Acceptor-Impurity Infrared Absorption in Semiconducting Synthetic Diamond

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The infrared-absorption spectra of a selection of aluminum-doped and nominally boron-doped semiconducting synthetic diamonds have been measured from 1 to 10 μ at temperatures near 100° and 300°K. These spectra are shown to be very similar to those obtained from natural semiconducting diamond. For large neutral-acceptor concentrations (10^{17} to 10^{19} cm^{-3}), line-broadening effects comparable with those reported in Si have been observed. An additional absorption feature has been found at 0.268 eV, and a tentative explanation of the transition involved is discussed.

WE have measured the infrared absorption spectra of two batches of doped synthetic diamond[1] from 1 to 10 μ (1.2 to 0.12 eV), at temperatures near 100 and 300°K. One batch of recent manufacture consisted of 3 aluminum-doped diamonds, GECAL 1, 2, and 3, which were pale steel-blue in color, similar to many natural type-IIb semiconducting diamonds, and of fairly large linear dimensions $\sim$0.5 to 1 mm. The second, less recent batch, numbered D1002, contained a large number of nominally boron-doped diamonds. A small proportion of these were relatively colorless or yellow-green, but the color of the majority ranged between pastel blue and indigo when viewed in a tungsten light on a microscope stage, and these were typically 0.2 to 0.5 mm in linear dimensions.

The specimens were mounted in a cryostat with CaF$_2$ windows which was placed at the intermediate focus of an infrared microscope with an image reduction of $\sim$10:1 and an aperture of $f/8$.[2] Spectra were recorded using a Perkin-Elmer model 99 monochromator with a thermocouple detector. After considerable modification, higher resolution in the range 1 to 5.4 μ was obtained using an InSb detector cooled by liquid oxygen. Signals proportional to the transmitted and incident light intensities I_t and I_0 were obtained with a strip chart recorder at suitable gain settings, respectively with and without the specimen (thickness t) in place. The ratio of the signal amplitudes was obtained point by point and normalized to $I_0/I_t = 1$ at 10 μ, where the absorption was negligible. The absorption coefficient μ was then found from the relationship $\mu = (1/t) \times \ln(I_0/I_t)$ cm^{-1}. Because of the irregular shape and rough surfaces of the diamonds, it was not possible to make explicit corrections for scattered and reflected light.

The top diagram in Fig. 1 shows the complete room-temperature infrared absorption spectrum of GECAL 3, which is seen to be very similar to that for natural IIb diamonds.[3] (The same lettering system as that in Ref. 3 has been used.) The absorption band f identified with

transitions to the third excited state is less well defined, however, and there is in addition, a disproportionately strong underlying continuum absorption. At temperatures $\sim$77°K complex absorption structure can be seen on and between the bands associated with the second and third excited states [(e) and (f)] in spectra from natural IIb diamonds.[3] This spectral region is compared in detail in Fig. 2, for GECAL 3 and a natural IIb diamond A100, at 100 and 300°K. The spectra of these two crystals were obtained at the same resolution and under identical conditions. It can be seen that although band e narrows between 300 and 100°K for GECAL 3, none of the detailed structure visible at this resolution for A100 is apparent. The diffuse nature of band f for GECAL 3, even at 100°K, is also apparent from Fig. 2. The phonon-assisted transitions become more clearly defined at 100°K, and it is possible to resolve the two peaks at 0.670 and 0.625 eV in the two-phonon-assisted region (h).

The colorless and yellow-green nominally B-doped diamonds show absorption features virtually identical with those for the GECAL series. The absorption of the blue specimens is, however, very much stronger, and the underlying continuum is predominant. The blue color evidently arises from this continuum absorption,
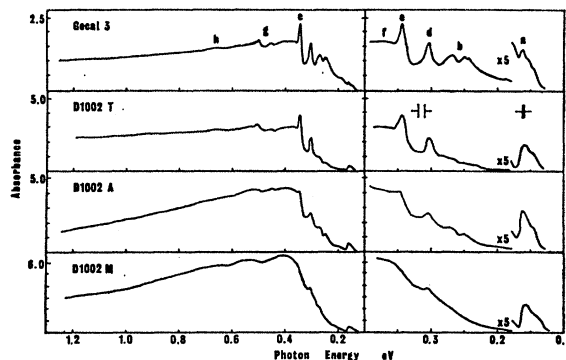

FIG. 1. Complete and expanded acceptor-impurity absorption spectra of synthetic diamonds GECAL 3 and D1002 T, A and M at 300°K, showing the concentration dependence of the line spectra. (a) One-phonon region; (b) two-phonon region; (d) transition to first excited state, 0.305 eV; (e) transition to second principal excited state, 0.348 eV; (f) transition to third principal excited state; (g) one-phonon-assisted absorption bands, 0.462 and 0.508 eV; (h) two-phonon-assisted region.

[1] Manufactured at the General Electric Research Laboratories, Schenectady, New York. Made available through the good offices of Dr. P. Cannon and Dr. R. H. Wentorf.

[2] K. P. Norris, J. Sci. Instr. 31, 284 (1954).

[3] S. D. Smith and W. Taylor, Proc. Phys. Soc. (London) 79, 1142 (1962).

which decreases slowly in strength with increasing photon energy. In general, the more intense the blue color, the stronger is the continuum absorption due to the photoionization of the neutral acceptor centers. The infrared-absorption spectra of specimens D1002 T, A and M, which have progressively stronger absorption, are compared in Fig. 1 with the spectrum of GECAL 3. This comparison is somewhat deceptive, since the lattice absorption (b) for GECAL 3 is relatively much stronger than for the other diamonds, and gives the appearance that the continuum extends to a lower energy than is in fact the case. A more realistic comparison would be obtained if it were possible to subtract the lattice absorption correctly (as in Ref. 3). The thicknesses of these four diamonds are, respectively, 0.057, 0.011, 0.031, and 0.021 cm. Because of the gross inhomogeneity of most of the D1002-series diamonds, the absorption coefficients calculated using these dimensions are unrealistically low ($\sim$350 cm^{-1} for D1002M, which is an order of magnitude lower than one would anticipate from the degree of broadening observed). The absorbance $\mu t' = \ln(I_0/I_t)$ is, therefore, plotted for these diamonds in Fig. 1, since the value of t' to be used in this equation is unknown ($t' \ll t$).

The inhomogeneous distribution of the acceptor centers in the D1002-series crystals is also evident from the relative intensity variations within the edge recombination luminescence spectra excited with a finely focused beam of low-energy (60-KeV) electrons.[4]

Similar concentration broadening has been observed in the line spectra of bound holes in silicon.[5,6] This broadening can be detected at neutral-acceptor concentrations of $\sim$3$\times$10^5 cm^3,[6] but only reaches the degree of broadening shown in Fig. 1 for D1002M at concentrations near 10^{18} cm^{-3}.[5] The equivalent Bohr radii of the impurity wave functions in diamond are $\sim$5$\times$ smaller than those in silicon, which would indicate a neutral acceptor concentration of $\sim$5$\times$10^{18} cm^{-3} in D1002M. This is consistent with the aluminum concentrations of 200 ppm ($\sim$10^{19} cm^{-3}) measured by slow-neutron-activation analysis. The degree of compensation by deep-lying nitrogen donors has been estimated to be $\sim$50% in the deep blue crystals, and much higher in the paler specimens and the GECAL series, which all contained similar amounts of aluminum.[4]

The absorption in the single-phonon region (a) commencing at the Raman energy (0.165 eV) becomes easily discernable for the strongly absorbing D1002 diamonds, and is apparently similar to that observed in natural IIb diamonds.[3] This absorption band sharpens up somewhat at 100°K, but no detailed structure has been observed.

An additional weak band is observed in the spectra from the thin but strongly absorbing crystals in which
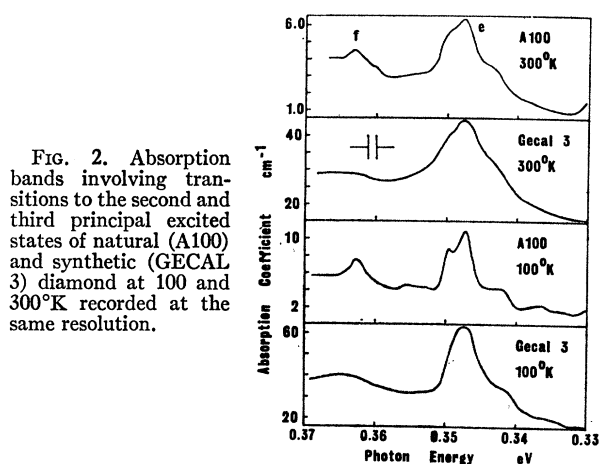

FIG. 2. Absorption bands involving transitions to the second and third principal excited states of natural (A100) and synthetic (GECAL 3) diamond at 100 and 300°K recorded at the same resolution.

the intrinsic two-phonon lattice absorption is relatively weak. This band, at 0.268 eV, is more easily seen in the chart recorder (transmission) presentation (Fig. 3). The new band is close to the calculated position of a forbidden transition at 0.266 eV which was introduced to explain the anomalous width of the first state in the spectra from natural IIb diamonds.[3]

Since strong allowed transitions have been seen in acceptor spectra from silicon between the ground state derived from the upper ($p_{3/2}$) valence bands and the excited states from the splitoff ($p_{1/2}$) valence band,[7] it is tempting to identify the 0.268-eV band with transitions between the two ground states of the aluminum acceptor center in diamond. This transition is normally strictly forbidden, but may become partially allowed because of the mixing of states derived from the two valence-band extrema when the spin-orbit splitting is small.[8] This interpretation, which will be discussed in more detail in a subsequent paper,[9] requires that the
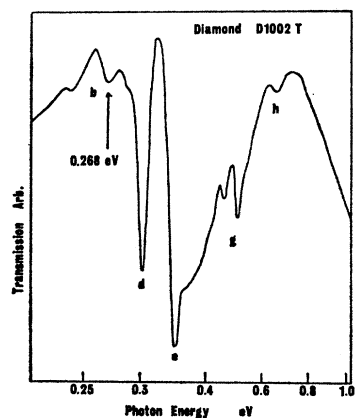

FIG. 3. Original chart-recorder trace of the absorption spectrum of D1002 T showing the additional absorption peak at 0.268 eV.

[4] P. J. Dean, E. C. Lightowlers, and D. R. Wight, Phys. Rev. 140, A352 (1965).
[5] R. Newman, Phys. Rev. 103, 103 (1956).
[6] K. Colbow and R. Barrie, Phys. Letters 5, 98 (1963).

[7] S. Zwerdling, K. J. Button, B. Lax, and L. M. Roth, Phys. Rev. Letters 4, 173 (1960).
[8] W. Kohn, in Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, p. 257.
[9] P. A. Crowther, P. J. Dean, and W. F. Sherman (unpublished).

binding energy of the $p_{3/2}$-band acceptor ground state is ~0.26 eV greater than that of the $p_{1/2}$-band ground state. Calculations based on Fig. 3 show that the 0.268-eV band would not be observed in the spectra from natural IIb diamond, in the presence of the comparatively strong two-phonon absorption.

Effect of Intense Illumination on Impurity Scattering in Semiconductors

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A phase-shift analysis is given of the scattering of electrons and holes by intense light when in the presence of ionized acceptors, the calculation being appropriate to a simple, direct band-gap, semiconductor. The scattering occurs when there is a near resonance of the optical frequency with the frequency of the transition from conduction band to acceptor state, and a mobility change results because a virtual transition through a bound state need not conserve carrier momentum. The oddest feature of this type of scattering is that states of higher l become progressively more important as the carrier energy decreases, a peculiarity that results from the hydrogenic nature of a set of simple acceptor states. The effect of a high density of acceptors on this result has not been determined. The optical scattering of holes by acceptors turns out to be unimportant; the scattering of electrons appears to become substantial at a light intensity that, in GaAs, is about five times greater than the intensity corresponding to the onset of laser action, and increases rapidly with further increase in the intensity of the light.

I. INTRODUCTION

THE high intensity of light in the active region of a semiconducting laser diode suggests that some form of optical scattering may be effective there in determining the mobility of the current carriers. Such a contribution to the mobility must result from transitions involving donor or acceptor states, since the momentum transfer in direct interband transitions is negligible. A simple physical picture of the effect involved can be obtained by considering the scattering of valence-band electrons from an ionized donor: No real transition can occur if the energy difference between the electron and the donor state is not equal to the photon energy, unless phonon-assisted transitions are invoked, but the virtual transition in which the electron is first excited to one of the donor states and then returns to the valence band with the same energy but with a different momentum can occur. This type of scattering is strongest when resonance is approached, i.e., when the energy of the electronic transition is close to the photon energy; in laser diodes, however, the photon energy is close to the value of the band gap, with the result that all states near the top of the valence band will be affected.

The optical scattering of conduction-band electrons by ionized acceptors is less easy to visualize than scattering by donors, since the acceptor is already negatively charged. The process is most readily described in terms of an alteration in the basis states available to the electron, rather than in terms of virtual transitions, and this is the point of view that will be adopted in calculation. Scattering by acceptors is generally much stronger than scattering by donors since the effective mass of the electrons is commonly much smaller than the effective mass of the holes, with the result that donor radius and electron mobility are much greater than acceptor radius and hole mobility. The large radius of the donor states makes them much weaker scatterers than are the acceptor states, and the density of donors is nearly always made much less than the density of acceptors as a result of the disparity in carrier mobilities. Scattering by donors has therefore been ignored. It should be noted that the direct interband transition links the valence-band states to those of the conduction band, and therefore allows the scattering of valence-band electrons by acceptors.

Real induced transitions have been ignored for two reasons: (1) Such transitions affect the current in a band by removing current carriers from it, rather than by altering their distribution within it; they are therefore best described in terms of the change they produce in the recombination rate, not in terms of the mobility. (2) The only electrons in the band that can undergo direct induced transitions are those that are actually at the resonance energy, and these make up only a small fraction of the population. By contrast, virtual transitions through the bound states affect the mobilities of all the electrons in the band.

This work was undertaken with particular reference to GaAs. It is generally (though not universally) believed that the optical transition responsible for laser action in this material is the transition between the