

Spectroscopy of the interaction between nitrogen and hydrogen in ZnSe epitaxial layers

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We report on detailed optical-spectroscopy investigations of nitrogen-doped ZnSe epitaxial layers of various doping levels and N contents which have been exposed *ex situ* to a hydrogen/deuterium plasma. The influence of this treatment is studied through temperature-dependent photoluminescence and selective photoluminescence. The results are similar for all samples, irrespective of their doping properties. We show that the N_{Se} acceptor is strongly passivated and that the deep compensating-donor disappears after plasma exposure. In addition, the nature of the main shallow compensating-donor is changed by the H/D treatment. The shallow donor in ZnSe:N which we have previously identified as a N-related defect is suppressed while the usual residual impurities of ZnSe are uncovered. Our results directly demonstrate that all compensating donors in ZnSe:N material are N-related defects, and that N may participate to nonradiative recombination centers at heavy doping. Finally, this helps selecting a few models for the deep compensating-donor and further support the implication of N interstitials in carrier compensation in ZnSe:N.

I. INTRODUCTION

The doping properties of wide-band-gap semiconductors are currently under the focus of attention driven by both the perspective to fabricate optoelectronic devices operating in the visible—ultraviolet range and the will to understand the intimate relationship existing between doping and carrier compensation. ZnSe is a case-study material in this respect: not only have several decades of work¹ been necessary before a viable acceptor could emerge,^{2,3} but it appeared soon that the acceptor impurity itself may be involved in the carrier-compensation affecting p -type material.⁴

In fact, plasma-activated nitrogen (N) and molecular-beam epitaxy (MBE) remain the unique dopant and unique growth technique, respectively, allowing to achieve reproducible p -type conductivity in ZnSe epitaxial layers. However, compensating donors are generated concurrently with p -type doping from the very onset of N incorporation.⁵ As a result, the net-acceptor concentration (NAC) $N_a - N_d$ is limited to around 10^{18} cm^{-3} even though $[N]$, the N content, can be orders-of-magnitude higher.⁶ In addition, compensation manifests itself in the low-temperature photoluminescence (LT PL) spectra of moderately to highly doped ZnSe:N layers by the presence of two distinct series of donor-acceptor pair (DAP) bands which arise from recombinations between the N acceptor and two distinct—a shallow and a deep—compensating donors.^{4,7,8}

Most work on carrier-compensation in ZnSe:N layers has focused on the deep compensating donor D^d . Experimental results appear to support an attribution to complex defects involving N.^{4,9,10} The activation energy of this deep donor however remains controversial, in the 45–57 meV range,^{4,8,11–13} which might indicate that various mechanisms may still be invoked. The shallow compensating donor, re-

sponsible for the D^s AP bands in the PL spectra, has in contrast attracted little attention and it has often been ascribed to residual impurities.^{4,8,9,11,13} We have however demonstrated that N doping of ZnSe is accompanied by the formation of a N-related shallow-compensating donor D_N^s with an activation energy of 29.1 meV.^{12,14,15}

From the theoretical point of view, many models have been considered in order to explain carrier compensation in ZnSe:N material: incorporation of N onto various interstitial sites,^{16,17} limited solubility of N in ZnSe^{18,19} formation of AX centers^{20,21} or of impurity-native defect complexes,^{22–25} and host bond breaking.²⁶

The nature of the defects responsible for carrier-compensation in ZnSe:N epitaxial layers remains thus under debate. For other semiconductors, such as Si or III-V compounds, investigating the interactions between dopant and intentionally incorporated hydrogen has shed some light onto the doping and compensation properties of the materials.^{27,28} Despite, very few similar studies have been reported up to now for ZnSe:N. Both Yasuda *et al.*²⁹ and Prior *et al.*³⁰ have observed a strong influence of the presence of H onto the LT PL spectra of ZnSe:N layers.

We have recently presented some results on the interaction between hydrogen/deuterium (H/D) and N in ZnSe:N.³¹ To summarize, we have varied many parameters such as the ZnSe:N sample doping level, the compensation ratio, the sample temperature during H/D plasma-exposure and the duration of this exposure. As far as the diffusion profiles and the electrical characterizations are concerned the results were similar, whatever the initial and experimental conditions. All samples turned to be semi-insulating after H/D plasma exposure, irrespective of the initial $N_a - N_d$ and compensation ratio. In addition, the characteristics of the H/D profiles were analogous whatever the plasma conditions. Besides a surface

accumulation layer, the H/D profiles exhibit a plateau the height of which corresponds, within the experimental uncertainty, to the total N content in the layer. Finally, the LT PL spectra of ZnSe:N layers are drastically affected by the presence of H/D. These results indicate that H/D strongly interacts with N species in ZnSe:N regardless of their electronic nature, and that it passivates the N acceptor in ZnSe:N.³¹

The aim of the work presented here is to study in detail the influence of an H/D plasma exposure on the properties of ZnSe:N layers in order to shed some light onto the nature of compensating centers. For that purpose we have carried out an extensive spectroscopic investigation of ZnSe:N H/D samples by LT PL, temperature-dependent PL, and selective PL (SPL). Together with previously published data,³¹ our results directly demonstrate that all compensating donors in ZnSe:N material are N-related defects which helps selecting a few models.

The samples and experimental techniques are described in Sec. II. We give in Sec. III a few general considerations on SPL investigations of semiconductors and on the PL properties of ZnSe:N material. The experimental results are presented in Sec. IV and discussed in Sec. V before concluding in Sec. VI.

II. EXPERIMENT

The ZnSe:N samples have been grown in a Riber Epineat system by solid-source MBE on semi-insulating (001) GaAs substrates. The growth temperature and growth rate were 280 °C and 0.14 nm/s, respectively. *p*-type doping was achieved with RF-plasma-activated N using an Oxford Applied Research (RFK)-30 cell. The epitaxial layers were between 1 and 3 μm thick. As-grown samples have been exposed to a H/D RF-plasma in a parallel plate capacitance reactor. Nitrogen as well as H/D concentrations have been measured for some samples by secondary-ion mass-spectroscopy (SIMS) using a Cs⁺ primary ion beam and implanted ZnSe epitaxial layers as references. NAC were measured at room temperature by the capacitance-voltage (*C-V*) technique either between coplanar Au-contacts or using a Hg-probe system.

For temperature-dependent PL the samples were mounted on the cold finger of a closed-cycle He cryostat. PL was excited by the 325 nm line of an He-Cd exciting laser ($P_{\text{exc}} \sim 5 \text{ W cm}^{-2}$) and detected at the exit of a 64-cm spectrometer equipped with a 1200 grooves/mm grating blazed at 500 nm. Selective PL (SPL) measurements were performed at 1.8 K in an 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/mm gratings blazed at 400 nm. In all experiments a CO₂-cooled GaAs photomultiplier was used as detector.

III. GENERAL CONSIDERATIONS

We give here the few relevant considerations on the SPL technique applied to impurity spectroscopy in semiconductors,^{32,33} and on the PL properties of ZnSe:N epitaxial layers.

A. Two-electron-transitions, two-hole-transitions

During PL spectroscopy, the electron remaining after recombination of the neutral-donor bound-exciton (NDBE) I_2 can be either in the fundamental ($1s$), or on an excited (ns, np) state of the donor. A series of resonances, the so-called “two-electron-transitions,” may thus be detected at the energies of $E(I_2) - E(1s \rightarrow ns, np)$. Although two-electron-transitions can in principle be seen in any PL spectrum excited above the band-gap energy, they are best seen when exciting resonantly with I_2 . Similarly, “two-hole-transitions,” which involve recombinations of the neutral-acceptor bound-exciton (NABE) I_1 are best seen when exciting resonantly with I_1 . The separation between the two-electron-transitions (two-hole-transitions) depending only on the spectrum of the excited states of the donor (acceptor) involved in the process, two-electron-transitions (two-hole-transitions) spectroscopy is a very powerful tool for identifying the impurities present in the material.

B. Donor-acceptor pair (DAP) spectroscopy

During SPL experiments, an incident photon with an energy E_{exc} can excite a (shallow or deep) donor in a state i and an acceptor in a state j . There results a neutral excited $D_i A_j P$ at a pair separation $R_{i,j}$ such as:

$$E_{\text{exc}} = E_g - [E(A_j) + E(D_i)] + \frac{e^2}{\epsilon R_{i,j}} + J_{i,j}(R_{i,j}), \quad (1)$$

where E_g is the band-gap energy, ϵ is the static dielectric constant, $E(A_j)$ and $E(D_i)$ are the binding energies of the acceptor and donor excited states, respectively. $J_{i,j}(R_{i,j})$ is a correction to the Coulomb effect $e^2/\epsilon R_{i,j}$ which takes into account the overlap between excited donor and acceptor wave functions.

After excitation the DAP rapidly thermalizes into its ground state and then gives rise to a PL line at

$$E_{\text{lum}} = E_g - [E(A_{1s3/2}) + E(D_1)] + \frac{e^2}{\epsilon R_{1,1}} + J_{1,1}(R_{1,1}). \quad (2)$$

The energy shift between excitation and emission is then

$$E_{\text{exc}} - E_{\text{lum}} = E(A_{1s3/2}) - E(A_j) + E(D_{1s}) - E(D_i) - \Delta J_{i,j}(R_{i,j}), \quad (3)$$

where

$$\Delta J_{i,j}(R_{i,j}) = J_{1,1}(R_{i,j}) - J_{i,j}(R_{i,j}). \quad (4)$$

C. ZnSe:N photoluminescence properties

Residual impurities in ZnSe are group-III and group-VII donors which have been well characterized.^{34–36} Their activation energy lies in the 25–28 meV range. The NDBE lines I_2 fall around 2.796 eV. N_{Se} on the other hand is a shallow acceptor with an activation energy $E_A = 111$ meV and a NABE line I_1^N at 2.791 eV.³⁷ The zero-phonon bands of the two distinct shallow, D^sAP, and deep, D^dAP, series observed in the PL spectra of ZnSe:N layers peak at about 2.70 and 2.68 eV, respectively. At very heavy doping levels how-

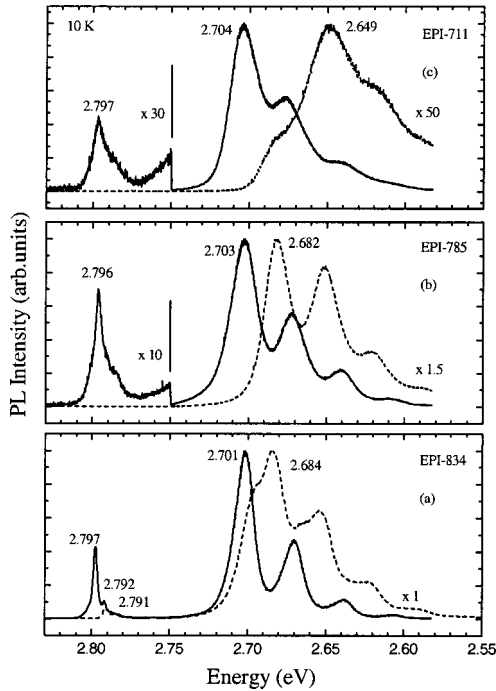


FIG. 1. PL spectra taken at 10 K from as-grown (dotted lines) and deuterated (solid lines) ZnSe:N samples. (a) EPI-834, $N_a - N_d = 1 \times 10^{17} \text{ cm}^{-3}$, (b) EPI-785, $N_a - N_d = 5 \times 10^{17} \text{ cm}^{-3}$, $[N] \sim 3 \times 10^{18} \text{ cm}^{-3}$, (c) EPI-711, $N_a - N_d = 1 \times 10^{18} \text{ cm}^{-3}$, $[N] \sim 1 \times 10^{19} \text{ cm}^{-3}$.

ever, statistical fluctuations in local impurity concentration lead to the formation of spatially separated potential wells in the material resulting in broad band states.²² Unstructured, red-shifted broad DAP bands are then observed.^{6,38,39}

For high-quality MBE-grown ZnSe:N layers, the line-shape of the LT-PL spectra can be used as an indicator for $N_a - N_d$, and $[N]$.⁶ The LT-PL emission of lightly-doped samples ($N_a - N_d < \sim 1 \times 10^{17} \text{ cm}^{-3}$ and $[N] < \sim 5 \times 10^{17} \text{ cm}^{-3}$) is dominated by the NABE line I_1^N . Upon increasing the doping level, the near bandedge emission vanishes progressively at the expense of both D^s AP and D^d AP bands. D^d AP bands generally take over for $N_a - N_d > \sim 1 \times 10^{17} \text{ cm}^{-3}$ and $[N] > \sim 1 \times 10^{18} \text{ cm}^{-3}$. Finally, the red-shifted unstructured DAP band is observed for very-heavy doping, typically for $[N] > \sim 1 \times 10^{19} \text{ cm}^{-3}$.

IV. EXPERIMENTAL RESULTS

A. Photoluminescence spectroscopy

We show in Figs. 1(a)–1(c) the LT PL spectra taken before (dotted lines) and after (solid lines) H/D plasma exposure for three representative samples, the $N_a - N_d$ of which are 1×10^{17} (EPI-834), 5×10^{17} (EPI-785) and 1×10^{18} (EPI-711) cm^{-3} , respectively. Before hydrogenation, the increase of $N_a - N_d$ when going from (a) to (c) is well confirmed by the evolution of the LT PL spectra (Fig. 1). The N contents in samples EPI-711 and EPI-785 have been measured by SIMS to be $\sim 1 \times 10^{19} \text{ cm}^{-3}$ and $\sim 3 \times 10^{18} \text{ cm}^{-3}$, respectively, which fits well also with the LT PL spectra. $[N]$ has not been measured for sample EPI-834 but from the shape of the LT PL spectrum one can estimate it to be $\sim 1 \times 10^{18} \text{ cm}^{-3}$. Finally, it is noticeable that before

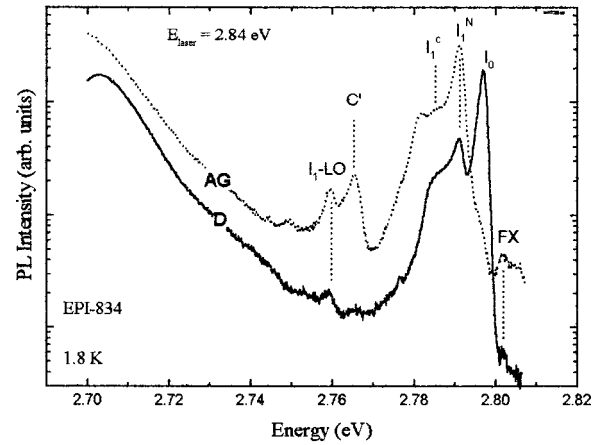


FIG. 2. Near bandedge emission taken at 1.8 K by exciting at 2.84 eV sample EPI-834 as grown (dotted line) and after deuteration (solid line).

hydrogenation a NABE line I_1^N at 2.791 eV can be detected only from EPI-834 which is the most lightly doped sample (Fig. 1).

After hydrogenation the LT PL spectra of all samples are dominated by a shallow DAP band with a zero-phonon line around 2.70 eV (Fig. 1). A particularly salient feature of these spectra is that *all* deep D^d AP bands have completely vanished away after H/D plasma exposure. In addition, the near bandedge spectra of all samples are now dominated by a peak labeled I_0 at 2.796–2.797 eV, i.e., in the region typical for NDBE recombinations. Reminiscence of a NABE I_1^N peak can be clearly seen at 2.792 eV in the spectrum taken from sample EPI-834 while it appears as a shoulder in the spectra taken from samples EPI-785 and EPI-711 (Fig. 1). The influence of H/D plasma exposure on the near bandedge emission is better seen on the spectra displayed in a logarithmic scale on Fig. 2 which were taken at 1.8 K by exciting at 2.84 eV, i.e., slightly above the ZnSe band gap. The near bandedge emission of the as-grown sample is dominated by the NABE line I_1^N . The peaks labeled I_1^c at 2.785 eV and C' at 2.766 eV are also seen in ZnSe:N samples.^{8,9} Their precise origin has yet not been uncovered, although I_1^c is thought to arise from exciton complexes.⁴⁰ After deuteration, the near bandedge emission is largely dominated by the line labeled I_0 in the NDBE spectral range while the intensity of the N-related peaks I_1^N , I_1^c , and C' is greatly reduced. Finally, a weak free exciton line FX is seen in both as-grown and deuterated samples.

The detection of a shallow DAP band after H/D plasma exposure indicates that shallow acceptors and shallow donors are present in the material after hydrogenation. The lineshape and position of the DAP bands together with Eq. (2) show that the concentration of these impurities increases again from (a) to (c). The question then arises of the nature of these acceptors and donors.

We show on a logarithmic scale in Fig. 3 the evolution of the PL spectrum taken from sample EPI-834 after deuteration. Above 20 K a line emerges progressively above the zero-phonon line of the DAP band. This line takes over in the DAP-band region above 50 K when the shallow donors are ionized. It can thus be ascribed to $e-A^0$ recombinations involving free electrons and neutral acceptor. Its position

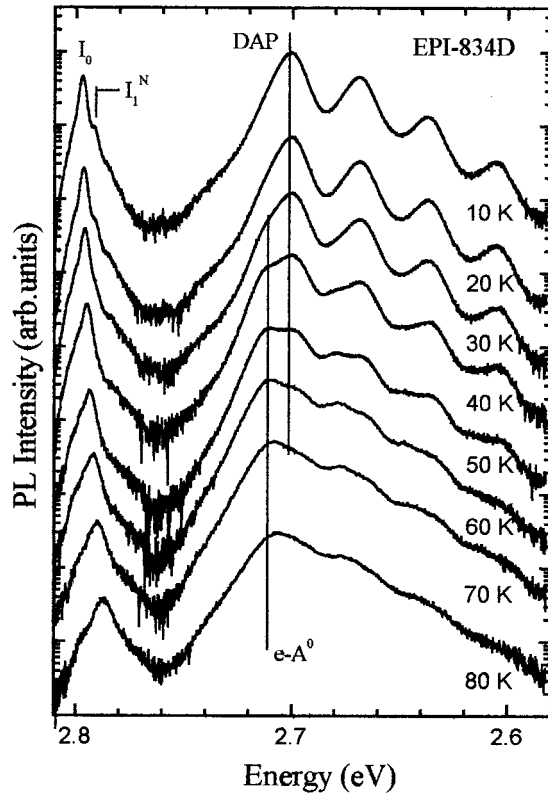


FIG. 3. Evolution with the temperature of the PL spectra taken from deuterated EPI-834.

which can be accurately determined on Fig. 3 is 2.711 eV at 40 K. It corresponds well to an acceptor with an activation energy of $E_A = 111$ meV, which indicates that the shallow acceptor involved in the DAP band is N. It thus appears that H/D does not passivate all N acceptors during plasma exposure.

Finally, one can note from Fig. 1 that the PL efficiency is higher after H/D plasma-exposure, and the higher doped the sample, the stronger this effect. This reveals that H/D passivates non-radiative recombination centers originally present in ZnSe:N.

B. Selective photoluminescence spectroscopy

All investigated samples behave in a similar manner. We present here the data obtained on sample EPI-834 which exhibits the better resolved PL spectra.

We show in Fig. 4 SPL spectra taken by exciting sample EPI-834 in the NDBE region and by detecting around 40 meV below the laser line. The spectrum is totally flat for the deuterated sample. In contrast, for the as-grown sample a somewhat broad-band which is centered at 41.5 meV below the excitation line emerges from the background (see arrow in Fig. 4). Now, a donor with an activation energy $E_A = 45$ –50 meV, i.e., within the range of the deep compensating-donor D_N^d in ZnSe:N^{4,8,11–13} will give $1s \rightarrow 2s$ and $1s \rightarrow 2p$ transition energies precisely in this spectral range. In spite of the lack of clearly-resolved resonances, the concomitant disappearance of this band (Fig. 4) and of the D^d AP-band series (Fig. 1) after H/D plasma-exposure supports its assignment to two-electron-transitions involving D_N^d .

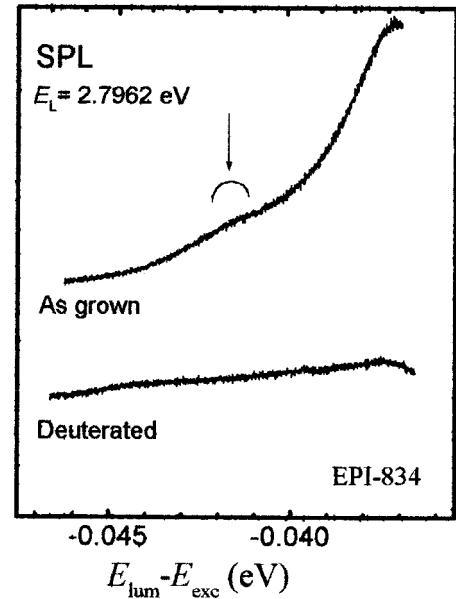


FIG. 4. SPL spectra taken from sample EPI-834 by exciting in the NDBE and detecting in the D_N^d two-electron-transition spectral ranges.

We now turn to the identification of the shallow donors. We display in Fig. 5 the SPL spectra taken by exciting sample EPI-834 again in the NDBE region but by detecting in the shallow-donor two-electron-transitions spectral range. In that way we evidence the main shallow donors in the samples. For the as-grown sample, a weak resonance appears at 22.5 meV below the laser line. It corresponds to the $1s \rightarrow 2p$ two-electron-transitions of the D_N^s shallow donor with

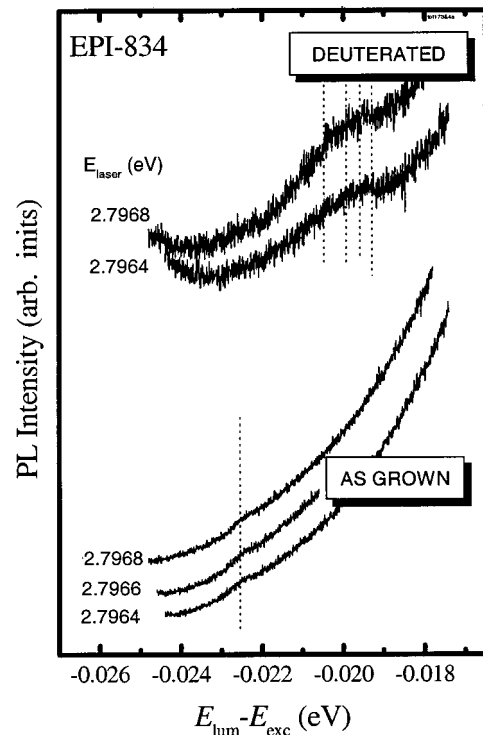


FIG. 5. SPL spectra taken from sample EPI-834 by exciting in the NDBE and detecting in the shallow-donor two-electron-transition spectral ranges.

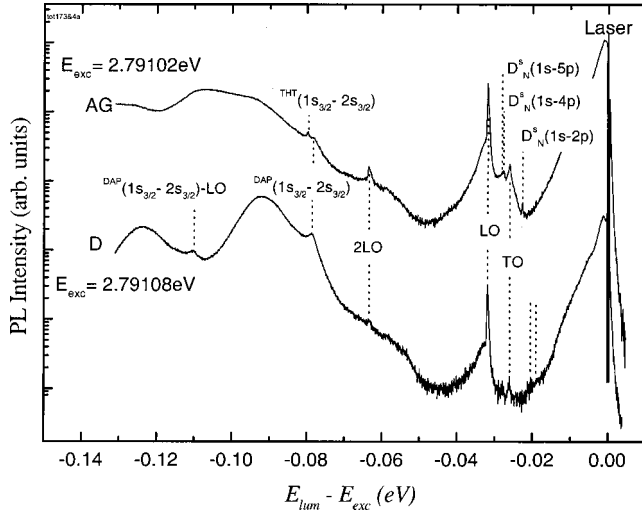


FIG. 6. SPL spectra taken from as-grown (AG) and deuterated (D) EPI-834 by exciting in the NABE and detecting down to the two-hole-transition spectral ranges.

an activation energy of 29.1 meV that we have previously discovered in ZnSe:N samples.^{12,14,15} No other lines can be seen. In contrast, after H/D plasma-exposure this resonance has completely disappeared. Other weak resonances are now uncovered in the spectral range between 19 and 20.5 meV. They correspond to the two-electron-transitions of Al_{Zn}, Cl_{Se}, and Ga_{Zn}, the usual residual impurities in ZnSe.^{34–36} These lines are in fact the only ones detected when performing two-electron-transition spectroscopy on nominally undoped ZnSe epitaxial layers grown in our MBE system.¹² This figure thus shows that the nature of the donor involved in the shallow DAP band changes during H/D plasma exposure.

Next we have performed SPL by exciting in the vicinity of the large absorption threshold, i.e., near the NABE line at 2.791 eV (Fig. 6). In the one-LO phonon range, resonances corresponding to various transitions of the D_N^d shallow donor are detected for the as-grown sample while they have completely vanished away after H/D plasma exposure. In contrast, resonances near 19–20 meV are detected in this case which are the signature of the residual shallow donors of ZnSe.^{34–36} This figure thus supports the results deduced from Fig. 5.

In the two-hole-transition spectral range, a resonance corresponding to the $1s_{3/2} \rightarrow 2s_{3/2}$ transition of the neutral acceptor N (Ref. 37) is detected for the as-grown sample only. In contrast, resonances corresponding to the selective excitation of DAP pairs in the $2s_{3/2}$ state of the N acceptor are observed for as-grown as well as deuterated samples.

Finally, we show in Fig. 7 SPL spectra obtained from both as-grown as well as deuterated samples by exciting with exactly the same energy for both kind of samples. PL emission which corresponds to neutral DAP excited in the $2s_{3/2}$ state of the N acceptor is observed in both spectra. In that case, the general Eq. (3) and Eq. (1) can be rewritten, respectively, as

$$E_{\text{exc}} - E_{\text{lum}} = E(A_{1s3/2}) - E(A_{2s3/2}) - \Delta J_{1,j}(R_{1,j}), \quad (5)$$

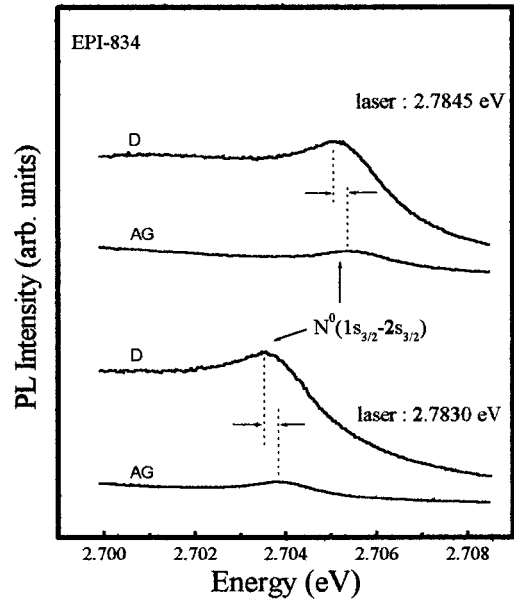


FIG. 7. PL spectra taken from as-grown (AG) and deuterated (D) EPI-834 by selective excitation of the DAP.

$$E_{\text{exc}} - E_g + E(A_{2s3/2}) + E(D_{1s}) = \frac{e^2}{\epsilon R_{1,j}} + J_{1,j}(R_{1,j}). \quad (6)$$

The shift in the PL-peak position seen in Fig. 7 and Eq. (5) show that $\Delta J_{1,j}(R_{1,j})$ is smaller for the deuterated sample than for the as-grown sample. Now, on the one hand, $\Delta J_{i,j}(R_{i,j})$ decreases when $R_{i,j}$ increases,⁴¹ and on the other hand, changing the donor activation-energy, i.e., changing the nature of the donor involved in the DAP, does not affect $J_{i,j}(R_{i,j})$.⁴¹ From Eq. (6), an increase of $R_{1,j}$ implies a decrease of $E(D_{1s})$, all other terms being constant. Consequently, we deduce from Fig. 7 that after deuteration the binding energy of the donor involved in the selectively excited DAP is smaller as compared to the as-grown ZnSe:N epitaxial layer.

V. DISCUSSION

A simple comparison of the PL spectra displayed in Fig. 1 taken prior and after H/D plasma exposure reveals that most N_{Se} acceptors and deep compensating-donors D_N^d are passivated, but that even though donors and acceptors are present in the material after treatment. We now discuss the origin of these defects.

Investigations of the shallow DAP bands detected after H/D plasma exposure by temperature-dependent PL (Fig. 3) and two-hole-transition spectroscopy (Fig. 6) reveal that N_{Se} is the acceptor involved in these DAP. This is in agreement with the fact that no residual acceptor is detected in undoped ZnSe material grown in our system,¹² and this indicates that not all N acceptors are passivated by H/D. On the other hand, total passivation of the deep compensating-donor D_N^d is confirmed by the disappearance of the corresponding-band detected in SPL spectra of as-grown ZnSe:N samples (Fig. 4).

Another, most interesting, point is the influence of the H/D plasma exposure on the nature of the donors involved in the shallow DAP. The crucial result obtained here is that the

main shallow donors are not the same in the as-grown ZnSe:N and in the treated ZnSe:N:H/D samples. Indeed, Figs. 5–7 confirm that the main shallow donor present in ZnSe:N samples is the donor D_N^s with an activation energy $E_D = 29.1$ meV that we have previously detected in other samples.^{12,14,15} In contrast, all spectral signatures of this donor disappear after the treatment while weak resonances typical for the group-III and group-VII residual impurities in ZnSe emerge (the weakness of these resonances stems from the very low residual-doping achieved in our MBE system). This shows that H/D completely passivates the original shallow compensating-donor. Finally, a line that we have initially labeled I_0 appears in the NDBE range. Two-electron-transition spectroscopy indicates that we can now unambiguously identify it as being the NDBE line traditionally observed in ZnSe and labeled I_2 . Its intensity being higher than that of the reminiscent NABE line I_1^N (Figs. 1 and 2) the residual-donor density is larger than the unpassivated N_{Se} acceptor density. Since the residual carrier-concentration in not-intentionally doped ZnSe layers grown in our system is in the $5 \times 10^{14} - 10^{15} \text{ cm}^{-3}$ range, we conclude that after plasma exposure only about 10^{14} cm^{-3} , i.e., a 10^{-3} to 10^{-4} fraction of the initially active N_{Se} acceptor remain unpassivated. This explains why C - V measurements indicate that all samples turn to be semi-insulating after the treatment.³¹

In addition, one has to remind that after H/D plasma exposure of ZnSe:N samples, the H/D profiles measured by SIMS follow within the experimental uncertainty the N profile, whatever the N content and compensation ratio.³¹ This demonstrates that H/D interacts with *all* N-related species, regardless of their nature. Thus, the passivation of the deep compensating-donor and the change of the nature of the shallow compensating-donor described in the previous paragraph provide direct evidence that both the deep and shallow compensating-donors in ZnSe:N are N-related defects. As for the deep compensating-donor D_N^d , one should then consider only models involving N such as the formation of AX

centers^{20,21} or of impurity—native defect complexes^{22–25} and disregard the others. All these defects however are expected to give rise to deep donors so they cannot be considered for explaining the origin of the shallow compensating-donor D_N^s . We have previously proposed that it rather involves N sitting on interstitial sites.^{14,15} In fact, a particular interstitial configuration, the so-called “⟨100⟩ split interstitial” has a low formation energy¹⁷ and forms a shallow donor level in ZnSe:N.¹⁶ This defect involves a N-interstitial bonded either to a Se host atom or to a N_{Se} atom, the bond being aligned along the ⟨100⟩ crystal direction. In this last case there is in fact formation of a $(N-N)_{Se}$ pair. To our knowledge this defect remains the only one calculated to form a shallow donor-level in ZnSe:N.

Finally, another interesting point drawn from Fig. 1 is that the PL intensity of strongly compensated samples drastically increases after H/D plasma exposure which suggests that N impurity may be involved in non-radiative recombination centers at high doping levels.

VI. CONCLUSION

We have investigated by detailed PL spectroscopy the interactions between the N impurity and H/D incorporated *ex situ* by plasma exposure in ZnSe:N epitaxial layers with various N content and compensation ratio. The results are similar for all samples. We have shown that the N_{Se} acceptor is strongly passivated and that the deep compensating-donor D_N^d disappears after plasma exposure. In addition, the main shallow compensating-donor in ZnSe:N which we have previously identified as a N-related defect D_N^s is suppressed by the H/D treatment and the usual residual impurities of ZnSe are uncovered. Our results directly demonstrate that all compensating donors in ZnSe:N material are N-related defects, and that N may participate to non-radiative recombination centers at heavy doping. Finally, our results helps selecting a few models for the deep compensating-donor and further support the implication of N interstitials in carrier-compensation in ZnSe:N.

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