Optical evidence for 630-meV phosphorus donor in synthetic diamond

H. Sternschulte,* K. Thonke, and R. Sauer[†]
Abteilung Halbleiterphysik, Universität Ulm, D-89069 Ulm, Germany

S. Koizumi
National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba, 305-0044, Japan
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Diamond samples doped with phosphorus either during high-pressure/high-temperature synthesis or during chemical vapor deposition growth are studied by cathodoluminescence at low temperatures. Some of the specimens unintentionally contain boron acceptors in low concentrations as demonstrated by the observation of boron-bound exciton emission at 5.215 eV. Other samples show a lower energy-bound exciton line at 5.175 eV relating in intensity to the phosphorus concentration and indicative of a phosphorus impurity or a phosphorus complex. Four samples phosphorus doped by different techniques reveal almost identical discrete donor-acceptor pair-line spectra between 5.2 and 4.7 eV. The appearance of these spectra gives firm evidence for a phosphorus-related donor. Analysis of the spectra assuming boron as the acceptor involved yields an ionization energy of (630 ± 50) meV for the phosphorus donor. [S0163-1829(99)06219-0]

The advent of low-pressure/low-temperature chemical vapor deposition (CVD) techniques for the growth of diamond layers on various substrates and recent improvements in texture, orientation, and morphology of such layers have opened up new perspectives for diamond applications as sensors, actuators, and electronic devices. Whereas it is often sufficient in electronic applications to use p-type layers doped with the acceptor boron other applications require n-type material or, at least, make n-type conductivity highly desirable. Nitrogen as a ''natural'' substitutional donor with an ionization energy of $E_D = 1.7$ eV (Ref. 1) is generally little helpful as it provides a too-low carrier concentration though pn junctions with boron acceptors and nitrogen donors have been successfully demonstrated.[2] Theoretical candidates for shallow donors are phosphorus (substitutional), and lithium and sodium (interstitial). Their ionization energies as calculated by different theoretical approaches vary strongly with values of 200 meV (Ref. 3) or 1090 meV (Ref. 4) for phosphorus, 100 meV for lithium, and 300 meV for sodium.[3] Experimentally, these species have been introduced into diamond by doping diamond layers during CVD growth either on Si substrates[5,6] or on diamond substrates[7,8] and by ion implantation of natural and synthetic diamonds.[9–12] Phosphorus has also been introduced into high-pressure/high temperature (HPHT) diamonds by using this elemental species as a catalyst.[13] In electrical measurements, a direct correlation of n-type conductivity with the prospective donor species introduced is often difficult, since it might be due to defects created by damage during irradiation which is not completely annealed out. Also, hopping conductivity has often been found revealing itself by a thermal behavior $\sigma \sim \exp(T/T_0)^{1/4}$ instead of impurity-to-band activation of donor electrons characterized by $\sigma \sim \exp(-E/kT)$.[10] Recently, Koizumi *et al.*[8] and Kalish *et al.*[14] in Hall measurements on phosphorus-doped homoepitaxial CVD films observed n-type conductivity with exponential activation, and from Arrhenius plots determined apparent activation energies of approximately $(430 \ldots 460)$ or 500 meV, respectively. They

suggested that phosphorus donors on substitutional lattice sites were responsible for the conductivity.

In the present paper we employ luminescence techniques to study phosphorus-doped diamond. First, we find a bound-exciton recombination line at 5.175 eV photon energy, which is tentatively ascribed to the TO-phonon replica of an exciton transition at a substitutional phosphorus atom or a phosphorus-related complex. Second, in four samples containing unintentionally boron and doped with phosphorus by different techniques we observe almost identical line-resolved donor-acceptor pair spectra. The analysis provides firm evidence for phosphorus as a donor. The present spectra in the band-edge region $(5.2 \ldots 4.7$ eV$)$ are different from previously reported donor-acceptor pair-line spectra at much lower energy $(2.67 \ldots 2.07$ eV$)$ which were ascribed to boron as the acceptor and to a deep donor with 3.57 eV ionization energy.[15]

The samples studied are HPHT synthetic single crystals and CVD-grown homoepitaxial diamond films. The HPHT diamonds were doped with phosphorus during the HPHT synthesis with phosphorus as the catalyst. The crystals spontaneously nucleated in the pressure chamber have sizes of only 50–100 μm. Therefore, no secondary-ion-mass spectroscopy (SIMS) studies were possible to determine the phosphorus concentrations. The CVD diamond films were grown on (111) HPHT-Ib diamonds by microwave-assisted CVD. They were doped during the CVD growth by adding phosphine to the reaction gases. These samples were grown under similar conditions and have film thicknesses between 300 nm and 2 μm, and phosphorus concentrations between $10^{18}/\text{cm}^3$ and $\approx 10^{19}/\text{cm}^3$ as studied by SIMS. In the cathodoluminescence (CL) measurements the samples were glued on the copper sample holder of a continuous-flow crystat that was cooled either with liquid nitrogen or liquid helium. The temperatures on the sample surface could be varied between 20 and 300 K. The luminescence was excited by 8 keV electrons from a conventional reflection high-energy electron diffraction electron gun. The CL signal was focused with Al-
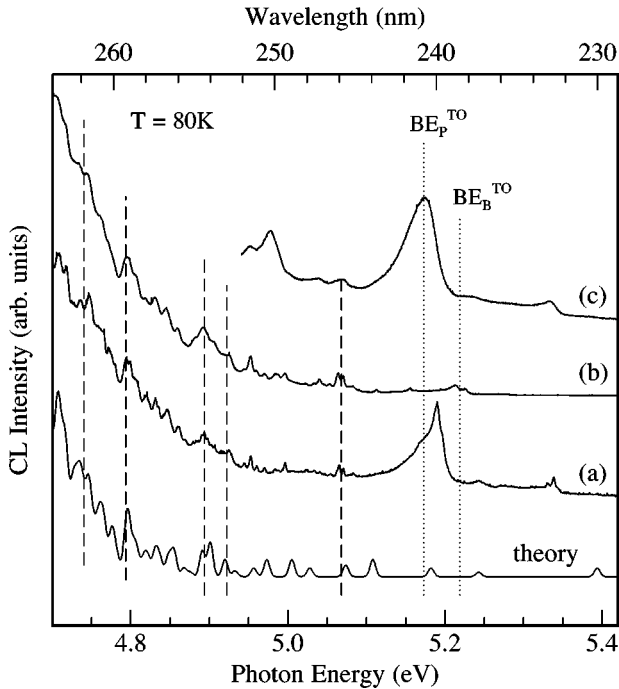
FIG. 1. Near-band-edge CL spectra of phosphorus-doped diamonds: (a) Microwave-assisted CVD layer (NIRIM, Japan) (b) HPHT-crystal (NIRIM, Japan) (c) hot-filament CVD layer (Technical University, Vienna, Austria). Theory: Simulated spectrum ($\varepsilon_0 = 5.7$ and $a_0 = 3.568$ Å) with $E_A = 370$ meV (boron) and an assumed donor ionization energy of $E_D = 630$ meV. For the assignment of lines to shell numbers, see Fig. 2. Vertical-dotted and -dashed lines are eye guides.

coated parabolic mirrors onto the entrance slit of a 1 m-monochromator and detected with a LN$_2$-cooled UV-optimized charge-coupled device camera. The accuracy of the energetic positions quoted is ≈ 0.3 meV, and the resolution was typically 2 meV.

Figure 1 depicts near-band-edge CL spectra at 80 K of a phosphorus-doped CVD diamond film (spectrum a) and of a phosphorus-doped HPHT diamond (spectrum b). Two other HPHT diamonds show spectra very similar to those in Fig. 1 in the whole range of photon energies. In spectrum (b), the TO phonon replica of the bound-exciton recombination at boron acceptors (BE_B^{TO}) is weakly detected. The doublet structure with lower energy peak position at 5.215 eV is well documented in the literature.[16] Boron was not intentionally doped in this sample but is due to traces of this element in the growth apparatus possibly from previous experiments. At 5.175 eV a transition emerges in two of the spectra [(a) and (c)] which we have recently seen in several phosphorus-doped diamonds and ascribed to a TO-phonon-assisted exciton transition at phosphorus donors or phosphorus-related complexes.[17] The set of sharp lines down to 4.7 eV is novel. The lines are more closely spaced for decreasing photon energy. At the same time they become broader forming unresolvable groups of transitions. These features are characteristic of donor-acceptor pair (DAP) line spectra. Here, the recombination energy $h\nu$ of an electron at a donor with a hole at an acceptor at distance R_i is given by[18]

$$h\nu(R_i) = E_g - E_D - E_A + e^2/(4\pi\varepsilon\varepsilon_0 R_i) + J(R_i). \quad (1)$$

The Coulomb term describes the interaction of the charged donor and acceptor after recombination and depends on the discrete-valued spatial distance of the two impurities. The Coulomb integral $J(R_i)$ involves the interaction between the electron and the hole, and the interaction of the electron and the hole with the donor and acceptor ions, respectively. $J(R_i)$ can be neglected for large R_i. In diamond, the wave functions are strongly localized at the impurities (the wave function radius is comparable to the lattice constant a_0) and $J(R_i)$ plays no significant role in the following assignment of line energies to R_i values.

In a crystalline semiconductor, the dopants can occupy discrete lattice sites only. If the donors and acceptors are on substitutional sites, R_i can take the following values[19]

$$R_i(m) = a_0\sqrt{(m-b)/2}, \quad (2)$$

with $b = 0$ for type I donor-acceptor pairs (donors and acceptors are on the same sublattice) and $b = 5/8$ for type II donor-acceptor pairs (donors and acceptors are on different sublattices). m is a positive integer and called the shell number, and a_0 represents the lattice constant.

The lower trace in Fig. 1 represents a simulated DAP spectrum resulting from Eqs. (1) and (2). 50 transitions with shell numbers up to $m = 25$ for both types of pairs were superimposed. They were Gaussian broadened with 10 meV halfwidth, and their relative intensities correspond to the calculated number density of pairs at the individual shell numbers m.[19] The transition probability was assumed to remain constant for these first 100 transitions in total. The simulated spectrum was then shifted in energy so as to reproduce most satisfactorily the essential experimental features. As mentioned above, simulated lines at low-shell number values are not expected to coincide with experimental lines due to the $J(R_i)$ term. Two other assignments of the simulated spectrum to the experimental spectra, within ± 50 meV shift from the assignment shown in Fig. 1, seem possible but were less convincing. In Fig. 2, we have plotted the line positions of the discrete DAP transitions against the inverse of the normalized distances. A linear relationship results, supporting our interpretation of the experimental line spectra as discrete DAP transitions. Extrapolation of the straight line to $R_i \rightarrow \infty$ yields an intersection with the coordinate at $(E_g - E_A - E_D) = 4.50$ eV. Consideration of the two neglected assignments yields finally an uncertainty of ± 0.05 eV.

Three of the phosphorus-doped diamonds under investigation show the boron-bound exciton line at 5.215 eV, indicating that boron on substitutional lattice sites is incorporated in low concentrations. Therefore, we assume the acceptor involved in these DA pair transitions is boron. At moderate concentrations, boron has an ionization energy of $E_A = 370$ meV.[20] With the band-gap energy of diamond, $E_g = 5.50$ eV,[16] a donor ionization energy of $E_D = 630$ meV results with an uncertainty of ± 50 meV. We have observed the DAP transitions in different samples grown either by HPHT or CVD, but only after intentional phosphorus-doping. Therefore, the donor involved is likely isolated phosphorus or a phosphorus-related complex with donor behavior.

Hall measurements on similar phosphorus-doped homoepitaxial CVD diamond films have confirmed the n-type
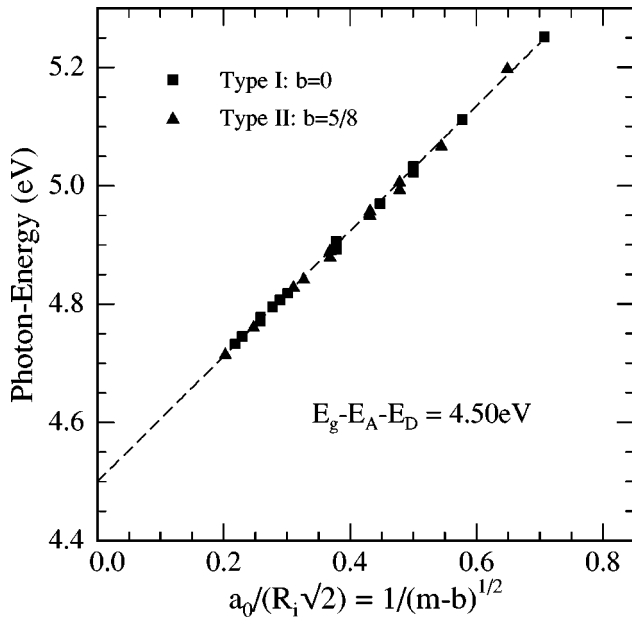
FIG. 2. Energy positions of the discrete DAP lines against inverse, normalized pair separations $R_i\sqrt{2}/a_0$. The full line is a least-squares fit to the data points intersecting the coordinate (for $R_i \rightarrow \infty$) at $(E_g - E_A - E_D) = 4.50$ eV.

conductivity of such samples. Temperature-dependent Hall data yielded an apparent activation energy for the donor of $E_D = (430 \ldots 460)$ meV or ≈ 500 meV, respectively.[8,14] Our resolved DAP transitions were only detectable in the CVD sample with the lowest nominal phosphorus doping concentration, which shows no significant electrical conductivity. In turn, we were unable to detect DAP lines in the higher phosphorus-doped samples. This is consistent with the cases of galliumphosphide[21] and silicon[22] where discrete DAP spectra can only be observed for a limited range of donor and acceptor concentrations. Thermal activation energies obtained from Hall measurements generally have the disadvantage that they can represent the full donor or acceptor ionization energy or half of this value in the extreme limits of high or low compensation, respectively, which may not well be known. Also, they might suffer from contact problems or the existence of parallel conductivity channels. For high-concentration levels, further corrections due to impurity overlap have to be taken into account, which in diamond amount to ≈ 80 meV for a donor concentration of 2×10^{18} cm^{-3}. Also, in general, the Hall factor possibly deviates from the value 1 and might be temperature dependent, leading to additional corrections. Such problems do not exist

in the luminescence measurements suggesting that the present optically determined value of E_D may be more reliable than the electrically determined values.

Finally, we compare the ionization energies E_i of the acceptor boron ($E_A = 370$ meV) and the phosphorus donor ($E_D = 630$ meV) with the binding energies $E_{loc,X}$ with which the excitons are localized at these impurities. The latter values are the spectroscopic spacings between the bound-exciton recombination lines and the low-energy threshold of the free exciton (FE) radiation. In silicon, this relation follows an empirical rule $E_{loc,X} \approx 0.1 \; E_i$ as first established by Haynes.[23] In other semiconductors, the proportionality factor is different and constant energy offset terms have to be added. In diamond, using for all luminescence transitions TO-phonon-assisted lines, $h\nu(BE_B^{TO}) \approx 5.215$ eV, $h\nu(BE_P^{TO}) \approx 5.175$ eV, and $h\nu(FE^{TO}) \approx 5.270$ eV, we obtain $E_{loc,X}(B) \approx 55$ meV and $E_{loc,X}(P) \approx 95$ meV. The latter two values would constitute an equivalent of Haynes' rule in diamond $E_i \approx 0.15 \; E_{loc,X}$. Argued from a different point of view, if this relation valid in diamond in the well-known case of boron is assumed to hold also for a phosphorus donor, the exciton transition at the donor would be positioned at 5.175 eV (where it is actually observed) lending support to our suggestion of a phosphorus donor with $E_D = 630$ meV.

To summarize, cathodoluminescence studies on phosphorus-doped CVD diamond films and HPHT diamonds were presented. In four samples studied, discrete donor-acceptor pair lines were observed in a spectral range near the band-gap energy of diamond. Knowing that boron is contained in these samples besides the phosphorus dopant, we derive from the DAP spectra an ionization energy of (630 ± 50) meV for the donor involved. A bound-exciton transition observed at 5.175 eV depends on intentional phosphorus doping and is ascribed to the TO phonon replica of an exciton transition at the new donor. Combining the donor ionization energy of 630 meV from the DAP spectra with the exciton localization energy of 95 meV at the donor we obtain the relation $E_{loc,X}/E_D \approx 0.15$ as for the boron acceptor. This could be considered the analogue of Haynes' rule in silicon.

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*Present address: Experimentalphysik IV, Universität Augsburg, D-86135 Augsburg, Germany.

†Electronic address: rolf.sauer@physik.uni-ulm.de

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