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Ga-bound excitons in 3*C*-, 4*H*-, and 6*H*-SiC

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We report a photoluminescence (PL) study from p-type gallium-doped SiC epilayers, which reveals a PL spectrum constituted of a set of sharp lines and interpreted as excitons bound to the Ga acceptor. The PL spectrum consists of several zero-phonon lines, which are very close to or superimposed on the nitrogen-bound excitons in the 4H- and 6H-SiC. The intensity of the PL spectrum depends on the Ga concentration introduced during the growth of the epilayers. The applicability of the Haynes rule is shown for the acceptors in SiC. A comparison with the aluminum-bound exciton is also presented.

Today SiC attracts much attention, due to its potential application for high-power, high-frequency, and high-temperature devices. Recent efforts in crystal growth have led to significant improvements of the material quality, which now makes the performance of more detailed and fundamental spectroscopic studies possible. The acceptor impurities were earlier only studied via the donor-acceptor-pair emission;[1,2] however, recently, a report revealing photoluminescence (PL) lines associated with the aluminum-bound exciton (BE) has been published.[3]

We present PL excitonic lines associated with the acceptor gallium in SiC material grown by chemical vapor deposition (CVD). The spectra are found to be dependent on the growth conditions, such as the flux and vapor pressure of the trimethylgallium (TMG) used as the doping source. A comparison with the aluminum-bound exciton spectrum is also presented to understand the multiplicity of the observed no-phonon lines. Moreover, the gallium impurity is found to be a good alternative p-type dopant, since a lower memory effect in the CVD reactor and probably a better doping uniformity of the layer are observed in comparison with the aluminum case.

The samples used in this study are CVD epitaxial films grown in a hot-wall reactor with a SiC coated graphite susceptor previously described elsewhere.[4,5] The films are typically 15–20 μm thick and grown on off-axis Si(0001)-face n-type (10^{18} cm^{-3}) substrates from Cree Research Inc. The growths were performed by passing reactive gases (silane and propane diluted to 1%) through the susceptor inside which the substrates were placed. Hydrogen was used as the carrier gas and the p-type doping was achieved by small additions of TMG, for which the flux and vapor pressure could be controlled. The mole fraction of Ga could thus be varied from 0 to 0.208. All growths were performed at a temperature of 1550 °C and with a C/Si ratio of 3.

Low-temperature PL spectra of the near-band-gap emission of the different SiC polytypes were recorded at a temperature of about 1.8 K, using the UV line at 334.5 nm of an Ar^{+}-ion laser as an excitation source. The luminescence was dispersed by a SPEX 1404 0.85-m double grating monochromator, fitted with two 1200 grooves/mm gratings blazed at 5000 Å and detected by a UV sensitive Hamamatsu photomultiplier tube operating in a photon-counting mode.

Figure 1(a) shows a typical PL spectrum recorded in the near-band-gap region of a low-doped n-type 6H-SiC epilayer, which contains several sharp lines related to the recombination of three zero-phonon N-BE lines,[6] labeled as the P_0, R_0, and S_0, respectively, and to the recombination of the free exciton (FE), which is denoted as I, where the subscript denotes the energy of the assisting phonon (in meV) involved in the recombination process.[6] For this n-type sample, no contribution from the Al impurity was observed, which should give rise to a set of sharp BE lines in the energy range of 3000–3005 meV (4132–4125 Å). The I_{77} line intensity as compared to the R_0 and S_0 N-BE lines leads, according to Ref. 7, to a nitrogen impurity concentration of 4×10^{14} cm^{-3}.

When a small amount of TMG is added to the gas flow during growth, PL lines with an energy position close to the N-BE lines can be observed. This part of the spectrum will be discussed in more detail below. A decrease in intensity of the I_{77} FE line relative to the N-BE lines [Fig. 1(b)] is also noticed. As the flux of the TMG is increased, more acceptor impurities are introduced into the epilayers [Fig. 1(c)], and the I_{77} FE line will decrease[7] to finally vanish for growths with high TMG fluxes [Fig. 1(d)].

Figure 2 shows PL spectra recorded with higher resolution than in Fig. 1. The dashed lines show the energy posi-

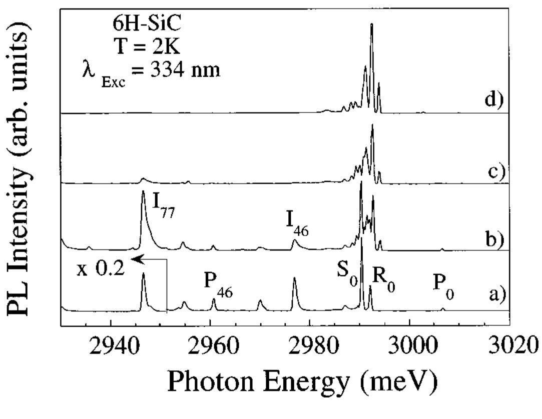

FIG. 1. Photoluminescence spectra at 2 K from the near band-gap emission of 6H-SiC epilayers from the n-type undoped-reference sample (a), and various Ga-doped epilayers with the mole fraction of Ga during growth equal to 0.01 (b), 0.034 (c), and 0.068 (d).

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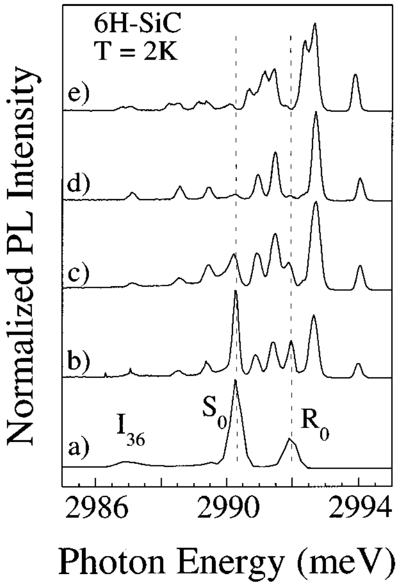

FIG. 2. High-resolution photoluminescence spectra of the undoped reference (a), and of various Ga-doped epilayers with the mole fraction of Ga during growth equal to 0.01 (b), 0.034 (c), 0.068 (d), and 0.205 (e).

tion of the well-known nitrogen BE lines. When the TMG is added to the gas flow during growth, sharp lines interpreted as Ga-BE lines are observed around the N-BE lines from the samples. With a high TMG flux, the N-BE lines are very weakly seen, and almost only the Ga-BE lines are observed. At very high Ga doping, a structure appears in the Ga-BE spectrum [Fig. 2(e)], which could be interpreted as a splitting of some of the BE lines of the previous spectrum [Figs. 2(b)–2(d)]. The intensity of the Ga-BE lines first increases with increasing TMG flux, but reaches rapidly a saturation. We, thus, associate this series of very sharp and closely spaced lines with the recombination of excitons bound to Ga impurities without emission of phonons. The exciton binding energy (E_{BX}) of the Ga-BE in 6H-SiC is deduced from the excitonic band gap (E_{GX}) to be in the range 29–37 meV. Weak but distinct phonon-assisted replicas of the Ga-BE zero-phonon lines are observed with the dominant phonon energies of 77, 97, and 106 meV, which are similar to the phonon energies observed for the N-BE lines or FE emissions in 6H-SiC.

For the N-BE lines, as well as for the PL spectrum related to the Ga-BE, a slight blueshift, with a maximum value of 0.5 meV, of the energy position could be observed on some spots of the samples. This behavior could be associated with small inhomogeneities of the samples, mainly induced by strain effects.

The PL intensities of all the sharp lines associated with the Ga-BE show a similar excitation power dependence. This behavior indicates that the series of the observed sharp lines cannot be associated to multibound exciton complexes.[8] The temperature dependence of the PL spectrum associated with the Ga-BE in 6H-SiC shows a decrease of the PL intensity from about 25 K, with a complete quenching above 85 K. Polarization measurements were carried out and the observed luminescence was found to be predominantly polarized perpendicular to the growth direction.

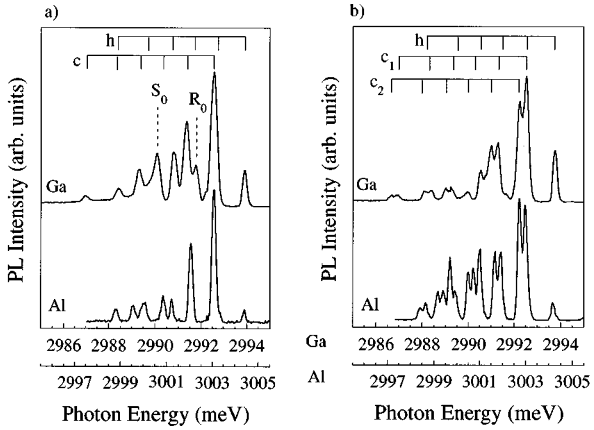

FIG. 3. Comparison of the photoluminescence spectra of Ga- (top spectra) and Al- (bottom spectra) doped 6H-SiC epilayer for (a) low- and (b) high-acceptor concentration, respectively. The drawing on the top of each part shows the possibility of superposition of the PL lines.

Preliminary lifetime measurements of the dominant Ga-related line (4141.8 Å–2992.6 meV) were carried out and a decay time faster than our detection limit (150 ps) was observed at 2 K. This fast decay time is believed to be related to a strong Auger effect in the recombination process, as suggested for the N-BE emission.[9]

In Figs. 3(a) and 3(b), a comparison between the PL spectrum of the Ga-BE and that of the Al-BE is presented for low-doped and highly doped 6H-SiC material, respectively. The spectra are plotted for an easy comparison by shifting the horizontal axis in such a way that the highest-energy lines coincide in the plot. A very good correlation can be observed for the structure in both cases of doping. The sample with low Al doping was grown in the same CVD reactor as the Ga-doped samples. However, the growth parameters were different from those for the reference sample [Fig. 1(a)] giving a lightly compensated p-type material with a carrier concentration below 10^{14} cm^{-3}. The PL spectra recorded in the Al-BE region were, however, spot dependent: on some spots of the sample, the PL spectrum was as presented in Fig. 3(a), whereas other spots show a similar PL spectrum to that of Fig. 3(b), indicating an inhomogeneity of the Al impurity distribution in the layer. This behavior was more weakly observed for the Ga-doped epilayers. The highly Al-doped layer was grown in a high-temperature CVD reactor, which was recently presented.[10] As can be seen from these figures, a very good correlation between the Al- and Ga-BE spectra can be observed. For low-doped samples, up to eight lines are first observed for Ga-BE and nine for Al-BE, respectively. A superposition of lines can, however, be assumed and we propose tentatively that two families of six lines give rise to the PL spectrum, as indicated in Fig. 3(a). One family is supposed to arise from the Ga atoms at the hexagonal site, whereas the other could be from Ga atoms at the two inequivalent cubic sites. From comparison with the N-BE's, the energy separation between the BE lines, arising from the cubic sites (1.7 meV between the R_0 and S_0 N-BE lines), is very small compared to that between the hexagonal related site (P_0 line) and the cubic sites (about 14.5 meV). Since the energy spectra of the ac-

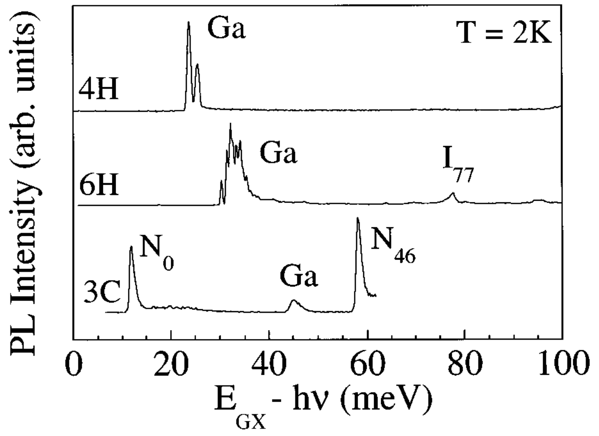

FIG. 4. Photoluminescence spectra of 3*C*-, 6*H*-, and 4*H*-polytype epilayers doped with gallium.

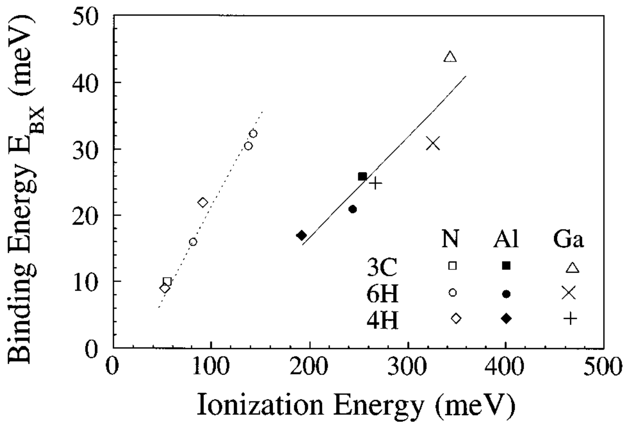

FIG. 5. Exciton binding energies, as a function of the ionization energies in various SiC polytypes.

ceptor BE is much more condensed than that of the N-BE, it is likely that the Ga-BE's at the two cubic sites are indistinguishable. When the doping concentration increases, however, the lines originating from these cubic sites can be seen as two components. The observed splittings or separations are almost equidistant with a maximum energy separation of about 0.3 and 0.5 meV for the Ga- and Al-BE, respectively, leading to the appearance of three families of six lines in the PL spectrum [see Fig. 3(b)]. The splitting occurs for the Al-BE already at relatively low Al concentration, which may indicate clustering effects of the Al impurities.

Investigations of Ga-doped 3*C* and 4*H* polytypes were also carried out. Figure 4 illustrates the PL spectra recorded for the three investigated polytypes, where the data are plotted so that the horizontal axis indicates the exciton binding energy. For the 3*C* polytype, a quite broad asymmetric line is observed around 2346 meV, leading to $E_{\mathrm{BX}}=44$ meV. This line probably consists of several unresolved zero-phonon lines. Weak phonon replicas were also observed with energies close to those reported for the N-donor BE or Al-acceptor BE.

In 4*H*-SiC, at least two broad PL lines are suggested to be the Ga-BE zero-phonon lines with an E_{BX} of about 23.8 and 25.6 meV, respectively. With high-resolution measurements, these broad lines are observed to be composed of three components, leading to the observation of six different lines. Just as for 6*H*-SiC, the Al-BE and Ga-BE PL spectra are similar, also, for the 3*C* and 4*H* polytypes.

The closely spaced series of very sharp and shallow lines of lightly aluminum-doped *p*-type SiC have previously been observed and associated with the recombination of a neutral Al-acceptor bound exciton.[3] Although the authors were not able to assign the specific transitions at that time,[11] a group theoretical model originally developed by Dean *et al.*[12] was applied to explain the multiplicity of the observed transitions. We propose, thus, in analogy with the work done on Al-doped SiC, that the series of sharp lines reported here is due to the recombination of excitons bound to Ga impurities. For each inequivalent Ga site the model predicts 6, 3, and 12 states for 6*H*-, 4*H*-, and 3*C*-SiC, respectively, leading to a total of 18, 6, and 12 recombination lines for the three polytypes. For 4*H*, we actually observe six PL lines (2×3 lines). We cannot resolve the 12 PL lines for 3*C*. Following the tentative assignment in Fig. 3 for 6*H*, we have 12 lines (although some of them are superimposed on others) in the low-doped case and 18 lines in the highly doped case. It is not clear why 18 lines appear for the high doping. It may be related to strain-induced splitting of orientational degeneracy or to the interaction between close BE pairs residing at cubic sites.

The exciton binding energy (E_{BX}) can often be described in semiconductors as a simple, linear function of the ionization energy of the impurity. This Haynes rule was shown to be applicable relatively well for the N donors in various polytypes.[1] We present in Fig. 5 the data obtained for the N donor (E_D is the ionization energy of the donor from recently published works[13–15]). For the acceptor BE's in Fig. 5, we plot only the binding energy of the most intense PL BE line. The ionization energies of the acceptors (E_A) in this figure are an average of the energies published for acceptor impurities occupying the hexagonal-like and cubiclike sites from Ref. 1. The least-squares linear fit of these data yields the relations

$$E_{\mathrm{BDX}}=-3.58\ \text{meV}+0.25E_D, \tag{1}$$

$$E_{\mathrm{BAX}}=-14.9\ \text{meV}+0.16E_A, \tag{2}$$

for the donors and acceptors, respectively.

In summary, we have observed a set of closely spaced, very sharp and shallow lines in the low-temperature PL spectrum of gallium-doped SiC epilayers. These PL lines are believed to be due to the recombination of excitons bound to the gallium impurity. The Haynes rule is shown to be applicable for the acceptors in SiC.

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