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RADIATIVE RECOMBINATION IN β-SiC DOPED WITH BORON

H. KUWABARA, S. YAMADA and S. TSUNEKAWA
Research Institute of Electronics, Shizuoka University, 3-5-1 Johoku, Hamamatsu, 432 Japan

There are two kinds of photoluminescence in β-SiC associated with boron atoms, one of which is caused by the nitrogen donor–boron acceptors pair recombination, and the other is caused by an electronic transition between the conduction band and the boron acceptor. The ionization energies of the nitrogen donor and the boron acceptor are estimated to be 0.055 and 0.735 eV, respectively.

1. Introduction

There are two types of near-infrared emission bands in β-SiC doped with boron. One of them, designated as an A emission, is predominant at room temperature region, and the other B emission predominates at lower temperatures [1,2]. As for the B emission, the peak of the no-phonon band (B_0) shifts toward the higher energy side with increasing excitation intensity and boron concentration. It is suggested that this B emission is caused by the nitrogen donor–boron acceptor pair transitions. On the other hand, the no-phonon band (A_0) of the A emission shows no appreciable peak shift and broadening with excitation intensity and boron concentration. The A_0 emission band is located at about 40 meV higher energy with respect to the B_0 emission band.

This paper describes the experimental and analytical results of these two emission bands.

2. Experimental

The β-SiC crystals used were grown from a silicon solution at about 1550°C in a graphite crucible [3]. The SiC crystals containing various amounts of boron and nitrogen were prepared. The boron concentrations in SiC crystals were estimated from the dopant concentration in the silicon melt using published data [4]. For photoluminescence measurements, the crystals were excited by the 488 nm line of an Ar^+ ion laser.

3. Results and discussion

The spectra of the high energy portion of the B_0 band at 1.6 K are shown in fig. 1. The spectra are rather complicated owing to the presence of isotopes of boron. We selected the emission lines corresponding to the boron of mass number 11 for the analysis. From consideration of the correlation between the luminescence intensity and the number of equivalent lattice sites at a given shell number, and also on the lack of spectral lines at the special shell numbers, the spectrum is concluded to be Type I D–A pair emission: i.e. both the nitrogen and the boron atoms substitute at the same kind of host lattice. The photon energy corresponding to the infinite separation is expressed as $h\nu_\infty = E_g - (E_D + E_A)$, and is estimated to be 1.614 eV, where E_g is the bandgap energy and E_D and E_A are the ionization energies of a donor and an acceptor, respectively.

The half-width of the A_0 band increases with temperature, and is about $2.2\,kT$ in the temperature range from 65 to 160 K. This A emission is examined by a free-to-bound transition model. The rate of radiative recombination of an electron of kinetic energy E_k with a hole bound to an acceptor is given by [5]

$$R(E_k) = CE_k^m \exp(-E_k/kT) \tag{1}$$

where C is a constant, and the capture cross section for an electron is assumed to be proportional to some power of E_k. As the energy of the emitted photon in the no-phonon band is given by $(E_g - E_A + E_k)$, the spectral shape of this transition should be described by (1). A comparison of the spectral line shape for the A_0 band with the calculated one from (1) is shown in fig. 2. The agreement is good when the value of m is assumed to be 0.7. This value of m yields the half-width of $2.1\,kT$,

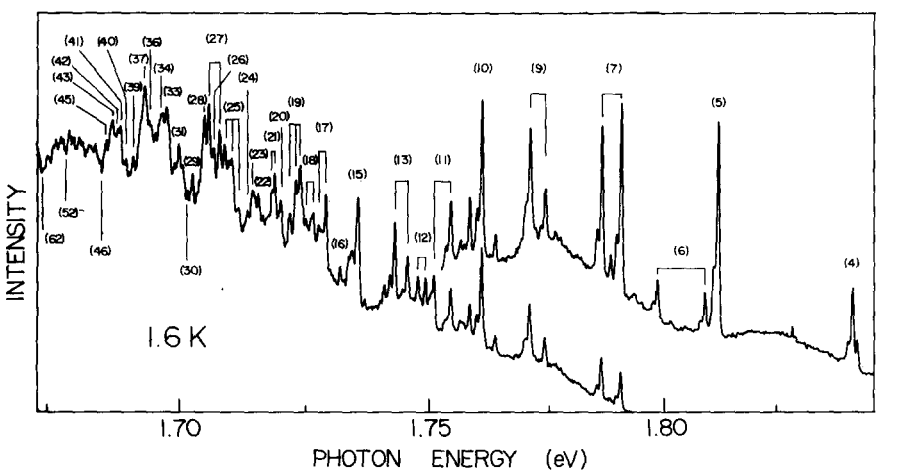

Fig. 1. Luminescence spectra measured at 1.6 K. Shell numbers are shown in the brackets.

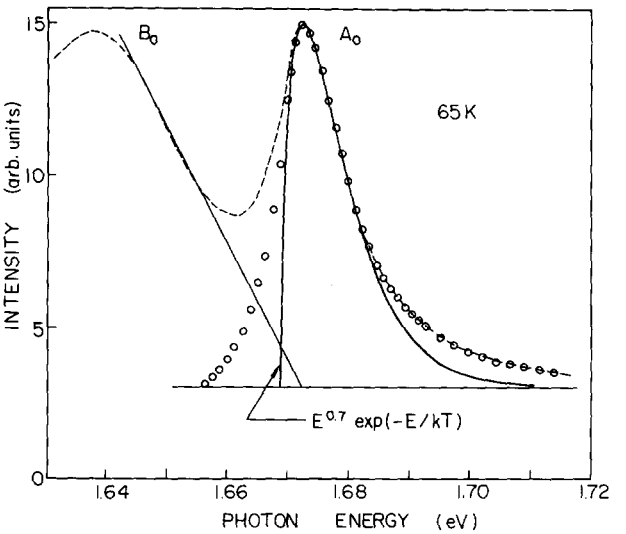

Fig. 2. Comparison between the measured spectral shape and the calculated curve, $E^{0.7}$ $\exp(-E/kT)$ at 65 K. The background for the A_0 band is approximated by two lines shown in the figure.

showing good consistency with the experimental half-width of 2.2 kT within the experimental error.

According to (1), the energy difference between the low energy threshold, $h\nu_0$, of the no-phonon band and its peak energy must be mkT. The energy $h\nu_0$ should correspond to $(E_g - E_A)$, and is expected to show similar temperature dependence to that of E_g. Fig. 3 shows $h\nu_0$ as a function of temperature assuming $m = 0.7$, and exciton bandgap energy E_{gx} of 6H-SiC. Exact temperature dependence of E_g of

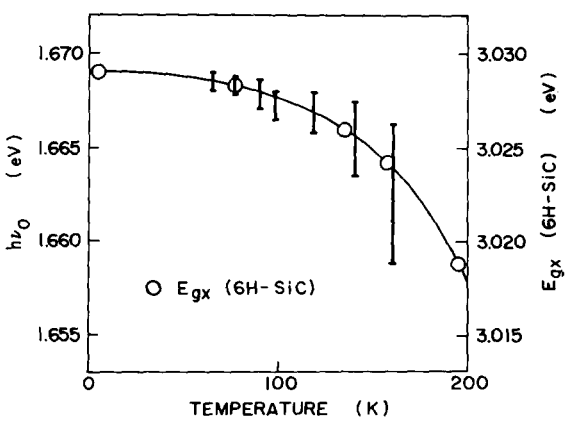

Fig. 3. Temperature dependence of $h\nu_0$ (=A_0 peak − 0.7 kT). Open circles show E_{gx} of 6H-SiC. Possible energy range of $h\nu_0$ are illustrated by vertical bars.

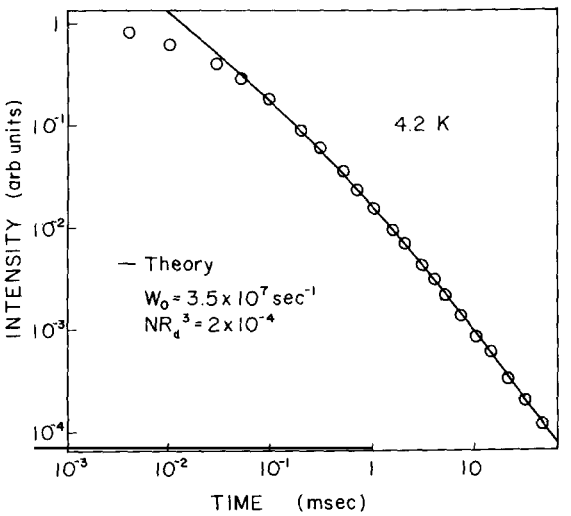

Fig. 4. The time decay of integrated intensity of the B emission. The curve is calculated under the assumption that all the pairs are initially saturated and donors are in excess.

β-SiC is not known yet, but is considered to be not so much differ from that of other polytypes such as 6H-SiC [6]. The exciton ionization energy is much smaller than E_g. Therefore, it is considered that there is a similarity between experimental temperature dependence of $h\nu_0$ and that of bandgap of β-SiC.

From these consideration, we concluded that the A emission of β-SiC doped with

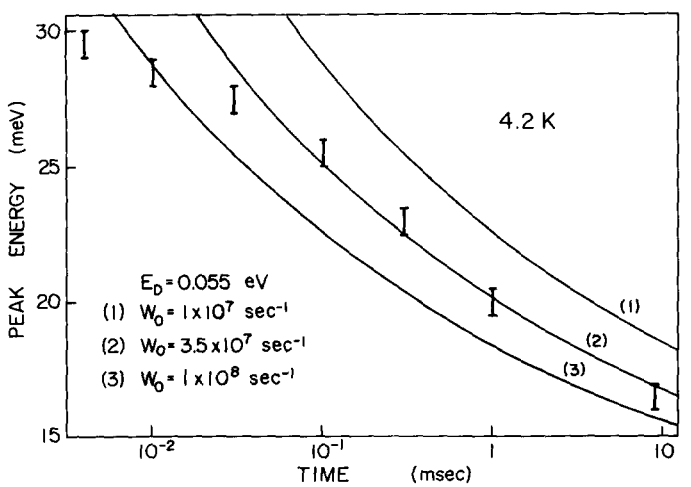

Fig. 5. Spectral shifts of the B_0 peak (E_p) in time resolved spectroscopy. The peak energy is reckoned from the $h\nu_\infty$. Theoretical curves are calculated from $W_0 t = \{1 - (E_p/E_D)\} \times \exp(4E_D/E_p)$ [10] assuming $E_D = 0.055$ eV.

boron is due to the recombination of an electron in the conduction band with a hole bound to boron acceptor.

From fig. 3, the value of the energy difference $(E_g - E_A)$ is obtained as 1.669 eV. Using 1.614 eV for $E_g - (E_D + E_A)$, and 2.390 eV for E_{gx} of β-SiC [7] and assuming 13.5 meV for the value of exciton ionization energy [8], the value of ionization energies of the nitrogen donor and the boron acceptor are estimated to be 0.055 and 0.735 eV, respectively.

The time decay of integrated intensity of the B emission and the peak shift of the B_0 during the decay are shown in figs. 4 and 5. In the calculation of the theoretical curves [9,10], it is assumed that all pairs are initially saturated and that the transition probability is given by $W_0 \exp(-r/R_d)$, where R_d is half the Bohr radius of the shallower center, and W_0 is a transition probability corresponding to separation $r \to 0$. The excitation intensity used in the experiment seems to be not strong enough to saturate all the pairs, and this results in deviation of the decay characteristics from the theoretical curves in the early stage of the decay. In these two figures, appropriate fit is obtained when the value of W_0 is assumed to be 3.5×10^7 s^{-1} and NR_d^3 equals 2×10^{-4}. The nitrogen concentration N is estimated to be 6.5×10^{17} cm^{-3}.

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Discussion

H. Mitsuhashi: I understood that you used an CW argon laser. I think it is important to select adequate light source for the analysis of time resolved spectra. Would you comment on the use of light sources other than CW argon laser.

H. Kuwabara: For low level excitation, we used a Xenon lamp and also a Hg discharge lamp.

H. Matsunami: How did you determine the energy levels of donors and acceptors as 0.055 eV and 0.735 eV, respectively?

H. Kuwabara: The summation of ionization energies of donor and acceptor is determined from the line structure of donor–acceptor pair precisely. The ionization energy of acceptor is deduced from the analysis of A_0 emission, under the assumption that the A_0 emission is caused by the transition of electrons from the conduction band to the acceptors.

A.T. Vink: You derive for the transition probability at $R = 0$ a value of 3.5×10^7 s^{-1}. For an indirect band gap semiconductor this is an extremely high value, those normally found being in the range of 10^5 to 10^6 s^{-1}. S. Hagen of our laboratory also obtained such values for N-Al pairs in SiC (see e.g. J. Luminescence 9 (1974) 180 and reference cited there). The value you give is more characteristic for a direct band gap semiconductor. Do you have an explanation for this large value?

H. Kuwabara: Yes, the value of 3.5×10^7 s^{-1} for the maximum transition probability, W_0, seems to be too large with respect to that expected for indirect materials. Now further investigation on the total light decay and the time resolved spectra are in progress.