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# Optical Absorption in $n$-Type Cubic SiC†

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Nitrogen doping of cubic SiC increases the optical absorption in two regions. The free-carrier intraband absorption has a wavelength dependence of $\lambda^{2.8}$. An additional narrow band near 3.1 eV is shown to be the direct interband transition from the $X_{1c}$ conduction band to the higher $X_{3c}$ band. The relationship to Biedermann's work on other SiC polytypes is indicated.

## I. INTRODUCTION

We have compared the optical absorption of $n$-type samples of cubic SiC with that of relatively pure specimens. The $n$-type samples have additional absorption of two kinds, one of which is the usual free-carrier *intraband* absorption.[1] The other $n$-type absorption is a rather narrow band with a maximum at 3.1 eV, and can be attributed to the transition of electrons in the $X_{1c}$ conduction band to the higher $X_{3c}$ band. This is an allowed direct transition.

Such *interband* transitions in $n$-type crystals were observed by Biedermann in several SiC polytypes.[2] They are responsible for the well-known colors of nitrogen-doped samples, e.g., green $6H$ and yellow $15R$. The cubic $n$-type interband absorption differs from those reported for the other polytypes in three respects. (1) No part of the absorption band lies in the visible range, hence it does not contribute to crystal color. (2) The direct $n$-type absorption falls within the energy range of the intrinsic indirect interband absorption. (3) Only a single isotropic absorption band is found, because of the high symmetry of the cubic SiC band structure.

The lower limit of the interband transitions, approximately 3.05 eV, yields a value of the $X_{1c}$-$X_{3c}$ band separation which is in good agreement with some of the calculated values.[3,4] We discuss the possibility of distinguishing between absorption by electrons in the conduction band and by those bound to donor atoms. The wavelength dependence of the free-carrier intraband absorption yields information on the electron scattering mechanisms. Either polar or impurity scattering (or both) appear to be consistent with the experimental results.

## II. EXPERIMENTAL

### A. Crystal Preparation

All measurements were made on vapor-grown crystals that originated as cubic overgrowths on hexagonal crystals,[5] the overgrowths being deposited during the cooling period of the crystal-growing furnace.[6] The hexagonal parts were ground off, leaving small but good quality single crystals of cubic SiC, as shown by Laue transmission x-ray pictures. Various pressures of nitrogen were used in the furnace during crystal growth. No electrical measurements were made on the small cubic crystals, but measurements on hexagonal crystals grown in the same furnace show donor densities ranging from $10^{17}/\text{cm}^3$ at the lowest nitrogen pressures to $10^{19}/\text{cm}^3$ or more at the highest.

### B. Experimental Results

The absorption of an $n$-type crystal is compared with that of a pure crystal in Fig. 1. The relatively pure $A$ crystal probably has a donor density of order $10^{17}/\text{cm}^3$, but no evidence of the donors is found in the optical measurements. It has an indirect absorption edge at 2.39 eV.[7] The $n$-type $B$ crystal is thought to have a donor density of order $10^{19}/\text{cm}^3$. Other crystals were found to have different intensities of the 3.1-eV absorption band, and the intensity correlated qualitatively with the nitrogen pressure in the crystal-growing furnace, and with a color change to be described later.

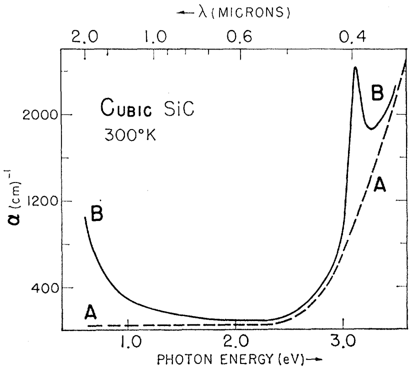

FIG. 1. Absorption spectra of cubic SiC crystals A (dashed) and B (solid) at 300°K. Crystal A is relatively pure; crystal B is strongly $n$-type (perhaps $10^{19}/\text{cm}^3$ donors).

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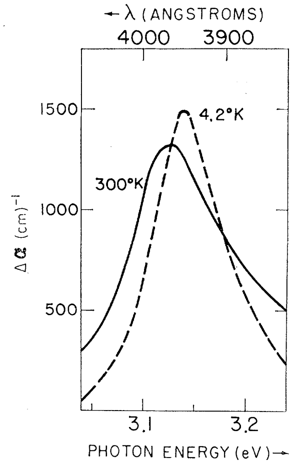

FIG. 2. Difference ($\Delta\alpha$) of crystal A and B absorption coefficients near 3.1 eV, at 300°K (solid) and at 4.2°K (dashed).

The additional $n$-type absorption near 3.1 eV' $\Delta\alpha=\alpha_B-\alpha_A$, is plotted in Fig. 2. It is an asymmetric band, but the shape cannot be determined accurately because of the uncertainty in $\Delta\alpha$ in the wings. Because of the difficulty of measuring absolute absorption coefficients on small crystals, the difference $\Delta\alpha$ between the two crystals is not reliable when it is much smaller than $\alpha_A$. At 4.2°K, the 3.1-eV band narrows considerably and moves to a slightly higher energy. At 77°K, the width of the band is close to that at 4.2°K.

## III. DISCUSSION

### A. Interband Absorption

Cubic SiC has the zinc-blende structure. Both theory and experiment suggest that the extra interband absorption in $n$-type samples should be attributed to direct transitions from the $X_{1c}$ conduction band to the higher $X_{3c}$ band.[8] Recent band calculations by Herman, Van Dyke, and Kortum show an $X_{1c}$-$X_{3c}$ separation of about 2.7 eV, compared with about 3.05 eV for the observed absorption edge (Fig. 2). The energies of the phonons emitted in the indirect exciton recombination transitions have been measured.[7] These phonons conserve crystal momentum, and therefore have the same $\mathbf{k}$ values as the conduction-band minima. The degeneracy of the transverse phonon modes in the exciton spectrum shows that the conduction-band minima lie in directions of high symmetry. The $L$ positions are then excluded by noting that the phonon energies are different from those found for $L$ in Raman-scattering experiments.[9] Thus, we conclude that the conduction-band minima are very likely at $X$.

A similar transition, also at $X$, is observed in $n$-type GaP at 0.4 eV.[10] Bassani remarks that the $X_{1c}$-$X_{3c}$ splitting, which is due to the antisymmetric portion of the crystal potential, is large for small atoms.[11] Biedermann made absorption measurements on $n$-type samples of several other SiC polytypes, and attributed the absorption to direct transitions from the conduction band to higher bands.[2] However, the bands between which the transitions take place have not been identified for these polytypes, because the exact positions of the conduction-band minima are not yet known.

In recent measurements[12] on the donor-induced transitions in 6$H$ SiC, an attempt was made to distinguish between absorption by electrons bound to donors and by conduction-band electrons. In cubic SiC we find only a single absorption band, which narrows and shifts to higher energy at 4.2°K. The shift of about 15 meV is possibly due to a change in interband separation. The band shape and the band narrowing at low temperature are not unlike those observed for the inter-valence-band transitions between bands 1 and 3 in $p$-type Ge. A comparison of experimental and calculation absorption was possible for Ge,[13,14] but it requires band parameters which are not known for cubic SiC. In any case, the absorption band shape is not well known experimentally, as noted above, and it is not expected to be very different for electrons bound to donors or in the conduction band.[13] Thus, we think that the experimental results do not answer the question of the initial location of the electrons.

If we examine the data for the 6$H$ absorption band in Ref. 12, we find that a thermal shift in the interband spacing and thermal broadening can qualitatively explain the observed temperature dependence. Hence, we feel that the presence of two distinct absorption mechanisms has not yet been shown. In both the cubic and the 6H SiC data, impurity banding may blur the distinction between bound and free electrons, for the donor densities were of order $10^{19}/\mathrm{cm}^3$.

### B. Intraband Absorption

The free-carrier intraband absorption (0.6–2.0 eV) is similar to that found for other polytypes by Biedermann[2] and others.[15] It is customary to plot this portion of the absorption on log-log paper to find the index $s$ that best describes the wavelength dependence in the formula $\alpha=\text{const.}\times\lambda^s$. The classical value $s=2$ is not found for the photon energies employed here, which are large compared with either the thermal energy $kT$ or the SiC phonon energies. Instead, $s$ is expected to depend on the electron scattering mechanism that

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[8] The optical transition is allowed. The group product of $X_1$ and $X_3$ is $X_3$. Dipole transitions are $X_3$ or $X_5$.

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transfers the absorbed energy to the lattice. Visvanathan finds $s=2.5$ for polar mode scattering, and $s=3$ for impurity scattering.[16] For the data in Fig. 1 we find $s=2.8$, in fair agreement, considering theoretical and experimental uncertainties, with either or both of these mechanisms.

For the room-temperature electron mobility in cubic SiC, polar mode scattering is unimportant because of the high LO phonon energy of 0.12 eV.[9] However, in optical absorption, the intermediate-state electron is effectively a "hot" electron, having an energy $>0.6$ eV, thus making emission of LO phonons an important mechanism of energy loss.

### C. Crystal Color

The coloring of SiC crystals by nitrogen has often been noted. The common 6*H* and 15*R* polytypes are transparent when pure, but green and yellow, respectively, when enough of the donor nitrogen is present. Presumably, any other donor would be equally effective. Crystals of these polytypes are uniaxial, and Biedermann's measurements show a strong dichroism. However, the typical SiC crystal platelet has its large dimension perpendicular to the *c* axis, so that only the ordinary ray color is observed unless windows are polished on the narrow crystal edges. The complexity of these absorption bands is a reflection of the complex band structure of such polytypes as 6*H* and 15*R*, which, in turn, has made it difficult to locate the positions of their conduction-band minima precisely. In contrast, cubic SiC has the relatively simple zinc-blende structure, and, consequently, a simple isotropic absorption band.

Unlike the other polytypes, cubic SiC is not colored by the $n$-type interband absorption, for 3 eV is beyond the range of sensitivity of the eye. Nevertheless, strong nitrogen doping is observed to change the crystal color from a pale canary yellow to a greenish yellow, as previously noted.[17] The yellow of pure crystals is due to the intrinsic but weak absorption in the blue. The shift towards the green in nitrogen-doped crystals is due to the free-carrier intraband absorption, which absorbs red preferentially.

## ACKNOWLEDGMENT

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