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The effect of growth conditions and N_2/O_2 ambient on LO-phonon replicas during epitaxial growth of ZnO on c-sapphire

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Abstract High quality heteroepitaxial thin films of ZnO:N were grown by pulsed laser deposition using a two-step growth method and annealed in situ at different temperatures and ambient conditions. Films were analyzed by X-ray diffraction (XRD), electrical measurements, and photoluminescence experiments at low temperatures to investigate the effect of nitrogen doping. The XRD results demonstrate epitaxial growth on the c-sapphire substrates, with average grain size of 57 nm. Photoluminescence spectra reveals a peak at 3.061 eV (405.1 nm) which is part of the longitudinal-optical-phonon replicas of excitons bound to neutral acceptors $A_1^0 X_A$ at 3.348 eV (370.4 nm), attributed in recent investigations to a newly reported donor–acceptor pair. Electrical resistivity and Hall effect measurements were performed using standard four point van der Pauw geometry at room temperature. Fresh films exhibited a resistivity of 3.1×10^{-3} Ω cm, a carrier density of 1.3×10^{19} cm^{-3}, and a mobility of 53 cm^2/V s. During approximately 2 weeks the as-deposited films presented a p-type behavior, as shown by the positive sign of the Hall constant measured. Thereafter, films reverted to n-type. From electrical measurements and photoluminescence spectra, the acceptor energy was determined to be 150 meV, in close agreement with reported values. These results are consistent with those presented in the literature for high purity crystals or homoepitaxial thin films, even though samples for the present study were processed at lower annealing temperature.

Introduction

In recent years, an increasing need for short-wavelength, high power solid state emitters and detectors have encouraged research on wide bandgap semiconductors. Hexagonal (wurtzite structure) ZnO, with a 3.37 eV bandgap at 300 K, has merited extraordinary attention in this respect. This is mostly due to its large free-exciton binding energy (60 meV) contrasting with its near competitor GaN (21–25 meV at room temperature). Özgür et al. [1] recently provided a complete review of the state of research on ZnO. In state of the art optoelectronics devices, it is mandatory to have high quality materials of both n-type and p-type characteristics. However, while crystalline ZnO is naturally n-type, p-type ZnO is very difficult to achieve. There have been many reports on ZnO doping through native defects (intrinsically) and by unintentional impurity or intentional doping (extrinsically). The results of Zhang et al. [2] show that ZnO cannot be intrinsically doped p-type via shallow native acceptors O_i (oxygen interstitial) or V_{Zn} (zinc vacancies) in an equilibrium process because Zn_i (zinc interstitial) or Zn_o (substitutional zinc in oxygen sites) defects, which have low formation enthalpies under both Zn- and O-rich conditions, may be compensating them. Vanheusden et al. [3, 4] have proposed that V_o (oxygen vacancies) defects are responsible for the appearance of the green–yellow band in the PL spectra because they act as electron–hole recombination centers. Look et al. [5] suggested that Zn_i is the dominant shallow donor which impedes production of intrinsic p-type ZnO.

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Ab initio calculations which suggested nitrogen as a candidate to obtain p-type ZnO, also demonstrated that at a low dopant regime V_o (donors) is the principal defect which compensate the acceptors. Similarly, at high nitrogen doping levels, Zn_o forms deep defect complexes which compensate the acceptors. Ab initio calculations by Yan et al. [6] explain the results of Joseph et al. [7] for ZnO by pulsed laser deposition (PLD) with or without use of a plasma source, and doped by using N_2O or N_2, ambient gases. Their films grown with N_2O and deposited with the plasma source turned on presented p-type characteristics, with a resistivity of 5.0×10^5 Ω cm, while those deposited with the plasma source turned off were n-type, with a resistivity of 4.3×10^{-2} Ω cm. In addition, the films exhibited high hole concentration but a low mobility. Films grown in N_2 (with plasma source on) were n-type, with a resistivity of 0.17 Ω cm, a carrier density of 1.3×10^{19} cm^{-3}, and a mobility of 1.3 cm^2/V s.

Another difficulty is related to diffusion of hydrogen in ZnO, since hydrogen is present in most thin film growth environments as a residual gas or in residual water vapor. It has been argued that hydrogen can act simply as a shallow donor in ZnO, as suggested initially by Van de Walle [8, 9]. On the other hand, according to theoretical considerations, it has been predicted that it can cause a passivation effect [10]. Recently, Lyons et al. [11] using ab initio calculations with hybrid functionals found compelling evidence that nitrogen acceptors are not energetically favorable for p-type ZnO.

It is important to note that new nitrogen-related donor–acceptor pairs (DAPs) have been reported by several groups, while there is no consensus with respect to the DAP assignment [12, 13]. For example, Monteiro et al. [12] found, assuming that there are shallow donors at 67 meV involved, a DAP1 located at 3.220 eV (385.1 nm) and DAP2 located at 3.238 eV (383 nm), both nitrogen related, in high quality crystals, with acceptor levels of 250 and 232 meV, respectively. Adekore et al. [13] reported a single donor acceptor–transition at 3.067 eV (404.3 nm), and its phonon replica at 2.995 eV (414 nm), for nitrogen ion-implanted wafers. They also found a single acceptor at 3.057 eV (405.6 nm) in homoepitaxial films grown by metalorganic vapor deposition. The nitrogen acceptor binding energy was determined to be 333 meV, which they argue is comparable to the DAP peak at 3.235 eV (383.3 nm) with binding energy of 165 meV, and cited in Ref. [3] therein, for nitrogen-implanted crystals annealed at 900 °C.

Recently, Thonke et al. [14] found strong evidence that the emission at 3.31 eV in unstrained films and nanostructures of ZnO is attributed to a recombination of free electrons with neutral acceptor-like defects in the basal plane stacking fault (SF), with an acceptor binding energy of 130 ± 3 meV.

In the present work, structural and optical properties of ZnO:N deposited by PLD in N_2/O_2 ambient were investigated by X-ray diffraction (XRD), photoluminescence spectroscopy (PL) at cryogenic temperatures, and resistivity and Hall effect measurements using standard four point van der Pauw geometry at room temperature. The nitrogen-related effects were detected by PL and confirmed by the sign of the Hall constant (R_H) determined for samples grown at different background pressures in N_2/O_2 or O_2 ambient, and at different annealing ambient and temperatures. Hall constant values were measured for samples at different times after deposition.

Experiment

Samples were deposited onto polished (0001)-cut sapphire crystals. For cleaning, substrates were immersed in successive ultrasonic baths, of ethanol, trichloroethanol, and methanol, during 10 min each and finally dried with flowing N_2. A commercial 99.998% purity ZnO ceramic disk (Praxair, Inc.) was employed as target. The films were grown by PLD technique with an excimer laser (Lambda Physik, Compex 110) using KrF excimer ($\lambda = 248$ nm emission), and with an average fluence of 2 J/cm^2 at the target. N_2 and O_2 were used as reactive gases at 14 and 8 sccm flows, respectively, independently adjusted with mass flows controllers (MKS Instruments, Inc.). No plasma source was used. The chamber was evacuated with a turbomolecular pump to a background pressure in the 10^{-7} Torr range. Pressures during growth and in situ annealing were monitored with a capacitance diaphragm gauge (Varian Ceramicel). The target–substrate distance was held at 5 cm for all depositions. With an initial temperature of 400 °C and initial pressure of 10 mTorr a buffer layer was growth during 10 min while firing the laser at a repetition rate of 1 Hz. Thereafter, temperature and pressure were, respectively, increased to 520 °C and 30 mTorr, while the rate of firing was also increased to 4 Hz for the rest of the deposition. At the end of the deposition, the films were annealed in situ at 520 °C in O_2 ambient at 5.0 mTorr constant pressure during one hour, and then were slowly cooled down to room temperature while keeping the same pressure. The films were kept in a desiccator afterwards and in-between characterization experiments.

The crystal structure of deposited films was measured by XRD in a Bruker Discover D8 Diffractometer, using Cu K_α radiation. Some XRD scans required Cu $K_{\alpha 1}$ radiation, which was obtained by inserting a 4-reflection Ge crystal monochromator in the beam line. Photoluminescence spectra at 8 K were measured using a RMC cryostate, a SPEX 1403 double spectrometer, and a Coherent Innova 306 Ar laser. The ultraviolet line of the Ar laser at 351 nm was used to excite the samples. Hall measurements using four point van der Pauw geometry were performed at room temperature attaching fine gold wire on the corners of square (1 cm^2) samples. The structural and electrical parameters were measured during periods of more than 20 days after depositions. The PL spectra and Hall measurements were conducted with samples aged almost the same time.

Results for electrical and XRD characterization

For fresh ZnO:N films the resistivity obtained was $3.1 \times 10^{-3}\ \Omega$ cm. For films with an average thickness of 1000 Å, as measured with an Alphastep stylus profilometer, and using a magnetic field of 0.5 T, the Hall constant obtained was $+1.63 \times 10^{-1}\ \mathrm{cm}^3/\mathrm{C}$, and mobility was 53 cm^2/V s. After 2 weeks, samples exhibited a resistivity of $1.7 \times 10^{-5}\ \Omega$ cm and a Hall constant of $-1.46 \times 10^{-4}\ \mathrm{cm}^3/\mathrm{C}$.

XRD analysis of all samples evidenced very strongly oriented structure, with parallel *c* directions for the ZnO film and the *c*-cut sapphire substrates. Figure 1a shows a θ–2θ scan taken with monochromatic Cu $K_{\alpha1}$ radiation. Only the (0002) peak and the second order (0004) peak (not shown in the figure) were found for the film. The narrower peak in the graph is the sapphire (0006) peak. For this sample the integrated peak breadth, corrected for instrument breadth, is 0.146°, corresponding to an average coherent crystallite length along the direction normal of the sample surface (Scherrer size) of 570 Å, which is consistent with the full film thickness of the sample. In θ–2θ scans at higher beam intensity (with Cu $K_{\alpha1}$ radiation) no peaks other than those corresponding to the (0001) planes were found, confirming the strong out-of-plane orientation. Rocking curves with Cu $K_{\alpha1}$ radiation, such as the scan in Fig. 1b show a typical full width at half maximum of less than 0.25°, which is further confirmation of strong out-of-plane orientation. Peak positions for the (0002) ZnO reflections in the samples are slightly higher than the expected values (as given, for example, in the ICDD Powder Diffraction File # 36-1415). This indicates that the ZnO/sapphire films are in tension after growth.

In-plane film texture of the samples was studied with azimuthal (Φ angle) scans taken with Cu $K_{\alpha1}$ radiation. Figure 1c shows two azimuthal scans for the same ZnO/sapphire sample as in Fig. 1a at tilt angles (X) corresponding to those between the (0001) surface plane and, respectively, the $\left(01\bar{1}2\right)$ plane for sapphire (black trace), and the $\left(01\bar{1}1\right)$ plane for ZnO (blue trace). The equally spaced peaks correspond to the three and sixfold crystal symmetry of sapphire and wurtzite ZnO, respectively, demonstrating the epitaxial arrangement of the ZnO film over the sapphire *c* plane. The 30° shift between the two scans corresponds to the rotation by this same angle of the ZnO lattice structure over the sapphire lattice, so that the in-plane directions are ZnO $\left[10\bar{1}0\right]\|$sapphire $\left[11\bar{2}0\right]$. This heteroepitaxial arrangement reduces the effective lattice mismatch between ZnO and *c*-cut sapphire [1]. The width of the ZnO peaks in this Φ scan is $\sim 0.5°$, which is relatively small, considering the expected mosaicisity due to the substantial lattice mismatch with the substrate.

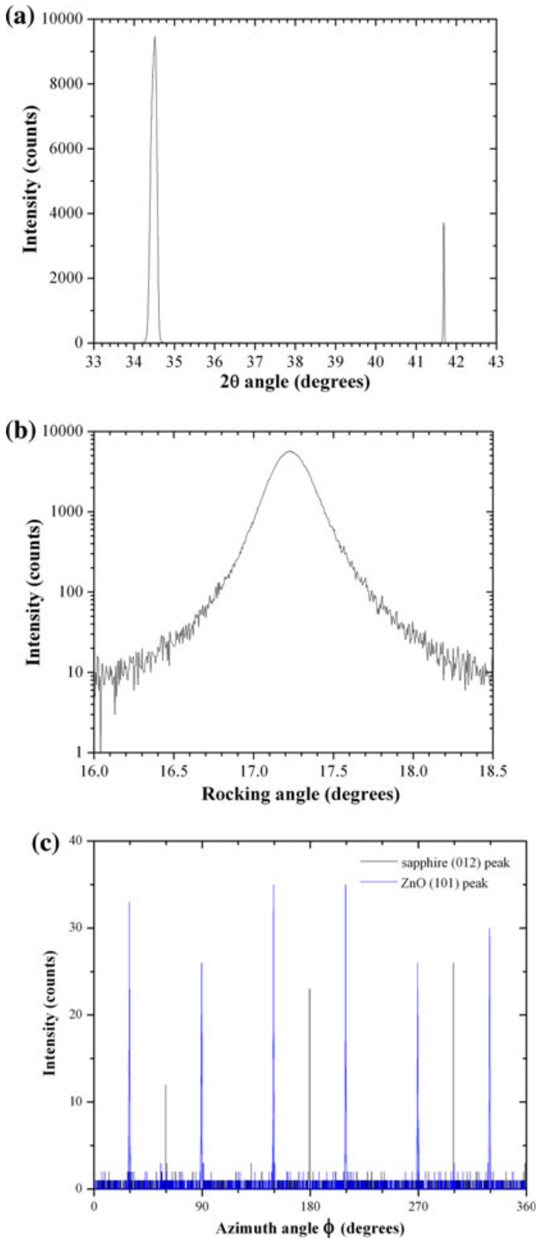

Fig. 1 **a** (*Left*) XRD θ–2θ scan spectra of undoped ZnO. Sample was grown at 520 °C and 32 mTorr, and annealed in O_2 at 520 °C for 1 h. **b** (*Center*) XRD rocking curves scan for ZnO:N. Sample was grown at 520 °C and 32 mTorr, and annealed in O_2 at 520 °C for 1 h. **c** (*Right*) XRD azimuthal scans for undoped ZnO film. Sample was grown at 520 °C and 32 mTorr, and annealed in O_2 at 520 °C for 1 h

Photoluminescence spectra

Photoluminescence spectra of films annealed at 520 °C

Figure 2 shows the PL spectra at 8 K of a ZnO:N thin film sample grown at 520 °C and annealed at the same temperature in O_2. Peak assignment can follow those reported in the literature for bulk ZnO [15, 16]. Emission peaks observed at 3.416 eV (363.0 nm) and around 3.373 eV (367.6 nm), are designated as free excitons ($FX_A^{n=2}$) and ($FX_A^{n=1}$), respectively. An energy separation between exciton A and its first excited state of 43 meV corroborates this assignment. Satellites (or shoulders), at 3.382 eV (366.6 nm), 3.370 eV (368 nm), and 3.362 eV (368.8 nm) [17], correspond, respectively, to free excitons ($FX_B^{n=1}$), lower polariton branch (LPB$_A$), and excitons bound to neutral donors ($D_1^0X_A$). Note that the energy separation Δ_{AB}, between A and B free excitons is in the range 9–15 meV [1].

The dominant emission peak at 3.357 eV (369.3 nm), weak shoulders at 3.282 eV (369.7 nm) and at 3.348 eV (370.4 nm) within the long tail, and the peak located at 3.329 eV (372.4 nm), are attributed, respectively, to excitons bound to neutral acceptors $A_1^0X_B$, $A_2^0X_B$ and $A_1^0X_A$, and two-electron satellite $\left(D_1^0X_A\right)_{2e}$transitions. The peak located at 3.313 eV (374.3 nm), which is attributed to exciton complexes from deep defect centers, and the peak at 3.287 (377.2 nm) attributed to free electron to acceptor level ($FA_1^0X_B$), were also observed. The broad peak whose center is located near 3.313 eV (374.3 nm) was recently associated with an acceptor in the basal plane SF [14]. It is also associated with substitutional nitrogen in the ZnO lattice, and has been observed by several groups in p-type ZnO and also, with weaker intensity, in n-type ZnO:N [18, 19]. Although this peak falls in the range of phonon replicas according to some authors [15, 16], we cannot assign it to a phonon replica of $A_1^0X_B$ (369.3 nm), because the separation between these lines is substantially shorter than the longitudinal-optical (LO)-phonon energy in ZnO ($E_{LO} =$ 72 meV, [20]). Neither can it be assigned to a phonon replica of two-electron satellite (TES) transitions, because the separation between these lines is substantially shorter than the energy of the LO phonon in ZnO. Furthermore, for DAP transitions the energy of the bound exciton depends on the donor–acceptor distance. Multiple DAP transitions with different donor–acceptor distances are expected to occur. As a result, broadened or overlapped multi-peaks may be detected in this spectral range. This is just what was observed near the peak at 3.313 eV (374.3 nm), with a line width at half maximum (FWHM) of 8 meV, contrasting with 4.5 meV for the dominant peak in Fig. 2a for a fresh p-type ZnO:N thin film.

It is expected that Zn$_i$ may trigger the basal plane SF formation under zinc-rich growth conditions. Hence, unintentional defects such as Zn$_i$, may be present in the samples, which are more diffusive than V$_o$. The formation of such a basal plane SF requires the precipitation of a double layer of zinc and oxygen atoms, which activates the diffusion of surrounding oxygen atoms to complete the (0002) double layer [21]. The V$_o$ defect, which is thermodynamically unstable, could be compensated more likely by the substitution of molecular nitrogen in oxygen sites $(N_2)_o$ due to its relatively low formation energy, by the substitution of atomic nitrogen in oxygen sites (N$_o$), or by complexes involving nitrogen impurities. The further assignment of the broad peak located near 2.254 eV (550 nm) will be discussed in "Temperature dependent effects due to annealing in O_2" section.

For peaks in Fig. 2b the following assignments are proposed: exciton emission at 3.287 eV (377.2 nm) corresponding to $FA_1^0X_B$, $A_1^0X_B$-1LO at 3.284 eV (377.6 nm), $A_2^0X_B$-1LO at 3.282 eV (377.8 nm), $A_1^0X_A$-1LO at 3.276 eV (378.5 nm), $\left(D_1^0X_A\right)_{2e}$-1LO at 3.258 eV (380.6 nm), $\left(D_1^0X_A\right)_{2e}$-2LO at 3.185 eV (389.3 nm). The peak at 3.266 eV (379.7 nm) was not assigned but might be related to a phonon replica of a transition within the tail, which begins to develop at 3.338 eV (371.5 nm) and falls in the TES region, with an energy separation of 72 meV. The relative intensity of the LO-phonon replicas must be roughly two orders of magnitude less than the intensity of the exciton bound to neutral donors [1], which is in agreement with the results presented in Fig. 2b. Around 383 nm (Fig. 2b) a broad band, or several bands centered near 3.239 eV (382.8 nm), can be observed which may be assigned to the DAP-1LO of the DAP at 3.313 eV (374.3 nm). This peak's position is near that reported by Monteiro et al. [12]. The broad peak at 3.232 eV (383.7 nm) was not assigned but could be related to DAP-1LO. A broad peak is also observed centered at 3.215 eV (385.7 nm), shoulders near 3.212 eV (386.1 nm) and 3.209 eV (386.4 nm), a weak peak at 3.205 eV (386.9 nm), and a better defined peak at 3.142 eV (394.7 nm). These can be assigned as follows, respectively: $FA_1^0X_B$-1LO, $A_1^0X_B$-2LO, $A_2^0X_B$-2LO, $A_1^0X_A$-2LO, and $FA_1^0X_A$-2LO. In the lower energy part presented in Fig. 2c the phonon replicas corresponding to DAP-2LO, $A_1^0X_B$-3LO, $A_1^0X_A$-3LO, and $A_1^0X_A$-4LO are observed, respectively, at 3.167 eV (391.5 nm), 3.139 eV (395 nm), 3.133 eV (395.8 nm), and 3.061 eV (405.1 nm).

The observation of the fourth order LO-phonon replicas ($A_1^0X_A$-4LO) is associated with the high epitaxial quality of the ZnO:N samples. The peak has nearly the same position as that reported by Adekore et al. [13] at 3.057 eV (405.6 nm) for homoepitaxial films and which they attributed to DAP. However, if that interpretation is applied in our case, no peaks can be attributed to phonon replicas.

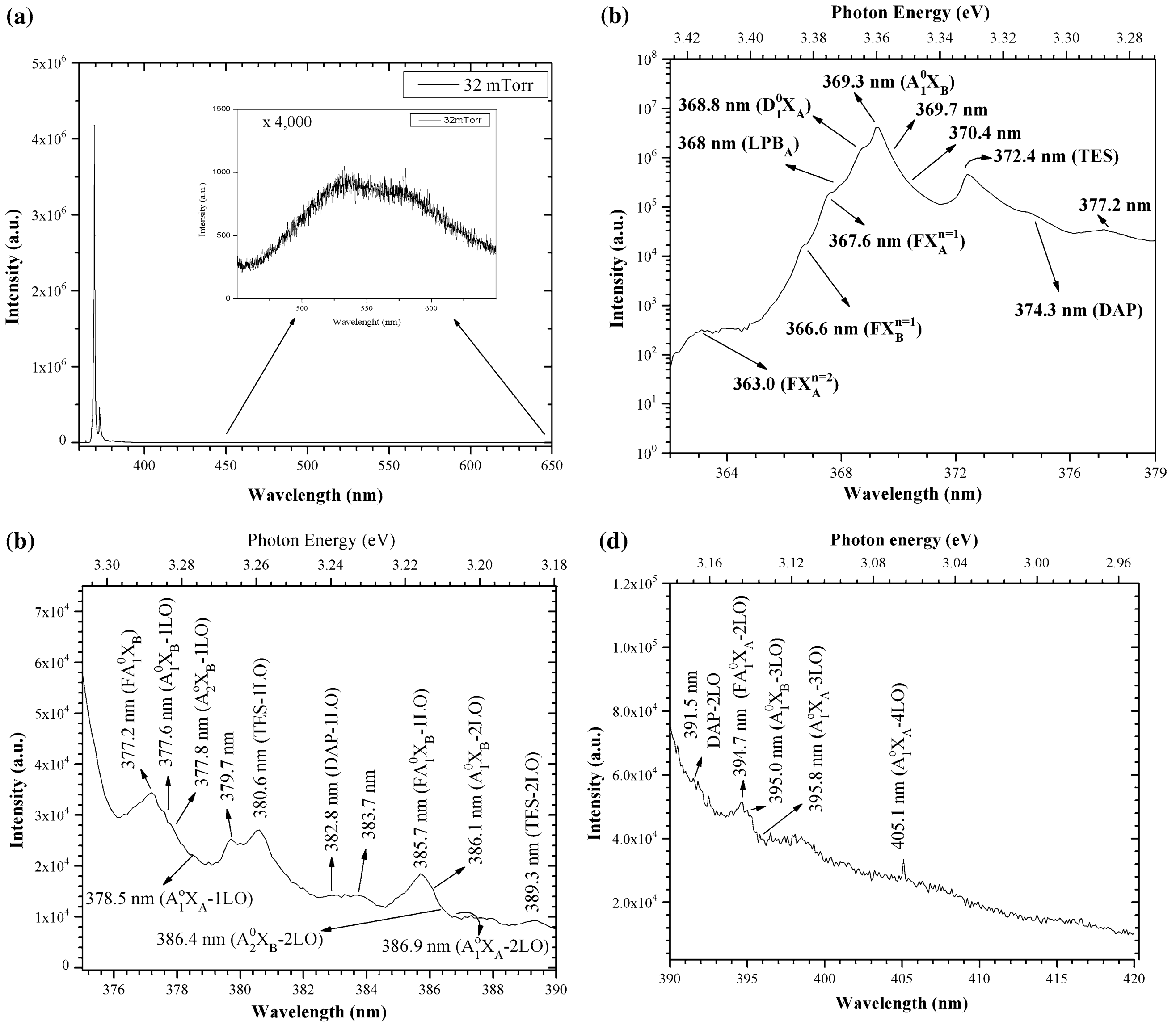

Fig. 2 **a** PL spectra of ZnO:N at 8 K. Sample was grown at 520 °C and 32 mTorr, and annealed in O_2 at 520 °C for 1 h. **b** Amplified spectral region from 363 nm to 379 nm. **c** PL spectra from 375 to 390 nm of ZnO:N at 8 K. Sample was grown at 520 °C and 32 mTorr, and annealed in O_2 at 520 °C for 1 h. **d** PL spectra from 390 nm to 420 nm of ZnO:N at 8 K. Sample was grown at 520 °C and 32 mTorr, and annealed in O_2 at 520 °C for 1 h

The appearance of this peak and, in general higher orders of LO-phonon replicas, rely strongly on crystal quality. This is supported by the PL results presented in Fig. 2a–c, including the 4.5 meV FWHM of the dominant peak, along with the XRD results presented above.

The results presented in Fig. 2 are for a sample annealed at 520 °C, which is much lower than the temperature commonly required, to achieve similar results [1]. The exciton phonon replicas can customarily be observed in samples with extremely high quality, such as those studied by Adekore et al. [13], but the intensity of the LO-phonon replicas must be roughly two orders of magnitude less than the intensity of the emission for the exciton bound to neutral donors [1], as previously commented, which is not in accordance with the results presented in Ref. [13]. Moreover, from Ref. [13] results, the Huang-Rhys factor inferred for the DAP assignment is much lower than the expected value for such a large binding DAP energy.

In order to further investigate the origin of the N-related peaks, and the assignment of the DAP at 3.313 eV (374.3 nm) in the SF, the PL spectra for films grown at double pressure, but with the other deposition parameters fixed were analyzed. This analysis is presented in "Effect of the growth pressure of nitrogen" section. Similarly, and for consistency purposes, the PL results presented previously, along with the PL spectra of films annealed at a different temperature and ambient conditions (and other fabrication parameters fixed), will be discussed in "Temperature dependent effects due to annealing in O_2" and "Effect of N_2/O_2 annealing ambient in the photoluminescence spectra" sections, respectively.

Effect of the growth pressure of nitrogen

Figure 3 shows PL results for a film grown at twice the pressure used for growth of the sample described in "Photoluminescence spectra of films annealed at 520 °C" section. In this case the $A_1^0X_B$ emission at 369.3 nm is broadened and overlapped with other peaks, resulting in a dominant peak located at 368.8 nm ($D_1^0X_A$). Because of additional stress produced by nitrogen substitution in the lattice a red shift of the peak is expected, similar to the red shift due to substrate mismatch reported in the literature [22, 23]. In addition, the peak at 3.313 eV (374.3 nm) is further broadened with overlapped structure, and a peak with higher relative intensity and FWHM of 22.9 meV appears at 3.306 eV (375 nm). The energy difference between the dominant peak at 3.362 eV (368.8 nm), and the peak at 375 nm is 55.6 meV, which does not fit the energies of the phonon replicas [16, 18, 20]. In consistency with "Photoluminescence spectra of films annealed at 520 °C" section, the exciton bound to the neutral acceptor$A_1^0X_B$, and the weak shoulders attributed to excitons bound to neutral acceptors, $A_2^0X_B$ and $A_1^0X_A$, are more defined in this case, and are clearly observed at 3.359 eV (369.2 nm), 3.355 eV (369.6 nm), and 3.348 eV (370.4 nm), respectively. In addition, two TES, $(D_2^0X_A)_{2e}$ and $(D_1^0X_A)_{2e}$, were found at 3.339 eV (371.4 nm) and 3.324 eV (373 nm), respectively. Unassigned peaks similar to those presented in Fig. 2c were also observed, as shown in the lower energy part of Fig. 3b.

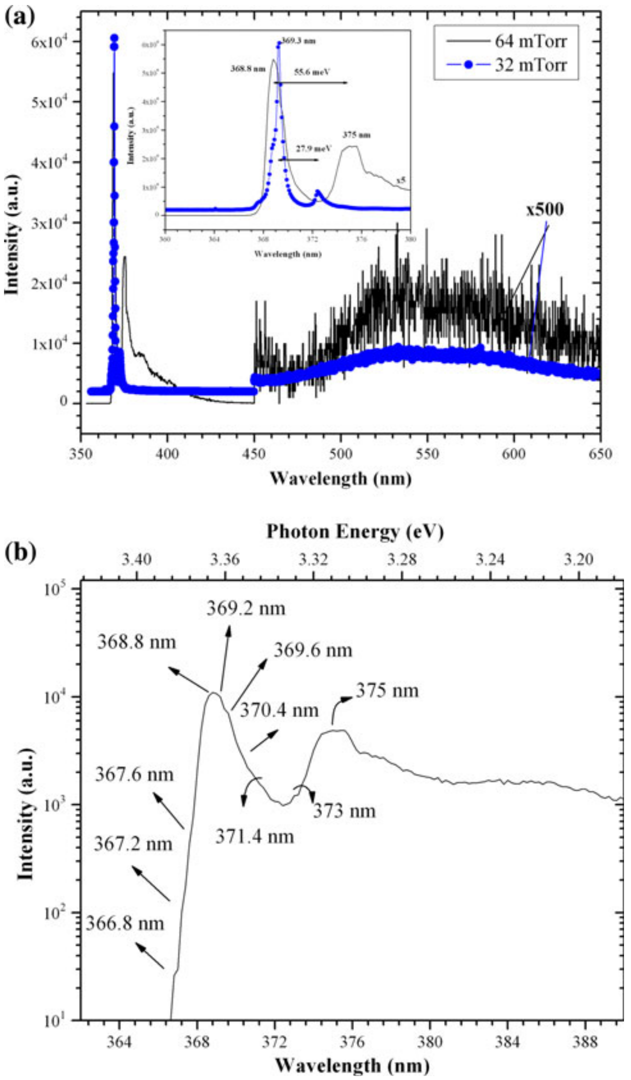

Fig. 3 **a** Comparison of PL spectra of films grown at 32 and 64 mTorr at 8 K annealed in O_2 at 520 °C for 1 h. **b** PL spectra from 363 nm to 389 nm of ZnO:N at 8 K. Sample was grown at 520 °C and 64 mTorr, and annealed in O_2 at 520 °C for 1 h

The dominant peak was also broadened, with the FWHM increasing from 4.5 to about 12.7 meV. Furthermore, N-related DAP emissions become stronger at the expense of decreasing and broadening of the free and bound ($A_1^0X_B/D_1^0X_A$) excitons. The acceptor binding energy for a distant DAP transitions in the SF, can be estimated using the equation:

$$h\nu_{DA} = E_g - E_D - E_A + \frac{e^2}{4\pi\varepsilon R_{DA}} \tag{1}$$

where E_g and ε are the band gap and dielectric constant of ZnO, respectively, E_D and E_A are the donor and acceptor binding energies, and R_{DA} is the relative distance between the donor and acceptor concerned. Because of the expected random distribution of nitrogen in ZnO, R_{DA} may vary. Hence, with an increase in population of donor and acceptor centers, R_{DA} is supposed to decrease, which explains the peak broadening effect of the DAP band in N-doped films. Therefore, N-related DAP emission in the basal plane SF can be expected to be a broad band or several overlapped bands, which can explain the results shown in Figs. 2 and 3.

From the Hall measurements ("Results for electrical and XRD characterization" section) for samples with growth conditions given in "Photoluminescence spectra of films annealed at 520 °C" section, the residual acceptor density was about 3.8×10^{19} cm^{-3} for fresh ZnO:N. An estimated value of R_{DA} is then calculated from the equation:

$$R_{DA} = \left(\frac{3}{4\pi N_D}\right)^{\frac{1}{3}} \tag{2}$$

From this, the Coulomb energy term in (1) can be calculated, which results in 92.1 meV. Using this value, and the ZnO band gap of 3.437 eV [24–26], the acceptor energy is estimated to be 156 meV, which is within the limits of 160 ± 45 meV reported by Zeuner et al. [19] Alternatively, from the equation:

$$E_A = E_g - E_{FAX} - \frac{k_B T}{2} \qquad (3)$$

and the peak position at 3.287 eV (377.2 nm) assigned to $FA_1^0X_B$ in section (a), the estimated acceptor energy is 150 meV, in agreement with the results previously presented.

Temperature dependent effects due to annealing in O_2

It is expected that oxidation occurs more favorably during annealing at higher temperatures, so that some oxygen vacancies are removed and some oxygen may substitute for nitrogen. To verify this argument, PL spectra were obtained for thin films grown under similar conditions, but annealed at just 400 °C in O_2.

The results presented in Fig. 4a and b are contrasted with the PL spectra previously analyzed in "Photoluminescence spectra of films annealed at 520 °C" section. The emission peaks observed as satellites (or shoulders), at 3.382 eV (366.6 nm), 3.375 eV (367.6 nm), and 3.362 eV (368.8 nm), are designated as free excitons ($FX_B^{n=1}$), ($FX_A^{n=1}$), and excitons bound to neutral donors ($D_1^0X_A$), respectively, in close agreement with those presented in "Photoluminescence spectra of films annealed at 520 °C" section. The other peaks were not assigned. The dominant $A_1^0X_B$ peak located at 3.359 eV (369.2 nm) is at a similar position as in Fig. 2a. Also, the weak shoulders at 3.355 eV (369.6 nm) and 3.348 eV (370.4 nm), attributed to $A_2^0X_B$ and $A_1^0X_A$, respectively, which are seen more clearly in this case, presented comparable and consistent positions to those reported in "Photoluminescence spectra of films annealed at 520 °C" and "Effect of the growth pressure of nitrogen" sections.

The TES peak at 372.4 nm $\left(D_1^0X_A\right)_{2e}$ was observed for both samples, followed by two additional peaks at 3.316 eV (374 nm) consistent with the DAP assigned in "Photoluminescence spectra of films annealed at 520 °C" section, and 3.299 eV (375.8 nm) related to the DAP assigned near 3.306 eV (375 nm) in "Effect of the growth pressure of nitrogen" section. The FWHM of the dominant peak is 3.6 meV for samples annealed at 400 °C. At 520 °C in O_2 oxidation is favorable, and thin films are expected to improve in crystal quality, which is verified by the line width and the emission intensity. For samples annealed in O_2 ambient at 400 °C the DAP relative intensity is higher while the N-related peaks are broader. Thus, by annealing the thin films in O_2 at lower temperature, the N-related DAP emission increased, which indicates that nitrogen can easily enter into the ZnO lattice even at 400 °C.

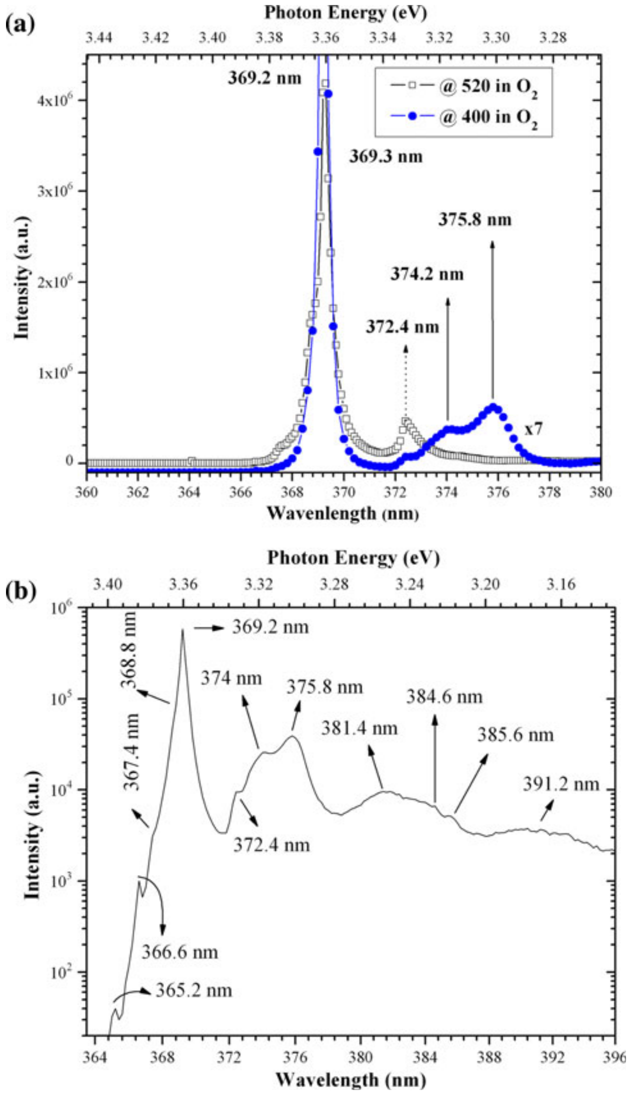

Fig. 4 **a** Comparison of PL spectra of films annealed in O_2 at 520 and 400 °C at 8 K. **b** PL spectra from 364 to 396 nm at 8 K. Sample was grown at 520 °C and 32 mTorr, and annealed in O_2 at 400 °C

The above results support the argument that at lower annealing temperature (400 °C) nitrogen incorporation is more effective. As previously discussed, because the energy of the bound exciton depends on the donor–acceptor distance, a broadening effect of DAP peaks of the samples prepared at lower annealing temperatures is expected. This result supports the assignment as DAP peaks to those observed at 3.299–3.314 eV [27], especially for the DAP in the SF of ZnO at 3.314 eV [14]. It is noted in relation to the lower part of Fig. 4b that no clear emission comparable to the $A_1^0X_A$-4LO peak at 3.061 eV (405.1 nm), nor to LO-replicas, such as those presented in Fig. 2b and c, were observed.

The broad green emission (GE) peak located near 2.254 eV (550 nm) in Fig. 2 is attributed to oxygen vacancies. Vanheusden et al. [3, 4] have suggested that the green peak is due to radiative recombination of a photon-generated hole in the valence band (VB) with an electron-occupied singly ionized oxygen vacancy, which is located well below the bottom of the conduction band (CB). In a model proposed by van Dijken et al. [28, 29] in relation to the influence of nanocrystalline ZnO in PL spectra, they proposed that the oxygen vacancy defects were located above the VB. Based on this model, the oxygen vacancies can accept one (V_o^*) or two (V_o^{**}) electrons and remain as ionized acceptors. These ionized acceptors can trap holes from the VB. Hence, according to this model, the green emission originates from a recombination between electrons in the CB or in shallow trapping centers (shallow donor states) and the holes trapped in the acceptors (V_o). Very low relative intensity of the GE band with respect to the dominant peak, as revealed in Fig. 2, indicates a low concentration of oxygen vacancies in our films. The most interesting result from the films grown at higher pressures (O_2), and even those annealed at lower temperature in O_2, is that the PL green emission is still very weak, in a relative proportion of 1:1000 with respect to the dominant peak, as opposed to those reported on by Jin et al. [30], for example. These authors reported that the relative GE intensity increased when the oxygen pressure during growth was increased from 1 to 200 mTorr, for thin films grown on sapphire at 400 °C by PLD. For our samples, in contrast, either prepared at higher oxygen pressures or annealed at lower temperatures in O_2, the GE observed remained at a low level of relative intensity.

Effect of N_2/O_2 annealing ambient in the photoluminescence spectra

To further elucidate the nature of these DAPs, and to corroborate their assignment, the PL results from samples presented in Fig. 2 are compared in detail with PL spectra from samples grown with identical conditions but annealed in N_2/O_2 ambient. For these samples, as shown in Fig. 5, a similar behavior as before was found, but red shifted as expected by the inclusion of nitrogen. In agreement with previous cases, these samples presented peaks or shoulders which can be attributed to excitons bound to neutral donors: $D_2^0X_A$ at 3.365 eV (368.5 nm), and $D_1^0X_A$at 3.360 eV (369 nm) with a FWHM of 3.6 meV; two types of excitons bound to neutral acceptors: $A_1^0X_B$ at 3.355 eV (369.6 nm), and $A_1^0X_A$ at 3.346 eV (370.6 nm); and also two TES: $(D_2^0X_A)_{2e}$ and $(D_1^0X_A)_{2e}$, found at 3.339 eV (371.4 nm) and 3.328 eV (372.6 nm), respectively. These assignments are consistent with those reported in "Photoluminescence spectra of films annealed at 520 °C" through "Temperature dependent effects due to annealing in O_2" sections. The main DAP peak, with a FWHM of 17.6 meV, is located at 3.303 eV (375.4 nm), followed by a peak at 3.286 eV (377.4 nm), attributed to free electron to acceptor level ($FA_1^0X_B$), in accordance once more with the results presented in previous sections.

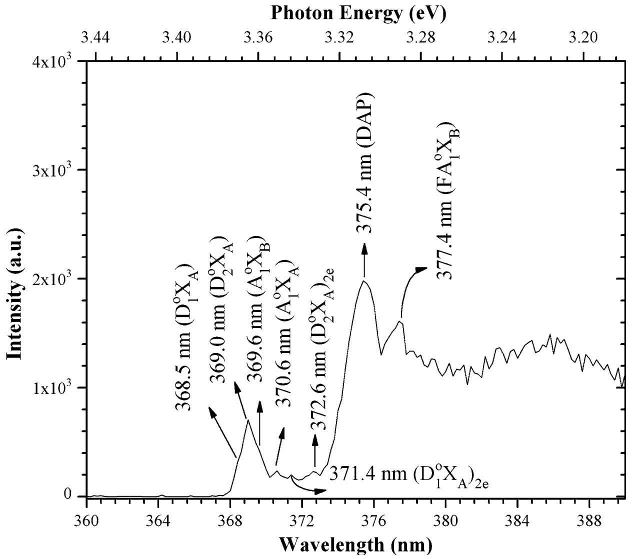

Fig. 5 PL spectra of films annealed in N_2/O_2 at 520 °C for 1 h at 8 K. Sample was grown at 520 °C and 32 mTorr

In the lower energy part of the spectrum in Fig. 5, a broad band centered at 3.214 eV (385.8 nm) is observed. This could include several narrow peaks which were not assigned. However, in consistency with the DAP assignation, the broad band, 72 meV from $FA_1^0X_B$, at 3.286 eV (377.4 nm), can be assigned to $FA_1^0X_B$-1LO. In addition, its relative intensity is roughly less than two orders of magnitude lower than that of the exciton bound to neutral donors [1]. These assignations are at variance with those made by Monteiro et al. [12] for peaks near 3.220 (385.1 nm) and 3.238 eV (383 nm).

Conclusions

In the present work, we have grown ZnO:N thin films on sapphire by PLD in N_2/O_2 atmosphere with a two-step deposition process and in situ annealing at a temperature no higher than 520 °C. Films were characterized with XRD, PL, and electrical measurements. The excellent crystal quality of the films for the growth conditions implemented was evidenced by their epitaxial characteristics and average crystal size of 57 nm, FWHM of 4.5 meV for the dominant PL peak, as well as by observation of free excitons and LO-phonon replicas of higher orders. These results are comparable to those reported in the literature for high purity crystals or homoepitaxial thin films annealed at a higher temperature. Hall measurements show p-type behavior for fresh films, which reverts to n-type after approximately 2 weeks. The Hall constant also reveals a DAP relaxation process when reverting to n-type, because calculated R_{DA} values increased as the measured R_H values increased. From the results presented, the calculated R_{DA} was 18.4 Å for fresh films, which is in agreement with the vibrational calculation showing that the pair separation beyond which an electron cannot be bound is 25 Å [31 and references therein]. The donors and acceptors peak positions for PL experiments were consistent for samples grown at the same conditions but annealed at 520 °C in O_2 or N_2/O_2, or even annealed at 400 in O_2. Samples grown at double pressure and annealed at 520 °C in O_2 also presented those consistent peak positions. The DAP peaks found in the 3.299–3.314 eV region [27] are consistent with those recently reported in the literature [14]. While formation of a basal plane SF may in principle causes V_o [21], samples prepared either at higher oxygen pressures or annealed at lower temperatures in O_2, with PL emission at 3.314 eV attributed to the SF [14, 32], presented a low level of relative intensity for the yellow emission.

The acceptor binding energy obtained, based on different calculations from the PL spectra, was approximately 150 meV, which is in agreement with results of electrical measurements performed on the fresh samples. For samples annealed at 520 °C in O_2 the peak found near 3.239 eV (382.8 nm) which was assigned to DAP-1LO with respect to the main DAP at 3.313 eV (374.3 nm), presented a low Huang-Rhys factor. Samples annealed at 520 °C in O_2 or N_2/O_2 presented $FA_1^0X_B$ and $FA_1^0X_B$-1LO peaks positions in close agreement. The peak at 3.061 eV (405.1 nm) found for samples annealed at 520 °C, which has a comparable position to those annealed at higher temperature and reported in Ref. [12], was assigned to $A_1^0X_A$-4LO, in variance with the conclusions in Ref. [12]. Otherwise, a similar peak was not observed for samples either grown at higher pressure, annealed at lower temperature or different reactive ambient, mainly because of deterioration in crystal quality as evidenced by the FWHM values in the PL spectra.

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