PHYSICAL REVIEW B **71**, 241201(R) (2005)

Ionization energies of phosphorus and nitrogen donors and aluminum acceptors in 4*H* silicon carbide from the donor-acceptor pair emission

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(Received 16 February 2005; revised manuscript received 18 April 2005; published 7 June 2005)

This paper deals with fitting the donor-acceptor pair luminescence due to P-Al pairs in 4*H*-SiC. It was possible to identify P at the Si cubic site as the shallower donor with ionization energy of 60.7 meV, as well as to distinguish the contribution in the spectrum from pairs involving this donor and Al acceptors from both the cubic and hexagonal lattice sites, leading to justification of their ionization energies. The case of N-Al pair luminescence was revisited and the ionization energy of the deeper N_c donor at the cubic site was determined, 125.5 meV.

DOI: 10.1103/PhysRevB.71.241201 PACS number(s): 78.55.−m, 71.55.−i, 71.35.−y, 78.55.Hx

In the past few years a considerable amount of work has been dedicated to the investigation of phosphorus as an alternative for nitrogen as *n*-type dopant of both 6*H* and 4*H* polytypes of SiC. While the 4*H* polytype is more interesting for industrial applications, most of the papers consider only 6*H* SiC,[1] and very scarce data is available in the literature considering the optical properties of the phosphorus shallow donor in 4*H* SiC.[2] A recent study of *in situ* P-doped 4*H*-SiC based on Hall measurements resolves two donor levels with ionization energies about 50–52 and 78–80 meV.[3] An electron paramagnetic resonance (EPR) study of P in 4*H* and 6*H* SiC assigned the observed level to P at the hexagonal site, but the assignment for 4*H* SiC was based only on the analogy with 6*H* SiC.[4] The hyperfine interactions observed in this work identify the isolated P donor as substitutional for Si.

The purpose of this study is to use the donor-acceptor pair (DAP) luminescence from phosphorus-aluminum (P-Al) pairs for characterization of the phosphorus donors in 4*H*-SiC. The fitting of the DAP spectrum can be used to obtain accurately the ionization energy of (at least) the shallower P donor, as well as identify its position in the crystal lattice. The approach is the same as the one described in Ref. 5, where it was used for fitting the nitrogen-aluminum (N-Al) pair luminescence. It will be convenient to distinguish the ionization energies of the different donors or acceptors by a subscript identifying the species, e.g., E_{N_h} relates to the donor N_h etc., where the index after the chemical symbol denotes the lattice site, *h* for hexagonal and *k* for cubic. Since the acceptor, aluminum in our case, is the same as in Ref. 5, and the ionization energy of the shallower N donor is accurately known, 61.4 meV,[6] the ionization energy of the shallower phosphorus donor can be obtained by comparison of the corresponding quantities $\hbar\omega_\infty$, obtained from the fits of the N-Al and P-Al pair spectra. Here we use the notation

$$\hbar\omega_\infty = E_g - (E_D + E_A), \tag{1}$$

where E_g is the energy of the electronic band gap, and E_D and E_A are the ionization energies of the relevant donor and acceptor, respectively.

The samples used in this work are epitaxial layers (about 16 μm thick) grown in a hot-wall chemical vapor deposition (CVD) reactor. The doping was performed *in situ* using as dopant sources trimethylaluminium [TMA, $Al(CH_3)_3$] for aluminum and tertiarybutylphosphine (TBP, $C_4H_9PH_2$) for phosphorus. Both Si-face and C-face off-axis substrates (8° off) were used. The doping concentrations for the Si-face sample (sample no. 1) as measured by secondary-ion mass spectroscopy (SIMS) are $[Al]=8.3\ 10^{16}$ and $[P]=2.4\ 10^{16}\ cm^{-3}$. For the sample grown on C face (sample no. 2) the concentrations are estimated to $[Al]\leqslant 6\times 10^{16}$ and $[P]\sim 7-8\times 10^{16}\ cm^{-3}$ from previous experience. The nitrogen concentration is at the background level (high 10^{13}–low $10^{14}\ cm^{-3}$ for the CVD reactor used). This was expected and confirmed to be low enough to avoid any contribution in the DAP spectrum from N-Al pairs. Sample no. 3 used for the N-Al pair emission is described as no. 1 in Ref. 5.

The PL spectra obtained at 2 K using as excitation the 244 nm line from a frequency-doubled Ar laser are shown in Fig. 1. A spectrum of a N-Al doped sample (sample no. 3) is also given for comparison. Both samples [no. 1 and no. 2, Fig. 1(a) and 1(b)] show strong DAP emission with identical structure, which is, however, essentially different from that of the N-Al DAP spectrum in Fig. 1(c) [see also Fig. 2]. As an example, the line at 3087.5 meV marked in Fig. 2 is strong in the N-Al DAP spectrum and missing in the P-Al-doped samples. This leads us to conclude that the observed DAP emission in samples no. 1 and no. 2 can be entirely attributed to P-Al pairs.

We note that, although the structure of the sharp features in the P-Al DAP spectrum is different from that of the N-Al one, the broad bands peaking at about 3060 and 2990 meV are very similar to the corresponding bands in the N-Al case. This is an indication that phosphorus also introduces two donors with significantly different ionization energies, the energy difference being of the order of the difference between the peaks, i.e., about 60–70 meV. Since the peak positions are close in the P-Al and the N-Al cases, the shallower and the deeper levels due to phosphorus are expected to have roughly similar energies to the shallower (N_h) and the deeper (N_k) nitrogen donors, respectively.

Phosphorus is expected to substitute for Si atoms,[7] al-

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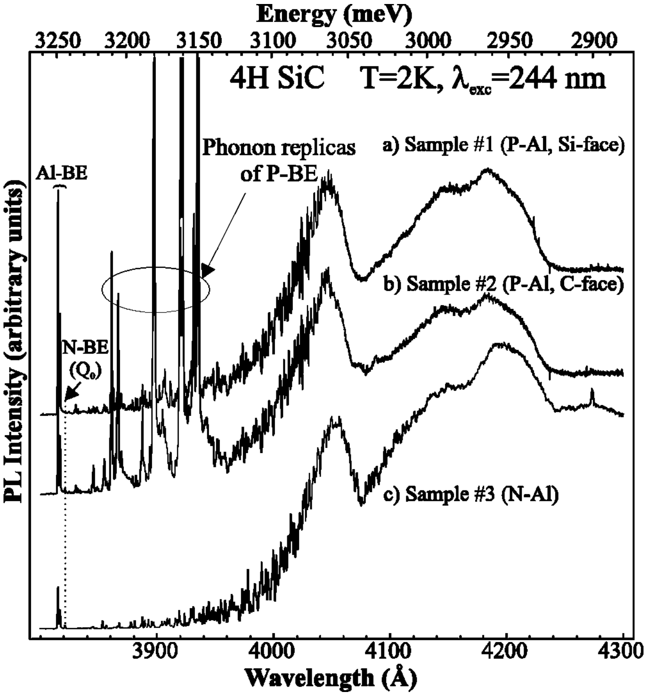

FIG. 1. General view of the photoluminescence spectra of P-Al doped 4*H*-SiC samples compared with the spectrum of the N-Al doped sample. The zero phonon bound exciton (BE) lines of the Al-BE and N-BE are marked. The P-BE spectrum shows mainly phonon replicas with polarization perpendicular to the crystal axis, in accord with Ref. 2.

though, unlike N, it may reside on the both sublattices.[8] Therefore, the fit of the spectrum must be tried with all possible sets [*hh*, *hk* (or its equivalent *kh*) and *kk*, see Ref. 5 for the definition] for both type I and type II arrangements of the donor acceptor pairs. Provided that the Al acceptors reside on the Si-sublattice, in the former case (type I), the donors are also on this sublattice, whereas for type II arrangements (the N-Al case) the donors are on the C sublattice. We shall denote the arrangement type as a subscript of the set, for instance, hk_I denotes the *hk* set of type I. We stipulate that the donor site is written first, hence the donors are at cubic sites in the *kh* set and at hexagonal ones in the *hk* set. Theoretically, for any DAP arrangement these two sets have identical structure but, of course, different value of the shift $\hbar\omega_\infty$ when applied to the spectrum.[5]

The function used to fit the experimental spectrum has the form:

$$f(E) = at_s[E - \hbar\omega_\infty(s)] + P(E), \qquad (2)$$

where E is the variable (photon energy), $\hbar\omega_\infty(s)$ is the energy shift between the experimental spectrum and the theoretically synthesized one, $t_s(E_C)$, for a specific arrangement $s = hh_I, hk_I, kk_I, hh_{II}, hk_{II}$, or kk_{II}, and $P(E)$ is a polynomial (usually of third degree) added to account for smooth variations of the background below the sharp features in the experimental spectrum. The theoretical curves $t_s(E_C)$ were synthesized exactly in the same way as described in Ref. 5 using as a variable only the Coulomb energy E_C of interaction between the donor and acceptor. Parameters of the fit are the amplitude a, the coefficients of $P(E)$, and, of course, the shift $\hbar\omega_\infty(s)$. In practice, a part of t_s is chosen, corresponding to "intermediate" pairs (typically between $32\ \text{meV} < E_C < 62\ \text{meV}$, so that multipole and other corrections can be neglected),[5] and this part is moved along the experimental spectrum by varying the shift. For each value of the shift, a and the coefficients of $P(E)$ are determined using the least-

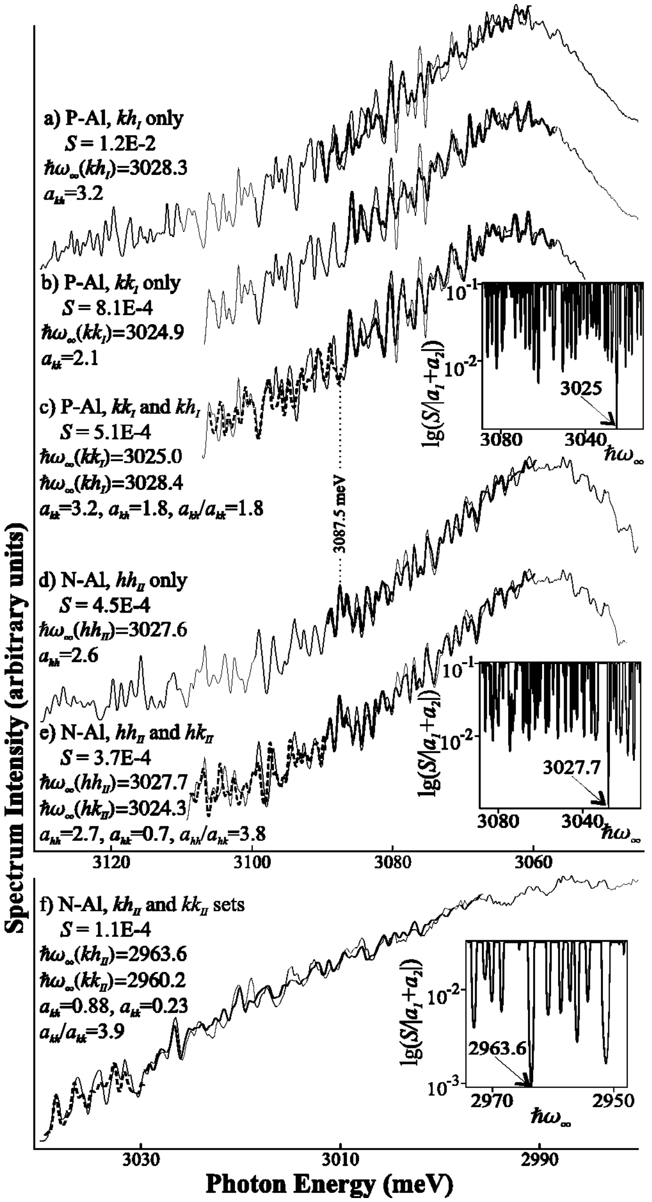

FIG. 2. Fit of the DAP PL for the cases of P-Al and N-Al pair emissions. The black solid lines represent the fit in the fitted region, whereas the dashed lines are the extension of the theoretical curves beyond this region. The variation of the factor $S/|a_1 + a_2|$ is illustrated in the insets next to the curves representing the fits with two sets. All energies are in meV. The least-squares sum S and the amplitudes are displayed in arbitrary units, which, however, are the same for all fits. The amplitudes of the single fits are displayed for comparison with the amplitudes of the double fits. The line at 3087.5 meV is an example of a strong line in the N-Al spectrum, which is absent in the P-Al one.

squares method (LSM). The criterion used in Ref. 5 for selection of the best fit among the different fits obtained for different values of $\hbar\omega_\infty(s)$ was the maximum positive value of the amplitude a, together with the visual inspection of the fit. In this work we use as a criterion the minimum value of the quantity $S/|a|$, where S denotes the sum of the squares of the deviations between the experimental intensity points $I(E_i)$ and $f(E_i)$ [Eq. (2)], and E_i represent the discrete photon energies, at which the experimental spectrum is recorded. The division by $|a|$ is necessary in order to make unfavorable a situation when no modulation in the experimental spectrum is present (consequently, $|a| \approx 0$) and the spectrum can be fitted well with $P(E)$ alone. As will be seen, the dependence of $S/|a|$ on the shift $\hbar\omega_\infty(s)$ exhibits a sharp minimum at the correct value of the shift. The fit is further confirmed by visual inspection.

In the case of N-Al DAP emission, the spectrum was fitted reasonably well with the hh_{II} set alone.[5] In the case of P-Al DAP emission, we found that there are *two* sets that provide an acceptable fit to the corresponding part of the spectrum, namely, kh_I (equivalently, hk_I) and kk_I. However, each of these fits is of significantly worse quality than the fit for N-Al pairs, as illustrated in Fig. 2(a) and 2(b). This prompts us to test a fit with *both* kh_I and kk_I, mutually shifted by the energy value $\Delta = \hbar\omega_\infty(kh_I) - \hbar\omega_\infty(kk_I) = 3.4$ meV. Hence, $f(E)$ needs modification, which in this particular case takes the form:

$$f(E) = a_1 t_{kk_I}[E - \hbar\omega_\infty(kk_I)] + a_2 t_{kh_I}[E - \hbar\omega_\infty(kk_I) + \Delta] + P(E), \tag{3}$$

where now both amplitudes a_1 and a_2 are determined independently using the LSM. When necessary, we shall label the amplitudes with the notation of the relevant set (without indicating its type) instead of the index 1 or 2, see Fig. 2. The criterion for a best fit becomes $S/|a_1 + a_2| = \mathit{minimum}$. The use of two sets results in a much better fit, as shown in Fig. 2(c) together with the variation of $S/|a_1 + a_2|$ over the spectrum. Not only does $S/|a_1 + a_2|$ exhibit a sharp and unambiguous minimum at $\hbar\omega_\infty(kk_I) = 3025.0$ meV, but also all experimentally observed peaks and valleys find their match in the theoretical curve. Moreover, if the theoretical spectrum is extended towards higher energies [the dashed curve in Fig. 2(c)], we find also in the extended region a very good agreement with the experiment. On the high-energy side of this region deviations between the experimental and theoretical peaks become noticeable, which is expected because corrections to the purely Coulomb term become more important for closer pairs. In addition, we have also varied the value of Δ and verified that $\Delta = 3.4$ meV indeed provides the best fit. Thus, we can unambiguously conclude that the values $\hbar\omega_\infty(kk_I) = 3025.0$ and $\hbar\omega_\infty(kh_I) = \hbar\omega_\infty(kk_I) + \Delta = 3028.4$ meV obtained from the fit are correct within 0.1–0.2 meV.

Let us consider the sets used in the fit. The kk_I set certainly involves Al acceptors and P donors at cubic sites in the Si sublattice. The other set is either kh_I, or hk_I, but from the present information we cannot decide whether the acceptor is at the hexagonal site, or the donor. If the donor was at the hexagonal site, then we would have to conclude that the considered part of the spectrum is dominated by emission involving Al_k acceptor and both P_h and P_k donors, and it would be difficult to understand why in the case of N-Al pairs the dominant emission involves mainly the Al_h acceptor. Difficulties arise also with understanding the structure of the broad bands in Fig. 1, similar in the cases of P-Al and N-Al pairs. On the other hand, if we assign the observed emission to the joint contribution of P_k-Al_h and P_k-Al_k pairs, then we are led to conclude that the difference in the ground-state energies of Al_h and Al_k is only 3.4 meV, the former being shallower. This relatively small separation between E_{Al_h} and E_{Al_k} is in good agreement with the results of previous work.[9] In order to confirm or reject this assignment, we will have to reexamine also the N-Al pair spectra.

We are now led to the assumption that both the hh_{II} set and the kh_{II} set are responsible for the observed N-Al DAP emission in the region above ~3060 meV, and the shift between them must be equal to $\Delta = \hbar\omega_\infty(hh_{II}) - \hbar\omega_\infty(hk_{II}) = 3.4$ meV but, possibly, the contribution from the second set is too weak to lead to a significant disagreement of the fit with the hh_{II} set only. Indeed, we do observe a significant improvement of the fit with both sets, as illustrated in Fig. 2(d) and 2(e); the least-squares sum decreases by about 20%. The contribution of the hk_{II} set is a factor of 4 smaller than that of the hh_{II} set [cf. the ratio a_{hh}/a_{hk} in Fig. 2(e)], which explains why the fit is good even with the hh_{II} set alone.

Furthermore, we may consider now the region below ~3050 meV in the N-Al pair spectrum. The fit of the sharp features in this region with only one set (either kh_{II}, or kk_{II}) was attempted in Ref. 5, but did not produce satisfactory results. It is natural to assume that both the kh_{II} and the kk_{II} sets contribute in this region, and in this case the shift between them must again be equal to $\Delta = \hbar\omega_\infty(kh_{II}) - \hbar\omega_\infty(kk_{II}) = 3.4$ meV. In fact, using both sets, it was straightforward to find a much better fit to the experimental spectrum also in this region, as illustrated in Fig. 2(f). It is also remarkable that the corrections in the region of higher Coulomb energies (see the dashed curve) seem to be smaller than in the case when the shallower N_h donor is involved, as should be expected, because the N_k donor responsible for the pair emission below 3050 meV has a significantly larger binding energy (and smaller effective Bohr radius) than N_h. The ionization energy $E_{\mathrm{N}_k} = 125.5$ meV is easily deduced using the difference $\hbar\omega_\infty(hh_{II}) - \hbar\omega_\infty(kh_{II}) = 64.1$ meV and adding it to the known energy $E_{\mathrm{N}_h} = 61.4$ meV.[6]

Note that the ratio of the amplitudes given for the three double fits is a measure of the relative contribution of the two sets in the DAP emission. Thus we find that in all cases the contribution from the set involving Al_h is stronger than from the other set involving Al_k. However, in both cases involving N_h and N_k the contribution from the pair emission involving Al_k is approximately a factor of 4 weaker than that involving Al_h, whereas in the case of the P_k donor this factor is closer to 2. This means that the donor and acceptor effective Bohr radii are not the only factors governing the recombination rate.

Thus our assignment is confirmed and we can conclude that the P-Al DAP spectrum in the region above approximately 3050 meV is, indeed, governed by P_k-Al_h and

P_k-Al_k pair emissions. As mentioned above, the presence of a second broad band centered around 2990–3000 meV is an indication for the presence of a second donor related to phosphorus with roughly 60 meV larger ionization energy than P_k, in analogy to nitrogen. Since P is anticipated to occupy also the hexagonal site on the cubic sublattice, this band probably originates from P_h-Al_h and P_h-Al_k pair emissions. Unfortunately, the sharp features on the high-energy side of this band are too weak to make possible unambiguous identification using the fit, whereas in the case of N-Al DAP luminescence the sharp features in the analogous region 3000–3050 meV are strong enough [cf. Fig. 2(f)] to identify the second donor, N_k, and to determine its ionization energy, 125.5 meV, as described above. Any presence of phosphorus on the carbon sublattice cannot be revealed from the available spectra, probably because of its much lower concentration, in agreement with the theoretical estimations.[10] The results are summarized in Table I.

In conclusion, the analysis of the P-Al DAP luminescence enables us to identify the shallower P donor as P substitutional for Si at a cubic site, as well as to successfully determine the contributions from both Al_k and Al_h in the P-Al DAP emission. Consequently, we were able to determine $E_{P_k}=60.7$ meV, and to justify the difference between the ionization energies $E_{Al_k}=E_{Al_h}+3.4$ meV. Revisiting the case of N-Al DAP emission, we were able to improve the fits presented in Ref. 5 by accounting for the contributions from N_h-Al_k and N_k-Al_k in the spectrum, as well as to determine $E_{N_k}=125.5$ meV. While the values of the donor ionization energies given here are deduced by comparison with the known energy of the shallower nitrogen donor N_h, $E_{N_h}=61.4$ meV,[6] the calculation of the Al-acceptor ionization energies involves the value of the electronic band gap, Eq. (1). Therefore, the values for E_{Al_h} and E_{Al_k} given in Table I depend on the accuracy of E_g (we use $E_g=3287$ meV).[5] However, their difference, $E_{Al_k}-E_{Al_h}=3.4$ meV has the same tolerance as the donor binding energies, i.e., approximately 0.1 meV. Finally, our values for the phosphorus ionization energies are larger than those obtained from the Hall measurements,[1,3] but we notice that underestimating the binding energies when Hall data is interpreted seems to be a rule.

TABLE I. Characteristics of shallow P and N donors and Al acceptors in 4*H*-SiC.

Species	Identification	Ionization energy (meV)
N_{C_h}	on C hexagonal site	61.4[a]
N_{C_k}	on C cubic site	125.5
Al_{Si_h}	on Si hexagonal site	197.9[b]
Al_{Si_k}	on Si cubic site	201.3[b]
P_{Si_k}	on Si cubic site	60.7
P_{Si_h}	on Si hexagonal site	120±20[c]

[a] Accoding to Ref. 6.

[b] Based on the value of the band gap $E_g=3287$ meV from Ref. 5.

[c] The remote-DAP band around 2990 meV is most probably due to the remaining P_h donor on Si site, and the estimate for its energy is based on the analogy with the N-Al DAP spectrum.

We wish to thank Okmetic AB for supplying some of the samples. Support from the SSF program SiCMAT and the Swedish Research Council is gratefully acknowledged.

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