any specimen, with the phase-sensitive detector, indicating an absence of measurable resistance. This was further confirmed by driving the cavities in higher harmonics. A finite bulk resistance caused by the field would result in a larger decay for the frequency-dependent thermal wave, and the reduction in the transmitted amplitude would be enhanced. This too could not be detected. From several independent estimates we were able to conclude that, even for the thickest samples, the bulk contribution could not exceed 10%. Our final conclusion, therefore, is that the main reason for the variation in energy flow is a change in h_K caused by the electrons.

*Work supported by the National Science Foundation under Grants No. GH 33385 and No. GH 40901.

†Work supported in part by a Fellowship from The University of Ohio and in part by the Deutsche Forschungsgemeinschaft.

‡Now at the Department of Metallurgy.

[1]I. M. Khalatnikov, Zh. Eksp. Teor. Fiz. 22, 687 (1952).

[2]W. A. Little, Can. J. Phys. 37, 334 (1959).

[3]W. A. Little, Phys. Rev. 123, 435 (1961).

[4]A. F. Andreev, Zh. Eksp. Teor. Phys. 43, 1535 (1962) [Sov. Phys. JETP 16, 1084 (1963)].

[5]N. S. Snyder, *Thermal Conductance at the Interface of a Solid and Helium II (Kapitza Conductance)*, U. S. National Bureau of Standards Technical Note No. 385 (U. S. GPO, Washington, D. C., 1969).

[6]J. D. N. Cheeke, in *Proceedings of the Eleventh International Conference on Low Temperature Physics, St. Andrews, Scotland, 1968*, edited by J. F. Allen, D. M. Finlayson, and D. M. McCall (St. Andrews Univ. Press, St. Andrews, Scotland, 1969), Vol. 1, p. 567.

[7]L. J. Challis, J. Phys. C: Proc. Phys. Soc., London 7, 481 (1974).

[8]L. J. Challis and R. A. Sherlock, J. Phys. C: Proc. Phys. Soc., London 3, 1193 (1970).

[9]R. I. Boughton and M. Yaqub, Phys. Kondens. Mater. 9, 138 (1969).

[10]R. J. von Gutfeld and A. H. Nethercot, Jr., Phys. Rev. Lett. 18, 855 (1967).

[11]W. A. Reed and J. A. Marcus, Phys. Rev. 126, 1298 (1962).

[12]W. A. Reed, Phys. Rev. 188, 1184 (1969).

[13]J. C. Kimball and R. W. Stark, Phys. Rev. B 4, 1786 (1971).

[14]F. W. Gorter and L. J. Noordermeer, Physica (Utrecht) 46, 507 (1970).

Picosecond Ellipsometry of Transient Electron-Hole Plasmas in Germanium

D. H. Auston
Bell Laboratories, Murray Hill, New Jersey 07974

and

C. V. Shank
Bell Laboratories, Holmdel, New Jersey 07733

(Received 28 February 1974)

An ellipsometer has been used with picosecond pulses to measure the time evolution of optically generated plasmas in intrinsic Ge. By measuring the change in optical ellipticity of a weak probe beam following the absorption of an intense excitation pulse, the time evolution of the plasma density can be determined with a precision of a few picoseconds. At a density of 1.7×10^{20} cm^{-3}, the ambipolar diffusivity of the plasma was observed to be a factor of 3 greater than the low-density value, consistent with a simple theoretical model of diffusion in the degenerate regime.

In this Letter we report measurements on optically generated electron-hole plasmas in germanium using a new technique which combines ellipsometry and optical picosecond pulses to measure small changes in index of refraction ($\delta n/n < 10^{-3}$) on a picosecond time scale. The physical properties of semiconductor plasmas produced by interband optical absorption have been measured previously by a number of techniques, including infrared[1] and millimeter-wave reflectivity[2] and free-carrier absorption.[3] The ellipsometric technique allows a direct time-resolved measurement of the plasma contribution to the optical refractive index. In addition, both

the magnitude and sign of the real and imaginary parts of the dielectric response can be determined.

We have used picosecond optical pulses for both generation and probing of the plasma. By introducing a variable delay between excitation and probing, the transient properties of the plasma can be measured with a temporal precision limited only by the optical pulse duration. Also, the use of intense single picosecond pulses permits the generation of extremely high plasma densities, making possible the study of transport properties in the degenerate regime in high-purity material on a time scale where recombination is negligible. Since the ellipsometric technique involves a reflection from the crystal surface, its sensitivity is limited to changes in the optical constants within a fraction of a wavelength of the surface. We have utilized this property to study the diffusive transport of degenerate plasmas by observing the time decay of the surface density as the plasma diffuses into the bulk following its generation in a thin layer near the surface.

Figure 1 is a sketch of the experiment. The ellipsometer consists of two polarizing prisms (commonly referred to as the "polarizer" and "analyzer"), and a quarter-wave plate (fast axis at 45° to horizontal). The germanium crystal was situated as in Fig. 1 so that the probing beam was reflected from a polished face at an angle, φ (in all of our measurements, $\varphi = 70°$). The crystal was an intrinsic sample of room-temperature resistivity 40 Ω cm whose (111) face was cut and polished with a standard siton etch, a procedure known to produce reliable measurements of the linear optical constants by conventional ellipsometry. A mode-locked Nd:glass laser at 1 06 μm with a single pulse selector was used as the source of optical pulses. The probing beam was attenuated by a factor of 20 relative to the excitation beam. Initially the ellipsometer analyzer and polarizer were adjusted for extinction (ratio = $1:3\times10^{-5}$) with no excitation pulse. The absorption of the strong excitation pulse in the crystal produced an incremental change in the refractive index at the crystal surface and a consequent increase in the probe beam transmission which was proportional to $|\delta n/n|^2$ for small δn. The sign of δn can readily be determined by offsetting the ellipsometer extinction by rotating the analyzer prism and observing whether the excitation pulse causes the probe transmission to increase or decrease.

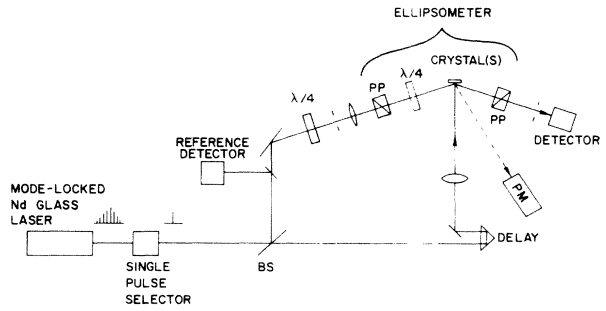

FIG. 1. Picosecond ellipsometer used to measure the time evolution of optically generated electron-hole plasmas in Ge. The zero time reference was determined by second-harmonic generation of the excitation and probe pulses in reflection from a GaAs crystal and was detected by the photomultiplier (PM).

A variable delay in the excitation arm controlled the relative timing of excitation and probing. The setting on this delay corresponding to the exact overlap of the two pulses at the crystal surface (i.e., zero time) was determined by a separate second-harmonic generation experiment. A crystal of GaAs was mounted above and coplanar with the Ge crystal on an adjustable mount so they could be readily interchanged without affecting the alignment or delay. Second-harmonic generation at 0.53 μm produced by the 1.06-μm probe and excitation beams in reflection at the GaAs was then detected by a photomultiplier at an angle of 28° with respect to the crystal normal (Fig. 1), as determined by the laws of nonlinear reflection.[4] By varying the delay, the second-order intensity correlation of the pulses was obtained, from which the zero-delay setting was determined and the pulse width was found to be 10 psec [full width at half-maximum (FWHM)]. The measurement includes a small broadening effect of approximately 1 psec due to the imperfect spatial overlap of the probe and excitation beams at the crystal surface. The overall accuracy of the zero-delay setting is estimated to be ± 2 psec.

In Fig. 2 the response of the ellipsometer is shown as a function of delay, following the absorption of an intense excitation pulse in the germanium crystal. The ellipsometer transmission was observed to increase to a maximum approximately 11 psec after excitation and then decay slowly. Typically, a pulse of approximately 10^{-2} J cm^{-2} produced a peak negative index change of $\delta n/n = -0.05$. Assuming rapid thermalization of the excess electron and hole energies, the plasma refractive index can be estimated from the

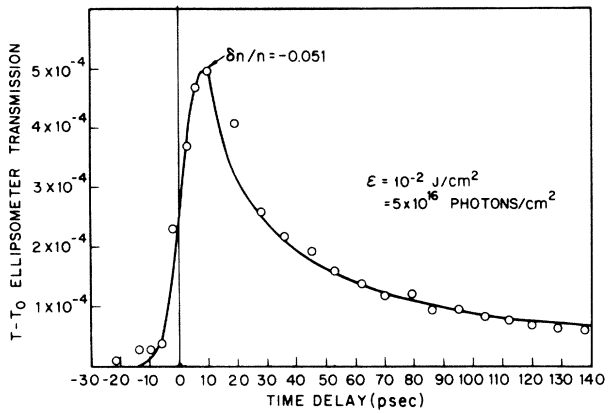

FIG. 2. Ellipsometer transmission, $\Delta T \propto |\delta n/n|^2$, versus time delay between plasma generation and probing. The background transmission due to a finite extinction has been subtracted. Each point is a simple (unweighted) average of ten laser shots. The dispersion in the data was typically 11% per shot and 4% for the mean. The solid line is the solution, Eq. (3), of the diffusion equation for the parameters $\alpha = 1.4\times10^{4}$ cm^{-1}, and $D = 230$ cm^2 sec^{-1}.

simple Drude model of a free electron-hole gas:

$$\frac{\delta n}{n} = -\frac{2\pi N e^2}{n^2\omega}\left(\frac{1}{m_e}+\frac{1}{m_h}\right), \tag{1}$$

where $N = 4n\alpha\mathcal{E}/\hbar\omega(n+1)^2$ is the plasma density, $\mathcal{E}$ is the excitation pulse energy, α is the absorption constant at the optical frequency ω, and m_e and m_h are the electron and hole effective masses. Using the known properties[5-7] of Ge, namely, $\alpha = 1.4\times10^{4}$ cm^{-1} at 1.06 μm, $m_e = 0.12m_0$, $m_h = 0.35m_0$, and $n = 4.35$, we find that the plasma density is 1.7×10^{20} cm^{-3} for $\delta n/n = -0.05$. A pulse energy of 1.3×10^{-2} J/cm^2 would be required to produce this excitation level, in excellent agreement with the experimental results. At these excitation levels the crystals were undamaged and the results were highly reproducible. Surface damage was observed at approximately 5×10^{-2} J cm^{-2}, or $N \simeq 10^{21}$ cm^{-3}. The choice of the correct effective mass for holes in determining the plasma frequency has recently been discussed by Combescot and Nozières.[8] For the particular conditions of density and optical frequency encountered here, the contribution to the dielectric constant of heavy-to-light hole transitions is not important and consequently we have chosen an effective mass dominated by the heavy-hole band. Also, we do not expect to observe any appreciable excited state absorption due to heavy-to-light hole transitions.

Since the ellipsometer involves a reflection from the crystal surface, its response is essentially a measure of the square of the plasma density at the surface. The effective probing depth is only $\lambda/4\pi n \simeq 200$ Å at $\lambda = 1.06$ μm. The surface density thus decreases with time because of the diffusion of carriers into the bulk following their generation on a thin layer near the surface of thickness α^{-1}. To determine the diffusive transport properties of the plasma, we have solved the linear equation for ambipolar diffusion[9] with a generation term equal to $\alpha\mathcal{E}(t)\exp(-\alpha x - t^2/\tau_p^2)$, where x is the distance into the crystal, and τ_p is the excitation pulse width (assumed to be Gaussian). Recombination was neglected and space-charge neutrality was assumed to prevail. Surface recombination can also be neglected because of the low surface recombination velocity at the etched Ge surface. The resulting surface plasma density was then squared and convolved with the probing pulse to simulate the ellipsometer measurement. The transmission of the probe beam through the ellipsometer is given by

$$T(t) = \int_{-\infty}^{+\infty}\left\{\int_{-\infty}^{\tau} N(0,\xi) I_P(\tau-\xi)\,d\xi\right\}^2 I_S(t-\tau)\,d\tau, \tag{2}$$

where

$$N(0,t) = N_0 \exp(\alpha^2 Dt)\,\mathrm{erfc}\,\alpha(Dt)^{1/2} \tag{3}$$

is the impulse response, I_P and I_S are the pump and probe pulses, and D is the diffusivity, which is assumed to be a constant. We have fitted expression (3) to the experimental data assuming $\alpha = 1.4\times10^{4}$ cm^{-1} (Ref. 5), $\tau_p = 6.7$ psec (8 psec FWHM), with D the variable parameter. As seen in Fig. 2, an excellent fit to the experimental data is obtained for $D = 230 \pm 50$ cm^2 sec^{-1}. This value is 3.5 times larger than the low-density ambipolar diffusion constant in Ge given by $D = 2D_eD_h/(D_e+D_h) = 65$ cm^2 sec^{-1}.

At densities of $\sim10^{20}$ cm^{-3} the plasma is degenerate and consequently we would expect the diffusivity to differ from its nondegenerate value. The density dependence of D can be readily estimated from the solution of the Boltzmann equation using a relaxation-time approximation:

$$D = \frac{1}{3}\int \tau v^2 \frac{\partial f}{\partial \mathcal{E}}\,d^3k \left(\int \frac{\partial f}{\partial \mathcal{E}}\,d^3k\right)^{-1}, \tag{4}$$

where τ is the momentum relaxation time, v the electron (or hole) velocity, and $f(\mathcal{E})$ the Fermi-Dirac distribution function. Assuming that the relaxation time has an energy dependence of $\tau \propto \mathcal{E}^{-1/2}$ characteristic of lattice scattering, the

integrals can be evaluated for spherical energy surfaces in terms of the Fermi-Dirac functions $\mathfrak{F}_k(\eta)$,[10] to give the result $D(\eta)/D_0 = \mathfrak{F}_0(\eta)/\mathfrak{F}_{-1/2}(\eta)$, where η is the quasi-Fermi level normalized to kT and D_0 is the nondegenerate diffusivity. In the degenerate limit, $\eta \gg 1$, $D(\eta)/D_0 \simeq \frac{1}{2}(\pi\eta)^{1/2}$ and the diffusivity has an approximate density dependence of $N^{1/3}$. For $N = 1.7\times10^{20}$ cm^{-3}, the quasi-Fermi level for electrons is approximately 0.2 eV ($\eta = 8$) and for holes is 0.3 eV ($\eta = 12.5$), and the diffusivities are increased by factors of 2.5 and 3.1, respectively. Consequently the ambipolar diffusivity should be 2.9 times the nondegenerate diffusivity in fair agreement with the observed result.

A more rigorous analysis of the diffusion dynamics would incorporate the density dependence of D in the solution of the diffusion equation. However, we do not expect the inclusion of a nonlinear D to be significant for the range of densities observed in our experiment. Although T was measured over a range of 7:1 and N over a range of ~ 2.6:1, the expected variation in D is only 1.3:1. This variation would be further reduced through spatial averaging in the diffusion equation, and consequently should not appreciably affect the accuracy of our determination of D. Further experiments are currently in progress to measure the diffusive transport properties of a variety of materials for a range of excitation intensities and different excitation wavelengths. We expect that the measurement technique employed in this experiment will be of general interest for applications requiring the measurement of small transient index perturbations with picosecond time resolution.

The authors are grateful for stimulating discussions with W. F. Brinkman, T. M. Rice, and W. W. Van Roosbroeck. We also thank P. LeFur and F. Beisser for technical assistance and W. L. Mammel for computations.

[1]G. N. Galkin, L. M. Blinov, V. S. Vavilov, and A. G. Golovashkin, Zh. Eksp. Teor. Fiz., Pis'ma Red. 7, 93 (1968) [JETP Lett. 7, 69 (1968)].

[2]R. F. Leheny, R. E. Nahory, and M. A. Pollack, Phys. Rev. B 8, 620 (1973).

[3]H. J. Fossum, W. S. Chen, and B. Ancker-Johnson, Phys. Rev. B 8, 2857 (1973); J. C. Herper, I. Palocz, N. N. Axelrod, and R. A. Stern, J. Appl, Phys. 45, 224 (1974).

[4]J. Ducuing and N. Bloembergen, Phys. Rev. Lett. 10, 474 (1963).

[5]W. C. Dash and R. Newman, Phys. Rev. 99, 1151 (1955).

[6]E. Conwell, Proc. IRE 46, 1281 (1958), and 40, 1327 (1952).

[7]H. R. Philipp and E. A. Taft, Phys. Rev. 113, 1002 (1959); R. J. Archer, Phys. Rev. 110, 354 (1956).

[8]M. Combescot and P. Nozières, Solid State Commun. 10, 301 (1972).

[9]W. Van Roosbroeck, Phys. Rev. 91, 282 (1953).

[10]J. S. Blakemore, *Semiconductor Statistics* (Pergamon, New York, 1962), p. 346.

Photoemission Observations of π-d Bonding and Surface Reactions of Adsorbed Hydrocarbons on Ni(111)†

J. E. Demuth and D. E. Eastman
IBM Watson Research Center, Yorktown Heights, New York 10598
(Received 24 January 1974)

Ionization energies for chemisorbed acetylene, ethylene, and benzene exhibit π-orbital bonding shifts (~ 0.9–1.5 eV) as well as large nonchemical-bonding relaxation shifts of ~ 1–3 eV for both π and σ orbitals. Dehydrogenation of chemisorbed ethylene to acetylene for $T \gtrsim 230$°K is directly observed. We estimate π-d bonding interaction strengths and chemisorption energies from spectroscopic energy levels and predict that this surface reaction becomes exothermic because of π-d bonding.

It has been postulated that π-d bonding plays an important role in hydrocarbon chemisorption on group-VIII transition metals (Ni, Pd, Pt), and also in catalytic reactions (hydrogenation, dehydrogenation, dimerization, etc.).[1] We report photoemission valence orbital energy levels for condensed (weakly bound) and chemisorbed hydrocarbons which give a clear picture of the chemical state of the adsorbed species, i.e., a monitor for surface reactions, and which show