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Red luminescence in phosphorous-doped chemically vapor deposited diamond

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Luminescence studies have been performed on phosphorous-doped diamond films deposited by hot-filament chemical vapor deposition. A broad luminescence band, centered around 1.9 eV is revealed, in the cathodo luminescence spectra of homoepitaxial and polycrystalline films, whereas the blue band-A luminescence, which is characteristic for undoped diamond, is quenched in the presence of phosphorus. The 1.9 eV luminescence band could not be excited by Ar⁺ laser light (2.54 eV) and did not show a zero-phonon line in the spectrum. Therefore, we suggest that this band is a red form of band-A luminescence, related to electron-hole recombination at substitutional phosphorous and a phosphorus-vacancy complex. © 1997 American Institute of Physics. [S0021-8979(97)02213-5]

INTRODUCTION

Incorporation of phosphorus in diamond has been studied extensively,¹ with the purpose of obtaining *n*-type conduction in diamond, but the results are inconsistent. From electron paramagnetic-resonance spectroscopy on phosphorous-doped polycrystalline diamond films, it has been observed that phosphorus in diamond forms impurity-vacancy complexes.² In contrast to this, Zvanut *et al.* have found that phosphorus incorporates substitutionally in diamond,³ as was predicted from *ab initio* pseudopotential calculations with plane wave methods.⁴ The donor level according to these calculations is located at 0.2 eV below the conduction band. On the other hand, from local density approximation cluster calculations a donor ionization energy of 1.09 eV is found.⁵ Experimentally, donor energies for phosphorus in diamond between 0.1 eV (Ref. 6) and 1.16 eV (Ref. 7) have been reported, although it is believed that the first result most probably can be attributed to nondiamond *sp*²-bonded components at the grain boundaries. Furthermore, all electrical measurements on phosphorous-doped diamond reveal high resistivities,⁸⁻¹⁰ instead of *n*-type conduction. A satisfying explanation for the absence of this *n*-type conduction has not yet been given, although several possibilities are considered.¹⁰

The optical activity of phosphorus in diamond has been studied recently by Prins. He observed quenching of the blue band-A signal in cathodoluminescence spectra of type IIa diamond after implantation of phosphorus ions.¹¹ In the present study, it is shown that in our chemically vapor deposited diamond films not only the blue band-A luminescence is quenched, due to the presence of phosphorus, but also a new transition has been revealed in cathodoluminescence (CL) spectra. This luminescence band has also been observed in the CL spectra of nitrogen-phosphorous-codoped diamond by Cao *et al.*¹⁰ In their paper, it was as-

cribed to the nitrogen-vacancy related vibronic band with the zero-phonon line at 1.945 eV. However, this vibronic band can only be observed in photoluminescence (PL) spectra and not in CL spectra.¹² In this study we show that the newly found transition is not a vibronic band, but can probably be ascribed to electron-hole recombination at a donor-acceptor pair. Since the properties are comparable, it is suggested that this new transition is a red variant of the well-known band-A luminescence.

EXPERIMENT

The phosphorous-doped diamond films have been grown in a conventional hot-filament chemical vapor deposition (CVD) reactor, operating at a total pressure of 50 mbar.¹⁰ The gases used for the diamond deposition process were hydrogen and methane (4.5N) diluted in hydrogen (10%). For phosphorus doping, phosphine (PH₃) diluted in hydrogen (1000 ppm), was used. Silicon and single-crystal natural diamond were used as substrate materials. The single crystal silicon wafers were (100) oriented, whereas the diamond substrates were type IIa (100)7°(110) oriented crystal plates. Typical growth conditions for diamond films are as follows: the filament temperature was 2500 °C, the substrate temperature was 800 °C. The volume fraction of methane in the gas phase was 2% at a total flow rate of 300 sccm. The phosphine volume fraction was varied between 0 and 60 ppm.

RESULTS

The CL and PL experiments were performed as described by Cao *et al.*¹⁰ The CL spectra have been recorded at room temperature and at 77 K. The PL spectra were recorded at 77 K; no PL signal could be detected at room temperature.

Raman spectroscopy showed that the phosphorous-doped, polycrystalline diamond films are of a high quality.¹³ CL spectra of polycrystalline diamond films. Room temperatures deposited with four different phosphine concentrations, are shown in Fig. 1. In these spectra the emission from the plasma in the CL chamber is denoted by *P*. In the spectrum of the undoped sample (0 ppm PH₃) only a broad peak with

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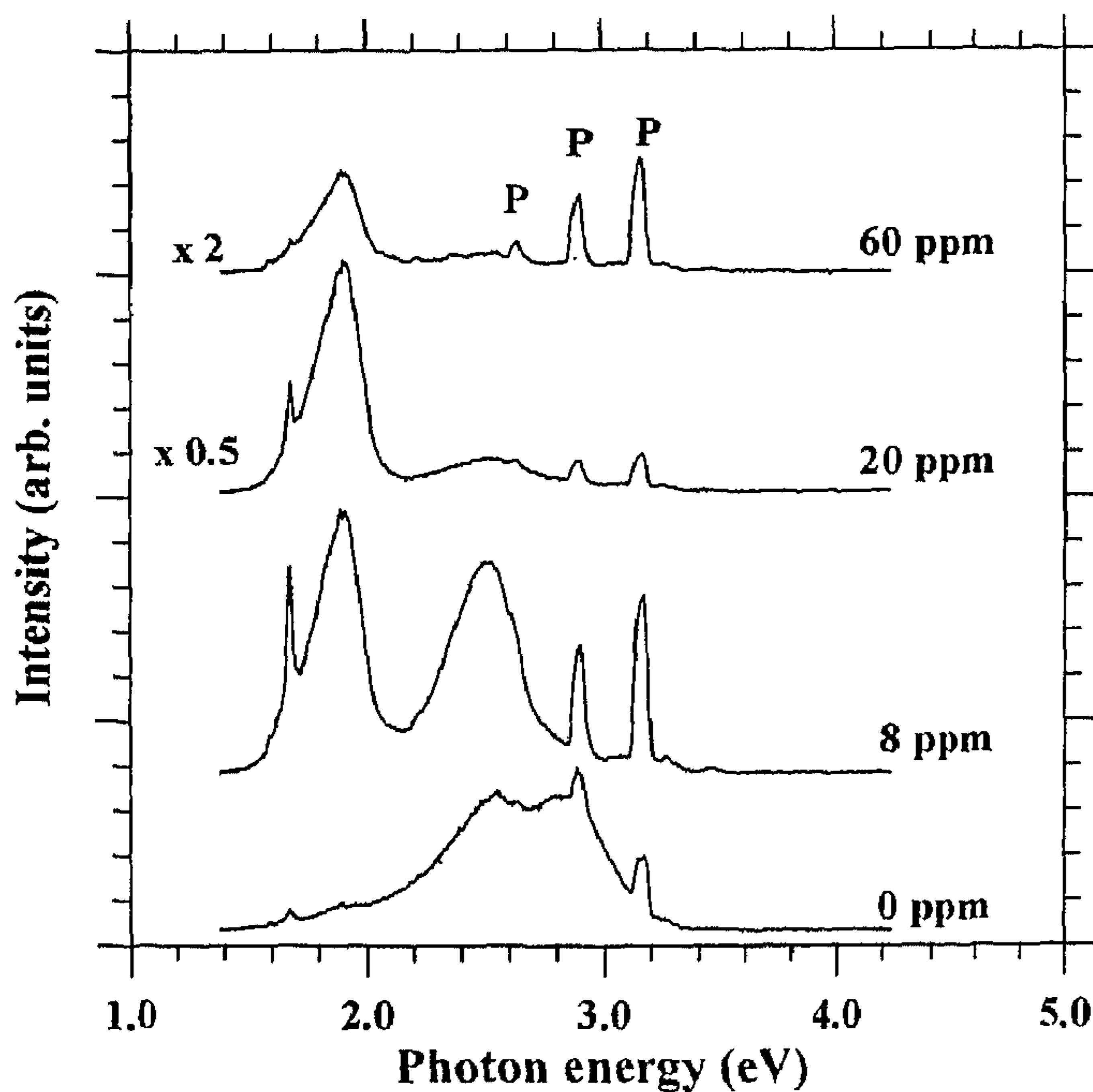


FIG. 1. CL spectra, recorded at 300 K, of four polycrystalline diamond layers, grown with phosphine concentrations in the gas phase as indicated. The plasma lines are marked by P. The intensities are multiplied by the factors as indicated.

its maximum at 2.6 eV is observed: the blue band-A emission, which is characteristic for undoped CVD diamond.¹⁴ In the spectra of the phosphorous-doped samples, the intensity of this peak decreases and finally at a concentration of 60 ppm PH_3 the blue band-A luminescence is hardly visible in the spectrum. On the other hand, in these spectra an intense red luminescence band centered at 1.9 eV starts to

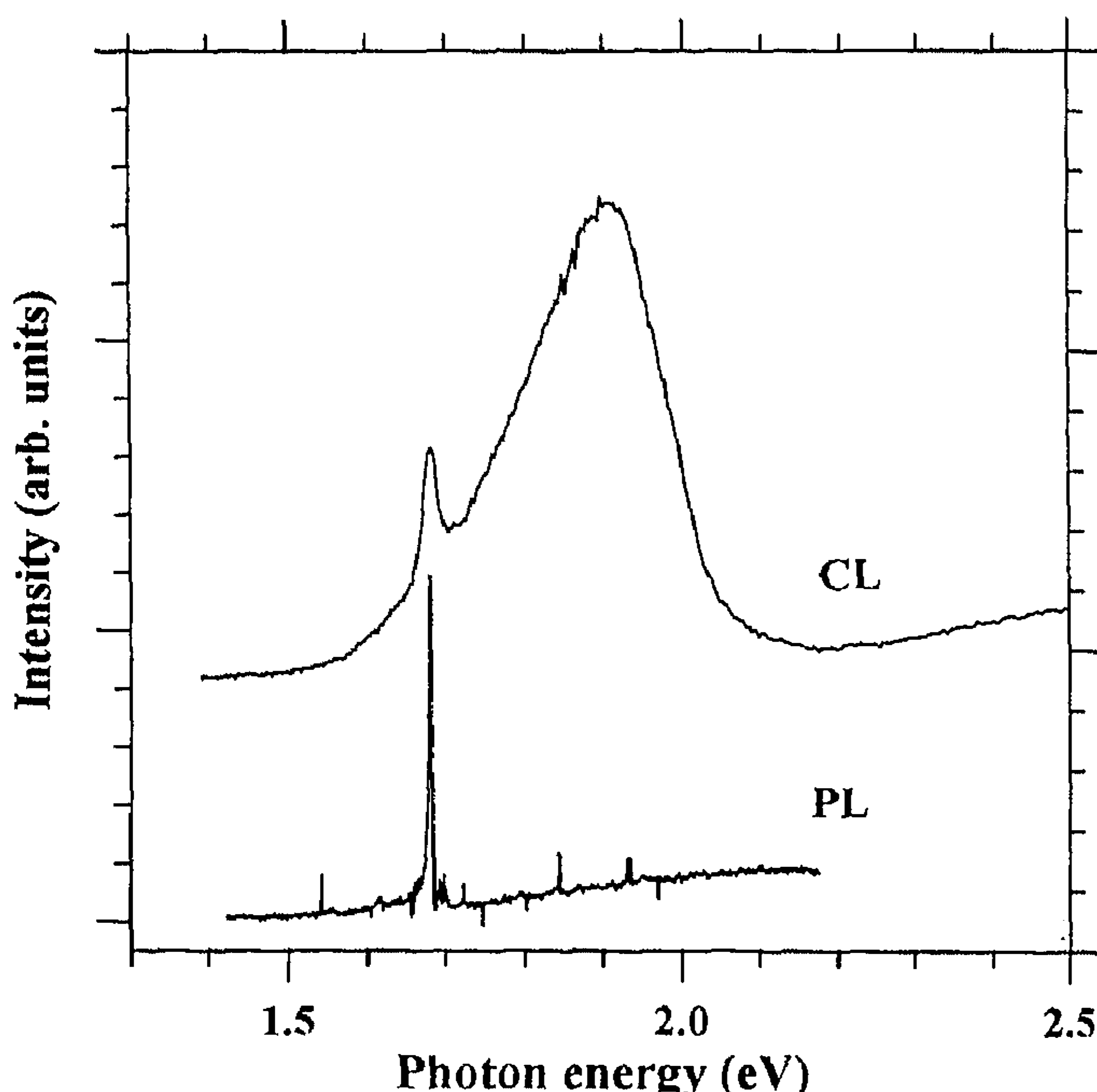


FIG. 2. CL and PL spectra, recorded at 300 and 77 K, respectively, of polycrystalline diamond grown with 20 ppm phosphine in the gas phase.

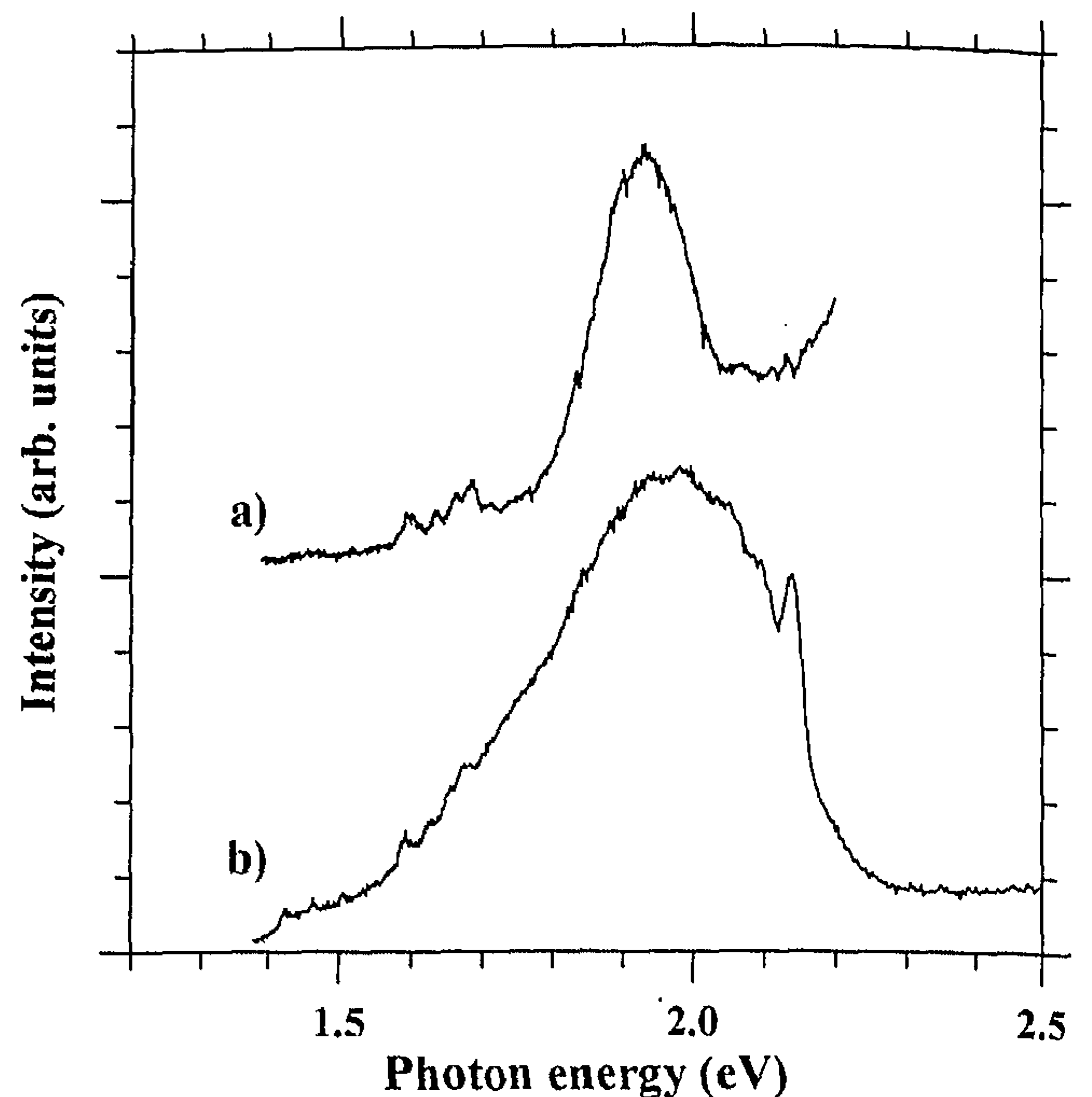


FIG. 3. Room temperature CL spectra of (a) phosphorous-doped HFCVD homoepitaxial diamond and (b) nitrogen-doped flame-grown homoepitaxial diamond.

evolve. Furthermore, a sharp line at 1.681 eV is observed in the CL spectra. This line is related to incorporation of silicon during growth.¹² The 1.9 eV luminescence band could not be excited by an Ar^+ laser light of 2.54 eV, as is shown in the PL spectrum in Fig. 2; in this spectrum only the silicon-related emission is observed. Therefore, our 1.9 eV emission does not have the same origin as that observed in type IIb boron-doped synthetic diamond by Freitas *et al.*,¹⁵ which already could be excited at laser energies of 2.41 and 2.33 eV.

A comparison of CL spectra of phosphorous-doped and nitrogen-doped homoepitaxial diamond is shown in Fig. 3. The nitrogen-doped diamond sample is a homoepitaxial layer grown by acetylene-oxygen combustion-flame diamond deposition.¹⁶ In the CL spectrum of this layer, a zero-phonon line is observed at 2.156 eV (the so-called 575 nm system) with the phonon-emission spectrum at lower energies. Collins and Lawson¹⁷ have concluded that this optical center is related to single nitrogen-vacancy pairs. This zero-phonon line is absent in the CL spectra of the phosphorous-doped diamond layers (see Figs. 1 and 3), showing that the 1.9 eV band observed in phosphorous-doped diamond is different from the nitrogen-related 575 nm system. The fact that the red luminescence band is also observed in homoepitaxial, phosphorous-doped diamond demonstrates that it is not related to the presence of grain boundaries in polycrystalline diamond. Because of the presence of the phonon-emission spectrum of the 575 nm system, it is not possible to conclude that the 1.9 eV emission band is totally absent in nitrogen-doped diamond; some overlap of these two spectra may occur. However, one can conclude that in the spectra of phosphorous-doped diamond in the absence of nitrogen, where the zero-phonon line at 2.156 eV is not present, the 1.9 eV emission band is observed as an isolated system,

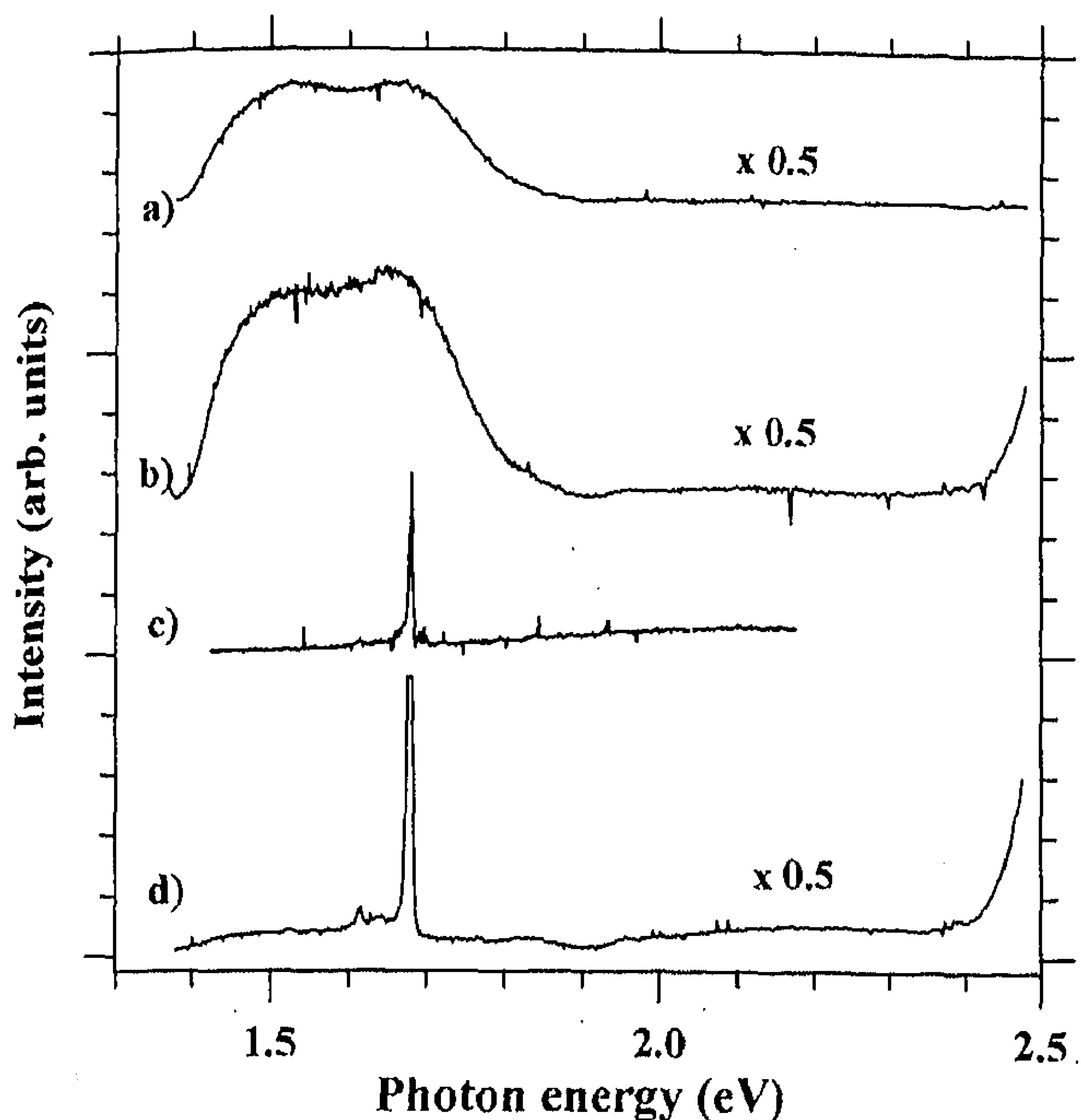


FIG. 4. PL spectra, recorded at 77 K of (a) nitrogen-doped, (b) phosphorous-nitrogen codoped, (c) phosphorous-doped, and (d) undoped polycrystalline HFCVD diamond.

without any overlap of other emission spectra.

Another indication that the 1.9 eV emission band does not originate from the presence of nitrogen in the diamond lattice is obtained from a comparison of the PL spectra of phosphorous-doped, nitrogen-doped, phosphorous-nitrogen codoped, and undoped polycrystalline diamond, as is shown in Fig. 4. In the samples in which nitrogen is present [(a) and (b) in Fig. 4] two broad emission bands centered at about 1.5 and 1.7 eV are observed. In the undoped and the phosphorous-doped samples [spectra (c) and (d) in Fig. 4] again only the silicon-related line at 1.681 eV is observed. This shows that the broad band in the PL spectra in nitrogen-doped diamond does not have the same origin as the 1.9 eV emission band in the CL spectra in phosphorous-doped diamond.

Summarizing, a new luminescence peak is observed at 1.9 eV in the CL spectra of diamond, which is related to the presence of phosphorous. On this broad peak, no zero-phonon line is observed, implying that very probably it is not a vibronic transition between local levels. This transition is only detected with CL; it could not directly be excited with PL with an laser energy of 2.54 eV), as can the silicon-vacancy complex, but only via the diamond host material. The excitation energy must exceed the band gap of diamond to excite this transition, as is the case with the band-A transition.¹² This behavior is different from that of the broad red emission band, observed by Freitas *et al.* in type IIb boron-doped synthetic diamond.¹⁵ The latter emission band, peaking at 1.84 eV, could be observed using sub-band gap excitation by laser light of energies of 3.53 eV (351 nm), 2.41 eV (514 nm), and 2.33 eV (532 nm), which are lower than the band gap energy of diamond. During the present experiments the 1.9 eV red luminescence could not be ex-

cited by laser of an energy of 2.54 eV, which is in the same energy range as used in Ref. 15.

It is generally believed that the relatively broad band-A luminescence originates from electron-hole recombination at donor-acceptor pairs.¹⁸ Thus far, band-A emission is known to occur in the range between 2.1 and 3.1 eV. However, since the properties of the above described 1.9 eV emission line are comparable to those of band-A luminescence, we suggest that this CL line is a phosphorous-induced variant of band-A luminescence.

A possible explanation for the origin of the 1.9 eV emission may be obtained from the spin-polarized *ab initio* calculations on phosphorous in diamond by Jones *et al.*¹⁹ It has been found that phosphorous in the presence of vacancies forms a phosphorous-vacancy (P-V) complex, similar to the split-vacancy Si-V complex. These complexes act as deep acceptors with an energy level, situated at 2.7 eV below the conduction band,¹⁹ i.e., 2.8 eV above the valence band. No internal transitions are possible for the ionized defect. However, if substitutionally incorporated phosphorous is considered to be a deep donor with an activation energy of 1.1 eV, as is shown theoretically⁵ as well as experimentally,⁷ donor-acceptor recombination can take place at pairs of substitutional phosphorous and the P-V complex, leading to band-A-like emission. Analogous to the calculation of the luminescence energy of the transition between substitutional nitrogen and the P-V complex given by Jones *et al.*,¹⁹ for this electron-hole recombination process an energy of around 2.1 eV can be derived. In this calculation a distance between donor and acceptor of 0.5 nm (Ref. 19) has been taken; it will decrease with increasing donor-acceptor pair separation (e.g., for a separation distance of 1.0 nm a luminescence energy of 1.85 eV will be derived). Therefore, the 1.9 eV band-A-like emission may be the result of the above described transition between substitutional phosphorous and a P-V complex.

In conclusion, an intense red luminescence band at 1.9 eV is revealed in phosphorous-doped CVD diamond. Since this luminescence could not be excited by an Ar⁺ laser light of 2.54 eV and no zero-phonon line has been observed, it is proposed that it is a red form of band-A luminescence, related to electron-hole recombination at substitutional phosphorous and a P-V complex.

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¹G. Popovici, and M. A. Prelas, *Diam. Relat. Mater.* **4**, 1305 (1995), and references therein.

²V. V. Tokiy, N. D. Samsonenko, D. L. Savina, and S. V. Gorban, in *2nd International Conference on the Applications of Diamond Films and Related Materials, Japan, August 25-27, 1993*, edited by M. Yoshikawa, M. Murakawa, Y. Tzeng, and W. A. Yarbrough (MYU, Tokyo, Japan, 1993), p. 757.

³M. E. Zvanut, W. E. Carlos, J. A. Freitas, Jr., K. D. Jamison, and R. P. Helmer, *Appl. Phys. Lett.* **65**, 2287 (1994).

- ⁴S. A. Kajihara, A. Antonelli, J. Bernholc, and R. Car, *Phys. Rev. Lett.* **66**, 2010 (1991).
- ⁵K. Jackson, M. R. Pederson, and J. G. Harrison, *Phys. Rev. B* **41**, 12641 (1990).
- ⁶K. Okano, H. Kiyota, T. Kuruso, and M. Ida, *Diam. Relat. Mater.* **3**, 35 (1994).
- ⁷M. Kamo, H. Yarimoto, T. Ando, and Y. Sato, in *Proceedings of the 2nd International Conference on New Diamond Science and Technology*, edited by R. Messier, J. T. Glass, J. E. Butler, and R. Roy (Materials Research Society, Pittsburgh, 1991), p. 637.
- ⁸H. Shiomi, K. Tanabe, Y. Nishibayashi, and N. Fujimori, *Jpn. J. Appl. Phys.* **29**, 34 (1990).
- ⁹S. N. Schauer, J. R. Flemish, R. Wittstruck, M. I. Landstrass, and M. A. Plano, *Appl. Phys. Lett.* **64**, 1094 (1994).
- ¹⁰G. Z. Cao, F. A. J. M. Driessen, G. J. Bauhuis, L. J. Giling, and P. F. A. Alkemade, *J. Appl. Phys.* **78**, 3125 (1995).
- ¹¹J. F. Prins, paper presented at the 6th European Conference on Diamond, Diamond-like and Related Materials, Barcelona, Spain, 1995; *Indust. Diam. Rev.* **56**, 22 (1996).
- ¹²A. T. Collins, *Diam. Relat. Mater.* **1**, 457 (1992), and references therein.
- ¹³J. te Nijenhuis, W. J. P. van Enkevort, and L. J. Giling (unpublished)
- ¹⁴R. J. Graham, T. D. Moustakas, and M. M. Disko, *J. Appl. Phys.* **69**, 3212 (1991).
- ¹⁵J. A. Freitas, Jr., P. B. Klein, and A. T. Collins, *Appl. Phys. Lett.* **64**, 2136 (1994).
- ¹⁶J. J. Schermer, W. J. P. van Enkevort, and L. J. Giling, *Diam. Relat. Mater.* **3**, 408 (1994).
- ¹⁷A. T. Collins, and C. S. Lawson, *J. Phys., Condens. Matter.* **1**, 4029 (1989).
- ¹⁸P. J. Dean, *Phys. Rev.* **139**, 588 (1965).
- ¹⁹R. Jones, J. E. Lowther, and J. Goss, *Appl. Phys. Lett.* **69**, 2489 (1996).