# Isoelectronic δ doping in a ZnSe superlattice: Tellurium as an efficient hole trap

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Spatially selective introduction of Te isoelectronic traps into ZnSe-based quantum-well structures allows the probing of this strongly binding center for excitons with direct microscopic insight. In particular, we show how the hole wave function is strongly localized at Te sites to an orbit size comparable to that of the unit cell. The electron wave function, Coulomb bound to the hole, is not measurably altered following the shrinkage of the hole orbit.

## I. INTRODUCTION

In the past two decades there have been many studies about the nature of substitutional isoelectronic dopants in semiconductors. Generally speaking, the existence of bound states at such centers remains an uncommon occurrence. Theoretical models have yielded qualitative insight for preferred conditions for the formation of bound states in terms of the choice of the isoelectronic impurity to a particular host but large quantitative discrepancies remain, for example, between calculated and experimentally observed binding energies.[1] Among the best studied cases involve GaP:N and InP:Bi, for which the energy scale for binding of excitons is typically tens of meV.[2,3]

In this paper we show how the advent of artificial semiconductor microstructures is making it possible to access new insight to the nature of particular isoelectronic centers. The case studied here involves Te as the isoelectronic impurity in ZnSe,[4,5] a physically interesting situation with unusual characteristics which have recently been discussed in terms of exciton extrinsic "self-trapping,"[5] i.e., with strong photocarrier-induced lattice relaxation deepening the effective binding at the impurity site.[6(a)] Similar effects have also been encountered earlier in ZnS:Te.[6(b)] The energy scale in such trapping can be well in excess of 100 meV and the process has been speculated[6(b)] to be dominated by hole capture at Te sites, with the electron simply Coulomb bound to the self-trapped hole. In work reported here the isoelectronic centers are introduced in a spatially selective fashion by using atomic-layer epitaxy (ALE) to deposit monolayers of ZnTe into ZnSe-based quantum-well structures. This "δ doping" provides a high degree of spatial control over the location of the isoelectronic traps in a semiconductor microstructure; the presence of a surrounding superlattice or quantum well can in principle be used to "tune" the exciton wave function further. Central to this paper is our choice of a diluted magnetic semiconductor $Zn_{1-x}Mn_xSe$ (with its "giant" $g$ factor) as the barrier material in the quantum well. This arrangement makes Zeeman spectroscopy especially useful by permitting direct probing for the spatial extent of the quasiparticle wave functions as shown below.

## II. EXPERIMENTAL RESULTS AND ANALYSIS

A number of ZnSe-based layered structures containing spatially selective incorporation of ultrathin ZnTe layers have been recently grown at Purdue University.[7] Of several different geometries we focus in this paper on one type, which provides the most appropriate illustration of the principal physical ideas. This structure consists of a molecular-beam-epitaxially (MBE) grown multiple quantum well (MQW) of $ZnSe/Zn_{1-x}Mn_xSe$ ($x=0.21$) where a molecular monolayer on ZnTe was incorporated within each ZnSe quantum well by ALE. The monolayers of ZnTe are subject to both interdiffusion and strain. As for the latter we note that the lattice mismatch between ZnTe and ZnSe is very large, approximately 7%, nevertheless for the ultrathin layer structures considered here we believe that the epitaxy is essentially pseudomorphic. The optical properties of "undoped" strained layer $ZnSe/Zn_{1-x}Mn_xSe$ quantum wells have been studied recently so that information about band offsets and exciton features is available.[8] Comparison between the photoluminescence (PL) spectra of such an undoped multiple quantum-well sample with another including the δ doping is shown in Figs. 1(a) and 1(b), respectively, at $T=2$ K.[7] The undoped sample had ZnSe quantum wells of 67 Å in layer thickness; the isoelectronically doped structure contained 44-Å-thick ZnSe layers with a monolayer of ZnTe in the middle of each well. Both structures were highly quantum efficient at this measurement temperature; their amplitudes are normalized in the figure. Figure 1(c) shows the PL excitation spectrum for the Te-doped structure displaying the principal $n=1$ exciton absorption features [light and heavy hole exciton, respectively, where the former is at lower energy due to the uniaxial component of the ZnSe-(Zn,Mn)Se lattice mismatch strain]. Comparison with the excitation spectrum of undoped structures of similar well thicknesses[8] shows that the addition of the ultrathin "sheet" of ZnTe has very little effect on the absorbing exciton which is measured in excitation spectroscopy. For qualitative purposes we note that simple atomic-orbital estimates suggest that a thin layer of ZnTe would introduce an approximately

 

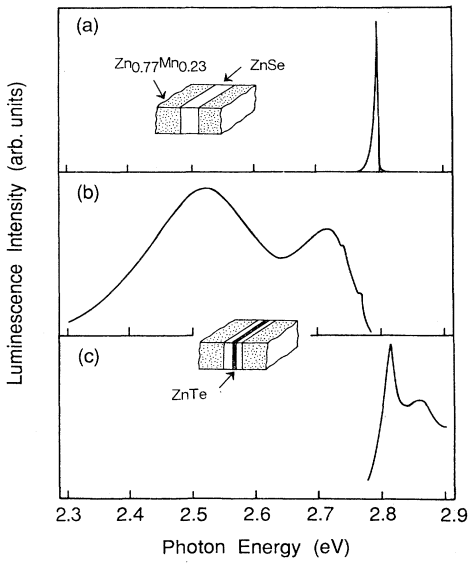


FIG. 1. Photoluminescence spectra at $T=2$ K of (a) a ZnSe/(Zn,Mn)Se multiple quantum well, (b) a similar structure but with the Te isoelectronic δ doping in the middle of the quantum wells. The amplitudes in (a) and (b) are normalized; the dimensions of the structures are given in text. The photoluminescence excitation spectra of sample (b) in the vicinity of the $n=1$ exciton is shown in the bottom panel (c).

0.5-eV potential barrier in the conduction band of ZnSe quantum well and an approximately 1.0-eV well in the valence band; for a perfect ZnTe monolayer these additional potentials are estimated to produce corrections to the excitation spectrum on a scale of less than 10 meV in a simple Kronig-Penney or tight-binding model.

The large differences between the PL spectra of the δ-doped and undoped $ZnSe/Zn_{1-x}Mn_xSe$ quantum wells have been briefly commented in Ref. 7. First, the emission from the δ-doped structure shows large Stokes shifts (considerably in excess of 100 meV) in relation to the lowest absorbing resonance at 2.82 eV (the undoped structure has a redshift of less than 5 meV in its PL, presumably due to exciton localization effects by quantum-well thickness fluctuations on monolayer scale). Second, the emission at low lattice temperatures is composed of two principal features, both of which exhibit a large amount of linewidth broadening ($\cong 100$ meV). Such general features have also been observed in the dilute bulk alloy $ZnSe_{1-x}Te_x$ and $ZnS_{1-x}Te_x$ for $x \lesssim 0.05$.[4,5,6(b)] The interpretation of this behavior in bulk material evokes self-trapping of excitons at small Te clusters, of which single Te sites (denoted as $S_1$) and double Te sites (Te atoms on nearest-neighbor anion sites, denoted as $S_2$) produce the higher and lower energy peaks at 2.72 and 2.52 eV in Fig. 1, respectively. The trapping involves a combination of short-range and long-range exciton-phonon interactions and physically results in a locally distorted lattice about the capture center.[5] The relative amplitudes of the $S_1$ and $S_2$ features for the superlattice indicate a comparable density of the two sites, respectively, under assumption of a comparable capture cross section and decay. Assuming statistical distribution of the anion we can calculate that this is consistent with approximately one monolayer worth of interdiffusion at the ultrathin ZnSe sheets, the result of which is to produce a thin layer ($\cong 6$ Å) of $ZnSe_{1-x}Te_x$ at the center of each ZnSe quantum well ($L_W=44$ Å). In other words, while the distribution of Te sites is spatially still quite anisotropic and confined to a fraction of each quantum-well thickness, one monolayer of interdiffusion makes Te pairs and singles the most numerous species in the distribution of clusters. We also make the point that the relatively low growth temperature employed here ($T=320$ °C) should discourage the formation of Te aggregates, especially when compared with bulk growth. At higher temperatures ($T>150$ K) the principal emission lines in Fig. 1 become weak due to thermal dissociation effects and other low energy emissions below the $S_2$ feature appear;[7] these are associated with higher Te-related complexes. We have also studied structures with 2-monolayer-thick ZnTe layers where an isoelectronic impurity band apparently develops in the layer ($x$-$y$) plane; that is, percolation threshold is exceeded. This aspect will be discussed elsewhere in greater detail. For our purposes here the δ-doped quantum wells are suitable for investigating the details of the isoelectronic trapping at nearly isolated Te centers in the middle of ZnSe quantum wells, with weak minimal intersite energy transport of excitons (by tunneling) in the $x$-$y$ plane, especially for the more deeply trapped exciton state $S_2$ (see comments in connection with time-resolved measurements below).

Direct evidence about the vast changes in the hole part of the exciton wave function upon self-trapping was obtained through spectroscopic studies in external magnetic fields as follows. The very large effective $g$ factors which are characteristic of diluted magnetic semiconductor such as $Zn_{1-x}Mn_xSe$ are consequence of a short-range, contact potentiallike exchange interaction between the band-edge electron-hole states and the Mn-ion $d$ electrons. Hence, in a quantum-well structure the Zeeman splittings of the ground-state exciton give a direct measure of the extent of wave-function penetration of the confined quasiparticles into the barrier layers. Figure 2 compares the field-induced effects in both excitation and PL spectra in a 3-$T$ field at $T=2$ K parallel to the superlattice growth axis ($z$). Only a portion of the PL spectrum is shown near the peak of the $S_1$ emission (note expanded horizontal scale); however, similar conclusions apply to the $S_1$ and $S_2$ bands. While the excitation spectrum (absorbing exciton) shows a large Zeeman splitting of approximately 30 meV for the $n=1$ light hole exciton ground state, we have been unable to measure a distinct Zeeman effect (shift) in the emission. Here, however, the very broad emission lines together with finite experimental noise puts an upper limit to a possible shift of $\cong 1$ meV in our direct PL measurement.

In the simplest approach we write for the Zeeman splitting of the exciton state a direct sum of the electron and hole contributions as

$$\Delta E_X = N_0 \langle x \rangle [\alpha g_c(L) - \langle \beta \rangle g_v(L)] \langle S_z \rangle \ . \quad (1)$$

Our notation follows standard approach in describing

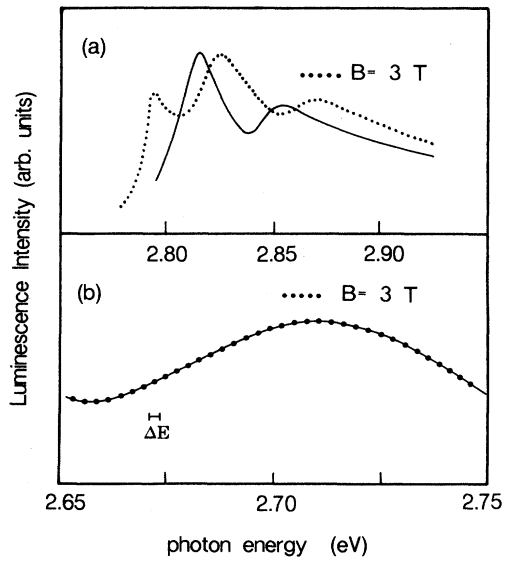


FIG. 2. Effect of an external magnetic field at $T=2$ K on the excitation spectrum of the "δ-doped" quantum well (a), and on the recombining exciton spectrum in the vicinity of the $S_1$ transition (note expanded scale). The solid lines are spectra in zero field and the dotted lines in a field of 3 T. The experimental resolution is also indicated.

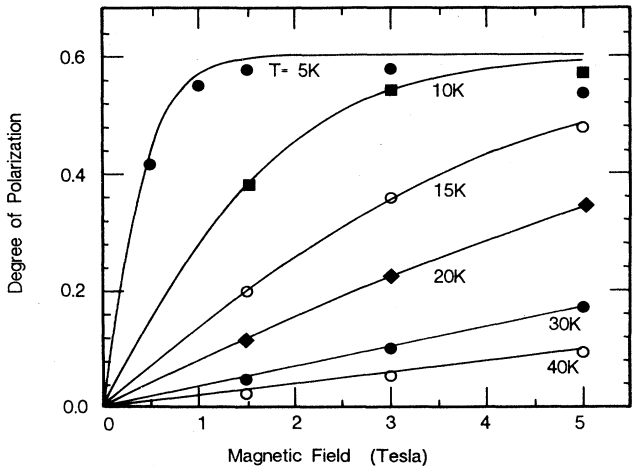


FIG. 3. Degree of circular polarization in the luminescence as a function of magnetic field at several temperatures. The points are experimental; the solid lines correspond to calculations of the model described in text.

the exchange interaction between band-edge states with the $d$-electron spins of the Mn ion. The cation density is given by $N_0$ and the quantity $\langle x \rangle$ indicates the effective concentration of Mn in the barrier layer by taking into account the antiferromagnetic interactions. The conduction- and valence-band exchange coefficients are given as $N_0\alpha=250$ meV and $N_0\beta=1250$ meV for $Zn_{1-x}Mn_xSe$,[9] the latter should be averaged for the $|m_j|=\frac{3}{2}$ and $\frac{1}{2}$ states due to the strain-induced valence-band anisotropy. $\langle S_Z \rangle$ is the average Mn-ion spin in the direction of the external field, and $g_c(L)$ and $g_v(L)$ are the fractions of integrated electron and hole probability densities within the barrier layers (obtained from solutions for a square-well potential problem for well thickness $L$; thus for bulk $Zn_{1-x}Mn_xSe$, $g_c=g_v=1$). The electron-hole Coulomb interaction is neglected in this estimate (apart from using the excitonic band gap as the zero field reference level). While the conduction- and valence-band offsets for the $ZnSe/Zn_{1-x}Mn_xSe$ heterojunction are not precisely known, it has been clearly established[8] that the valence-band offset is small (on the scale of the exciton Rydberg) and actually dominated by lattice mismatch strain contributions. Combination of the small valence band offset and large exchange coefficient means that for the "absorbing" exciton [Fig 2(a)] the *hole contribution dominates* the exchange interaction. For purposes of an estimate we take $\Delta E_c=100$ meV and $\Delta E_v=30$ meV, in accordance with earlier optical studies of $ZnSe/Zn_{1-x}Mn_xSe$ quantum wells of similar layer thicknesses and Mn concentration. This choice of $\Delta E_v$ is then compatible with Zeeman splitting of the excitation spectrum for $g_V\cong 0.5$. However, a more direct measurement for this value of $g_V$ was obtained by comparing the measured exciton splitting with that observed in a thin epitaxial film of $Zn_{1-x}Mn_xSe$ ($x=0.20$). With these considerations in mind, the principal conclusion of our measurements in a magnetic field is that for the recombining exciton [Fig. 2(b)] the reduction in the Zeeman effect at least by an order of magnitude must be due to the collapse of the hole wave function to the Te centers at the middle of the quantum wells. Considering the experimental resolution and allowing for a finite penetration by the electron wave function to the barrier to produce a finite exchange correction to the exciton energy then produces the estimate that the hole wave function must have shrunk to the scale of the unit cell (for a simple hydrogenic envelope function).

The penetration into the $Zn_{1-x}Mn_xSe$ barrier layer by the electron component of the recombining exciton wave function can be measured by the degree of circular polarization in the luminescence in magnetic field. This method circumvents the problem of experimental resolution in looking for small shifts in the broad PL spectra. Figure 3 shows the field dependence of polarization as a function of the applied field at several temperatures. The polarization is defined in the conventional way as $P=(I_+-I_-)/(I_++I_-)$. We have found that the degree of polarization is very nearly wavelength independent over most of the $S_1$ and $S_2$ bands. If, by keeping in mind the results of the Zeeman experiments above, we assume that the dominant contribution to $P$ is by the electron, we can calculate (ignoring the relatively modest exciton exchange in ZnSe) the expected electron polarization, for instance, by adapting a model by Heiman, Wolff, and Warnock.[10,11] This model self-consistently accounts for the electron-Mn-ion exchange including thermodynamical statistical fluctuations of the net Mn-ion magnetization within the carrier orbit, as well as possible spontaneous magnetic ordering effects (bound magnetic polaron). For electrons in a quantum well we write for the net effective magnetic moment in the electron orbit (normalized to Bohr magneton)

$$\mathbf{m} \equiv 10\pi g \langle x \rangle N_0 \int dz \int dr'\, r' B_{5/2}(5N_0\alpha \exp[-2\{[(r')^2+z^2]\}^{1/2}/a_e]/4\pi N_0 a_e^3 k_B(T+T_0)) \,, \tag{2}$$

where the integration in the $z$ direction limits the exchange interaction to the $ZnSe/Zn_{1-x}Mn_xSe$ barrier layer ($r'$ being the coordinate in the quantum-well layer plane). The Mn-ion $g$ factor is taken as $g=2$, $N_0$ is the density of unit cells per volume, and $a_e$ the Bohr radius of the electron. The antiferromagnetic interactions within the Mn-ion spin system are treated here by using an effective Mn concentration $\langle x \rangle$, together with a corrective temperature factor $T_0$ in the argument of the Brillouin function $B_{5/2}$.

With this effective magnetic moment, the electron polarization is obtained from

$$p_e = p_s \tanh(\mathbf{m}\mu B/k_B T) \,, \tag{3}$$

with $p_s$ an experimentally determined constant. The solid line in Fig. 3 is a fit to experimental points with Eq. (2) for a wide range of temperatures with $a_e=29$ Å, $\langle x \rangle = 0.03$, and $T_0 = 1.0$ K. The "saturation" moment has been taken to be $p_s = 0.60$, indicative of the approximate asymptotic limit observed experimentally at high fields and $T < 10$ K. The parameter values for $\langle x \rangle$ and $T_0$ are in reasonable agreement with extrapolated results from Ref. 9. The electron Bohr radius is within the accuracy of effective mass estimates for donor electrons in bulk ZnSe within the range of dielectric constants reported in the literature. For the quantum-well parameters in question (band offset and layer thickness) variational calculations show that confinement effects are weak so that the electron remains essentially three-dimensional. Since the maximum experimentally measured polarization exceeds 0.50, the value expected for a totally spin polarized electron and a randomly polarized hole, the implication is that the hole state participating in the recombination process must possess a partially anisotropic total angular momentum [so that $P=(p_e+p_h)/(1+p_e p_h)$]. Such a situation is not unexpected considering that the hole wave function is spread over much of the Brillouin zone and subject to considerable band mixing as well as influence by the large lattice mismatch strain at the ZnTe/ZnSe interface. In these circumstances the self-trapping is likely to be an anisotropic process.[12] Except at low temperatures ($T < 5$ K), the agreement with the calculation and experiment is good, therefore supporting the model of circular polarization which first and foremost reflects the exchange interaction of the electron with a finite number of Mn-ion spins in that part of its orbit which reaches into the (Zn,Mn)Se barrier layer. The experimentally observed decrease in circular polarization at $T=5$ K (and below) at fields somewhat in excess of the "saturation field" is puzzling; it may be due to field-induced changes in the quantum-well potential which are not included in our model. Finally, the effective moment $\mathbf{m}$ calculated from Eq. (2) at low temperature implies an experimentally expected Zeeman shift of less than 2 meV at $B > 5$ T in the luminescence spectrum of the recombining exciton; as mentioned above, this is the resolution in our experiment. (The Zeeman shift is also partially canceled by the exciton diamagnetic shift of $\cong 1$ meV.) Altogether then, the polarization measurements, which can be explained by considering the electron exchange alone, support the conclusion of a dramatically reduced hole wave function in the self-trapped exciton. Furthermore, within the accuracy of our experiment and model the electron Bohr orbit is not apparently altered in any significant way by the dramatic changes which have taken place in the hole charge distribution during its localization process.

The changes in the hole orbit which accompany exciton self-trapping at the Te sites also influence the exciton radiative lifetime. At the low lattice temperatures considered here, the overall lifetime is dominated by radiative recombination. We have made time resolved measurements in both quantum wells and the dilute bulk alloy $ZnSe_{1-x}Te_x$ ($x=0.01$) (Ref. 13) to show that, while the radiative lifetime of a quasi-2D exciton in an undoped ZnSe/(Zn,Mn)Se quantum well [Fig. 1(a)] at low temperatures is approximately 200 psec,[14] the introduction of the Te isoelectronic centers increases the lifetime by approximately 2 orders of magnitude. As discussed earlier by Rashba,[15] and Henry and Nassau,[16] the oscillator strength (hence radiative recombination rate) for an exciton where one of the quasiparticles has a much smaller orbit is proportional to $|\Phi_e(0)|^2 |\int \Phi_h(\mathbf{r}) d\mathbf{r}|^2$. For a highly localized hole we can here approximate the total exciton wave function as $\Psi \cong \Phi_e \Phi_h$ with

$$\Phi_e \sim \cos(\pi z/L) \exp\{-[(r')^2+z^2]^{1/2}/a_e\}$$

and $\Phi_h \sim \exp(-r/a_h)/r$, where $a_e$ and $a_h$ are the Bohr radii of the electron and the hole, respectively. This simplified exciton wave function shows that, while quantum-well confinement effects are no longer important for the hole in determining the oscillator strength (except for ultrathin wells), the electron wave function (hence its overlap with the hole) can in principle be "tuned" by varying the quantum-well thickness. For the $ZnSe/Zn_{1-x}Mn_xSe$ quantum wells, larger confining potentials ($x > 0.3$) and narrow wells ($L < 30$ Å) than those encountered here are needed for this effect to be significant, however. The second important factor influencing the exciton kinetics (including lifetime) is a consequence of the high isoelectronic center density in the quantum-well midplane, finite interdiffusion notwithstanding. This can allow the migration of exciton energy in the $x$-$y$ plane and involves transfer (most likely by tunneling) of highly localized holes between small Te clusters. Reflecting this, we measure a lifetime of 20 nsec for the $S_2$ emission band and approximately 6 nsec for the $S_1$ band. Details of time-resolved spectroscopy show,[13(a)] however, that the relatively short lifetime of the latter is entirely due to energy transfer into the former. Such energy-transfer processes have been studied in detail at steady state by Heimbrodt and Goede[13(b)] in ZnS:Te. Focusing on the $S_2$ band and employing realistic effective

mass parameters for ZnSe with assuming $a_e = 29$Å and $a_h \cong 6$ Å, we calculate a lifetime in good agreement with the measurement. In the case of a dilute bulk $ZnSe_{1-x}Te_x$ ($x \cong 0.01$), the long exciton lifetimes measured experimentally similarly reflect the reduced electron-hole overlap for the self-trapped excitons.[4,13]

## III. SUMMARY

In conclusion, we have employed magneto-optical measurements to study isoelectronic doping of a ZnSe quantum well by in a spatially selective way. In the particular geometry considered here, direct physical insight has been acquired to the nature of exciton self-trapping at elementary Te clusters, a process which produces very large effects in the exciton recombination spectra. In particular, we have directly shown how the principal effect is due to the large shrinkage in the hole Bohr orbit following the capture at the Te sites. From steady-state and time-resolved spectroscopy we conclude that the relaxed hole has an effective Bohr radius approximately equal to that of the lattice constant. On the other hand, the electron is not influenced by the changes in the hole charge distribution and remains Coulomb bound to the hole in a donorlike fashion. The hole capture must involve strong local lattice relaxation effects the microscopic details of which are not given by our experiments. Application, e.g., of time-resolved methods, to study the excitation of the local lattice vibrations at the capture sites should add physical insight to this part of the problem. Clearly, other designs of superlattice structures are also possible to further exploit both the fundamental science as well as application of these phenomena in connection with light emitting phenomena in the blue-green region of the spectrum.

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