Nitrogen donor excitation spectra in 3C-SiC

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Infrared transmission spectra of high-quality vapor-grown 3C-SiC in the region of 1s-2p donor excitation transitions reveal three sequences of donor transitions analogous to those found in donor-doped silicon and germanium. Two of these sequences, a broad sequence and a sharp one, occur when the sample is held near 4.2 K. The broad sequence is assigned to transitions arising from the $1s(A)$ ground state of nitrogen. On warming, a second broad sequence, assigned to transitions from the $1s(E)$ ground state of nitrogen, is observed. The measured separation of these sequences, the $1s(A)$-$1s(E)$ valley-orbit splitting, is 8.34 meV. Excellent correspondence with theory is found for a nitrogen binding energy of 54.2 meV, consistent with other optical determinations of the nitrogen donor binding energy, and a static dielectric constant of 9.8. The sharp sequence, similar to sharp sequences found in very pure germanium, is attributed to an unidentified second donor whose excitation transitions are not broadened by grown-in local strain, e.g., an impurity free of chemical shift.

Silicon carbide is becoming recognized as one of the most promising semiconductor materials for future electronic device applications. Frequently mentioned applications for SiC include high-temperature, high-power, high-frequency, and radiation tolerant devices. As a result of the interest produced by its device potential, the electronic properties of the various polytypes of SiC, including the effects of desired and undesired impurities, are important current issues.

Among those impurities frequently observed, nitrogen is the donor most often found in the highest concentrations. Although nitrogen appears in all cubic SiC at approximately 54 meV in photoluminescence, the conductivity of cubic SiC epitaxially grown on Si substrates is typically dominated by a shallow donor below 20 meV whose identification is still controversial. Studies of the properties of the nitrogen donors by techniques other than photoluminescence could help establish the conditions for which the electronic properties of nitrogen are understood.

Donor excitation spectra, that is photon absorption arising from donor ground- to excited-state transitions, have been measured in infrared transmission studies of modified Lely-grown 6H-SiC (Ref. 1) and 4H-SiC (Ref. 2) in which nitrogen was the dominant donor. Similar infrared transmission measurements for the cubic polytype have not been reported previously, although nitrogen donor excitation spectra of Lely-grown cubic SiC have been observed by the two-electron satellite method in photoluminescence studies of donor bound excitons.[3]

Silicon carbide, silicon, and germanium share a similar asymmetric conduction-band structure, characterized by longitudinal and transverse effective masses, and an indirect gap. As a result, it is expected that donors in cubic SiC will, like 6H-SiC, have excitation spectra which are similar to the well-studied excitation spectra of donors in Si and Ge. Ground states are expected to be split by the valley-orbit mechanism into a low-lying $1s(A)$ and higher $1s(E)$ levels.

In this paper we report excitation spectra for a vapor-grown *n*-type sample of cubic SiC of very high purity. Excitation spectra, dominated by nitrogen, similar in quality to those for float-zoned Si and pure Ge, are obtained. The sample also contains an unidentified donor, shallower than nitrogen, with uniquely sharp excitation lines. The observation of very sharp excitation transitions suggests that grown-in local strain, not impurity-impurity interaction, is the dominant broadening mechanism for the nitrogen transitions. The donor producing the sharp sequence is relatively immune to the variations in local environment which broaden the excitation transitions. This behavior is expected for donors free of chemical shift.

Excitation spectra taken on samples containing large amounts of grown-in strain or high donor concentrations are rarely of high quality. Strain and impurity-impurity interactions broaden the transitions and large strain can split and complicate the spectra. The spectra reported here were acquired from a vapor-grown sample of very high purity yielding relatively unbroadened excitation

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lines. The vapor-phase growth process utilized thermal decomposition of methyl trichlorosilane in hydrogen at 1700 °C on graphite needles.

Transmission measurements were made at two sample temperatures, one near 4.2 K and the other at some unknown higher temperature. In both cases the small sample was attached to a copper aperture which was clamped, with good thermal contact, in front of a gallium-doped germanium photoconductive detector, and the assembly was cooled to near 4.2 K. This arrangement provides high optical efficiency, adequate cooling, and high detector sensitivity.

For operation of the sample near 4.2 K the sample was packed into the copper aperture with pure indium. This mounting provided efficient cooling of the SiC and optical baffling to prevent IR radiation leaks around the sample. Measurements at the higher temperature used the same arrangement except that the sample was attached to the aperture with a small amount of insulating vanish. In large quantities this varnish provides considerable cooling, but when used sparingly allows the sample to warm above the heat sink temperature. No thermometer was used so we do not know the sample temperature in the low-thermal-conductivity configuration.

The sample and detector with a CsI window were placed at an F/1 detector port of a Bomem DA 3.02 Fourier-transform spectrometer with a 3-μm mylar beamsplitter.

An infrared transmission spectrum for a sample cooled to near 4.2 K is given in Fig. 1, obtained with 0.135-cm^{-1} resolution. This spectrum contains two sequences of lines, a broad sequence with an indicated binding energy of 54.2 meV and a sharp one lying 6.43 meV lower. The observation of both sequences near 4.2 K indicates that they are independent donors, not two ground states of the same donor. If the sharp sequence were a split-off ground state of the donor producing the broad sequence, then the split-off ground state would be sparsely occupied at 4.2 K due to the 6.43-meV energy separation.

The broad sequence is the stronger one; it is used to determine the identity of the final state of the transitions and the excited-state binding energies. Representative transitions are labeled in Fig. 1 with the final-state designation. Those not labeled in Fig. 1 are identified and transition energies are given in Table I. Transitions have been identified using both observed trends and theoretical characteristics. Specifically, we have used the calculations of Faulkner[4] and the observation that amplitudes of a given sequence, e.g., $p_\pm$, diminish as the principal quantum number increases. The excitation spectrum of SiC bears a strong resemblance to that of Si (Ref. 5) with a few differences. The state $4p_0$ lies below $3p_\pm$ in Si, whereas $4p_0$ appears above $3p_\pm$ in SiC. The calculations of Faulkner correctly predict the observed ordering of $4p_0$ and $3p_\pm$ in both Si and SiC. The identifications of $4p_\pm$ and $4f_\pm$ are based on the positions predicted by Faulkner, although the experiment shows $4f_\pm$ as the stronger of the two. This relative strength is not observed in Si or Ge, so appears to be anomalous. Table I gives the observed energies of donor excitation transitions for the three sequences observed. Table II gives the observed excited-state binding energies determined from the cold broad sequence.

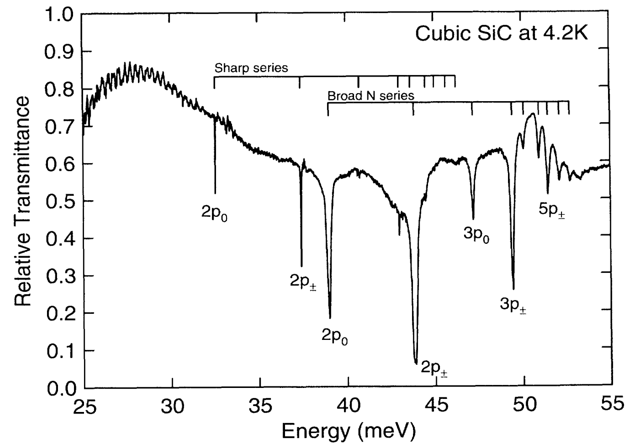

FIG. 1. Transmission of 3*C*-SiC containing nitrogen in the region of the donor excitations. The sample temperature was near 4.2 K. Major excitation lines are labeled with the identification of the final state of the transition.

Agreement between experiment and theory is excellent when optimum choices for the nitrogen binding energy and dielectric constant are made. In the calculations we have used $m_L^*=0.667m_0$ and $m_T^*=0.247m_0$ from cyclotron resonance measurements[6] which yield $\gamma^{1/3}=0.718$. Linear interpolation of Faulkner's tables provided parameters for calculating the theoretical excited-state positions. There are two variable parameters in establishing the fits: the donor ground-state binding energy and the static dielectric constant. Here, the donor ground-state binding energy was iterated for optimum fit with the static dielectric constant adjusted to yield agreement for the $2p_\pm$ level. Values used in the data of Table II are $E_D=54.2$ meV and $\varepsilon_s=9.82$. This choice of static dielectric constant and Faulkner's calculation predict the binding energy of the 1*s* ground state of a donor without chemical shift to be 47.2 meV. Since we have used both the nitrogen binding energy and static dielectric constant as parameters which are varied to optimize the agree-

TABLE I. Energies observed in meV for excitation transitions.

Initial state	Final state $2p_0$	$2p_\pm$	$3p_0$	$3p_\pm$	$4p_0$	$4p_\pm$	$4f_\pm$	$5p_\pm$	$6p_\pm$
$1s(A)$	38.99	43.84	47.19	49.43	50.09	50.95	51.45	52.1	52.69
$1s(E)$	30.63	35.5		41.1		42.61	43.17		
$1s(A)$,sharp	32.54	37.41		42.99		44.47	45.01		

TABLE II. Observed excited state binding energies in meV and calculated value. Ground-state binding energy and static dielectric constant were chosen to optimize the fit. Values used were $E_D = 54.2$ meV and $\varepsilon_s = 9.82$

	$2p_0$	$2p_\pm$	$3p_0$	$3p_\pm$	$4p_0$	$4p_\pm$	$4f_\pm$	$5p_\pm$	$6p_\pm$
Observed	15.21	10.36	7.01	4.77	4.11	3.25	2.75	2.1	1.55
Calculated	15.22	10.36	6.98	4.76	4.09	3.26	2.75	2.11	1.51

ment of theory with experiment, their values reflect the numeric accuracy of the effective-mass calculation as well as the characteristics of the sample.

The sharp series has a smaller binding energy and a smaller concentration than the broad one. The indicated binding energy of this shallow donor is 47.8 meV, which agrees very well with the 47.2 meV calculated by the effective-mass model for a donor with no chemical shift. We estimate the concentration of the donor producing the sharp series at approximately 5% of the nitrogen concentration, by assuming that its excitation transition absorption cross sections are equal to the nitrogen absorption cross sections.

The sharp lines seen here are exceptionally narrow. Typical excitation linewidths, even in very pure semiconductors like Si and Ge with impurity concentrations in the mid to low 10^{14}-cm^{-3} range, are of the order of 60 μeV. The width of the transitions in the sharp series here is approximately 30 μeV, which suggests that the concentration of 47.8-meV donors may be in the high 10^{13}-cm^{-3} range.

Coexistence of sharp and broad excitation lines in the same sample has been observed in ultrapure Ge containing donor concentrations in the 10^{10}-cm^{-3} range.[7,8] Coexistence of sharp and broad transitions requires either (1) that the centers producing the sharp and broad sequences occupy separate regions of the crystal, or (2) that the sharp sequence entails local conditions which mask the effects of interaction with random perturbations in the impurity's environment. The first possibility implies the existence of a distinct crystalline region of exceptionally high purity. The second could perhaps have several origins. For example, if the sharp sequence arises from a shallow donor free of chemical shift then it is possible that both the ground and excited states shift by the same amount with any local strain. The result would be a donor free of observable strain-induced broadening of its excitation lines.[9] Although this phenomenon was first discussed in the context of a lithium-oxygen donor complex, it can occur for any impurity free of chemical shift. Identification of the donor producing the sharp sequence observed here in SiC cannot be made with the available information but will require additional experimental work. Although the identity of the donor producing the sharp series is not established, the existence of the sharp series suggests that the SiC sample studied is of very high quality since the donor excitations can be very narrow, not limited by impurity-impurity interaction. This characteristic is usually observed only in the very purest semiconductors.

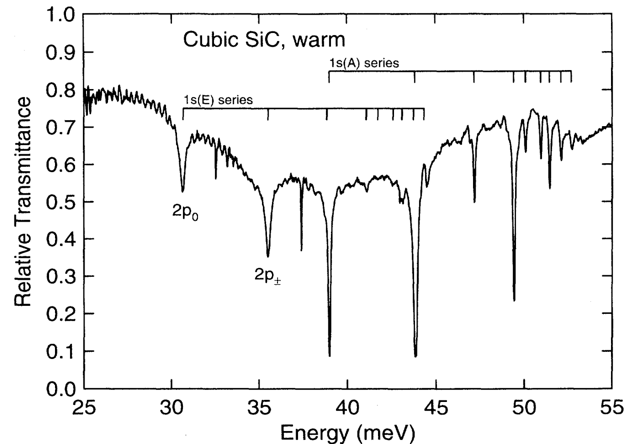

FIG. 2. Transmission of 3C-SiC warmed above 4.2 K. Two excitation lines present only in a warm sample are labeled with the identification of the final state of the transition.

Transitions observed when the sample is significantly above 4.2 K are shown in Fig. 2. All the transitions observed at lower temperature remain and a new sequence appears at lower energy. We identify the new sequence as originating from the $1s(E)$ ground state of nitrogen which places the $1s(A)$-$1s(E)$ valley-orbit splitting at 8.34 meV, and the $1s(E)$ ground state at 45.8 meV. Energies of transitions observed in the low-energy sequence are listed in Table I.

In summary, excitation spectra identified as those of nitrogen on the carbon site are observed. Indicated binding energies of the $1s(A)$ and $1s(E)$ ground states are 54.2 and 45.8 meV, respectively. In addition, a sharp excitation series is observed which is attributed to an unidentified donor, probably free of chemical shift, with a binding energy of 47.8 meV. Agreement of experiment with the theory of Faulkner is excellent. The observed linewidth of the narrow sequence suggests that the purity of this SiC sample is exceptionally high.

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