Optical Properties of Cubic SiC: Luminescence of Nitrogen-Exciton Complexes, and Interband Absorption

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Absorption measurements of cubic SiC at 4.2°K show that the absorption edge is due to indirect, exciton-creating transitions, with an exciton energy gap of 2.390 eV. The energies of the phonons participating in these transitions are 46, 79, 94, and 103 meV, and suggest that the conduction-band minima are at X, as predicted by recent calculations. The phonon energies are accurately determined from the 6°K luminescence spectrum of four-particle nitrogen-exciton complexes. Additional lines in the luminescence spectrum at higher temperatures are attributed to thermally excited states of the complex. Comparisons of cubic SiC with other polytypes are given. There is close agreement in some phonon energies, but energy gaps are very different. An empirical correlation of the energy gaps with percent "hexagonal" is given for seven polytypes.

I. INTRODUCTION

CUBIC SiC has the zinc-blende structure, with only one Si and one C atom per unit cell. Thus, the luminescence and absorption spectra are much simpler than those of the common SiC polytypes,[1] $6H$ and $15R$, in which the large unit cells result in inequivalent Si and C sites,[2] and in phonon spectra of many branches.[3] Nevertheless, few optical experiments on cubic SiC have been reported, apparently because it is difficult to grow good large single crystals at the relatively low temperature ($\approx 1950°C$) required to avoid contamination by other polytypes. We have grown crystals of good enough quality for low temperature luminescence measurements, and of large enough size (diam > 1 mm) for absorption measurements.

We find a well-resolved luminescence spectrum due to four-particle nitrogen-exciton complexes,[3] from which we derive phonon energies of 46, 79, 94, and 103 meV. These values are close to those of phonons at the extended zone boundaries of $6H$ and $15R$ SiC.[4] Thus, they are consistent with theoretical calculations[5] which place the conduction-band minima at the zone boundary in $<100>$ directions (at X).

The absorption edge is of the shape expected for indirect transitions in which excitons are created,[6] with portions corresponding to each of the phonons listed above. The exciton energy gap is 2.390 eV, which is considerably smaller than that of other polytypes. A table of energy gaps of seven polytypes is given, and a graph showing an empirical correlation of exciton energy gaps with the percentage of "hexagonal" planes in the

stacking sequence. In all seven polytypes the transitions are indirect.

II. CRYSTAL GROWTH AND IMPURITIES

Cubic crystals have been grown from the vapor in the furnace previously described,[7] starting with relatively pure silicon and carbon. Most of the crystals were grown in the temperature range 1950 to 2000°C, the lower limit being set by diminishing rates of evaporation, and the upper limit by the occurence of increasing amounts of other polytypes. To enhance vapor transport, the argon ambient pressure was reduced to about 10^{-3} atm. Most of the crystals have second-order twinning on two nonparallel octahedral composition planes,[8] resulting in a specimen with a common $<110>$ as growth axis. Equant untwinned specimens were also observed.

Other crystals were grown during the cooling period, after growth of $6H$ or $15R$ crystals at temperatures above 2250°C. These cubic crystals were used to identify the luminescence spectra due to the two common *shallow* impurities, N and Al, by correlating the cubic spectra with the known spectra of N and Al in $6H$ or $15R$ crystals grown in the same furnace run.

Another luminescence spectrum frequently found in cubic crystals is, we believe, due to N–Al pairs. It is qualitatively similar to one of the pair spectra in GaP reported by Hopfield *et al.*[9] In this paper we discuss only the nitrogen spectrum.

III. EXPERIMENTAL PROCEDURES

We used a helium cryostat for all measurements. The sample was not immersed, but for absorption measurements the difference between sample temperature and 4.2°K was insignificant. However, for luminescence, the intense exciting light raised the sample temperature to

[1] There are many SiC polytypes, with trigonal or hexagonal symmetry. See A. R. Verma, *Crystal Growth and Dislocations* (Butterworths Scientific Publications, Ltd., London, 1953), Chap. 7.

[2] Lyle Patrick, Phys. Rev. **127**, 1878 (1962).

[3] W. J. Choyke and Lyle Patrick, Phys. Rev. **127**, 1868 (1962).

[4] Lyle Patrick, D. R. Hamilton, and W. J. Choyke, Phys. Rev. **132**, 2023 (1963).

[5] F. Bassani and M. Yoshimine, Phys. Rev. **130**, 20 (1963).

[6] R. J. Elliott, Phys. Rev. **108**, 1384 (1957); T. P. McLean, in *Progress in Semiconductors* (Heywood and Company, London, 1960), Vol. 5, p. 55.

[7] D. R. Hamilton, J. Electrochem. Soc. **105**, 735 (1958).

[8] J. A. Kohn and D. W. Eckart, Am. Mineralogist **47**, 1005 (1962).

[9] J. J. Hopfield, D. G. Thomas, and M. Gershenzon, Phys. Rev. Letters **10**, 162 (1963).

about 6°K. The intensity of luminescence from thermally excited states of the exciton complex provided a good estimate of the actual sample temperature. For some measurements a thermal resistance was inserted between the sample holder and the helium reservoir to raise the sample temperature to about 15°K.

For a survey of the luminescence of over 100 cubic SiC samples, we used a grating spectrograph, with Kodak spectroscopic plates, type 103a-G. For the spectra shown here, we used an $f/9$ Fastie-Ebert monochromator, with resolution of about 0.1 meV, and photon-counting equipment.

IV. LUMINESCENCE AT 6°K

The existence of exciton complexes has explained many features of low-temperature semiconductor luminescence, in materials having either direct[10] or indirect[11] transitions. Such complexes were first discussed by Lampert,[12] and their luminescence was first observed in Si by Haynes.[13]

Ultraviolet illumination of the semiconductor creates excitons, which may be captured by impurities to form complexes[14] which subsequently decay by photon and phonon emission. In indirect materials, like Si or SiC, there is usually a phonon emitted, which has a propagation vector $\mathbf{k}$ determined by the positions of the conduction-band minima. However, photon emission without a phonon is also permitted, since the exciton is bound to an impurity atom.

Figure 1 shows the luminescence at 6°K of a cubic SiC sample in which nitrogen, substituting for carbon, is the principle *shallow* impurity. There are five strong narrow lines which are labeled according to the phonon emitted in the transition, with "0" indicating that in which no phonon is emitted. The exciton energy gap E_{Gx} is the usual energy gap E_G minus the unknown exciton binding energy. E_{Gx} is determined in our absorption measurements (Sec. VI) and its value, 2.390 eV, is indicated by the heavy arrow in Fig. 1. The displacement of the "0" peak from E_{Gx} is 10 meV, and is a measure of the energy by which the exciton is bound to the nitrogen. The small value of this binding energy is one indication that the complex is formed by an exciton and a *neutral* nitrogen (to form a four-particle complex). The binding of an exciton to *ionized* nitrogen to form a three-particle complex would be comparable with the ionization energy of the nitrogen (perhaps 100 meV).[11]

[10] D. G. Thomas and J. J. Hopfield, Phys. Rev. 128, 2135 (1962).
[11] D. R. Hamilton, W. J. Choyke, and Lyle Patrick, Phys. Rev. 131, 127 (1963).
[12] M. A. Lampert, Phys. Rev. Letters 1, 450 (1958).
[13] J. R. Haynes, Phys. Rev. Letters 4, 361 (1960).
[14] By exciton capture, un-ionized donors or acceptors form four-particle complexes, while ionized donors or acceptors form three-particle complexes. When luminescence from both four- and three-particle complexes is observed for the same impurity, it is possible to estimate the impurity ionization energy, as explained in Ref. 11.
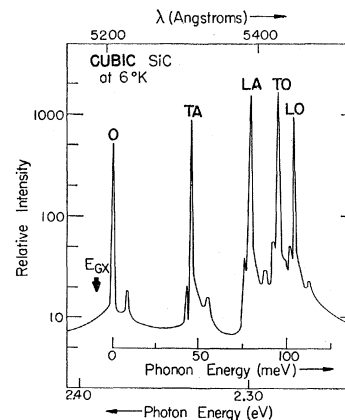
FIG. 1. The luminescence spectrum of four-particle nitrogen-exciton complexes in cubic SiC at 6°K. The phonon-free line is labeled "0" and its energy is used as the zero for the upper "phonon energy" scale, from which one may read directly the energies of TA, LA, TO, and LO phonons. The 10 meV between "E_{Gx}" and "0" is a measure of the binding energy of the exciton to the nitrogen atom.

We have not observed a three-particle spectrum for nitrogen in cubic SiC, although such a spectrum is usually quite strong in[11] 6H and[4] 15R SiC.

We have seen some lines at lower photon energy, which we think are due to simultaneous emission of a photon and two phonons, and we have seen other lines that appear to be due to one-phonon transitions which leave the nitrogen donor in an excited state.

The phonon energies derived from Fig. 1 are listed in Table I, together with the extended zone-boundary phonon energies in 15R and 6H SiC. We thus compare, for 3 polytypes, with 3 different symmetries, the phonons whose $\mathbf{k}$ vectors are determined by the positions of the conduction-band minima. For transverse phonons, the agreement is within experimental error (≈ 0.3 meV). For longitudinal phonons, a definite trend is observed in the sequence cubic, 15R, 6H: namely, LA decreases, while LO increases, with the sum of LA and LO remaining very nearly constant.

We conclude from this comparison that the conduction-band minima are very probably at the zone boundary, as predicted by Bassani and Yoshimine.[5] They place the minima at X, i.e., at the boundary in $<100>$ directions. Hence, the two TA momentum-conserving phonons should be degenerate, and likewise, the two TO phonons. This is consistent with our observation of 4, rather than 6, phonons. Furthermore,

TABLE I. Comparison of phonon energies in three polytypes. Energies in meV.

Phonon branch	Cubic	15R	6H
TA	46.3	46.3	46.3
LA	79.4	78.2	77.0
TO	94.4	94.6	94.7
LO	102.8	103.7	104.2

assuming the validity of the calculated band structure, one can show, by group theory, that optical transitions are allowed at both Γ and X, and that scattering is allowed for all branches of the phonon spectrum.

V. LUMINESCENCE AT 15°K

At 15°K two additional series of lines are observed in the luminescence spectrum, at energies greater by 2 and 5 meV. These lines are attributed to thermally excited states of the complex. Such excited states were observed in the spectra of[11] $6H$ and[4] $15R$ SiC, and could be separated into two kinds, depending on whether their energies were the same for all inequivalent sites in the polytype, or whether they depended on the particular site. The former were attributed to spin-orbit splitting, the latter to valley-orbit splitting.[15] In cubic SiC there is only a single nitrogen site, hence we cannot use the same criterion to identify the origin of the two excited states.

With the conduction-band minima at X, the number of degenerate minima is three, and there should be two valley-orbit states,[16] a singlet (A_1) and a doublet (E). However, in $6H$ and $15R$ spectra it appeared that doublet states were split (perhaps by the Jahn-Teller effect), so it is possible that we may observe three valley-orbit states. That is, it is possible that the ground state and the two excited states observed at 15°K are all due to valley-orbit splitting. On the other hand, the 5-meV energy is approximately the same as that attributed to the spin-orbit splitting in $6H$ and $15R$ SiC, so that we might alternatively attribute one exicted state to spin-orbit splitting and the other to valley-orbit splitting.

VI. ABSORPTION OF LIGHT AT 4.2°K

An earlier measurement[17] of the absorption of cubic SiC was made at 300°K, but no structure was observed in the absorption edge. Our results at 4.2°K, based on transmission measurements, are shown in Fig. 2. The square root of the absorption coefficient is plotted against photon energy. The shape of the edge is characteristic of indirect transitions in which excitons are created.[6] At higher photon energies, the plot is linear.

Transitions in which phonons are *absorbed* are entirely negligible at 4.2°K. The *emitted* phonons have energies of 46, 79, 94, and 103 meV, but these energies are derived more accurately from the luminescence. The beginning of the absorption in which each of the 4 phonons is involved is indicated by an arrow with the appropriate label. From Fig. 2 we derive a value of 2.390 eV for E_{Gx}, the exciton energy gap.
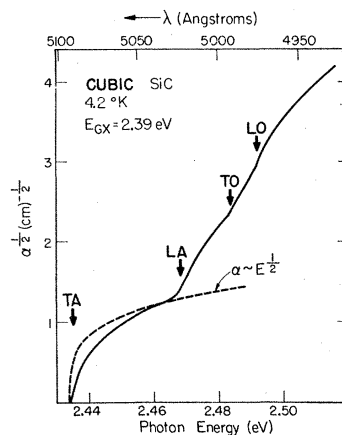

FIG. 2. The square root of the absorption coefficient as a function of energy for cubic SiC at 4.2°K. At photon energies shown by the arrows, emission of the indicated phonons becomes energetically possible. The dashed line is a plot of α against $E^{1/2}$, the initial energy dependence predicted by theory.

We have not made measurements at higher temperatures. Thus, we actually accept the value 46 meV for TA phonons from the luminescence measurements, and find that the other 3 phonon energies are consistent with those determined from the luminescence spectrum.

The largest crystal we used in absorption measurements had a light path of ≈ 2 mm, and an opening, or window, of about 1 mm^2. For accurate measurements we would prefer to have much larger crystals.[18] However, we think that the crystal size does not account for the lack of sharp structure in the absorption edge, as indicated by the deviation of the data from the dashed theoretical curve in Fig. 2. There are at least three other reasons for the discrepancy, which we list here. (1) The crystal quality is not as good as that of the high-temperature polytypes ($6H$ and $15R$). There is some twinning which may be equivalent to small inclusions of other polytypes. (2) There is a second valence band which may be about 5 meV lower in energy, but which has not been resolved, hence undoubtedly broadens the absorption edge. (3) Even in good Ge and Si crystals there is a deviation from the theoretical curves which has been attributed to collision broadening by Macfarlane et al.[19]

When better absorption measurements can be made, an analysis of the absorption-edge structure should yield the exciton binding energy.[6] In the meantime, we determine E_{Gx}, but not E_G.

VII. ENERGY GAPS FOR SiC POLYTYPES

Since E_{Gx} for cubic SiC is considerably smaller than that for other polytypes, it is of some interest to com-

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[15] In $6H$ and $15R$ SiC we observed valley-orbit splitting only in the three-particle spectrum, and spin-orbit splitting only in the four-particle spectrum.

[16] We consider only one of the electrons to be excited. Such a state may be thought of as an excited valley-orbit state of the nitrogen donor plus an exciton.

[17] H. R. Philipp, Phys. Rev. **111**, 440 (1958).

[18] Because the crystals were small, we did not use reflectivity data to correct the relative transmission measurements, but simply assumed that there was no absorption before the sharp edge at 2.435 eV.

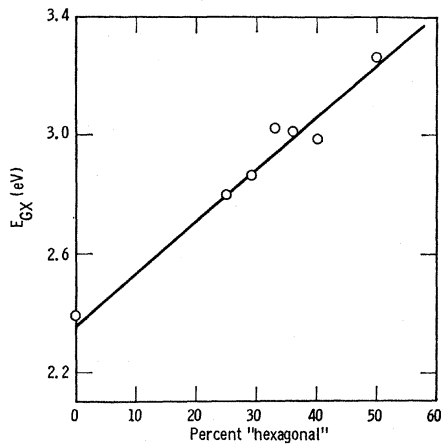[19] G. G. Macfarlane, T. P. McLean, J. E. Quarrington, and V. Roberts, Phys. Rev. **111**, 1245 (1958).

FIG. 3. A plot of E_{Gx} against percent "hexagonal" for seven SiC polytypes. The values of E_{Gx} are obtained from absorption measurements at 4.2°K, or luminescence measurements at 6°K, and are listed in Table II, together with the Jagodzinski notation used to define the percent "hexagonal."

TABLE II. E_{Gx} for seven SiC polytypes, with percent "hexagonal".

Polytype (Ramsdell notation)	Exciton energy gap, E_{Gx}	Jagodzinski notation	Percent h
Cubic	2.390	k	0
8H	2.80	$hkkk$	25
21R	2.86	$hkkhkkk$	29
15R	2.986	$hkhkk$	40
33R	3.01	$hkkhkkhkkhk$	36
6H	3.023	hkk	33
4H	3.263	hk	50

pare the 7 values of E_{Gx} which we have now determined. We find that it is possible to make an empirical correlation of E_{Gx} with percentage of "hexagonal" planes in the polytype, this parameter being obtained very easily from Jagodzinski's notation[1] in Table II. Jagodzinski obtains the required sequence of h's and k's by considering one of the sublattices in a SiC polytype, e.g., the Si sublattice, which can be thought of as a sequence of close-packed planes stacked along the c axis (or <111> in cubic). Each plane can be characterized as hexagonal (h) or cubic (k), depending on whether the relative orientation of atoms in the two neighboring planes is that found in wurtzite (h) or zinc blende (k). For a given polytype, one then writes down a sequence of h's and k's which is repeated endlessly in the actual structure.

For the 4 polytypes for which we have absorption measurements,[20] our values of E_{Gx} are given to four figures in Table II (estimated error ≈ 0.003 eV). To estimate E_{Gx} for the other 3 polytypes we use luminescence spectra[21] which can be identified as four-particle spectra, and which probably involve the nitrogen atom. The binding energies of excitons to neutral nitrogen atoms vary from 7 to 33 meV in other polytypes,[3,4] so we use the average value of 20 meV in estimating E_{Gx} for the polytypes 8H, 21R, and 33R. The error in E_{Gx} is probably not more than 0.015 eV.

A plot of E_{Gx} against percent "hexagonal" is shown in Fig. 3, indicating a roughly linear relationship. The 7 points represent the 7 polytypes of Table II. It will be interesting to see if this relationship also holds for the rare 2H polytype[22] (wurtzite, or 100% "hexagonal").

ACKNOWLEDGMENTS

[20] We have given a preliminary account of absorption in 4H SiC; Bull. Am. Phys. Soc. 5, 151 (1960).
[21] Our unpublished measurements.
[22] R. F. Adamsky and K. M. Merz, Z. Krist. 111, 350 (1959).