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Donor binding energies determined from temperature dependence of photoluminescence spectra in undoped and aluminum-doped beta SiC films

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Measurements of the temperature dependence of N-Al donor-acceptor pair photoluminescence spectra in cubic SiC films demonstrate that the thermal activation energy for the nitrogen donors is equivalent to the 54 meV binding energy for nitrogen determined from the spectral energies of the sharp-line close pair spectra. It follows that the 15–20 meV donor which dominates the electrical properties of *n*-type films is not isolated, substitutional nitrogen. Spatial variations observed in the intensity of a new 2.368 eV luminescence band demonstrate that the radiative recombination centers are inhomogeneously distributed in the films.

Recently, there have been several reports of temperature-dependent Hall measurements in *n*-type cubic SiC films grown by chemical vapor deposition (CVD) on Si substrates.[1-4] After some initial controversy, there appears to be agreement[3,4] that the electrical properties of *n*-type undoped films are controlled by a shallow donor with binding energy E_D of the order of 15–20 meV. These donors can be present in concentrations N_D in excess of 10^{18} cm^{-3}, but are highly compensated ($\sim 95\%$) by background acceptors. The only donor which has been identified in Lely- and CVD-grown cubic SiC [by photoluminescence (PL)[5-7] and electron paramagnetic resonance (EPR)[4-8] techniques] either as a contaminant or an intentional dopant is nitrogen, and Segall *et al.*[2,3] have assigned the $\sim$15–20 meV donor level in the SiC films to nitrogen. However, the nitrogen donor binding energy has been measured as 53.6 meV from studies of the two electron satellites of the nitrogen-bound exciton PL band[9] in undoped Lely crystals and, independently, as 53.5 meV from nitrogen-aluminum donor-acceptor pair (DAP) PL spectra in both Lely- and CVD-grown aluminum-doped samples.[4,9-11]

Segall *et al.*[2,3] explained this apparent discrepancy by suggesting that the donor binding energy as measured by temperature-dependent Hall effect (thermal activation energy) is a function of N_D and is reduced from the $\sim$54 meV "dilute" value measured in high-purity crystals to $\sim$15–20 meV in the CVD films for which $N_D \sim 10^{17}$–10^{18} cm^3. On the other hand, Suzuki *et al.*[1] have questioned the assignment of the shallow donors in undoped films of SiC to residual nitrogen and suggest that the electrical properties of these films are controlled by nonstoichiometric defects.

In the present work we have measured the nitrogen donor binding energy from the thermally activated quenching of the nitrogen-aluminum DAP PL intensity. The PL quenching data are consistent with the $\sim$53–54 meV E_D for nitrogen inferred previously from PL spectroscopic data and indicate that it is not likely that isolated, substitutional nitrogen is the unidentified 15–20 meV donor in CVD-grown cubic SiC. In addition, we report the observation of a new PL band in *n*-type, undoped, CVD SiC whose intensity reveals spatial inhomogeneities in the distribution of recombination centers in these films.

The nitrogen-aluminum DAP PL spectra were studied in Al-doped films grown on Si substrates by the CVD process[12] described previously. Aluminum doping was accomplished by introducing trimethyl aluminum with the source gases. Undoped *n*-type samples were prepared by the same procedure, but for several values of the source gas ratio C/Si. The films were removed from their substrates for the PL measurements which were carried out at temperatures ranging from 1.5 to 130 K. Optical excitation was provided by 476 nm light from an argon ion laser; the PL spectra were analyzed by a double-grating monochromator and detected by a GaAs photomultiplier tube.

The DAP PL spectrum obtained from an Al-doped sample at 1.5 K is shown in Fig. 1. The sharp-line spectra between 2.20 and 2.35 eV are equivalent in every detail to the DA-pair PL spectra reported by Choyke and Patrick[10] (CP) in Al-doped Lely-grown crystals of cubic SiC, which they attributed to radiative recombination at close N-Al pairs. The same interpretation is applicable to these Al-doped films in which EPR measurements under optical illumination[13] have detected the presence of residual nitrogen donors. Quantitative analysis of the spectral energies of the sharp-

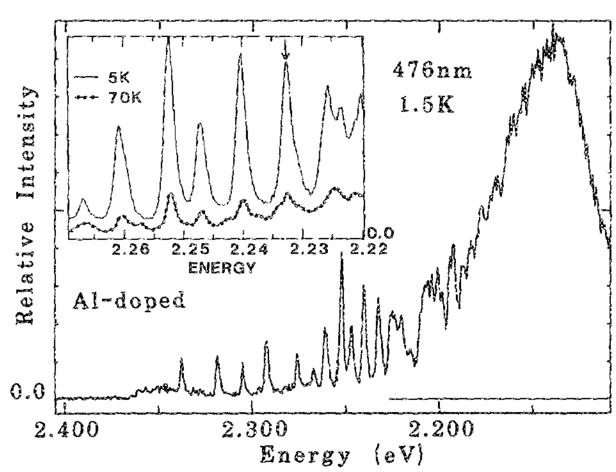

FIG. 1. Low-temperature photoluminescence spectra from an Al-doped cubic SiC film showing sharp-line close DAP spectra. The inset compares an expanded portion of the DAP spectra for 5 and 70 K, and illustrates the thermal quenching of the luminescence intensity. The arrow in the inset indicates the 2.233 eV PL band whose temperature dependence is plotted in Fig. 2 (curve *a*).

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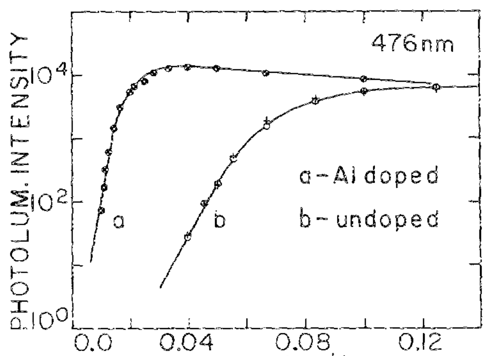

FIG. 2. Photoluminescence intensity as a function of reciprocal temperature for the 2.233 eV N-Al DAP line in an Al-doped film (curve *a*) and the 2.322 eV TA phonon replica of the new PL band in undoped films grown with C/Si ratios of 1.2 (O) and 1.6 (+) (curve *b*).

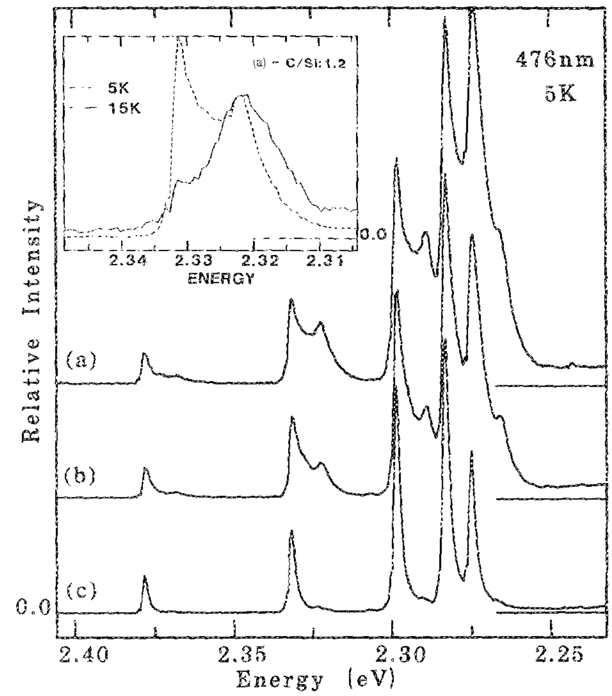

FIG. 3. Low-temperature photoluminescence spectra from three undoped SiC films grown with three different values of C/Si ratio: (a) 1.2, (b) 1.6, and (c) 2.4. The new PL band appears as low-energy shoulders on the ZPL and four phonon replicas of the sharp-line nitrogen bound exciton spectrum. The TA phonon replica portion of spectrum (a) is shown in the inset for 5 and 15 K.

line close pair spectra for the cubic SiC films confirms the 257 and 53 meV values for the Al acceptor and N donor binding energies, respectively, which were inferred[9,11] from the data of CP.[10]

A portion of the sharp-line close DAP spectrum is shown in expanded form in the inset in Fig. 1 for temperatures of 5 and 70 K, illustrating the quenching of the PL intensity with increasing temperature. Curve *a* in Fig. 2 shows the temperature dependence of the intensity of the 2.233 eV sharp close pair PL line labeled in the inset in Fig. 1 for temperatures from 8 to 95 K. The DA-pair PL spectra arise from the radiative recombination of electrons bound at neutral donors with holes bound at neutral acceptors.[14] Because the nitrogen donor binding energy is about one-fifth that of the aluminum acceptor, the holes will remain bound to the aluminum acceptors over the temperature range of the donor ionization, and the PL quenching curve is characterized primarily by the donor binding energy.[14] Thus the analysis of the PL quenching curve provides a thermal activation energy for the nitrogen donors which can be compared to the binding energy inferred from the spectral energies of the sharp-line DA-pair PL spectra.

The value of the donor binding energy is given by the slope, E_D/kT, of the exponential quenching curve at the highest temperatures, and the data are clearly consistent with the 54 meV value of E_D employed in the theoretical fit[15] of Fig. 2 (solid curve *a*). Thus for those nitrogen atoms which are involved in the DA-pair PL process there does not appear to be a discrepancy between the nitrogen donor binding energy inferred from the PL transition energies (the so-called optical or "dilute" value) and the thermal activation energy (which would be measured by the Hall effect if isolated nitrogen donors dominated the electronic transport). It follows that the ~15–20 meV shallow donor level which dominates the electrical properties of all undoped *n*-type SiC films cannot be ascribed to isolated, substitutional nitrogen. If nitrogen is associated with the ~15–20 meV shallow donor, it can only be in inhomogeneities in the films where nitrogen is incorporated at much higher concentrations (with lower effective binding energy[2,3]) or indirectly in the formation of other defects such as defect-impurity complexes or nonstoichiometric defects.

This conclusion is consistent with our observation of a new PL band in thin-film cubic SiC whose intensity demonstrates the existence of spatial inhomogeneities in the films. The near-band-edge PL spectra from undoped films of SiC grown with source gas ratios ranging from 1.2 to 3.0 are shown in Fig. 3. This spectral range is usually dominated for undoped samples by the five-line nitrogen-bound exciton (NBE) PL spectrum,[5,6,9] and this is true of the PL spectrum (c) in Fig. 3 for C/Si ratio of 2.4. The NBE spectrum, consisting of a zero phonon line (ZPL) at 2.378 eV and four sharp phonon replicas at lower energies, is regarded as a fingerprint for the presence of nitrogen in cubic SiC.[5,9] Careful examination of the NBE spectra from CVD films of cubic SiC reveals that most *n*-type samples exhibit weak shoulders on the low-energy side of the ZPL and each of the well-resolved phonon replicas (Fig. 3). In addition, we have now found that the relative strengths of the NBE spectrum and these low-energy shoulders are a function of the C/Si source gas ratio. As shown in Fig. 3 spectra (a) and (b), for the lower C/Si ratios the intensity of the shoulders is greatly enhanced, suggesting that the recombination centers giving rise to these PL transitions (shoulders) might be associated directly or indirectly with nonstoichiometric defects such as Si interstitials or C vacancies.

We have studied the line shape and temperature dependence of the ~2.322 eV transverse acoustic (TA) phonon replica of the new PL band because it is much stronger than its ~2.368 eV ZPL and is well resolved from the other replicas. The thermal quenching curves for the intensity of the 2.322 eV PL band (TA replica) in two undoped films are

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shown in Fig. 2. Curve b is a fit to the data (circles in Fig. 2) for the sample with a C/Si ratio of 1.2 by the procedure[15] used for curve a, and the resulting thermal quenching energy for the PL band is 17 meV. Similar measurements on the NBE PL spectrum produced a thermal quenching energy of about 11 meV, which is in good agreement with the binding energy of the nitrogen-bound excitons reported by Choyke *et al.*[5] Because the NBE PL spectrum quenches at lower temperatures than the new PL band, the line shape of the new PL band can be distinguished clearly without influence from the overlapping NBE spectrum for $T > 15$ K, as shown in the inset in Fig. 3. It is evident that the new PL band is much broader than the sharp-line features of the NBE spectrum.

The most probable alternative interpretations of the 2.368 eV ZPL and its phonon replicas are that it is either another donor-bound exciton band or a donor free-to-bound transition. We first consider the bound exciton alternative. At 2.368 eV the ZPL is positioned about 22 meV below the 2.390 eV exciton energy gap of cubic SiC[5]; thus the measured 17 meV thermal quenching energy for the PL band is approximately consistent with an exciton binding energy derived from the spectral position of the band. However, the width of the new PL band is approximately five times that of the NBE spectrum, and it is unlikely that two donor-bound exciton bands of such disparate widths could originate from the same regions of the sample, i.e., having comparable crystal quality. It seems more likely that the sharp-line NBE spectrum originates from isolated nitrogen donors which are substituted in a relatively high quality crystal lattice, while the broader 2.368 eV PL band, if it is a bound exciton spectrum, must arise from recombination centers in inhomogeneities in the SiC film. These unidentified centers could presumably be present at much higher concentrations or in highly strained environments which contribute to the spectral broadening of the PL bands. It should also be pointed out that if the 2.368 eV PL band is attributable to the recombination of excitons bound to neutral donors, the application of Haynes's rule[16] would yield an estimate of 90–120 meV for the binding energy of the postulated donors, and thus the new PL band could not be associated with the 15–20 meV donor level observed in the transport measurements.

The alternative interpretation is to assign the shoulders on the low-energy side of the NBE spectra to the ZPL and phonon replicas of a donor free-to-bound transition, that is, electrons bound at neutral donors recombining with free holes at the top of the valence band. In this interpretation the donor binding energy is given by the difference between the 2.368 eV ZPL and the 2.403 eV low-temperature band gap[11] of cubic SiC or $E_D = 35$ meV. Obviously this estimate is substantially larger than the 17 meV thermal quenching energy. Thus there are unresolved ambiguities in both of the proposed recombination mechanisms, and it must be concluded that it is not possible at this time to decide which of the alternative interpretations of the new PL band is correct.

The spectra of Fig. 3 were obtained with the exciting laser beam focused into a linear image a few mm in length in order to obtain PL from a relatively large area of the film. The exciting light was weakly absorbed so that the entire thickness of the film was excited. However, if the exciting light is focused to a 100–200 μm diameter spot, large variations in the relative intensities of the NBE and new PL spectra are observed as the spot is translated across the film. For some locations, the new PL bands (shoulders) were observed to dominate the PL spectrum. Thus the nitrogen donors and the unidentified recombination centers are distinctly different centers, and they appear to be inhomogeneously distributed throughout the films. If this indication of inhomogeneity is verified in terms of electrically active centers, it could pose difficulties for the interpretation of Hall measurements in such films.

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