

PROOF OF THE INVOLVEMENT OF Ti IN THE LOW-TEMPERATURE ABC
LUMINESCENCE SPECTRUM OF 6H SiC

A.W.C. van Kemenade and S.H. Hagen

Philips Research Laboratories, Eindhoven, The Netherlands

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An investigation of the low-temperature photoluminescence of Ti-doped 6H SiC crystals in which the naturally abundant ^{48}Ti has for the greater part been replaced by ^{46}Ti , shows that a proposed attribution of the well-known ABC luminescence spectrum to Ti is correct. The effect of the isotope substitution on a localized vibrational gap mode is discussed.

IT WAS shown recently that the attribution in references 1 and 2 of the low-temperature ABC luminescence spectrum in 6H SiC to exciton recombination at ionized nitrogen donors was incorrect.^{3,4} Choyke and Patrick have now raised the idea that this recombination centre could be due to Ti which they suppose to act as an isoelectronic substitute for Si.⁵ According to these authors the recombination steps would consist of the capture of an electron at a non-bonding e -level, the subsequent binding of a hole by the Coulomb force, and radiative recombination of the captured electron and hole. They base this attribution on the observation by Dean and Hartman³ of two satellites on either side of the ABC lines. Choyke and Patrick interpreted these satellites in terms of isotope shifts from a dominant ^{48}Ti zero-phonon line, due to the presence in natural Ti of small amounts of the isotopes ^{46}Ti , ^{47}Ti , ^{49}Ti and ^{50}Ti . Reported relative intensities of the satellites³ are roughly in agreement with the natural abundances of the isotopes. Early attempts made by us to identify the impurity by investigating the ABC spectrum of 6H crystals grown in the presence of a substantial amount of Ti were not successful since no significant increase in the luminescence intensity could be found. This might, however, be due to limited solubility of Ti and/or the simultaneous incorporation of other impurities leading to an increase in the number of competitive recombination channels.

To obtain more conclusive evidence of the possible role of Ti we investigated the photoluminescence of crystals grown in the presence of TiO_2 consisting of 73.8%, 20.1%, 2.6%, 1.7% and 1.8% by weight of $^{46}\text{TiO}_2$, $^{48}\text{TiO}_2$, $^{47}\text{TiO}_2$, $^{49}\text{TiO}_2$ and $^{50}\text{TiO}_2$ respectively. To reduce the incorporation of other impurities to a minimum we used for this experiment the high-purity preparation method described by Kapteyns and Knippenberg.⁶ The amount of TiO_2 added to the growth charge of about 100 g of pyrolytic SiC was 17 mg.

Photoluminescence measurements were performed at 4.2 K, using a Hilger Engis Monospek 1000 grating monochromator (dispersion 1.25 mm/Å) and a cooled XP 1002 photomultiplier. A Philips 1000 W super-high-pressure mercury lamp (type SP1000) was used as the u.v. excitation source.

The results of these photoluminescence measurements prove that the attribution of the spectrum to Ti is correct.

In Fig. 1 we show the zero-phonon lines A , B and C together with the A_{90} , B_{90} and C_{90} lines which are replicas involving a localized vibrational gap mode with an energy of 90 meV. The most important feature of these spectra is the fact that, in addition to the lines which are normally dominant in the ABC spectrum,

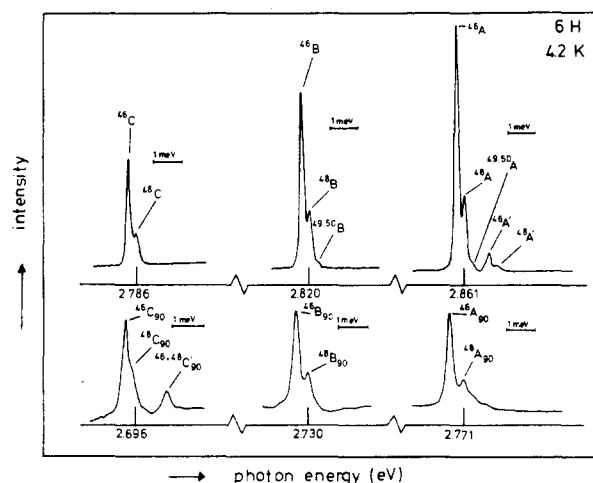


FIG. 1. Dominant luminescence lines of the 4.2 K ABC luminescence spectrum in 6H SiC which was doped with Ti consisting for the greater part of ^{46}Ti . The indices 46, 48, 49 and 50 refer to the relevant Ti isotopes. The marks on the abscissa indicate the location of these lines for a not intentionally doped sample containing only natural Ti in which ^{48}Ti dominates.

namely those with the index 48, additional lines of higher intensity are present at a slightly lower photon energy. The relatively high intensity of these lines is obviously due to the abundance of ^{46}Ti in the samples. That these are the lines due to ^{46}Ti was confirmed by a comparison with the spectrum of a crystal not intentionally doped with Ti. The photon energies of the A, B, C, A_{90} , B_{90} and C_{90} lines found for the latter spectrum are indicated by marks on the abscissa. They

coincide with the photon energies of the lines labelled with the index 48 in Fig. 1. Of the other two lines A' and C'_{90} (A_2 and C_{290} in reference 1) the former has also been resolved into a ^{46}Ti component and a ^{48}Ti component. In addition, the spectra of the A and B lines point to the presence of other isotopes, namely ^{49}Ti and ^{50}Ti . The relative strength of the ^{46}Ti and ^{48}Ti lines prevents the observation of a satellite due to ^{47}Ti . The observed intensity relation between the lines 46 and 48 is also in satisfactory agreement with the relative amounts of isotopes added.

The results also show that the replacement of ^{48}Ti by ^{46}Ti leads to a shift of the dominant zero-phonon line towards lower photon energy. This shift is about 0.30 meV for the A line and about 0.25 meV for the B and C lines.

The energy of the localized vibrational gap mode is about 0.15 meV larger for ^{46}Ti than for ^{48}Ti in the case of the A and B modes. The effect on the C mode is appreciably smaller and could not be determined. An estimate of the isotope effect on the gap mode may be made on the basis of Gaur's, Vetelino's and Mitra's⁷ theoretical calculations. For replacement of Si by ^{46}Ti instead of ^{48}Ti this estimate leads to an increase of about 0.1 meV, which is of the same sign and order of magnitude as found experimentally.

The conclusion that the ABC spectrum in 6H SiC is due to Ti should also apply to the corresponding spectra in other polytypes of SiC.

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Eine Untersuchung der Photolumineszenz von Ti-dotierten SiC Kristallen vom Polytyp 6H wobei ein Teil des in der Natur überwiegenden ^{48}Ti -Isotopes ersetzt war durch ^{46}Ti hat ergeben, dass der Vorschlag das ABC Lumineszenzspektrum dem Ti zuzuschreiben richtig ist. Der Effekt der Isotopensubstitution auf eine lokalisierte Gitterschwingung wird diskutiert.