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Low-temperature spectroscopic study of *n*-type diamond

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A spectroscopic study of epitaxial phosphorus-doped *n*-type diamond films, prepared by the chemical vapor deposition (CVD) technique, was carried out using the constant photocurrent method (CPM). Liquid nitrogen temperature CPM data show two new optically active defects in the gap of the P-doped CVD diamond film. A theoretical fitting of the optical cross-section data yields 0.56 eV optical excitation energy for the first level (denoted as X_{P1}) and 0.81 eV for the second level (denoted as X_{P2}). The X_{P1} optical data are in good agreement with Hall measurements, showing about the same value for the (thermal) activation energy of the carrier concentration for P-doped samples. The X_{P2}-defect level remains unidentified. Liquid helium temperature measurements for a high-electrical mobility *n*-type diamond sample show P-related oscillatory photoconductivity. [S0163-1829(99)02023-8]

The preparation of *n*-type diamond has always been one of the diamond-material physics challenges, never accomplished for synthetic and natural diamond, and it is of general interest for the semiconductor physic community. Only very recently, using the chemical vapor deposition method (CVD), the group at NIRIM has succeeded in the first preparation of thin (around 1-μm-thick) *n*-type phosphorus-doped homoepitaxial diamond films.[1] Recent Hall-effect measurements for P-doped samples showed an activation energy of the carrier concentration of about 0.40-0.60 eV.[1,2] But, so far, there has been no direct spectroscopic evidence of the phosphorus level in the gap of diamond. An observation of a P-bound exciton suggested an energy position about 0.64 eV below the conduction band for the phosphorus level.[3] These indications for the phosphorus level energy position differ from theoretical calculations, which suggested a shallower defect at about 0.2 eV below the conduction band.[4] Here, we present spectroscopic evidence of the phosphorus optical activity in diamond, using the constant photocurrent method (CPM).[5] Two new optically active defects are revealed by CPM in the *n*-type phosphorus-doped diamond films: one defect at 0.56 eV and the other one at about 0.81 eV optical excitation energy. Additionally, a low-temperature oscillatory photoconductivity is observed for a high-mobility *n*-type sample.

The investigated samples were phosphine (PH_3) doped, 0.5–3-μm-thick epitaxial CVD diamond deposited on polished top {111} facets of Ia- and Ib-type natural diamond crystals. The sample characteristics including the secondary-ion-mass spectroscopy (SIMS) measured P concentrations and the results of Hall-effect measurements are summarized in Table I. For preparation details see Ref. 2. The CPM technique is a common optical method used for investigations of the optical cross section of deep defects, and widely used in the past for studying defects in Si, GaAs, and other semiconductors.[5,6] Recently, the CPM has also been applied to CVD diamond.[7,8] The CPM allows us to determine the optical excitation energy of defects (e.g., their energy position within the forbidden optical gap). The quasisteady-state photocurrent (7-13 Hz modulation) and CPM setups, used for these measurements, are described in Refs. 7 and 9. The measurements are carried out at liquid nitrogen (LNT), liquid helium (LHeT), and at room temperatures (RT). The spectral resolution of the system at 2000 nm is typically 4 nm. Graphite/Au coplanar interdigitated contacts with 50 μm spacing (30 fingers) were deposited by lift-off photolithography on top of the diamond film. Eventually, two coplanar graphite contacts with a gap of 1 mm were used for smaller samples. The dark and photo I-V characteristics were linear up to an electric field of $4000\,\mathrm{V\,cm^{-1}}$. Samples were measured after an oxidation treatment.[1]

Figure 1 shows the RT photocurrent (PC) spectra of the Ia-substrate sample *A*. The substrate shape was triangular with two parallel optically polished {111} facets (see the inset of Fig. 1). The larger (back surface) facet was embedded during the diamond deposition and thus left intact. This allowed us to carry out a comparative spectroscopic measurement on the larger back surface facet only. The Ia substrate PC spectrum in Fig. 1 is similar to those available in the literature[10,11] and consists of PC continuum bands (two maxima at 3 and 3.3 eV) and a rise at about 4 eV.[11] In the IR region, there is no substrate absorption and the photocurrent falls off very sharply below the detection limit of the setup (about 10 fA). Surprisingly, the photocurrent measured for the smaller facet with the P-doped layer is quite different in the IR region. Two new shoulders, not present in the Ia-type substrate, appear in the spectrum. One shoulder (denoted here as X_{P1}) has an onset at about 0.6 eV. The other one, dominant at RT (see below), shows an onset at about 0.8 eV (denoted here as X_{P2}). The phase shift of the measured photocurrent spectra is shown in the inset of Fig. 1. Thus, the data in Fig. 1 indicate the presence of two new optically active defects in P-doped CVD diamond film.

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TABLE I. Characteristics of P-doped epitaxial CVD diamond films *A*-*C*, prepared by the PECVD technique using a CH_4:H_2 (0.075 volume percent) gas mixture and *in situ* doped by PH_3. Samples are prepared at substrate temperatures of 900-950 °C. Listed data show the part per million (ppm) concentrations of defects N_{SIMS} determined by SIMS, the RT carrier concentration values n_{RT} determined by the Hall measurements, and the optical photoionization energy E_I determined by CPM.

Sample no.	Substrate	PH_3 (ppm)	N_{SIMS} ppm	Film thickness (μm)	n_{RT} (cm^{-3})	μ ($cm^2\,V^{-1}\,s^{-2}$)	E_I (eV)
A	Ia	100	1.5	3			0.56; 0.81
B	Ib	1000	50	0.5	10^{12}	50	0.56
C	Ib	1000	50	0.5			0.56; 0.81

To investigate in detail the photoionization cross section of the new levels we have used the CPM. By keeping the photocurrent constant, the occupation of the gap states is fixed for a different light excitation energy and the CPM measured spectra correspond to the optical-absorption coefficient α. The related optical (photoionization) cross section σ_I for bound-to-free transitions can be determined by the relation[5]

$$\alpha = N_P \sigma_I \approx 1/N_{ph}, \tag{1}$$

where N_P is the concentration of defects associated with the investigated level, σ_I is the optical cross section, and N_{ph} is the number of incident photons necessary to keep the photocurrent constant. The RT and LNT CPM optical cross-section spectra of the measured samples are plotted in Fig. 2. Similar to the data in Fig. 1, the CPM spectra reveal two new optically active defects. The LNT measured spectrum is clearly sharper, less broadened by acoustic phonons as compared to the RT measurement and show well-defined optical cross sections of two defect levels.

For a numerical fitting of the optical cross section σ_I we use a convolution of the Inkson's formula with a Gaussian phonon-broadening[12,13]

$$\sigma_I(\varepsilon) = A \int_{-\infty}^{+\infty} \frac{(E-E_i)^{3/2}}{E(E-B)^2} \frac{\exp[-(E-E_i-\varepsilon)^2/2w^2]}{(2\pi w^2)^{1/2}} dE, \tag{2}$$

where *A* and *B* are constants, *E*, ε, is the energy, E_i is the photoionization threshold energy, and $2w$ is the full width at half maximum of the Gaussian phonon broadening term, related to the Huang-Rhys factor and the energy E_{ph} of the phonon involved in the optical transition.[13] Numerical fitting of the data yields $E_{XP1} = 0.56 \pm 0.03$ eV and $E_{XP2} = 0.81 \pm 0.03$ eV. The sample *A* exhibited rather low-electrical conductivity (it was beyond the reach of our van der Pauw method of the Hall-effect measurement). Nevertheless, in the coplanar gap-contact configuration we could measure the activation energy of the dark conductivity (see the inset of Fig. 2). Thus, our fit of the optical cross section is in very good agreement with the activation energy of the dark-conductivity measurement, which yields about 0.55-0.60 eV for the sample *A*. For the sample *B*, the Hall-effect measurements showed rather high mobility of 50 $cm^2\,V^{-1}\,s^{-1}$ and the activation energy of the carrier concentration of 0.57 eV.[14] For sample *C*, containing about the same amount of phosphorus, the dark conductivity was also too low to be detected by our Hall setup. The origin of the difference in the electrical conductivity for the samples *B* and *C* is not known, but the crystalline perfection of the epitaxial layer, induced for example by small variations in the CVD deposition temperature is one of the important parameters. The CPM measurements showed that in the sample *B* only the X_{P1} defect is present. On the other hand, the sample *C* exhibited both — the X_{P1} and the X_{P2} defects (see Table I). Thus, a compensation action of the X_{P2} defect is a possibility. This idea is supported by the observed phase-shift changes in the 0.5-0.9 eV energy region (see the inset of Fig. 1). In general, the photocurrent phase shift reflects changes in the response time τ, which are related to the occupation of the gap states[8] and/or changes related to a switch of photocarrier polarity.

By a detailed inspection of Fig. 2 it can be seen that the ratios of $\sigma_{XP1}(2E_{XP1})/\sigma_{XP2}(2E_{XP2})$ (e.g., a ratio of the photoionization cross section values at twice the energy of a

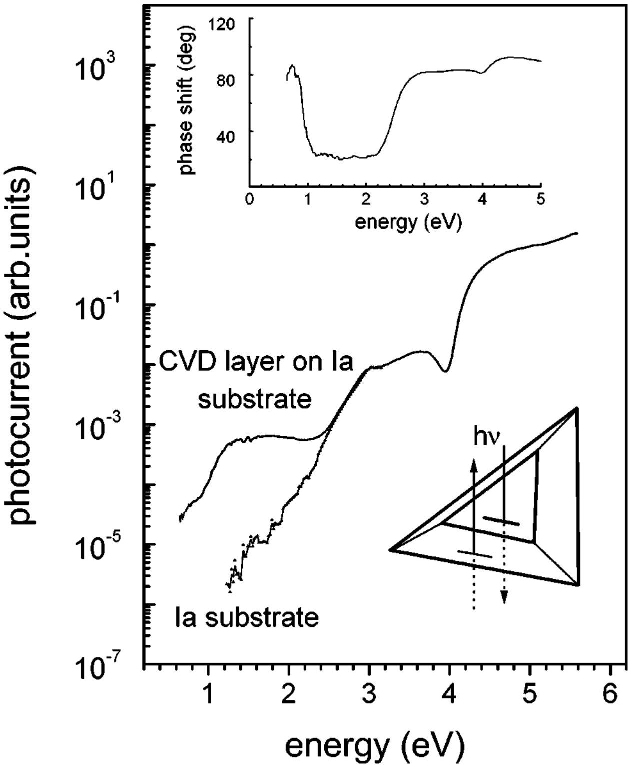

FIG. 1. Photocurrent (PC) and optical-absorption spectra for a Ia-type natural diamond crystal, compared with a spectrum for a P-doped epitaxial layer, deposited on the same crystal. The inset shows a photocurrent phase-shift spectrum

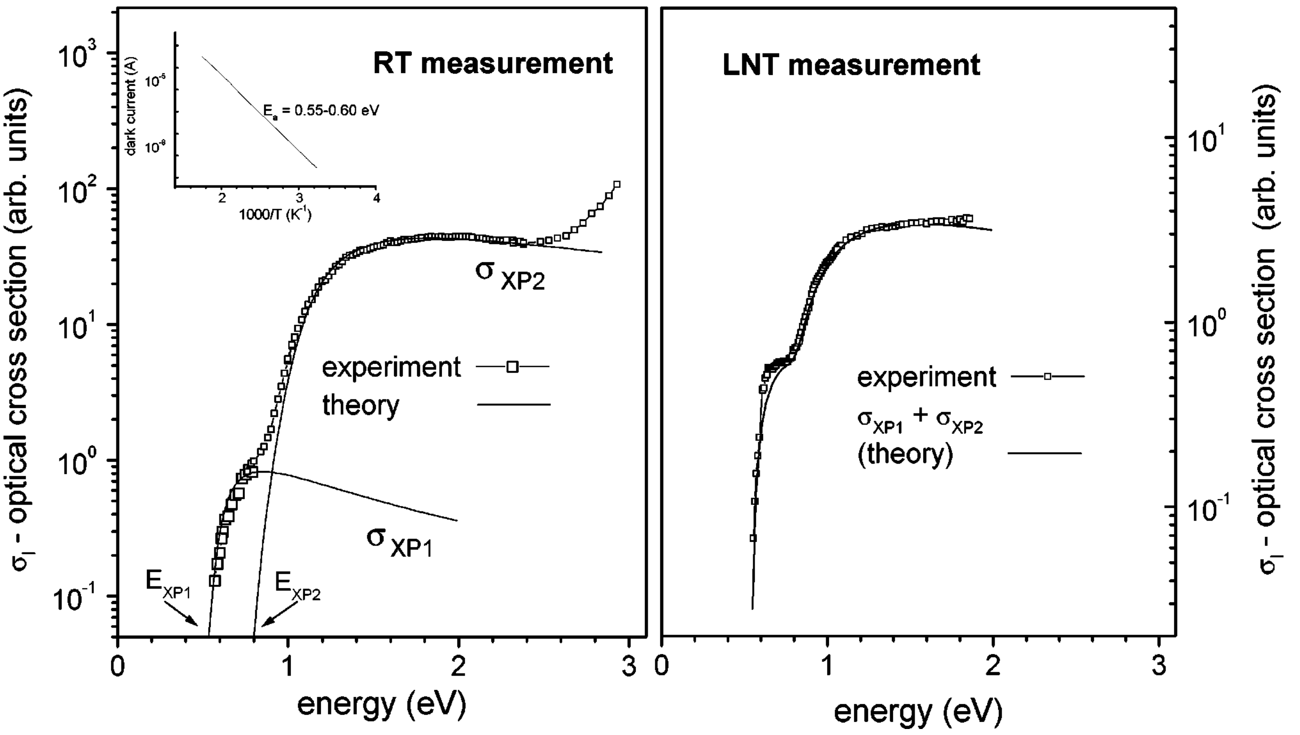

FIG. 2. Room temperature (RT) and liquid nitrogen temperature (LNT) optical cross-section spectrum for the P-doped epitaxial layer. Theoretical fit of the photoionization cross-section spectrum (Refs. 12 and 13) of X_{P1} and X_{P2} levels is indicated by the dotted line. The inset shows the activation energy of the dark conductivity E_a of 0.55-0.60 eV.

particular defect photoionization threshold E_i) are different for the LNT and RT measurements. In the Lucovsky's model[15] the $\sigma_I(2E_i)$ value is proportional to the defect concentration. In the case of a compensating acceptor level, such a difference can be induced by a change of both quasi-Fermi levels E_{fn} and E_{fp} with temperature, which may consequently cause a change in the recombination lifetime (and the photocurrent phase shift). Another possibility, indeed, is that the X_{P2} level can be a deep donorlike defect. In this case one should consider the movement of the electron quasi-Fermi level (E_{fn}) towards the conduction band upon lowering the temperature for the explanation of differences in $\sigma_{XP1}/\sigma_{XP2}$. The exact mechanism and the possible origin of the X_{P2} level are currently investigated in detail.

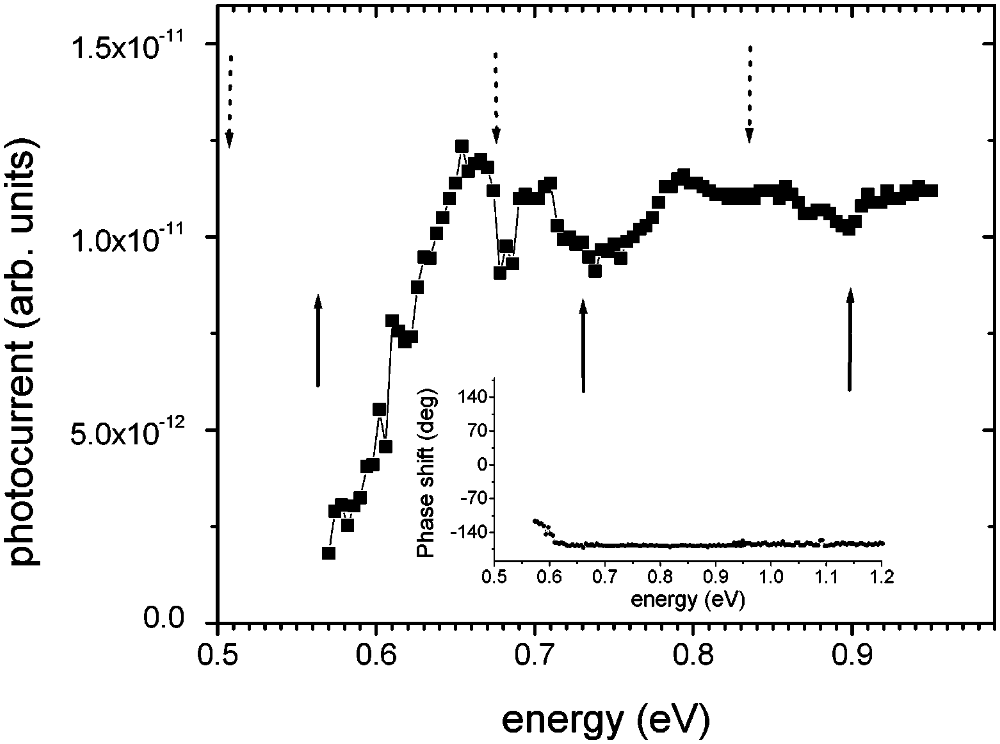

FIG. 3. Liquid helium temperature (LHeT) photoconductivity spectra for the sample *B*. The arrows indicate two sets of minima in photoconductivity, separated by a distance of about 165 meV. The inset shows the photocurrent phase shift.

In Fig. 3, the LHeT photocurrent spectra are plotted on the linear scale for sample *B*. This sample, as discussed above, shows only the X_{P1} defect at onset of about the 0.58 eV for the LHeT measurement. Additionally, we can clearly observe distinct minima in the photoconductivity. Similar spectra with photocurrent minima have been observed for boron-doped single-crystal diamond (IIb) and attributed to so-called oscillatory photoconductivity due to thermalization of photoexcited holes by an emission of LO phonons.[16] A fine inspection of the spectra in Fig. 3 suggests at least two sets of equidistant minima. The energy difference between the minima (marked by arrows in Fig. 3) agrees well with the energy of the LO phonon $E_{ph}=165$ meV in diamond. Existence of such sets of photoconductivity minima points towards collection levels near the bottom of the conduction band. The energy position of the collections levels, which are usually excited defects states,[16] can be calculated by subtracting the LO phonon energy from the lowest observed minimum of the cascade set (see Fig. 3). The photocurrent minima and the X_{P1} onset were observed for the above sample at different temperatures ranging from 5 to 77 K. The exact description of the oscillatory conductivity, including determination of the excited phosphorus levels by using the photothermal photoionisation spectroscopy, will be published in a separate publication.

To conclude, for the first time a spectroscopic study of *n*-type CVD diamond films has been carried out using the constant photocurrent method (CPM). The LNT measurement clearly points to the existence of two new defect levels in the gap of CVD diamond. A theoretical optical cross section fitting defines the position of the first level, denoted as X_{P1}, at about 0.56 eV optical excitation energy. The second level, denoted as X_{P2}, is positioned at 0.81 eV. The X_{P1} level position is in excellent agreement with Hall measurements of the activation energy of the carrier concentration. The X_{P2} is found in samples with a high resistivity and more information is necessary for its clear identification. The oscillatory photoconductivity is observed in the P-doped samples, which can be interpreted as being due to a rapid capture of electrons by collection levels near the conduction-band minimum with a simultaneous emission of LO phonons.

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