Properties of the As-related shallow acceptor level in heteroepitaxial ZnSe grown by molecular-beam epitaxy

Y. Zhang and B. J. Skromme
Department of Electrical Engineering and Center for Solid State Electronics Research, Arizona State University, Tempe, Arizona 85287-5706

S. M. Shibli* and M. C. Tamargo†
Bellcore, Red Bank, New Jersey 07701
(Received 2 April 1993)

The As-related shallow acceptor level in ZnSe is characterized in detail by low- and variable-temperature photoluminescence (PL), selective-pair luminescence, and magnetospectroscopy measurements, using intentionally As-doped material grown by molecular-beam epitaxy on GaAs. The shallow-acceptor-related PL features grow progressively stronger with Zn_3As_2 flux, while deep-level peaks at 2.20 and 1.7 eV are observed only at the highest doping levels. In addition to the previously reported donor-to-acceptor peak at about 2.693–2.697 eV, we observe a corresponding band-to-acceptor peak at temperatures of $\sim$25 K and above. The temperature dependence of the band-acceptor peak position yields a light-hole-acceptor binding energy of 114.6 ± 0.7 meV for thermally strained material, which compares to values of 114.1 ± 0.4 and 113.0 ± 0.6 meV we recently obtained in the same way for Li and N acceptors, respectively. The corresponding value for unstrained material is calculated to be $E_A^{\mathrm{As}}=114.8\pm0.7$ meV. Selective pair luminescence is used to study the excited states. Four states are observed and assigned to the $2p_{3/2}$, $2s_{3/2}$, $2p_{5/2}$ (Γ_7), and $3s_{3/2}$ levels, respectively. These levels lie about 73.6, 83.9, 93.5, and 98.4 meV above the ground state, respectively, which agrees with calculations based on effective-mass theory. In the excitonic region, the previously reported As acceptor-bound exciton peak at 2.7888 eV is found to exhibit a high energy component at 2.7903 eV. The observed splitting, which is similar to that of other shallow acceptor-bound excitons in relaxed heteroepitaxial layers, is modeled by a calculation of the effects due to thermal mismatch strain. The splitting of the acceptor-bound exciton is studied in magnetic fields up to 12 T as a function of orientation. The results suggest that the As-related acceptor has the point symmetry of the lattice, implying that it may involve a simple substitutional acceptor involving As on the Se site. The results imply that the failure to obtain *p*-type conductivity to date with this dopant is not due to the nonexistence of a suitable shallow level. Further work is necessary to investigate improved incorporation methods and to determine if the shallow level is metastable with respect to lattice distortion.

I. INTRODUCTION

Zinc selenide, which has a band gap ($E_g=2.67$ eV) at room temperature that falls in the blue range of the spectrum, is considered to be a promising material for application to blue light-emitting devices. However, the difficulty of achieving *p*-type doping in this material has long been a key issue relevant to applications requiring the development of *p*-*n* junctions. Recently, workers at Matsushita[1] and the University of Florida[2] developed a nitrogen-plasma-doping method in molecular-beam epitaxy (MBE) yielding N_A-N_D as high as 3.4×10^{17} cm^{-3}.[2] Refinement of this technique by workers at 3M Corporation resulted in N_A-N_D of 1.0×10^{18} cm^{-3}.[3] This breakthrough demonstrates that the problem of *p*-type doping of MBE ZnSe (at least up to the 10^{18} cm^{-3} range) is not related to the existence or behavior of native defects, which has frequently been invoked as the dominant factor giving rise to compensation in bulk material grown at higher temperatures. The possibility of doping ZnSe *p*-type with N makes the study of other column-V dopants more urgent than ever, in order to understand why N can successfully dope the *p*-type material, while others, such as As, P, and Sb, have not proven effective to date.

Arsenic is known to be an effective *p*-type dopant in both bulk and epitaxial ZnTe (Refs. 4 and 5) and CdTe.[6,7] However, there are relatively few reports on the properties of As as an intentionally doped acceptor in ZnSe.[8–13] Arsenic-doped bulk material shows only strong deep-level photoluminescence (PL) peaks,[8,9] which suggest that As may not be an effective *p*-type dopant for the material. Similar deep PL bands have also been observed in As-doped material grown by organometallic chemical-vapor deposition (OMCVD) (Ref. 11) and MBE.[12,13] The electron paramagnetic resonance studies of the bulk material suggested that these deep levels involve substitutional As on a Se site, but which has undergone a Jahn-Teller distortion to C_{3v} symmetry.[8] However, more recent studies of As-doped material grown by liquid-phase epitaxy, MBE, and OMCVD have given evidence of a shallow acceptor-bound exciton (I_1) peak[11–13] and donor-acceptor pair (D^0-A^0) emission[10–13] believed to involve a shallow As-related level. [Note, however, that there is

 ©1993 The American Physical Society

significant variation in the position of the reported (D^0-A^0) peaks from 2.693–2.712 eV, suggesting that the same level is not observed in all cases.] Photoconductivity thresholds at 125, 260, and 980 meV have also been observed in As-doped material.[13] Several groups have reported evidence of I_1 and/or (D^0-A^0) peaks believed to involve As coming from the GaAs substrate during growth or post-growth thermal anneals of undoped heteroepitaxial material.[14–17] In these cases, the observed (D^0-A^0) peak positions are more consistent (2.694–2.697 eV) and agree with the values observed in the present study.

Theoretical calculations have been performed to predict the behavior of acceptors in ZnSe.[18,19] A recent calculation[19] proposes that there are two acceptor states introduced in ZnSe by dopants such as As and P: a metastable effective-mass-like state with a small lattice relaxation, and a deep state with a large lattice relaxation. This deep state has been considered to be responsible for the absence of measurable conductivity in As- and P-doped ZnSe. So far, few experiments have been performed to confirm this model and determine the nature of the As and P shallow levels, or to study the possibility that these dopants can be used to introduce enough shallow acceptor levels in the material to obtain *p*-type conversion. In particular, no efforts to incorporate As or P from a plasma source, similar to the technique currently used for N, have yet been reported. The success of *p*-type ZnSe doped with N[3] makes the study of As and P more urgent than ever, even though As, P, and Sb have not proven effective to date.

In this paper, we have investigated the shallow acceptor level that consistently appears in As-doped MBE material in detail to address the key issues concerning this level, such as the accurate measurement of its binding energy, the energies of its excited states, the extent to which its energy levels obey effective-mass theory, and the point-group symmetry of the center producing the shallow acceptor level. The experimental probes include low-temperature photoluminescence (PL), variable-temperature PL, selective pair luminescence (SPL), and magnetospectroscopy measurements in fields up to 12 T. The variable-temperature PL measurements allow us to observe the (e-A^0) peak involving the As acceptor level at high temperature. From the theory of (e-A^0) line shapes[20] and the intercept of a linear fit to the position of the (e-A^0) peak as a function of temperature, we obtain the accurate binding energy of the shallow acceptor in As-doped material. Four excited states [$2p_{3/2}$, $2s_{3/2}$, $2p_{5/2}(\Gamma_7)$, and $3s_{3/2}$] are observed in the SPL measurements. Comparing their binding energies with theoretical calculations in the effective-mass approximation, we conclude that the level is effective-mass-like. The splitting of the As-related acceptor-bound exciton in different magnetic-field orientations has been compared with the splitting of the point defect Li acceptor-bound exciton at 11 T. The overall similarity of the splitting patterns for both acceptors (although not well resolved) suggests that the As-related acceptor level probably has the T_d symmetry of a simple substitutional point defect in ZnSe.

Our results demonstrate that As introduces a shallow acceptor level similar to those of the well-known dopants Li and N. The level is effective-mass-like and probably arises from a point defect. Therefore, the high resistivity observed in As-doped material to date cannot be simply blamed on the nonexistence of an appropriate shallow level, although we cannot rule out in the present study the possibility that this level might be metastable with respect to lattice distortion. We note further that the mere existence of As-related deep levels in the PL spectrum of As-doped ZnSe does not necessarily explain the absence of conductivity either, since similar deep levels have been observed in the PL spectrum of As-doped ZnTe, which nonetheless exhibits free hole concentrations as high as 1×10^{18} cm^{-3}.[5] While deep-level PL peaks are notably absent in moderately heavily doped *p*-type ZnSe:N,[1–3] the connection between the presence or absence of deep PL peaks and the ability to achieve *p*-type conduction is not yet clearly established.

II. EXPERIMENT

All of the samples were grown in one chamber of a dual chamber Riber MBE system on (100) undoped semi-insulating GaAs substrates, using metallic Zn and Se sources. High-purity Zn_3As_2 (99.9999%) was employed to dope the material. Details of the MBE growth of the As-doped samples have been published elsewhere.[12] Secondary-ion-mass spectrometry (SIMS) measurements were performed on some of the samples to measure the total As concentrations, as described previously.[12] The most heavily doped sample, grown at a Zn_3As_2 flux of 1.6×10^{-6} torr beam equivalent pressure (see Figs. 1 and 2), had an As concentration of about 10^{19} cm^{-3}. The As concentration increased in a strongly non-

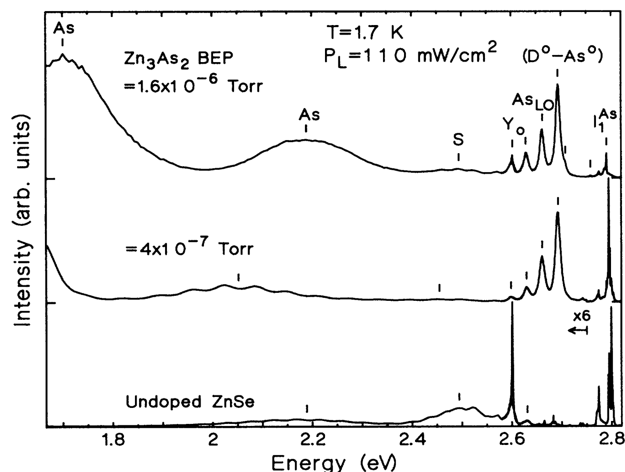

FIG. 1. Low-temperature PL spectra under low-level UV excitation for three ZnSe/GaAs samples as a function of Zn_3As_2 beam equivalent pressure (BEP), with growth temperatures of 330 °C, 270 °C, and 270 °C and layer thicknesses of 4.38, 3.22, and 1.00 μm, listed in order of increasing BEP. Note the $\times6$ scale expansion for the low-energy portion of the middle spectrum.

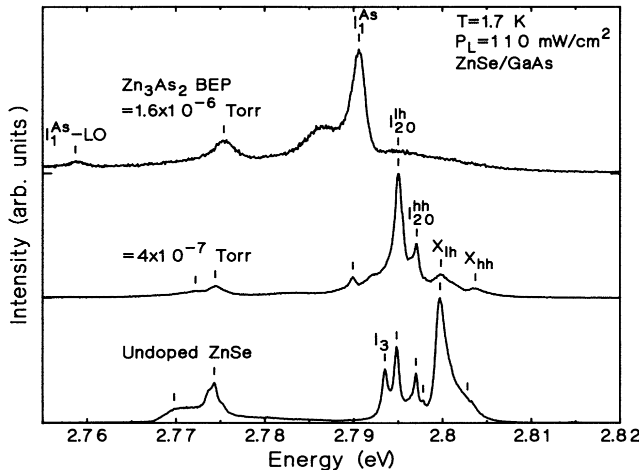

FIG. 2. Low-temperature PL spectra under low-level UV excitation in the exciton region for the undoped and As-doped ZnSe/GaAs samples of Fig. 1. Instrumental resolution is 0.07 meV for the lower two spectra and 0.44 meV for the upper one.

linear way with Zn_3As_2 flux, however, as discussed in Ref. 12, so that the more lightly doped samples which were measured had As concentrations at or below the SIMS detection limit (about 2×10^{17} cm^{-3}). In the following, therefore, we quote the Zn_3As_2 flux as a qualitative measure of As content, rather than actual concentrations.

The PL measurements were performed using cw excitation from either an UV Ar laser at 3.53 eV or from a Stilbene 3 dye laser operating in the blue. The blue laser light is passed through a Cambridge Research electro-optic power stabilizer to eliminate noise. A Janis optical cryostat and a 13-T superconducting solenoid magnet were used for PL and magnetospectroscopy, respectively. Both Faraday and Voigt configurations were employed for magnetospectroscopy. Samples were immersed strain free in superfluid liquid He for the low-temperature measurements and suspended in flowing gaseous He for measurements above liquid-He temperature. Total powers of 0.8 mW or less were employed in the variable-temperature measurements in order to avoid heating the samples. The spectra are corrected when necessary for the spectral response of the measurement system. Further details of the instrumentation are given in Ref. 21.

III. RESULTS AND DISCUSSION

A. PL properties of the As-related shallow acceptor

1. PL spectra of As-doped material

Low-temperature PL spectra of undoped and As-doped ZnSe layers grown by MBE with different Zn_3As_2 beam equivalent pressures (BEP) are shown in Fig. 1 for the energy range 1.666–2.82 eV. There is no detectable shallow acceptor level in the PL spectrum of the undoped material. As the dopant flux increases, a $(D^0\text{-}A^0)$ peak at 2.6934 eV appears and becomes stronger in the more heavily doped sample. This peak matches the position of the As-related $(D^0\text{-}A^0)$ peak reported in at least several of the previous studies.[12,14–17] Two deep peaks at 2.49 (the "*S*" band) and 2.19 eV are observed in the undoped material. With increasing Zn_3As_2 flux these peaks become weaker relative to the near-band-edge emissions, due to the increasing strength of the impurity-related luminescence resulting from As incorporation. However, two new deep peaks occur at 2.20 and 1.73 eV in the heavily As-doped material. Very similar peaks were observed in As-doped bulk material[9] and other OMCVD (Ref. 11) and MBE (Ref. 13) material. Therefore, these peaks are logically assigned to As-related deep levels.

Similar deep levels are also observed at 1.96 and 1.60 eV in As-doped ZnTe material grown by MBE, along with a shallow As acceptor level which gives rise to free hole concentrations up to 10^{18} cm^{-3}.[5] Evidently, the existence of deep-level peaks in addition to the shallow levels does not necessarily preclude good electrical conductivity, unless they involve compensating donor levels or represent spontaneous distortion of substitutional As centers as proposed by Chadi for both ZnSe and ZnTe.[19] The successful attainment of *p*-type conductivity with As doping in both bulk[4] and epitaxial[5] ZnTe clearly shows that the theoretical prediction (which is only based on an estimate in this case[19]) is not valid for ZnTe. Therefore, more precise calculations for As acceptor levels in both ZnSe and ZnTe need to be done, as well as more detailed comparisons of the deep-level properties, in order to understand the behavior of As in these materials.

2. Acceptor-bound excitons

The excitonic part of the spectrum also changes dramatically with the As-doping level. An expanded view of this region for the samples of Fig. 1 is shown in Fig. 2. All of the exciton peaks are shifted to lower energy compared to their peak positions in bulk material,[22] due to the biaxial tensile thermal strain in this heteroepitaxial material.[23–25] The free exciton is split into heavy-hole (X_{hh} at 2.8035 eV) and light-hole (X_{lh} at 2.7998 eV) components, and the neutral donor-bound exciton is similarly split into heavy (I_{2o}^{lh}) and light hole (I_{2o}^{lh}) components at 2.7971 and 2.7950 eV, respectively. The dominant structure is the free exciton in the undoped material, which suggests that the material has relatively few impurities. An acceptor-bound exciton peak (I_1^{As}) at 2.7888 eV is resolved in the sample with moderate As-doping level. In the most heavily As-doped sample, the bound exciton peak at 2.7906 eV becomes the dominant structure in the excitonic region and exhibits a LO-phonon replica at 2.7587 eV. The strength of the phonon replica confirms that this peak involves an acceptor rather than a donor, which would be less strongly coupled to lattice vibrations due to the lower electron mass and more extended wave function. The 0.8-meV shift between the two spectra is due to the differences in the thermal strain in the two samples. The linewidths in the heavily doped sample are broader, due to higher-impurity content and the greater effects of the inhomogeneous strain associated with interfacial defects in this thinner layer. These re-

sults verify that As, just like several other acceptors, introduces a shallow acceptor-bound exciton in ZnSe.

A high-energy component of the I_1 peak (denoted $I_1^{As'}$) is resolved at 2.7903 eV in the PL spectra at high temperature shown in Fig. 3 for the moderately doped sample of Fig. 1. The high-energy component dominates the lower-energy component at 2.7888 eV at 10 K and above, evidently due to a stronger oscillator strength compared with that of the low-energy component. This observation of a doublet for I_1^{As} parallels the thermalization behavior of other acceptor-bound excitons that have been previously studied in strained ZnTe (Ref. 26) and ZnSe,[3,27–29] and suggests that the I_1^{As} complex splits in the biaxial strain field in the same way as do excitons bound to N (Refs. 3 and 28) and Li (Refs. 27 and 29) acceptors. The heavy- and light-hole components of the donor-bound exciton also exhibit thermalization, as previously reported.[24]

A detailed theoretical analysis of the strain splitting of acceptor-bound excitons in II-VI materials has been given in Refs. 26 and 29. Since no information is available on the zero-strain peak positions and exchange and crystal-field splitting of I_1^{As} in bulk material, we have used the same values of the parameters that we employed in the I_1^{Li} case[29] to calculate the splitting pattern in our strained material, using the measured free-exciton splitting to determine the strain. The experimental positions of the two components of I_1^{As} agree with the calculated values within experimental error. This result indicates that the As acceptor-bound exciton behaves very similarly to the Li acceptor-bound exciton. We further note that unlike Yodo and Yamashita,[15] we find no difference whatsoever between the position of I_1^{As} and I_1^{Li} in similarly strained samples. This result seems quite logical given the similarity in the binding energies of the two acceptors (see below).

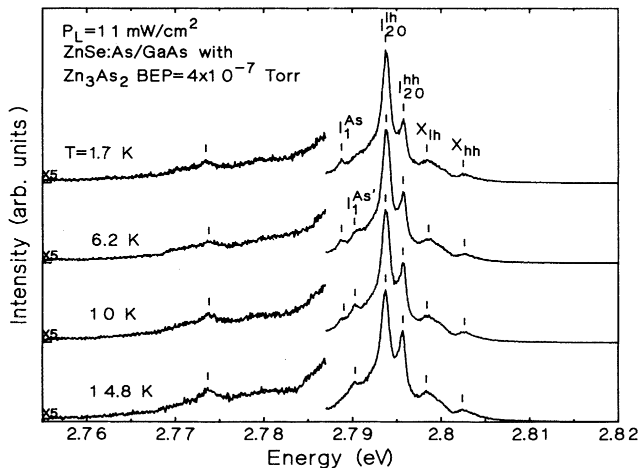

FIG. 3. PL spectra of the excitonic region as a function of temperature under low-level UV excitation for the sample of Fig. 1 with Zn_3As_2 BEP of 4×10^{-7} torr. Instrumental resolution is 0.22 meV.

3. *Donor-to-acceptor and band-to-acceptor peaks*

Figure 4 shows the temperature-dependent PL spectra in the $(D^0\text{-}A^0)$ pair range for the sample of Fig. 3. At low temperature, we observe an As-related $(D^0\text{-}A^0)$ peak at 2.6898 eV and its LO-phonon replicas. The Huang-Rhys factor which characterizes the phonon coupling strength has been determined to compare with those of other acceptors. The standard formula for the strengths of LO-phonon satellites[30] has been employed to fit our PL data for N-, P-, As-, and Li-related $(D^0\text{-}A^0)$ peaks and their LO-phonon replicas. Within an approximate 15% error in the peak fitting, a Huang-Rhys factor of 0.56 is obtained for the As acceptor level. This result implies a stronger phonon coupling strength than that of P acceptors with a Huang-Rhys factor of 0.30, but is comparable to that of Li and N acceptors with Huang-Rhys factors of 0.59 and 0.54, respectively. This observation indicates that the shallow As-related acceptor level has a similar degree of hole localization as do other substitutional acceptors. (As mentioned earlier, these data do not indicate whether or not this level is metastable.)

As the temperature rises above 26 K, a new peak occurs at 2.7068 eV along with LO-phonon replicas to lower energy, and becomes stronger and dominates the spectra at high temperature. This peak is considered to be a transition from electrons in the conduction band to the As acceptor level $(e\text{-}A^0)$, which results from thermal ionization of electrons bound to donors into the conduction band at high temperature. The temperature-

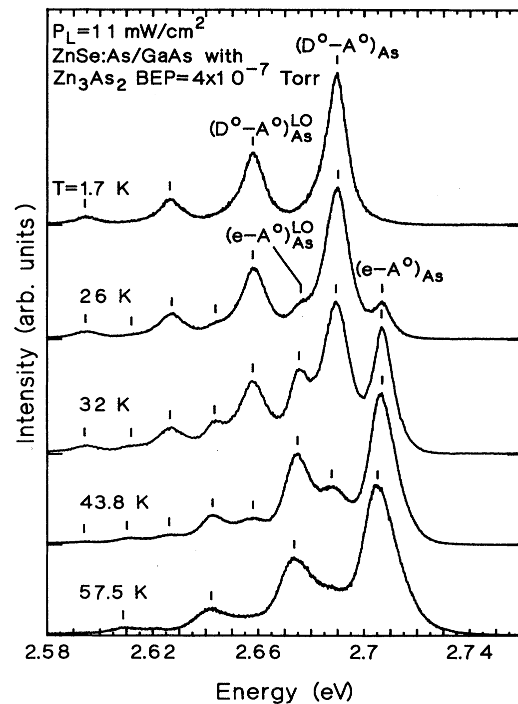

FIG. 4. Variable-temperature PL spectra of the $(D^0\text{-}A^0)$ pair region under low-level UV excitation for the sample of Fig. 3. Instrumental resolution is 0.36 meV.

dependent broadening of this peak strongly supports this interpretation.[20] From the position of the $(e\text{-}A^0)$ peak, the binding energy of the As-related acceptor can be determined with accuracy that greatly exceeds that available from crude estimates based on Haynes's Rule or $(D^0\text{-}A^0)$ peak positions.[29]

The method employed here to obtain the binding energy of the As acceptor from the temperature-dependent $(e\text{-}A^0)$ peak position is described in Ref. 29, which may be consulted for further details. The raw $(e\text{-}A^0)$ peak positions and corresponding values corrected for the variation of the band gap with temperature are shown in Fig. 5. The variation of the band gap is given in Ref. 29. A linear fit to the corrected data points gives a slope of 5.01×10^{-5} eV/K, which is in rough agreement with the theoretical value of $k_B/2=4.32\times10^{-5}$ eV/K,[20] and an intercept of 2.7065 eV. As the temperature increases, the linewidth of the $(e\text{-}A^0)$ peak (not plotted) increases linearly with a slope of $1.8k_B=2.4\times10^{-4}$ eV/K, in fair agreement with the theoretical value of 1.6×10^{-4} eV/K.[20] We assume, as discussed in Ref. 29, that the main component of the peak at the temperatures in question involves the heavy-hole acceptor level. The assumption is based on the three times larger oscillator strength of transitions involving the heavy-hole rather than light-hole level, which is expected to outweigh the thermalization into the light-hole state for the moderate splitting involved. With this assumption, we use the procedure described in Ref. 29 to obtain an accurate binding energy of the As-related acceptor from an average over similar data for three samples of strained material as 114.6 ± 0.7 meV. The binding energy of this acceptor level in unstrained material is calculated[29] to be $E_A^{\mathrm{As}}=114.8\pm0.7$ meV.

Our value of the binding energy is believed to be much more accurate than the rough estimates reported before.[10,11,13,14,17] The value we find in strained material can be compared to corresponding values we recently determined using identical procedures for Li (114.1 ± 0.4 meV) (Ref. 29) and N (113.0 ± 0.6 meV).[31] For practical purposes, it is therefore impossible to distinguish between residual Li and As acceptors in ZnSe without other information, although N can be distinguished from the other two. Our observation of the $(e\text{-}A^0)$ peak confirms the existence of an As-related shallow acceptor level in the Zn_3As_2-doped material.

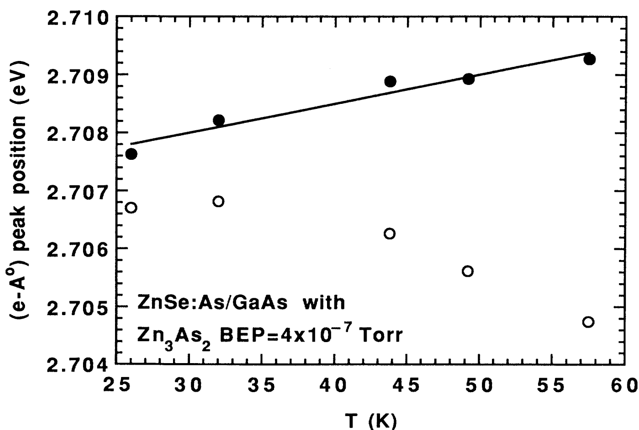

FIG. 5. Position of the $(e\text{-}A^0)$ peak as a function of temperature for the sample of Figs. 3 and 4 (open circles), together with corresponding values corrected for the shift of the band gap as a function of temperature (solid circles). The solid line is a linear fit to the corrected data points.

B. SPL measurements of the As-related shallow acceptor level

Selective pair luminescence measurements have been widely used to characterize excited states of acceptor levels in semiconductors and to determine whether or not a given acceptor follows effective-mass theory.[32] Previous SPL measurements have been performed for Li,[33] Na,[33,34] the "R" band in bulk ZnSe,[33] an unknown 56-meV acceptor level in OMCVD material,[35] Ag acceptors in bulk ZnSe,[36] and for N in homoepitaxial and heteroepitaxial ZnSe.[37,38] The results generally agree with effective-mass theory.[33–37] In the present work, we performed SPL measurements for the As-related acceptor level in ZnSe for the first time. Typical SPL spectra for an As-doped ZnSe layer are shown in Fig. 6. The main peaks are the nonselective As-related $(D^0\text{-}A^0)$ peak and its LO-phonon replica, which occur as a result of tunneling of the excitation from close to more distant pairs. As the energy of the laser line is tuned among various positions below the band gap of material, peaks assigned to the $3s_{3/2}$, $2p_{5/2}(\Gamma_7)$, $2s_{3/2}$, and $2p_{3/2}$ excited states of the As-related acceptor have been detected. The strongest

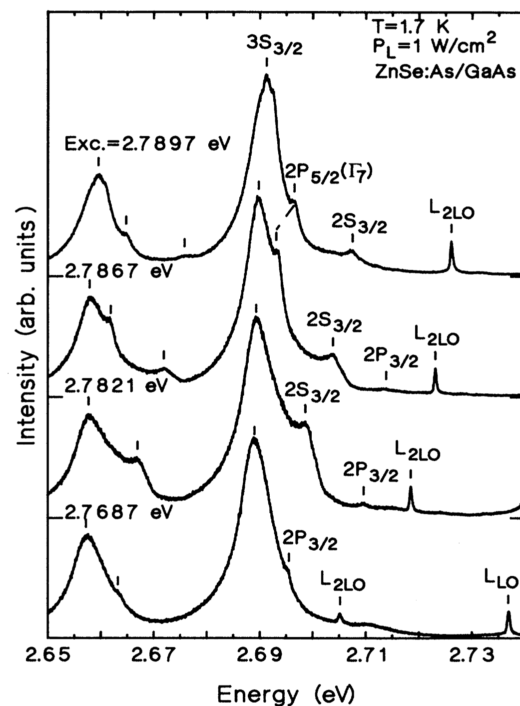

FIG. 6. Low-temperature SPL spectra of the $(D^0\text{-}A^0)$ pair region under dye laser excitation for a 3.75-μm-thick As-doped layer grown with Zn_3As_2 BEP of 4×10^{-7} torr. Instrumental resolution is 0.44 meV or better.

SPL peak is assigned to the $2s_{3/2}$ level, which is consistent with the fact that transitions involving the p states become allowed only due to the axial perturbation of the donor.[32] The SPL peaks all follow the laser line as it is tuned to progressively lower energies, as do their LO-phonon replicas, which supports their interpretation as SPL signals. Raman satellites of the laser are also identified in the spectra, based on their peak positions and linewidths.

The energy separations of the SPL peaks from the laser line as a function of luminescence energy for four different As-doped samples are plotted in Fig. 7. Decreasing luminescence energies correspond to increasing pair separation distances. The energy separation of SPL peaks from the laser line increases with increasing pair separation, due to a decrease in the interaction between the donor and acceptor wave functions with increasing pair distance. Therefore, the energy separation of the excited states from the ground state can be obtained from the SPL peaks in the limit of distant pairs, i.e., low luminescence energy. The corresponding values are about 98.4, 93.5, 83.9, and 73.6 meV for the peaks we assign to the $3s_{3/2}$, $2p_{5/2}(\Gamma_7)$, $2s_{3/2}$, and $2p_{3/2}$ excited states, respectively. The corresponding binding energies are determined by subtracting the separation energies from the binding energy of the $1s$ state determined in the $(e\text{-}A^0)$ peak position study.

A theoretical calculation of the excited states for an acceptor level in the effective-mass approximation (neglecting **q**-dependent screening and bound polaron effects, and assuming infinite spin-orbit splitting) has been given by Baldereschi and Lipari.[39,40] We have applied this calculation in the manner described by Tews, Venghaus, and Dean,[33] using the same experimental (renormalized) Luttinger parameters. In this approach, the entire spectrum is scaled by adjusting the effective Rydberg R_0 to match the experimental $1s_{3/2}$ binding energy and thereby account for central-cell corrections. This scaling method is not, in principle, valid for the p states, which are not expected to be affected by central-cell corrections. However, the As level probably has a very small central-cell correction, since it lies close in energy to the values for both Li and N acceptors. Thus, the scaling error should be negligible in this case. The calculated energy separations of the excited states from the ground state for the As acceptor level are listed in Table I. The $2p_{5/2}(\Gamma_8)$ state may be experimentally unresolved from the $2s_{3/2}$ state. We find good agreement between the experimental and theoretical values. This result indicates that the As-related shallow acceptor level in ZnSe is effective-mass-like.

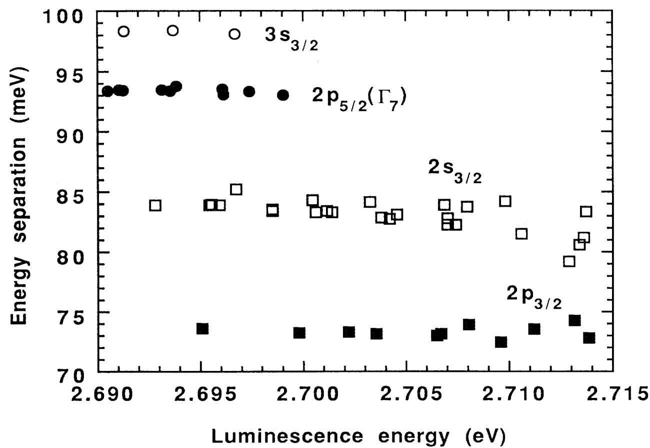

FIG. 7. Energy separations between the ground and excited states (i.e., between the laser and observed SPL peak) of the As-related shallow acceptor level as a function of luminescence energy for four different As-doped samples, including those of Figs. 3 and 6.

TABLE I. Experimental and theoretical separations between ground and excited states for the shallow As-related acceptor level in ZnSe.

Identification	Experiment (meV)	Theoretical (meV)
$1s_{3/2}$-$2p_{3/2}$	73.6	72.2
$1s_{3/2}$-$2s_{3/2}$	83.9	84.0
$1s_{3/2}$-$2p_{5/2}(\Gamma_8)$		84.6
$1s_{3/2}$-$2p_{5/2}(\Gamma_7)$	93.5	92.3
$1s_{3/2}$-$3s_{3/2}$	98.4	98.0[a]
$1s_{3/2}$-$2p_{1/2}$		99.6

[a]Estimate from the empirical rule $E_A^{ns}=(n^{-1.76})E_A^{1s}$.

C. Magnetospectroscopy

It is important to determine the nature of the center producing the shallow As-related level in ZnSe in order to understand this behavior. Magnetoluminescence has been used to measure the splitting of the As acceptor-bound exciton as a function of the magnetic-field direction. This type of experiment should, in principle, permit us to distinguish between full point group (T_d) or reduced (e.g., axial) symmetries, which can help to establish whether the shallow As-related level involves a substitutional point defect on the Se site or a complex. An As-doped MBE layer grown on an $In_xGa_{1-x}As$ substrate with an In fraction of 4% shows a dominant I_1^{As} peak at 2.7900 eV with a full width at half maximum of 0.7 meV in the low-temperature PL spectrum in Fig. 8, which makes this sample interesting for the magnetoluminescence measurements. At $B=0$, poorly resolved heavy- (X_{hh}) and light- (X_{lh}) hole free excitons and a Cu-related deep acceptor-bound exciton (I_1^D) are observed at 2.8032, 2.8004, and 2.7813 eV, respectively. The broad peak at 2.7951 eV contains unresolved donor and ionized donor-bound exciton peaks, possibly involving one or more species of donors.

The low temperature σ-polarized PL spectra of the I_1^{As} peak at 11 T with the magnetic field parallel to the [100], [110], and [111] crystal axes, and at zero magnetic field are shown in Fig. 8. Compared with its position at $B=0$, the peak shifts approximately 0.7 meV to higher energy at 11 T, due to the diamagnetism of the loosely bound electron in the As-acceptor bound exciton complex. The

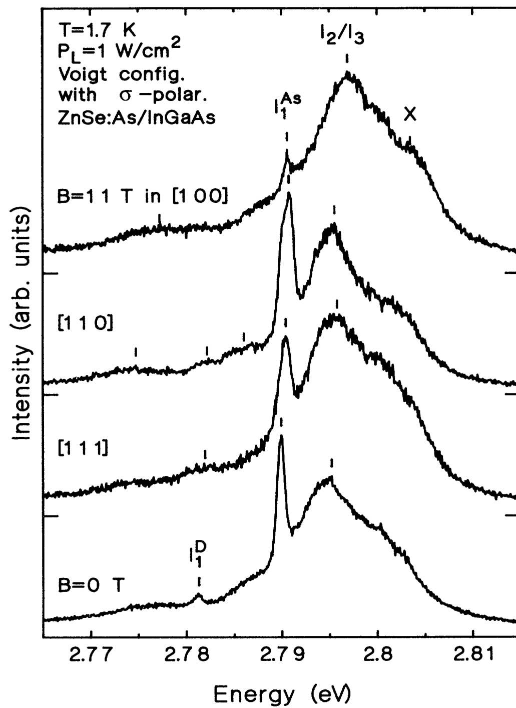

FIG. 8. Low-temperature σ-polarized excitonic PL spectra for $B=0$ and 11 T, with the magnetic field parallel to the [100], [110], and [111] crystal directions for an As-doped layer grown on an $In_{0.04}Ga_{0.96}As$ substrate. The layer thickness is 2.7 μm, and $T_g=270\,^{\circ}$C. Instrumental resolution is 0.58 meV.

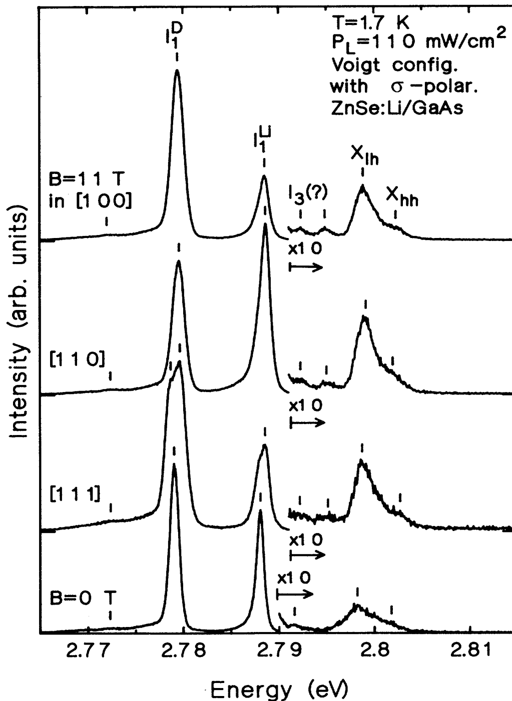

FIG. 9. Same as Fig. 8, but for a Li-doped ZnSe layer. Instrumental resolution is 0.13 meV.

linewidth of the As-acceptor bound exciton peak at high magnetic field is broader than that at zero magnetic field, due to the unresolved splitting of the peak. The π-polarized PL data were also recorded and showed essentially the same splittings as the σ-polarized spectra. The same low-temperature measurements were also performed on a lightly Li-doped MBE ZnSe layer grown on GaAs, and are shown in Fig. 9 for comparison. The I_1^{Li} peak is observed at 2.7881 eV at zero magnetic field. It shifts to 2.7886 eV at $B=11$ T due to diamagnetism and becomes broader, for all three field directions. However, a 0.7-meV splitting between the peaks observed in σ and π polarizations for $\mathbf{B}\|[100]$ and [110], and a 0.35-meV energy splitting between σ and π polarizations for $\mathbf{B}\|[111]$ are detected. Compared with the splitting of the Li-acceptor bound exciton at $B=11$ T, the As-acceptor bound exciton shows similar splitting patterns and no pronounced anisotropy. This result suggests that As acceptors have the point symmetry of the lattice, which indicates that As is probably a point defect in ZnSe involving a substitutional As atom on the Se site. The linewidth of the I_1^{As} peak prevents any more definitive analysis.

IV. SUMMARY

The As-related shallow acceptor level has been characterized in As-doped ZnSe material grown by MBE. Variable-temperature PL spectra of the excitonic region have demonstrated the existence of a high-energy component of the As bound exciton, which can be explained by splitting due to thermal tensile strain in the heteroepitaxial material, similar to that observed for other shallow acceptors. A conduction band-to-As acceptor peak is detected at temperatures above 26 K, and dominates the $(D^0\text{-}A^0)$ pair region of the PL spectra at high temperature. Analysis of the position of this $(e\text{-}A^0)$ peak as a function of temperature has yielded an accurate binding energy of 114.6±0.7 meV for the As-related shallow acceptor in strained material, implying $E_A^{\text{As}}=114.8\pm0.7$ meV in unstrained material. Together, these results prove that As doping does indeed introduce a shallow acceptor level similar to those of other well-known dopants, such as N and Li. The possibility remains that this level could be metastable with respect to lattice distortion, although we do not yet have any evidence on this point.

Selective pair luminescence measurements have been performed for the first time to study the excited states of this level. Four excited states assigned as $3s_{3/2}$, $2p_{5/2}(\Gamma_7)$, $2s_{3/2}$, and $2p_{3/2}$ with energy separations of 98.4, 93.5, 83.9, and 73.6 meV, respectively, from the ground state have been clearly observed. A theoretical calculation based on the effective-mass approximation is in good agreement with the experimental results. Therefore, we conclude that the As-related shallow acceptor level is effective-mass-like. The splitting pattern of the As acceptor-bound exciton has been measured for different configurations and directions of the magnetic field. The results are compared to similar data for a Li-doped sample. We find similar (though not well resolved) splitting patterns in both cases and therefore conclude

that the As acceptor probably has the point defect symmetry of the lattice, which suggests that it may be substitutional As on the Se site.

Our results indicate that the absence of *p*-type conductivity in As-doped material is not due to the absence of an As-related effective-mass-like acceptor level, nor necessarily just due to the presence of two strong deep-level peaks observed in the PL spectrum, since similar peaks are observed in the PL spectrum of heavily As-doped ZnTe but do not impede its conductivity. Future efforts to obtain type conversion in As-doped ZnSe should be directed at achieving more effective incorporation of the shallow As acceptor level, possibly using the methods currently employed for N. Additional experiments are also needed to investigate whether the As acceptor shallow level in ZnSe is metastable, to provide evidence for or against the theoretically proposed behavior of As in ZnSe.[18,19]

ACKNOWLEDGMENTS

We are grateful to H. Cheng for providing the Li-doped sample. The ASU portion of this work was supported by the National Science Foundation under Grant No. DMR-9106359.

*Present address: Instituto de Fisica "Gleb Wataghin," UNICAMP 13081, Campinas/SP, Brazil.
†Present address: Department of Chemistry, City College of the C.U.N.Y., New York, NY 10031.

[1] K. Ohkawa, T. Karasawa, and T. Mitsuyu, Jpn. J. Appl. Phys. **30**, L152 (1991).
[2] R. M. Park, M. B. Troffer, C. M. Rouleau, J. M. DePuydt, and M. A. Haase, Appl. Phys. Lett. **57**, 2127 (1990).
[3] J. Qiu, J. M. DePuydt, H. Cheng, and M. A. Haase, Appl. Phys. Lett. **59**, 2992 (1991).
[4] See, e.g., H. Venghaus and P. J. Dean, Phys. Rev. B **21**, 1596 (1980).
[5] F. S. Turco-Sandroff, M. J. S. P. Brasil, R. E. Nahory, R. J. Martin, Y. Zhang, and B. J. Skromme, Appl. Phys. Lett. **59**, 688 (1991).
[6] N. C. Giles, K. A. Bowers, R. L. Harper, Jr., S. Hwang, and J. F. Schetzina, J. Cryst. Growth **101**, 67 (1990).
[7] M. Ekawa, K. Yasuda, T. Ferid, M. Saji, and A. Tanaka, J. Appl. Phys. **71**, 2669 (1992).
[8] R. K. Watts, W. C. Holton, and M. de Wit, Phys. Rev. B **3**, 404 (1971).
[9] A. R. Reinberg, W. C. Holton, M. de Wit, and R. K. Watts, Phys. Rev. B **3**, 410 (1971).
[10] B. J. Fitzpatrick, C. J. Werkhoven, T. F. McGee, III, P. M. Harnack, S. P. Herko, R. N. Bhargava, and P. J. Dean, IEEE Trans. Electron Devices **ED-28**, 440 (1981).
[11] M. Okajima, M. Kawachi, T. Sato, K. Hirahara, A. Kamata, and T. Beppu, in *Extended Abstracts of the 18th Conference on Solid State Devices and Materials* (Publication Office, Business Center for Academic Society Japan, Tokyo, 1986), p. 647.
[12] S. M. Shibli, M. C. Tamargo, B. J. Skromme, S. A. Schwarz, C. L. Schwartz, R. E. Nahory, and R. J. Martin, J. Vac. Sci. Technol. B **8**, 187 (1990).
[13] K. Hingerl, W. Jantsch, P. Juza, M. Lang, H. Sitter, J. Lilja, M. Pessa, D. J. As, and W. Rothemund, J. Cryst. Growth **117**, 341 (1992).
[14] T. Yao, M. Ogura, S. Matsuoka, and T. Morishita, Jpn. J. Appl. Phys. **22**, L144 (1983).
[15] T. Yodo and K. Yamashita, Appl. Phys. Lett. **53**, 2403 (1988).
[16] B. J. Skromme, N. G. Stoffel, A. S. Gozdz, M. C. Tamargo, and S. M. Shibli, in *Advances in Materials, Processing, and Devices for III-V Compound Semiconductors,* edited by D. K. Sadana, L. E. Eastman, and R. Dupuis, MRS Symposia Proceedings No. 144 (Materials Research Society, Pittsburgh, 1989), pp. 391–396.
[17] J. O. Williams, in *Spectroscopy of Advanced Materials,* edited by R. J. H. Clark and R. E. Hester (Wiley, New York, 1991), p. 215.
[18] D. J. Chadi and K. J. Chang, Appl. Phys. Lett. **55**, 575 (1989).
[19] D. J. Chadi, Appl. Phys. Lett. **59**, 3589 (1991).
[20] D. M. Eagles, J. Phys. Chem. Solids **16**, 76 (1960).
[21] B. J. Skromme, R. Bhat, H. M. Cox, and E. Colas, IEEE J. Quantum Electron. **25**, 1035 (1989).
[22] P. J. Dean, D. C. Herbert, C. J. Werkhoven, B. J. Fitzpatrick, and R. N. Bhargava, Phys. Rev. B **23**, 4888 (1981).
[23] T. Yao, Y. Okada, S. Matsui, K. Ishida, and I. Fujimoto, J. Cryst. Growth **81**, 518 (1987).
[24] B. J. Skromme, M. C. Tamargo, J. L. de Miguel, and R. E. Nahory, in *Epitaxy of Semiconductor Layered Structures,* edited by R. T. Tung, L. R. Dawson, and R. L. Gunshor, MRS Symposia Proceedings No. 102 (Material Research Society, Pittsburgh, 1988), p. 577.
[25] B. J. Skromme, M. C. Tamargo, F. S. Turco, S. M. Shibli, W. A. Bonner, and R. E. Nahory, in Proceedings of the Fifteenth International Symposium on Gallium Arsenide and Related Compounds, edited by J. S. Harris, IOP Conf. Proc. No. 96 (Institute of Physics and Physical Society, Bristol, 1989), p. 205.
[26] Y. Zhang, B. J. Skromme, and F. S. Turco-Sandroff, Phys. Rev. B **46**, 3872 (1992).
[27] M. A. Haase, H. Cheng, J. M. DePuydt, and J. E. Potts, J. Appl. Phys. **67**, 448 (1990).
[28] K. Ohkawa, T. Mitsuyu, and O. Yamazaki, Phys. Rev. B **38**, 12 465 (1988).
[29] Y. Zhang, B. J. Skromme, and H. Cheng, Phys. Rev. B **47**, 2107 (1993).
[30] See, e.g., K. K. Rebane, *Impurity Spectra of Solids* (Plenum, New York, 1970).
[31] Y. Zhang, B. J. Skromme, and J. Qiu (unpublished).
[32] See, e.g., P. J. Dean, Prog. Cryst. Growth Charact. **5**, 89 (1982), and references cited therein.
[33] H. Tews, H. Venghaus, and P. J. Dean, Phys. Rev. B **19**, 5178 (1979).
[34] M. Isshiki, T. Itoga, K. Masumoto, K. Mochizuki, and W. Uchida, Jpn. J. Appl. Phys. **30**, 623 (1991).
[35] P. Blanconnier, J. F. Hogrel, A. M. Jean-Louis, and B. Sermage, J. Appl. Phys. **52**, 6895 (1981).
[36] P. J. Dean, B. J. Fitzpatrick, and R. N. Bhargava, Phys. Rev. B **26**, 2016 (1982).
[37] P. J. Dean, W. Stutius, G. F. Neumark, B. J. Fitzpatrick, and R. N. Bhargava, Phys. Rev. B **27**, 2419 (1983).
[38] K. Shahzad, B. A. Khan, D. J. Olego, and D. A. Cammack, Phys. Rev. B **42**, 11 240 (1990).
[39] A. Baldereschi and N. O. Lipari, Phys. Rev. B **8**, 2697 (1973).
[40] A. Baldereschi and N. O. Lipari, Phys. Rev. B **9**, 1525 (1974).