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Photoluminescence of Ti in four SiC polytypes

Lyle Patrick and W. J. Choyke
Westinghouse Research Laboratories, Pittsburgh, Pennsylvania 15235
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The photoluminescence of Ti in SiC has been observed in four SiC polytypes. The no-phonon line energies are shown to be independent of the polytype energy gap. The experimental results are explained by a model in which Ti is an isoelectronic substituent for Si. The isotope structure of Ti in 4*H* SiC is reported.

I. INTRODUCTION

A prominent and common luminescence spectrum in several SiC polytypes is due to Ti as an isoelectronic substituent for Si. Ti is one of many low-level impurities detected in the chemical analysis of most SiC samples, and its very strong contribution to the luminescence was long unsuspected. When we first reported the 6*H* *ABC* spectrum in 1963 we attributed it to *ionized* nitrogen,[1] for it was found in relatively pure crystals in which the principal impurity was N, and in which a second spectrum had been correctly attributed to *neutral* N.[2] However, doubts were raised about the 1963 assignment because the deduced N ionization energies did not agree with the values found in electrical measurements.[3] Finally,[4] we reassigned the spectrum to Ti, following some high-resolution studies by Dean and Hartman[5] that showed each spectral line to be made up of five closely spaced components. We observed that the intensities of the five lines were in approximate agreement with the natural abundances of the five Ti isotopes.[4] Recently, van Kemenade and Hagen[6] have confirmed the role of Ti by recording the luminescence spectrum of a 6*H* sample that was intentionally doped with Ti enriched in the isotope ^{46}Ti.

A significant deduction from our isoelectronic Ti model is that the electron taking part in the hole-electron recombination is a Ti *d*-shell electron. Thus, the photon energies should be independent of the positions of the conduction-band minima, and therefore independent of polytype,[7] in spite of the large differences in SiC polytype energy gaps. We have replotted data for four polytypes to show that this is so to a very good approximation. The absence of the Ti spectrum in 21*R* and 3*C* polytypes is then easily explained. Photon energy differences due to inequivalent sites within each polytype are attributed to local differences in the crystal field. Apparently, similar photon energies can be attributed to similar sites in different polytypes. Some additional data are given for 4*H* SiC, showing the presence of the Ti isotopic structure.

II. ISOTOPE STRUCTURE OF Ti IN 4*H* SiC

Most of the work on the Ti spectrum in SiC has been done on the common 6*H* polytype, and the observation of isotope structure has been reported only for 6*H*.[5,6] However, the Ti luminescence has also been observed in polytypes 4*H*,[8] 15*R*,[9] and 33*R*,[10] where it was identified as the "same" spectrum and therefore at first assigned incorrectly to N. The spectrum was recognized by its characteristic phonon structure, especially by a sharp 90-meV localized mode line.[1] Other localized and resonant modes were observed, but no momentum-conserving phonons, apparently because the hole-electron recombination involves a strongly localized electron.

To confirm the presence of Ti in 4*H* SiC we have made some high-resolution measurements on the strong no-phonon *A* line at 4350 Å. This is one of two such lines in polytype 4*H*. The results are shown in Fig. 1, which is copied from a densitometer trace, and shows the five components labeled by isotope number and percentage of natural abundance. The sample was not intentionally doped with Ti. This 4.2 °K spectrum was recorded on a 103*aF* photographic plate, using a Jarrell-Ash spectrometer. The dispersion was 0.4 mm/Å, and the slit width was 20 μm. The weak ^{49}Ti line was not resolved. The identification of isotope lines in Fig. 1 follows the rule, established in 6*H*, that lower mass lines fall at lower energies.[6] The separation between successive isotope lines is 0.13 meV, consistent with that found in 6*H*.[6] The relative line intensities cannot be measured accurately by a photographic method, but they appear to be in accord with the natural isotope abundances.

III. POLYTYPE COMPARISONS

The exciton energy gaps (E_{Gx}) of the SiC polytypes vary from 2.390 to 3.265 eV for the polytypes listed in Table I.[11] This large range in E_{Gx} is a result of the polytype dependence of the positions of the zone-edge conduction-band minima.[7] When the Ti spectra were first reported (as N spectra), they were attributed to exciton recombination, and exciton binding energies (called

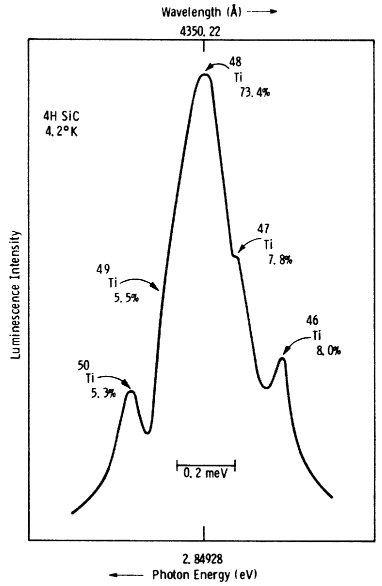

FIG. 1. Structure of the 4350-Å no-phonon line of Ti in *4H* SiC. The five equally spaced (0.13 meV) components are due to the five Ti isotopes, whose numbers and natural abundances are shown. The ^{49}Ti line was not resolved.

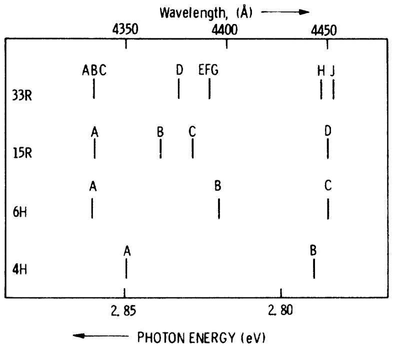

FIG. 2. Schematic spectra of Ti no-phonon lines in four SiC polytypes. The four spectra are purposely shown on the same wavelength and energy scales, in spite of differences in the polytype energy gaps. The coincidences of certain lines in different polytypes are discussed in the text. Lines in each polytype are lettered in the order of decreasing energy.

E_{3x}) were measured as the displacements of the no-phonon lines from the exciton gap

$$E_{3x} = E_{Gx} - h\nu \,. \tag{1}$$

The measured values of E_{3x} showed a large and puzzling polytype dependence, varying from 0.125 eV at one *15R* site[9] to 0.475 eV at one of the two *4H* sites.[8] However, now that we have identified the spectra as those of Ti, we can use a model in which the level of the trapped electron is unrelated to the positions of the conduction-band minima. It is then appropriate to compare photon energies directly for all polytypes, as we have done in Fig. 2, where vertical lines are placed at the energies of the observed Ti no-phonon lines. The number of lines is fewer than the number of inequivalent sites listed in Table I. Possibly the separate lines are not always resolved. In each polytype the observed lines are lettered in the order of decreasing energy. Each letter in Fig. 2 corresponds to a resolved line, although, for *33R*, the scale of the figure does not permit us to show the separate lines in two groups of three. These groups are shown resolved in Ref. 10.

TABLE I. Exciton energy gaps (E_{Gx}) of six SiC polytypes at 4.2 °K, with numbers of inequivalent Ti sites and resolved Ti no-phonon lines.

Polytype	E_{Gx} [a]	Inequivalent sites	Resolved Ti lines
3C	2.390	1	0
21R	2.86	7	0
15R	2.986	5	4
33R	3.003	11	9
6H	3.024	3	3
4H	3.265	2	2

[a] Reference 11 (revised).

The Ti no-phonon lines in each of the four polytypes shown in Fig. 2 span very nearly the same energy range, 2.79–2.86 eV. Photon energy differences at inequivalent sites can be attributed to site-to-site differences in the crystal field. The crystal symmetry requires the field to be reproduced in each unit cell, but permits differences at inequivalent sites. These differences can be traced to slight dissimilarities in neighborhood configurations. No scheme has yet been devised to unequivocally pair configurations with photon energies. We shall later consider the simplest case, polytype *4H* with only two equivalent sites.

In Sec. IV we briefly review the isoelectronic Ti model in order to justify the method of plotting the data in Fig. 2, with neglect of polytype energy-gap differences.

IV. MODEL OF ISOELECTRONIC Ti CENTER

The Ti atom has a $3d^2 3p^2$ configuration, isoelectronic with the $3s^2 3p^2$ of Si. In tetrahedral surroundings the d electrons split into sets of t_2 and e symmetry, and the t_2 set can mix with the p electrons on the four C ligands, which also have t_2 symmetry. Thus, ligand-field theory[12] indicates that the Ti states, shown on the left-hand side of Fig. 3, combine with the σ ligand states, shown on the right-hand side, to form the states shown in the center, which can be classified as bonding (superscript b), antibonding (superscript *), or nonbonding (no superscript). In other words, an sd^3 set from Ti combines with an sp^3 set from the

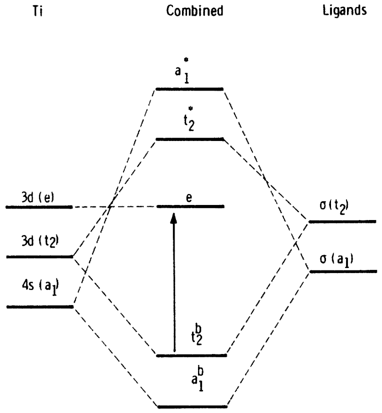

FIG. 3. Schematic diagram showing the combination of Ti and ligand states to form bonding (a_1^b and t_2^b), nonbonding (e), and antibonding states (a_1^* and t_2^*). Degenerate levels are shown separated for clarity. In the ground state the bonding levels are all occupied. It is suggested that exciton capture is equivalent to the transition indicated by the arrow, and luminescence to the reverse transition (from Ref. 4).

ligands to fully bond the Ti atom. The eight bonding electrons fill the a_1^b and t_2^b levels of the combined system. Exciton capture by the Ti atom is equivalent to the promotion of a bonding electron into the e level, as shown by the arrow in Fig. 3, and the reverse transition gives rise to the luminescence. The small departure from tetrahedral symmetry in the hexagonal and rhombohedral SiC polytypes will be neglected.

The work of Baldereschi and Hopfield[13] on isoelectronic impurities suggests that Ti does not differ enough from Si in size and electronegativity to form a hole trap. However, the presence of the empty e level makes Ti an electron trap, provided the e level falls below the bottom of the conduction band. A trapped electron then binds a hole by its Coulomb force, as in the usual kind of isoelectronic center.

In our model the e level electron is without significant contributions from the conduction band wave functions. Its energy level is therefore independent of polytype, for the values of the indirect energy gaps in SiC polytypes are determined by the polytype-dependent positions of the conduction-band minima.[7] This explains the constancy of the photon energy, as plotted in Fig. 2, in spite of energy gap differences as large as the 0.24-eV interval between 4H and 6H shown in Table I.

The measured no-phonon line energies range from 2.79 to 2.86 eV in Fig. 2. In cubic (3C) SiC,[11] with an energy gap of 2.39 eV, the e level would be resonant with the conduction-band levels, and would therefore not be able to function as an electron trap. Thus, the absence of Ti luminescence in 3C is consistent with the model. Polytype 21R, which also has no Ti luminescence,[14] has an exciton energy gap of 2.86 eV and is a marginal case on the basis of our model.

V. CRYSTAL-FIELD EFFECTS

The model of Fig. 3 schematically indicates the result of the covalent bonding of Ti at a Si site. Crystal field theory would consider the Ti energy levels to depend also on the positions of medium-distance neighboring atoms. Differences in such positions are found when the local stacking order is viewed from each inequivalent site in turn. Like the stacking order, site differences can be classified by a one-dimensional notation. The best scheme for showing the stacking order is the zigzag sequence in a (11$\bar{2}$0) plane. Figure 4 illustrates this for the simple 4H structure, with stacking order $ABAC$. Only one of the two sublattices is shown, which we arbitrarily take to be the Si sublattice.

Now consider the Si-to-Si distance along the c axis. As drawn, the 4H stacking sequence puts Si atoms at an interplanar separation of two planes on A sites and four planes on B and C sites, the B and C sites being equivalent under a screw-displacement operation 6_3 at A. Ti atoms substituted at the two inequivalent sites would have quite different neighborhoods, thereby explaining the considerable photon energy difference of the two no-phonon lines in 4H SiC. The ABC notation is a standard notation for stacking order in close-packed structures and should not be confused with our sim-

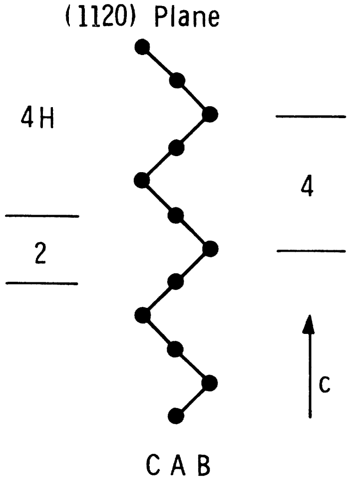

FIG. 4. Zig-zag sequence showing the $ABAC$ stacking order of 4H SiC. The circles represent Si atoms in a (11$\bar{2}$0) plane, with the c axis vertical. Atoms of each column are in one of the three sites denoted by A, B, and C in close-packed structures. The interplanar distance between Si atoms along the c axis is two for A sites but four for B and C sites.

ilar notation for the no-phonon lines in Fig. 2. We do not know which of the two sites in Fig. 4 should be matched with the *A* photon line at 4350 Å.

In more complex polytypes the zig-zag sequences show that two sites may have quite extensive similar neighborhoods, becoming inequivalent only at six or more interplanar distances. We presume that in such cases the no-phonon lines of Ti atoms at those sites are only slightly different in energy. For example, two configurations in polytype 6*H* are found to be like two of 15*R* over considerable neighborhoods, and this may account for the near coincidence of the *A* lines in these polytypes, and of the *C* line of 6*H* with the *D* line of 15*R*.

Another example is found in polytype 33*R*. The stacking sequence of 33*R* shows that it can be thought of as a combination of 6*H* and 15*R*.[10] The three inequivalent sites of 6*H* become six in 33*R* because of the symmetry reduction. Adding the five 15*R* sites, we obtain the 11 inequivalent sites of 33*R*. Only nine Ti no-phonon lines were resolved, of which three are the closely spaced lines *A*, *B*, and *C*, which fall at nearly the same energy as the *A* lines of 6*H* and 15*R*.[15] We conclude that two of them correspond to the doubled 6*H* line and the third to the 15*R* line. Other correspondences were pointed out in Ref. 10, but the comparisons were less immediate there because of our use of exciton binding energies (E_{3x}), now shown to be irrelevant.

From these correlations it appears that the photon energy of a Ti center has a moderate dependence on the configuration of neighboring atoms, but is very nearly independent of polytype. This is good evidence that the electron involved in the transition is well localized, as it would be within the *d* shell of Ti. However, the model is obviously oversimplified. In its present form it cannot account for the many thermally excited states of the Ti center.[1,16]

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[1] D. R. Hamilton, W. J. Choyke, and Lyle Patrick, Phys. Rev. 131, 127 (1963).

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

[3] S. H. Hagen and C. J. Kapteyns, Philips Res. Rept. 25, 1 (1970).

[4] W. J. Choyke and Lyle Patrick, in *Silicon Carbide* 1973 (University of South Carolina Press, Columbia, S.C., 1974), p. 261.

[5] P. J. Dean and R. L. Hartman, Phys. Rev. B 5, 4911 (1972).

[6] A. W. C. van Kemenade and S. H. Hagen, Solid State Commun. 14, 1331 (1974).

[7] Lyle Patrick, Mater. Res. Bull. 4, S129 (1969).

[8] W. J. Choyke, Lyle Patrick, and D. R. Hamilton, *International Conference on the Physics of Semiconductors* (Dunod, Paris, 1964), p. 751.

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

[10] W. J. Choyke, D. R. Hamilton, and Lyle Patrick, Phys. Rev. 139, A1262 (1965).

[11] W. J. Choyke, D. R. Hamilton, and Lyle Patrick, Phys. Rev. 133, A1163 (1964).

[12] C. J. Ballhausen, *Introduction to Ligand Field Theory* (McGraw-Hill, New York, 1962).

[13] A. Baldereschi and J. J. Hopfield, Phys. Rev. Lett. 28, 171 (1972).

[14] D. R. Hamilton, Lyle Patrick, and W. J. Choyke, Phys. Rev. 138, A1472 (1965).

[15] The three 33*R* lines are shown resolved in Fig. 7 of Ref. 10.

[16] I. S. Gorban and V. A. Gubanov, Fiz. Tverd. Tela 13, 2076 (1971) [Sov. Phys.-Solid State 13, 1741 (1972)].