Spectroscopy of the phosphorus impurity in ZnSe epitaxial layers grown by molecular-beam epitaxy

G. Neu, E. Tournié, C. Morhain,* M. Teisseire, and J.-P. Faurie
Centre de Recherche sur l'Hétéro-Epitaxie et ses Applications, Centre National de la Recherche Scientifique (CRHEA/CNRS), Rue Bernard Grégory, Parc Sophia Antipolis, F-06560 Valbonne, France
(Received 2 November 1999)

Phosphorus-implanted and plasma-doped ZnSe epitaxial layers grown by molecular-beam epitaxy are studied through photoluminescence (PL), selective PL, and PL-excitation spectroscopies. We show that with an activation energy of 85 ± 1 meV, the P-related shallow-acceptor level is the shallowest acceptor ever detected in ZnSe. The series of excited states of this acceptor reveals that it behaves like all substitutional acceptors. We thus identify it as being the simple P_{Se} substitutional impurity. Its excitonic emission definitely occurs at 2.791 eV. Negligible P-related deep levels can be detected by PL. However, a line which is relatively strongly coupled to phonons is detected at 2.796 eV. This line arises from P-related defects involving P incorporated on other-than-Se-substitutional sites. Finally, the lack of conductivity of our ZnSe:P samples, which does not stem from deep defects, could be explained by an *AX*-like behavior of the P impurity.

I. INTRODUCTION

P-type doping properties of ZnSe and related compounds have long been under the focus of attention owing to both fundamental and applied considerations.[1] On the one hand, the difficulty in obtaining stable *p*-type conductivity is a very intricate issue, which is neither experimentally nor theoretically fully understood. On the other hand, this problem still limits the progress of ZnSe-based devices. Only recently did plasma-activated nitrogen emerge as a suitable impurity for the growth of *p*-type ZnSe by molecular-beam epitaxy (MBE),[2,3] which remains the only technique allowing to reproducibly obtain stable *p*-type ZnSe films. However, the highest free-hole concentration in ZnSe:N epilayers reported so far is $(N_a - N_d) \sim (1-2)\times10^{18}\,\mathrm{cm}^{-3}$,[4] and at least two distinct N-related compensating donors have been detected,[5,6] which precludes any hope of reaching higher doping levels.

As a column-V element, phosphorus appears to be a potential candidate for *p*-type doping of ZnSe. In fact, over the past few decades much work to obtain *p*-type ZnSe:P material has been undertaken, but with unclear results. P has been reported to generate exclusively deep levels in bulk ZnSe (Refs. 7–10) as well as in epitaxial layers grown by metal-organic vapor phase epitaxy.[11] These deep centers were blamed for the sample lack of conductivity and, due to the absence of any other new transition in the photoluminescence (PL) spectra, were regarded as involving directly P_{Se}. However, in epitaxial layers deposited either by liquid-phase[12,13] or molecular-beam[14–20] epitaxy, P doping has been reported to give rise not only to deep- but also shallow-acceptor levels. Despite the emissions related to these shallow-acceptor centers, all samples were still insulating. The growth-technique dependence on the formation of shallow levels raises several questions: Do the deep centers really invoke P_{Se} or rather contaminating impurities in the dopant-material source, P clusters, or P incorporation on a site other than substitutional? Could a better incorporation of the P impurity favor shallow over deep levels in order to balance the deep center effect and to achieve a clear *p*-type conductivity?

Yet even when the P impurity forms a shallow level in ZnSe, its electronic properties are still badly comprehended. Although the optical studies previously reported agree with an acceptor activation energy in the 80–90-meV range, the related acceptor-bound exciton peak has, however, been detected at two different energies, either in the usual range for acceptor-bound excitons,[14,19,20] or more surprisingly, in the spectral range where donor-bound exciton lines usually emerge.[15,17,20] Further, this shallow acceptor has also been reported to be a P-related complex rather than the expected P_{Se} substitutional impurity.[17,18]

All these equivocal results call for a clarification. In this paper we report first a comprehensive spectroscopic study of the behavior of the P impurity in ZnSe, which encompasses experimental investigations of the formation of P-related deep levels and of the shallow donor-acceptor pair (DAP) and excitonic emissions. In order to avoid any unwanted incorporation or contamination, the samples were either implanted *ex situ* with P ions or doped *in situ* using plasma-activated P species, by analogy with the N doping of ZnSe known to be effective only when the N_2 dimers are activated in a plasma. Combining the results obtained from optical spectroscopy and confronting them to theoretical predictions, we discuss possible microscopic models to explain the lack of *p*-type dopability of ZnSe using P as a dopant.

II. EXPERIMENT

The samples under investigations were grown directly onto (001) GaAs substrates by solid-source MBE. The growth temperature was 280 °C and the growth rate 1.4 Å/s. The samples reported in this work are thick enough to be fully relaxed at growth temperature. *In situ* P doping was performed with a RFK 30 RF-plasma cell, purchased from Oxford Applied Research, which is specially designed to allow the production of solid-vapor plasmas. 6*N* purity red

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phosphorus was used as the source. We did not characterize the emitted plasma by spectroscopy. We assume, however, that atomic P is produced by the cell, as is the case with a similar although more recent cell.[20] The flux beam-equivalent pressures (BEP) were measured by means of a movable ion gauge. The phosphorus concentration in some layers was determined by secondary ion mass spectroscopy (SIMS). Electrical characterizations were performed by the capacitance-voltage (C-V) technique between coplanar Schottky gold contacts. For the purpose of comparison, P ions were implanted in nonintentionally doped layers [residual carrier concentration $(\mathrm{N}_d-\mathrm{N}_a)\sim(5-10)\times10^{14}\,\mathrm{cm}^{-3}$] with an energy of 100 keV resulting in a mean depth of about 1000 Å with a straggling of 480 Å.[21] Implanted doses are in the range from 5×10^{12} to $10^{15}\,\mathrm{cm}^{-2}$. As-implanted samples were annealed under a Zn atmosphere for 10 min at 500 °C in a vacuum-sealed ampoule. For PL spectroscopy the samples were mounted on the cold finger of a closed-cycle He cryostat, the temperature of which can be regulated between 9 and 300 K. PL was excited by the 325-nm line of an He-Cd laser and detected at the exit of a 64-cm spectrometer. Excitation power was set to $\sim5\,\mathrm{W\,cm}^{-2}$. SPL and PLE measurements were performed at 1.8 K in a He-bath cryostat. The samples were excited by a Stilbene-3 dye laser pumped by the uv lines of an Ar laser. PL was detected at the exit of a 1-m double spectrometer equipped with 1800 grooves/cm gratings blazed at 400 nm. The overall resolution of this setup is ~0.05 meV. Standard PL could also be performed with this equipment. In that case the excitation density was in the 1–100 $\mathrm{W\,cm}^{-2}$ range. In all experiments a CO_2-cooled GaAs photomultiplier was used as a detector. Finally, to evaluate the influence of the residual thermal strain, some layers were removed from their substrate by selective chemical etching.

III. EXPERIMENTAL RESULTS

A. Photoluminescence spectra of ZnSe:P samples

We show in Fig. 1 the PL spectra taken from samples doped with identical rf power but different P flux. The doping level increases from sample (a) to sample (c). The so-called Y line, arising from recombinations on extended defects, the nature of which is not yet completely understood,[22] is clearly seen in Fig. 1(a) and, to a lesser extent, Fig. 1(b). This line being more intense in purer material,[22] its presence in these spectra indicates that the corresponding samples are in fact comparatively lightly doped. Besides, only one series of DAP bands can be seen in all spectra. The zero-phonon line of this series lies near 2.72 eV, which fits well with the DAP bands previously detected in ZnSe:P epitaxial samples.[1] The rise of the DAP-band intensity with an increasing doping level confirms that they are due to a P-related shallow acceptor. Two peaks dominate the excitonic region of the spectra. One peak, located at 2.791 eV, i.e., in the spectra region corresponding to recombinations of neutral-acceptor bound excitons (NABE), is labeled I_1^{P}. Another peak, located at 2.796 eV, i.e., in the spectral region corresponding to recombinations of neutral-donor bound excitons (NDBE) or to neutral-donor to free-hole (D^0h) transitions, is labeled I_φ. The intensity of I_1^{P} with respect to I_φ increases with the P doping, as does the DAP-band intensity.

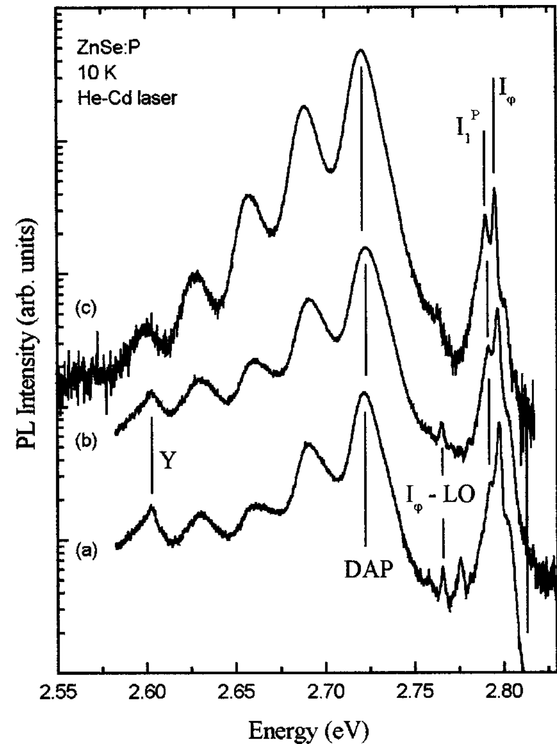

FIG. 1. PL spectra taken from *in situ* doped ZnSe:P epitaxial layers. Doping conditions: $\mathrm{P}_{\mathrm{rf}}=400\,\mathrm{W}$. Phosphorus beam-equivalent pressure during growth: (a) 1×10^{-7} Torr, (b) 2×10^{-7} Torr, (c) 4×10^{-7} Torr. The spectra have been vertically shifted for clarity. In this and the following figures the lines are identified in the text.

I_1^{P} thus appears to be clearly related to P doping. We show in Figs. 2(a) and 2(b) PL spectra taken from a P-implanted sample annealed at 500 °C for 8 and 16 mn, respectively. Besides the emergence of the I_1^{deep} line, which originates from point defects created during annealing, these spectra are very similar to those presented in Fig. 1 for samples that have been doped *in situ*. Considering the DAP-band blueshift induced by increasing the annealing time in Fig. 2, it is obvious that the electrically active impurity concentration increases in parallel. It can be inferred that such an effect partly manifests the kinetics for implanted phosphorus to reach acceptor sites. At higher PL-measurement temperature [Fig. 2(c)] an electron-acceptor recombination band emerges which clearly identifies the defect as a shallow acceptor. In any case, it can be concluded that the same P-related point defect is present in implanted and *in situ*–doped samples.

In addition, we show in Fig. 3 the PL spectra taken in a wide spectral range from two different P-doped, a N-doped, and a not-intentionally-doped ZnSe epitaxial layer. SIMS performed on sample EPI-649 revealed a P concentration of $[\mathrm{P}]_{\mathrm{SIMS}}=3\times10^{17}\,\mathrm{cm}^{-3}$, which confirms that our samples are efficiently P-doped. The shape and position of the deep PL bands in the 1.8–2.2-eV range vary with the sample characteristics. However, the intensity of these bands is three to four orders of magnitude lower than the DAP and near-band-edge (NBE) emissions for P-doped as well as N-doped samples, which reveals that, like N doping, P doping does not give rise to significant deep PL bands.

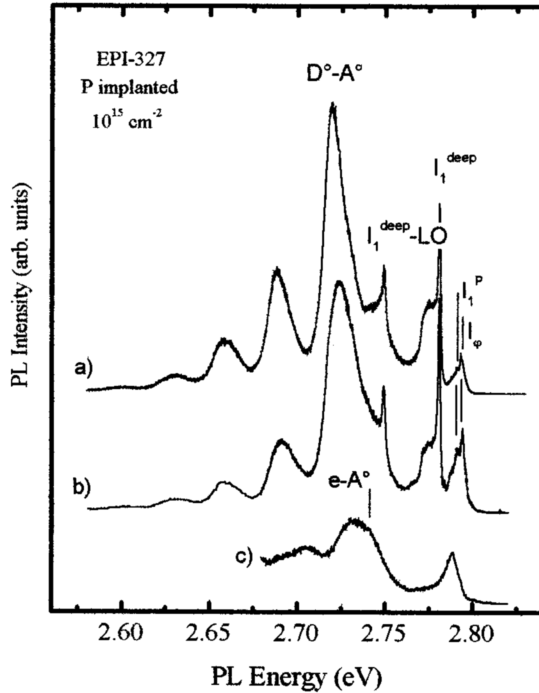

FIG. 2. PL spectra taken from a P-implanted ZnSe:P sample annealed for (a) 8 min and (b) 16 min at 500 °C. A spectrum taken at 30 K is also shown (c). The samples were excited by the Stillbene-3 dye laser operating at 2.879 eV (a), 2.888 eV (b), and 2.895 eV (c).

These figures thus demonstrate that P doping is accompanied by the appearance in the PL spectra of a DAP-band series and at least one line in the excitonic region, but a negligible deep PL band. We now investigate successively the DAP and NBE spectral ranges.

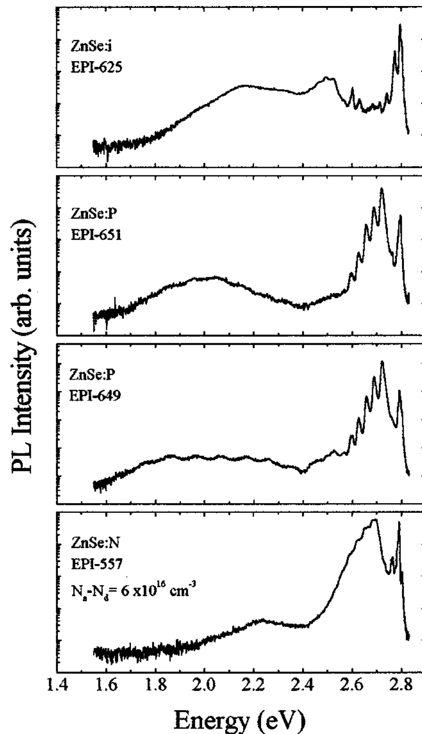

FIG. 3. PL spectra taken on a large spectral range for various ZnSe samples. Excitation by the He-Cd laser.

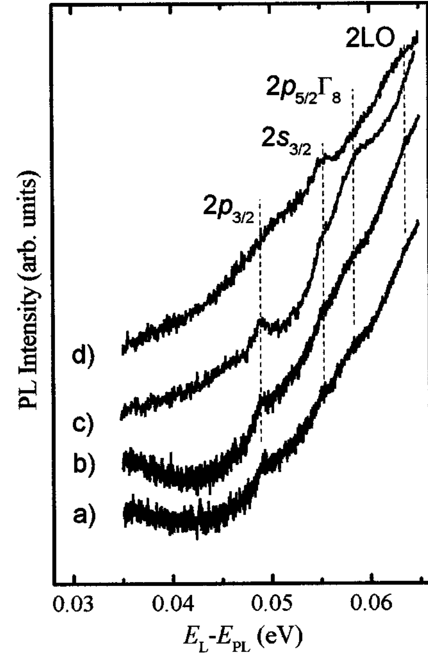

FIG. 4. PLE spectra taken taken from an implanted layer (a) and (b), a plasma-doped layer (c), and a substrate-free plasma-doped layer (d). Detection was set at 2.725 eV.

B. Donor-acceptor pair spectroscopy

We display in Fig. 4 PLE spectra taken from an implanted layer (a) and (b), a plasma-doped layer (c), and a substrate-free plasma-doped layer (d). The detection was set to 2.725 eV in all cases. Several resonances corresponding to transitions from the ground to excited states of the acceptor responsible for the presence of the DAP bands are detected. They have been labeled according to their origin. The coincidence of the transitions in all three spectra reveals that (i) the same acceptor is involved in the P-implanted and in the P-plasma-doped samples, and (ii) the strain does not alter significantly the acceptor binding energy. The loss of resolution observed on the PL excitation spectrum after the removal of the substrate could be due to the larger distances of selected DAP in stress-free samples.

The positions of the DAP bands in Fig. 1 and the energies of the acceptor transitions identified in Fig. 4 concur to indicate that the P-related acceptor is the shallowest acceptor known in ZnSe. It is thus difficult to understand that it behaves very differently from an effective-mass acceptor as claimed by Zhang *et al.*[18] We have then extensively studied the DAP region. We show in Figs. 5(a) and 5(b) the PLE and SPL spectra taken from a substrate-free layer by detecting and exciting in the DAP region, respectively. Figure 6 displays the results obtained under similar conditions for a strained layer. Up to five (six) excited states are detected for the substrate-free (strained) layer. The values of the transition energies extracted from these figures are listed in Table I, together with the results previously published by Zhang *et al.*[18] There are obvious discrepancies which might arise from the fact that Zhang *et al.* had not detected the transitions toward the first excited states, which led them to an erroneous conclusion.

In standard PL the ionization energy E_A of an impurity can be obtained accurately from the position of the free-

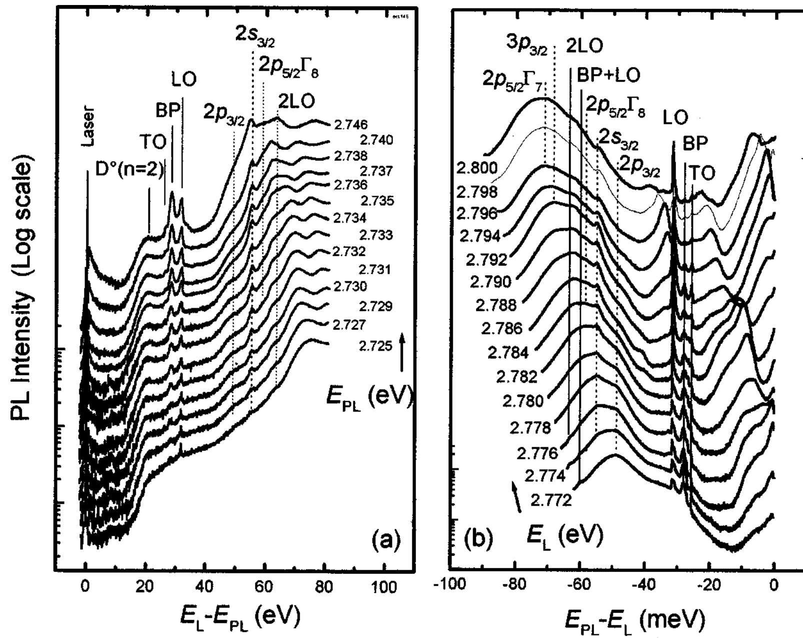

FIG. 5. PLE (a) and SPL (b) spectra taken from an *in situ* doped substrate-free layer taken by detecting (a) and exciting (b) in the DAP region.

electron-to-acceptor (e-$A°$) transition at low temperature, the position of the zero-phonon line of a DAP series giving only a crude estimate. However, in the case of the investigated ZnSe:P samples, no e-$A°$ line is seen at low temperature (Figs. 1 and 2). It emerges as a weak shoulder on the intense zero-phonon DAP band only when the donors ionize at higher temperature [Fig. 2(c)]. This technique can thus not be used to *precisely* determine E_A of the P-related shallow acceptor. Instead, we have used a more refined technique based on the detection of the absorption threshold corresponding to the ''acceptor-to-conduction-band'' transition. The principle is schematically given in Fig. 7. When the excitation energy E_L is larger than the difference $E_g - E_A$, where E_g is the band-gap energy, the acceptors involved in distant DAP are neutralized. The electrons which are released during this process can then be trapped by any ionized donor involved in a pair with a weak Coulombic interaction ($e^2/\varepsilon R_{DA} < E_D$, where E_D is the ionization energy of the donor). In turn, this increases the population of acceptors susceptible to be neutralized. Consequently, the PLE spectra of DAP recombining energies (E_{PL}) between $E_g - E_A - E_D$ and $E_g - E_A$ exhibit a nonselective threshold (i.e., occurring at fixed energy) at $E_L = E_g - E_A$, which can be used to determine E_A. We show in Fig. 8 the PLE spectra taken from a strained (a) and a substrate-free (b) ZnSe:P epitaxial layer. The detection was set in the one-phonon replica of the DAP band in order to facilitate the PLE threshold detection. One can note from this figure that the threshold difference between the strained and substrate-free cases just amounts to the strain-induced band-gap shift. This confirms the conclusion drawn from Fig. 4 that the strain does not alter significantly the binding energy of the P-related shallow acceptor. From the position of the threshold we thus deduce $E_A = 85 \pm 1$ meV for its ionization energy, after strain correction. We have reported in Table II the binding energies of the excited acceptor states for the P-related shallow acceptor, together with those for the Na, Li, and N acceptors in ZnSe. One should note that the binding energies of the $2p_{5/2}$ states are very similar for all acceptors, there is no influence of the central-cell correction on the $2s_{3/2}$ states, whereas the $2p_{3/2}$ states strongly depend on the chemical nature of the acceptor. These last two points reveal some departure of the acceptors from the effective-mass approximation. However, it concerns all shallow effective-mass acceptors in ZnSe, and not specifically the P-related acceptor.

C. Bound excitons in ZnSe:P

The examination of PL spectra in Figs. 1 and 2 showed that P doping of ZnSe/GaAs results in the appearance of a line labeled I_1^{P} which is located at 2.791_2 eV, i.e., in the region corresponding to the NABE recombinations. The occurrence of such NABE obeying the Haynes' rule[23] in P-doped ZnSe is scarcely mentioned in the literature. Only we[19] and very recently Calhoun and Park[20] reported the presence of an emission line at 2.791_9 eV attributed to the recom-

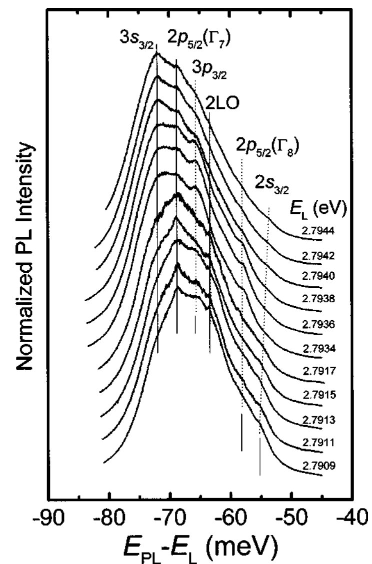

FIG. 6. SPL spectra taken from an *in situ* doped, strained ZnSe:P sample taken by detecting in the DAP region.

TABLE I. Transition energies between the ground and excited states of the P-related shallow acceptor in ZnSe.

Transition	Energy (meV) Zhang *et al.* (Ref. 18)	This work
$1s_{3/2}$-$2p_{3/2}$		49.9
$1s_{3/2}$-$2s_{3/2}$	69.3	55.2
$1s_{3/2}$-$2p_{5/2}(\Gamma_8)$	72.6	58.2
$1s_{3/2}$-$3p_{3/2}$		65.8
$1s_{3/2}$-$2p_{5/2}(\Gamma_7)$	73.9	68.8
$1s_{3/2}$-$3s_{3/2}$	75.6	72.0

bination of an acceptor bound exciton associated with atomic-phosphorus doping without specifying the exact nature of this acceptor. The detection of the electronic Raman scattering or the two-hole transitions[24] could allow to go beyond in the identification of the involved acceptor. In Fig. 9 we have reported a portion of the DAP spectra exhibiting features which are shifted by about the acceptor $1s_{3/2}$ to $2s_{3/2}$ transition energy from the laser excitation. The laser is tuned in the NABE region. When the laser is off-resonance ($E_L = 2.7924$ eV), the recombination of DAP neutralized with the hole in the $2s_{3/2}$ acceptor state is the only selectively excited transition detected. The reduction of the transition energy to the $2s_{3/2}$ excited state (54.0 meV here instead of 55.2 meV for distant DAP's) is due to the overlap of donor and acceptor wave functions, which introduces large deviations of the Coulomb interaction energy for close DAP's.[25] The reinforcement of the SPL signal at $E_L - 0.0552$ eV when the laser excitation is set in coincidence with $I_1^{\rm P}$ (2.791_2 eV) results from the resonant enhancement of a two-hole recombination line of NABE. The measured energy shift exactly corresponds to the acceptor $1s_{3/2}$ to $2s_{3/2}$ transition energy deduced in the preceding section (Table I) from SPL and PLE studies of a distant DAP emission band. SPL performed on $I_1^{\rm P}$ shows that this line is indeed related to the P-related shallow acceptor involved in the shallow-DAP band series. This result demonstrates that the P-related shallow acceptor behaves exactly like any shallow acceptors in ZnSe, in particular, by binding a usual NABE.

A second excitonic line, detected at 2.796 eV and labeled I_φ in Figs. 1 and 2, fits well with that of a neutral-donor

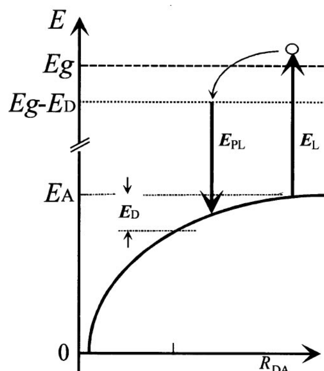

FIG. 7. Schematic principle of the detection of the absorption threshold corresponding to the ''acceptor-to-conduction band'' transition in PLE experiments.

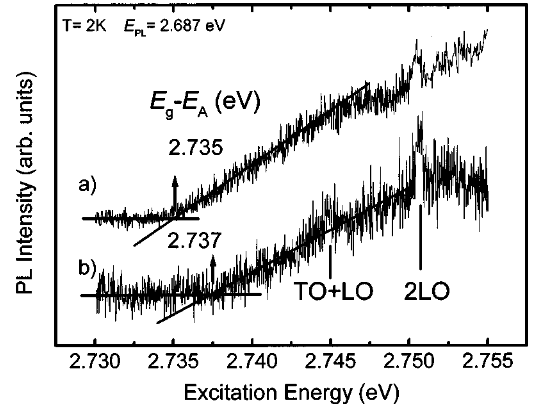

FIG. 8. PLE spectra taken from (a) a strained and (b) a substrate-free ZnSe:P layer. Detection was set in the DAP band at 2.687 eV. The nonselective threshold is indicated by vertical arrows.

bound exciton. The detailed SPL study of the donor associated electronic Raman scattering shown in Fig. 10 reveals the presence of Al and Cl residual donors.[26] Nevertheless, these experiments also show clearly that I_φ cannot be identified as a NDBE. A comparison of the intensities of the LO or the TO replica with those of the electronic Raman scattering signal shows that the resonance for each interaction process occurs at distinct excitation energies. The phonon interaction efficiency is maximum when the laser energy coincides with I_φ ($E_L = 2.7962$ eV) whereas the largest donor ERS process is observed for $E_L = 2.7970$ eV where no line is resolved on the standard PL spectrum (Figs. 1 and 2). As a consequence, SPL experiments definitely demonstrate that I_φ does not stem from recombinations of neutral-donor bound excitons. Further, this line is relatively strongly coupled to the LO phonon, with an I_φ-LO to I_φ intensity ratio of ~0.03 which allows to clearly detect the first-order replica in the PL spectra plotted on a semilogarithmic scale (Fig. 1). Such a ratio is indeed similar to what is usually obtained for excitons bound to shallow acceptors in ZnSe material.[15,17] This explains why this finding was wrongly taken as an argument to identify I_φ as due to an acceptor-bound exciton and to assign it to the P-related shallow-acceptor level.[15,17] However, we have shown above that $I_1^{\rm P}$ corresponds actually to this assignment.

TABLE II. Binding energies of acceptor states in ZnSe.

Identification[a]	Binding energies (meV) Na[a]	Li[a]	N[b]	P[c]
$1S_{3/2}$	128	114	110	85
$2P_{3/2}$	44.9	41.1	42.2	36.2
$2S_{3/2}$	30.4	31.4	30.1	29.8
$2P_{5/2}\Gamma_8$	27.6	28.2	27.4	27.1
$3P_{3/2}$	21.2	21.2	20.2	19.2
$2P_{5/2}\Gamma_7$	17.5	16.2	17.2	16.2
$3S_{3/2}$	15.0	14.0		13.0

[a]H. Tews, H. Venghaus, and P. J. Dean, Phys. Rev. B **19**, 5178 (1979).

[b]K. Shazad, B. A. Kahn, D. J. Olego, and D. A. Cammack, Phys. Rev. B **42**, 11 240 (1990).

[c]This work.

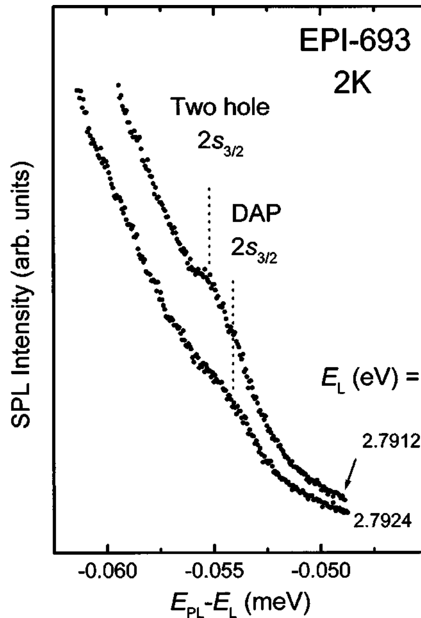

FIG. 9. Portion of the DAP spectra showing the recombination peaks corresponding to DAP selectively excited in the $2s_{3/2}$ state of the shallow acceptors ($E_1 = 2.7924$ eV). When the laser excitation is resonant with the exciton bound to the neutral acceptors I_1^{P} at $E_L = 2.7912$ eV, a second resonant peak appears due to the $2s_{3/2}$ two-hole recombination of I_1^{P}. The splitting between the two resonant peaks corresponds to the interaction energy between the close neutral donor and acceptor pair.

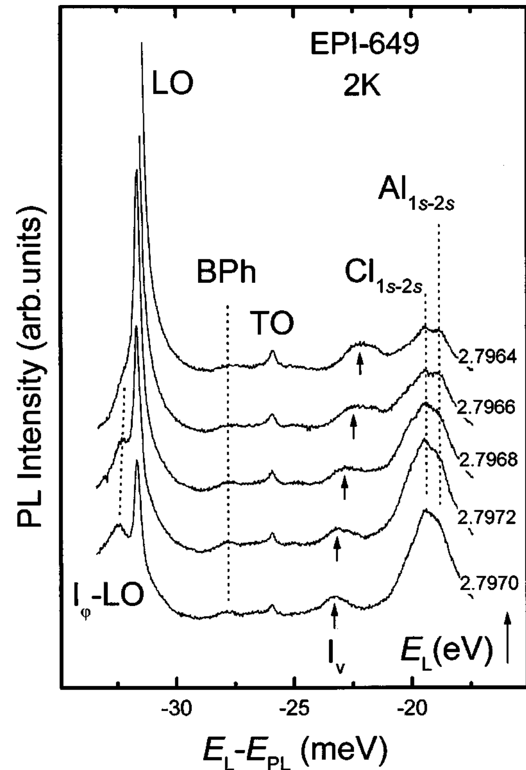

FIG. 10. SPL performed by exciting in the NDBE region. BPh indicates a bound-phonon related line.

IV. DISCUSSION

The set of data presented above unveils the following crucial properties of the P-related shallow acceptor in ZnSe: (i) the same level giving rise to a DAP-band series with a zero-phonon line near 2.72 eV is introduced upon *in situ* doping or implantation, (ii) its binding energy is $E_A = 85 \pm 1$ meV, and (iii) the spectrum of its excited states as well as its associated exciton line behaves exactly like those of all substitutional acceptors. As for item (iii), we feel that the discrepancy between our results and those of Zhang *et al.*[18] is due to the fact that these authors did not resolve the first excited states, which led them to an erroneous conclusion. Based on our results, the P-related shallow acceptor has to be ascribed to the $\mathrm{P_{Se}}$ substitutional impurity, which is then the shallowest acceptor ever detected in ZnSe.

Unlike previous studies using mainly Zn_3P_2 or ZnP_2 as P sources, the 1.95-eV-deep band, usually dominating the emission spectra of ZnSe:P samples, is not seen in our PL spectra. Investigations of the 1.95-eV-deep emission by optically detected magnetic resonance experiments show that this band is due to recombinations between shallow and deep acceptors.[9] However, the signature of the deep acceptor level on the electron-spin-resonance spectra corresponds to that of an unassociated paramagnetic defect, originally attributed to a $\mathrm{P_{Se}}$ atom undergoing a Jahn-Teller distorsion from a T_d to a C_{3v} site,[7,9] and more recently reinterpreted in terms of a $\mathrm{P_{int}}$ interstitial defect on the basis of pseudopotential total-energy calculations.[27] Our detailed study shows conclusively that the P-related shallow acceptor is in fact the simple $\mathrm{P_{Se}}$ defect. It thus confirms that the 1.95-eV-deep band is not related to that defect. In addition, it is noticeable that this band is not seen also by Calhoun and Park, who have used, as we have, plasma-activated P.[20] Phosphorus-plasma spectroscopy reveals the presence of P atoms in the plasma discharge[20] while Zn_3P_2 or ZnP_2 sublimate as Zn atoms and P_2 molecules. It is thus tempting to ascribe the 1.95-eV band to a recombination process involving P_2 clusters. The disappearance of this band for samples doped with plasma-activated P would then be due to efficient production of atomic P in the plasma discharge. We note that in the case of ZnSe:N, several defects involving paired N atoms have been invoked, including ($\mathrm{N_{Se}}$-$\mathrm{N_i}$), ($\mathrm{N_{Se}}$-$\mathrm{N_{Zn}}$), $(\mathrm{N_2})_i$, and $(\mathrm{N_2})_{\mathrm{Se}}$, to account for the partial electrical compensation of this material.[28]

Whatever the origin, $\mathrm{P_{int}}$ or P_2 of the defects involved in the 1.95-eV band, this emission has not been detected in our study, which refutes previous conclusions implying that these levels were responsible for the lack of conductivity of ZnSe:P samples.

In the preceding section, we noted the presence in the excitonic region of a line labeled I_φ, which appears to be affected by rather puzzling properties. Although it is located in the spectral range corresponding to shallow-donor bound excitons, the intensity of its phonon replicas suggests a large lattice coupling, characteristic of deep, localized defects. This is in accordance with the existence of single shallow DAP recombination, which involves the usual residual donors of ZnSe. We found that up to $[\mathrm{P}]_{\mathrm{SIMS}} = 4 \times 10^{17}\,\mathrm{cm}^{-3}$, the relative intensities of I_1^{P} with respect to I_φ are increasing with the phosphorus concentration, which is the opposite behavior to that reported by Calhoun and Park.[20] However, we have also observed that the choice of growth parameters such as the rf-plasma power, the P flux, or the VI/II flux ratio can

cause significant intensity variations of the bound-exciton lines without any obvious trend. This again confirms the attribution of I_{φ} to an exciton bound to a defect, as the intensity of I_{φ} compared to that of I_1^{P}, for identical [P] concentration, depends on the growth conditions. Excitons bound to deep defects and with a shallow binding energy have previously been detected in ZnSe. For example, I_1^{deep}, originally ascribed to Cu contamination and later thought to be related to a complex defect involving Zn vacancies,[29,30] similar to *A* centers,[31] peaks at a high energy (2.783 eV). Also, a line peaking at 2.785 eV, usually labeled I_C, is observed for ZnSe:N samples. The exact origin of I_C is still unknown, although an attribution to N_2-related defects has often been inferred.[32,33] As the intensity of I_{φ} is much stronger than that of I_1^{P} in the PL spectra of samples doped without activating P in a plasma discharge, we tentatively attribute this line to excitons bound to P_{int}- or P_2-related defects. Another candidate could also be a P_{Zn} antisite defect, which is a triple donor and shown to have a low formation energy.[27] The relatively high I_1^{P} to I_{φ} intensity ratio when plasma activated P is used, along with the absence of clear deep emission, indicate, however, a rather low density for the involved defect. Furthermore, we note that in the case of ZnSe:N, I_C largely dominates the excitonic emission in highly doped samples. Similarly, the defect involved in the emission of I_{φ} alone is not necessarily responsible for the lack of *p*-type conductivity.

In fact, all the samples investigated in this study are semi-insulating, despite stronger or lower I_{φ} intensities as compared to I_1^{P}, and despite a systematic absence of any deep emission. Considering the shallowness of the simple substitutional impurity P_{Se}, this is a rather unexpected result. We have performed an extensive investigation of the donors present in our samples. Only the group-III and group-VII impurities Al, In, and Cl, which are usual residual donors in ZnSe, could be detected. Thus, in contrast to N doping, no compensating donor appears to be generated during P doping of ZnSe.

With no evidence of large densities of point defects, the origin of compensation is thus to be searched for in a different direction. In fact, among the models reported in the literature, the occurrence of an *AX* center, as proposed by Chadi and Troulier,[34] could explain the experimental results. Within this model, P acceptors have two atomic configurations: a metastable effective-mass state with a small lattice relaxation and a stable deep state with a large lattice relaxation. The formation of such centers has been demonstrated recently in ZnMg(S)Se,[35,36] and thought to be the manifestation of a more general behavior for dopant impurities in II-VI semiconductors.[37] This configuration is consistent with all experimental data. At low temperature and under illumination, most of the deep stable states are expected to be ionized, resulting in PL spectra comprising only donor- to shallow-metastable acceptor-state recombinations, in a situation similar, albeit reversed, to the *DX* centers in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ alloys.[38] Further, all the attempts to detect the ground state of the *DX* center in $\mathrm{Ga}_{1-x}\mathrm{As}_x\mathrm{P}$ and in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ by EPR have also failed,[39–41] even though the paramagnetic nature of this level has been established by magnetic susceptibility measurements. This would explain the absence of deep emission in our ZnSe:P samples and why such a center has not been detected in ZnSe:P. Persistent photoconductivity measurements and deep-level transient spectroscopy, not available at this time, should allow us to gain an insight into the compensation processes and, in particular, validate or refute this model.

V. CONCLUSION

In conclusion, we have studied through PL spectroscopies P-implanted and P-plasma-doped ZnSe epitaxial layers grown by MBE. We have shown that the activation energy of the P-related shallow-acceptor level is 85 ± 1 meV, which corresponds to the shallowest acceptor ever detected in ZnSe. The series of excited states of this acceptor reveals that it behaves like all substitutional acceptors. We thus identify it as being the simple P_{Se} substitutional impurity. Its excitonic emission definitely occurs at 2.791 eV. No P-related deep levels can be detected. However, a line which is strongly coupled to phonons is detected at 2.796 eV. It arises from P-related defects involving P incorporated on other-than-Se-substitutional sites. Finally, the lack of conductivity of our ZnSe:P samples, which does not stem from deep defects, could be well explained by an *AX*-like behavior of the P impurity.

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*Present address: Department of Physics, Heriot-Watt University, Edinburgh EH14 4AS, United Kingdom.

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