LOW-TEMPERATURE LUMINESCENCE OF SILICON CARBIDE CRYSTALS

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The high-energy part of the blue fluorescence of α-SiC(6H) is found to be dependent on the nitrogen (donor) concentration. The line fluorescence spectrum is found to include a new series of lines due to radiative transitions to Al acceptor levels.

The most common of the numerous polytypes of SiC is α-SiC(6H), whose luminescence is of some interest. At present there is no agreed view on the nature and structure of the emission centers; the only real mode of solution lies in varying the concentrations of the most common impurities in SiC. The phonon spectrum of SiC has 36 branches, many of which lie in the infrared region (1,2), where the 0.046 and 0.067 eV lines and a group near 0.1 eV appear, although spectroscopic studies of indirect transitions do not allow this group to be resolved into its components. These transitions give the dissociation energy of the excitons as 0.045 eV and the width of the forbidden band at 77° K as 3.07 eV to better than 0.01 eV. The exciton width of the forbidden band is 3.023 eV.

The hydrogen-like approximation for an exciton gives a rough estimate of the effective mass as $\mu = 0.34 m_0$, in which m_0 is the mass of a free electron; the radius of the lowest exciton state is $r = 13.1$ Å.

Nearly all crystals contain in their low-temperature fluorescence spectra a blue band whose energy distribution is shown in Fig. 1a for several crystals at 77° K. Many crystals also show an emission at longer wavelengths, which starts at 2.2 eV; this will not be discussed here. The blue band consists of several components more or less prominent as peaks at 2.86, 2.79, 2.725, 2.675, 2.62, 2.56, and 2.525 eV. In addition, some crystals show less prominent shoulders, the commonest lying at 2.825, 2.7, and 2.59 eV. These do not occur simultaneously.
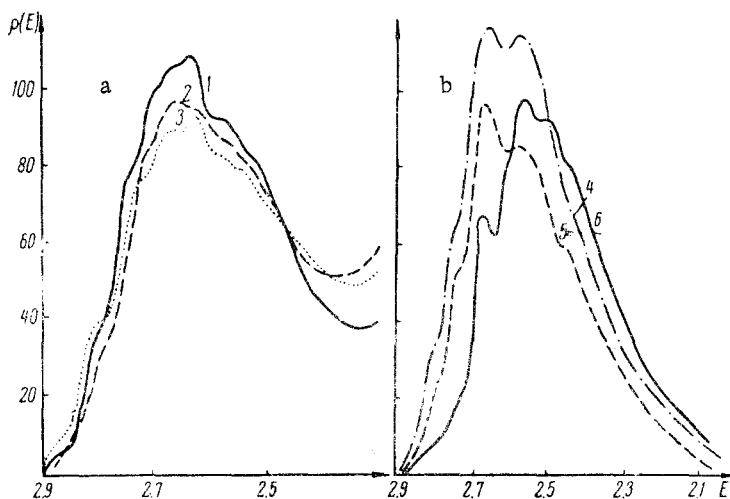

Fig. 1. a) Photoluminescence spectra at 77°K for n-type α-SiC(6H) crystals: 1) No. 197; 2) No. 204; 3) No. 93; b) structure of blue fluorescence band for 3) at temperatures of: 4) 77°K; 5) 83°K; 6) 90°K; $\rho(E)$ is the relative number of photons per unit time in unit energy range, while E is in eV.

The blue band is assigned [3] to transitions from nitrogen donor levels involving 0.07 eV phonons. A band of the form of Fig. 1a has been observed in our tests only for crystals with electron conduction, donor concentrations of 4×10^{18} to 10^{19} cm^{-3}, and activation energies of 0.02-0.06 eV; but Fig. 1a and the position of the peaks together show that the peaks have separations differing from 0.07 eV, which indicates that the explanation of [3] at best does not fully agree with the data.

Moreover, Fig. 1a also shows that the intensity ratios of the peaks vary from crystal to crystal under fixed conditions, which shows that the blue band is not homogeneous (due to centers of one type). This is clear also from the temperature dependence of the energy distribution within the band (Fig. 1b); even a small temperature for a crystal with a low activation energy for electron conduction causes loss of the short-wave peaks and occurrence of a more pronounced

structure at 2.6–2.7 eV. This can be understood if the shallowest donor levels cease to participate in radiative recombination due to thermal depletion. The deep valleys in the 2.6–2.7 eV region indicate that these levels give rise to more than one band.

We had available crystals containing only a little nitrogen (donor concentration 3.6×10^{17} cm^{-3}); some of these were n-type, and emission analysis indicated traces of Al, which in SiC is an acceptor forming local levels 0.22–0.27 eV from the valence band [4].

Another batch of nitrogen-depleted crystals was deliberately doped with Al during growth; emission spectra showed that these contained $1–8 \times 10^{18}$ cm^{-3} Al. These were p-type, the activation energy for the hole conduction being 0.16––0.18 eV. The hole conductivity was partly balanced by the donors, whose concentration was roughly as for the n-type crystals depleted of nitrogen.

Nitrogen-depleted SiC crystals, whether n-type or p-type, give spectra differring from those of Fig. 1a in that the over-all maximum lies at 2.45 eV, which corresponds to a photon energy reduced by 0.2 eV, while the region of the blue band has a linelike spectrum (full line in Fig. 2). The color of the emission is determined by the 2.45 eV band, which henceforth we call green. This green band has shoulders resembling the peaks and shoulders of the blue band (Fig. 1a). The lines at the shortest wavelength in the linelike part at 77°K have widths differing little from those of the emission lines of iron. This linelike spectrum of α-SiC(6H) at low temperatures has been observed previously [1] on crystals of unknown characteristics; it has been ascribed to three-particle complexes consisting of ionized donors (nitrogen atoms) and excitons localized near these. The linelike spectrum of [1] splits up into three series, which begin with the head lines A_0 B_0, and C_0, and which involve vibrational quanta of 0.030, 0.090, 0.094, and 0.107 eV. Between the lines of series A–C and to the short-wave side of A_0 lie much weaker lines, which may be related to thermally excited states. The energies of these vibrational states are close to the phonon energies. The three series arise from three types of donor center, which correspond to three nonequivalent positions of the nitrogen atom in the lattice of α-SiC(6H). The depth of the donor levels equals the difference between the width of the exciton forbidden band and the positions of the head lines, the values being ΔE_A = 0.16 eV, ΔE_B = 0.20 eV, and ΔE_C = = 0.235 eV. Of course, these depths are not equal to the dissociation energies of the donor centers.

Figure 2 shows the short-wave edge of the blue band, whose features lie in the same spectral positions as the groups of lines in the linelike spectrum. Thus that spectrum is transformed to the blue band at high N concentrations, when the interaction between centers cannot be neglected. This interaction, when the centers are randomly distributed, leads to broadening of the sets of lines into not very prominent peaks; it occurs at concentrations of the order of 10^{18} cm^{-3}, and it points also to concentration quenching that starts at the same N content. Figure 3 illustrates this by reference to the intensity as a function of N content; curve 1 is for the blue band, while curve 2 is the same for another batch of crystals containing more boron. Curve 3 relates to the green band, which is due to Al. Radiationless recombination evidently occurs via the nitrogen centers when these are sufficiently abundant.

The half width of the lines is much less than kT, which shows that the linelike spectrum of SiC is due to local levels, e.g., localized excitons. If the spectrum were due to recombination of electrons localized at donors with holes in the valence band, the width would be much greater, since the holes have an energy distribution of kT order.

This photoluminescence was excited by the UV light of a mercury lamp, whose photon energy is sufficient to transfer electrons from the valence band to the conduction band. The probability of capture of an electron by a hole to give a free exciton is very small at these low temperatures with this weak excitation. Moreover, the linelike spectrum is observed also in phosphorescence, so the dominant process cannot be formation of excitons localized at donors by localization of free excitons. We consider that the three-particle complexes are formed by capture of holes from the valence band at neutral donor centers. The state of a localized exciton in no way differs from the excited state of a center, so hole recombination should be considered as occurring in two stages. First there is the radiationless binding of a hole in a localized exciton state, which is followed by the radiative transition. This agrees with the temperature dependence of the blue band (Fig. 1b), in which the loss of some peaks causes dips to occur, this being caused by thermal ionization of
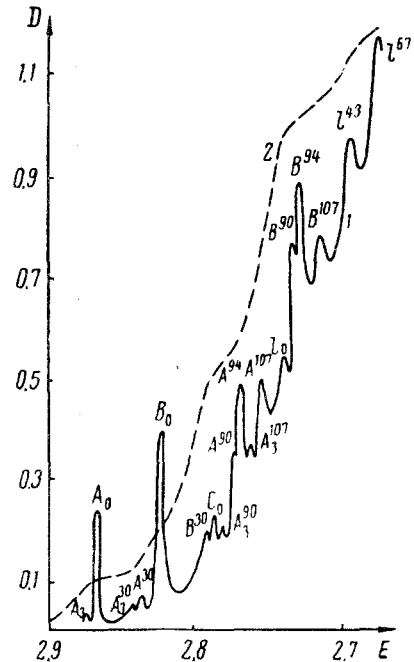

Fig. 2. Short-wave part of the low-temperature photoluminescence spectrum of α-SiC(6H) crystals: a) batch 214, nitrogen-depleted; b) batch 76, fairly high N concentration. D is the optical density of the film; E is in eV.

the type A donors (Fig. 2), which become incapable of hole capture. The structure of the linelike spectrum thus resembles that of optical spectra of the Mossbauer type, whose theory is considered in [5-7]; such spectra have been observed for other crystals [8].

The intensity ratio of the linelike spectrum and green band is not constant, which means that at least some part of the green band is not due to the nitrogen. The green band occurs in p-type crystals containing Al and in crystals with highly compensated n-type conduction. This indicates that the green band is due to Al, which acts as an acceptor in SiC.

If the fluorescence mechanism of the acceptor centers is as for donor ones, but with the three-particle complexes formed by trapping of conduction-band electrons at neutral acceptors, then we would expect a linelike spectrum due to excitons localized at the Al*. In fact, in certain crystals we find five fairly strong lines that cannot be fitted into the series associated with the donors; these lie at $l_0 = 2.74$ eV, $l_{43} = 2.699$, $l_{67} = 2.675$, $l_{43+43} = 2.655$, $l_{105} = 2.635$ eV (Fig. 2). The phonons of this l-series coincide with those involved in the indirect transitions that give rise to the structure at the edge of the principal absorption band. Taking l_0 as the head line of the l-series, the distance of the Al level from the valence band is $E_g - l_0 - E_l = 0.33$ eV $-E_l$, in which E_g is the width of the forbidden band and E_l is the energy involved in trapping an electron to form a three-particle center.
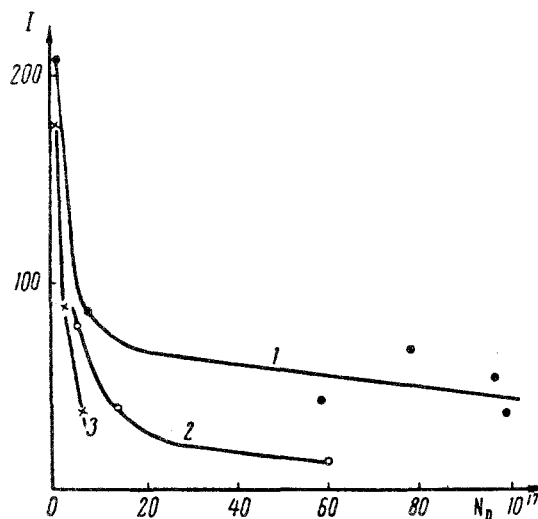

Fig. 3. Intensity I of the blue band for two batches of crystals (curves 1 and 2) and of the green band (curve 3) in relation to donor (nitrogen) concentration.

The lattice of α-SiC(6H) should have three nonequivalent positions for Al, which should give rise to three levels of acceptor type. Two of these are not observed in these spectra, perhaps because they are shallower, and in crystals with partly compensated p-type conduction are filled with electrons, thus not participating in forming three-particle complexes. This argument agrees with the data of [10], which indicate approximate energies of 0.18 and 0.12 eV for the Al levels. Thermoluminescence data [11] also indicate that the Al levels are shallow.

We consider that the green band with its peak at 2.45 eV is a phonon development of the linelike spectrum of excitons localized at Al. Unfortunately, the high Al concentration in our crystals prevents observation of a more detailed structure; but it is possible that some contribution to the green band comes from emission by donor-acceptor pairs formed by N and Al, the energy distance between the levels of such pairs corresponding to the spectral positions of the green band. At present there is no direct experimental evidence for such transitions.

Conclusions

1. The structure of the short-wave part of the blue luminiscence is dependent on the nitrogen concentration, nitrogen acting as a donor in α-SiC(6H). The linelike spectrum is converted to a rather featureless blue band by interaction between centers, which occurs at fairly high nitrogen concentrations.

2. The linelike spectrum is found to contain a new series of lines due to transitions to Al, which acts as an acceptor.

3. The low-temperature luminescence spectra agree with the idea that radiative recombination of nonequilibrium carriers occurs in two stages: capture by an emission center to give an excited state, which then goes over to the ground state.

4. The detailed structure indicates that the general peaks in the blue and green bands are due to interaction of phonons with the purely electronic transitions; the peak in the blue band is shifted relative to the purely electronic transition by 0.23 eV, while the shift for the green band is 0.28 eV.

5. This approach eliminates the apparent contradiction between the spectra and the electrophysical data on the energy structure of local centers; the spectra enable one to establish the general origin of the low-temperature luminescence.

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*Some other crystals [9] show emission due to excitons localized at acceptors.

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