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Brief Reports

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Exchange electron-hole interaction at the isoelectronic oxygen trap in zinc selenide

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We present photoluminescence (PL) and excitation data to show that oxygen substituting isoelectronically in ZnSe gives rise to a pair of transitions A^+(2.7895 eV) and B (2.7877 eV) as a result of the exchange interaction between the trapped electron-hole pair. The former is attributed to total angular momentum $J=1$, Γ_4 representation, and is electric dipole allowed while the latter is assigned to $J=2$ belonging to the $\Gamma_3+\Gamma_5$ representation and is electric dipole forbidden. Based on this model, we explain several experimental observations including varying PL intensity of the B line from sample to sample, the relatively rapid disappearance of the B line as a function of increasing temperature, and strong LO couplings of the A^+ and B lines.

Zinc selenide is a direct-band-gap semiconductor with the zinc-blende structure. It has a band gap of ~2.67 eV at 300 K, making it potentially very suitable for blue-light-emitting devices.[1] Due to the difficulty of achieving high-conductivity *p*-type material, there is currently intense effort directed towards finding suitable *p*-type dopants.[2–7] Recently, there has also been a report describing the achievement of *p*-type zinc selenide using oxygen as a dopant.[8] In this paper, we investigate optical properties of zinc selenide epilayers implanted with oxygen ions and show that our data are consistent with what is expected for an isoelectronic trap.

In Fig. 1 we show photoluminescence (PL) data taken with samples at ~5 K using uv lines of an Ar-ion laser. The samples are ~1-μm-thick epitaxial layers grown by molecular-beam epitaxy (MBE) on GaAs substrates at the University of Florida. The samples were subsequently implanted at 110 keV with either $^{16}O^+$ or $^{18}O^+$ at the doses and rapid-thermal-anneal temperatures indicated in the figure caption. Rapid thermal anneal was carried out in a zinc overpressure. All the spectra show very strong free-exciton-related transitions FX^+ (2.7980 eV) and FX^- (2.8027 eV), the splitting being caused by the tensile strain due to thermal mismatch between the epilayer and the substrate. The transitions due to the recombination of excitons bound to neutral donors are also clearly visible in the form of a strain-split doublet at 2.7935 eV (D^+) and 2.7961 eV (D^-).[9,10] One aspect of these spectra is that we additionally observe the two transitions labeled as A^+ (2.7895 eV) and B (2.7877 eV) as well as a transition appearing as a shoulder on the lower-energy side of the D^+ line, labeled as A^- at 2.7919 eV. The line A^+ was observed previously,[11] but the line B has not been reported. I_1^D at 2.7794 eV is quite often observed in bulk-grown or annealed samples and is believed to be related to a copper complex.[12,13] An important observation to note is that in the cases of free- and donor-bound-exciton transitions, the higher-energy strain-split components are much weaker compared with their lower-energy counterparts, due to thermalization effects at 5 K. However, the relative intensity of the A^+ and B lines is not constant and, in fact, A^+ is stronger than B in most cases. This is seen by comparing the PL spectra from samples 1, 2, and 4 in Fig. 1. In addition, the relative intensity of the aforementioned lines is found to vary *within* a sample, as seen by comparing the bottom two spectra taken at different spots for the sample 4. The full width at half maximum for the line A^+ is ~1.5 meV whereas that for the B line is ~2 meV. A closer look at the two lines reveals that the A^+ is *symmetrically* broadened, whereas the B line shows asymmetric broadening on the higher-energy side. The coupling strengths of A^+ and B to longitudinal-optical (LO) phonons is ~0.03 for both cases, rather comparable to the cases of typical acceptor-bound-exciton transitions in ZnSe.[14]

In Fig. 2 we present 1.9-K PL-excitation (PLE) data for sample 2. With the detector tuned at 1 LO below the A^+ line (A_{LO}^+), we observe strong PL when the excitation is in resonance with the A^+ line, as expected. The signal is weaker when exciting at the B line. The most noteworthy feature is the strong resonance enhancement of the A^- line. Recall that the A^- line appears as a weak shoulder at 5 K in PL (Fig. 1) (see also the temperature-dependent data presented later). The rest of higher-energy features are due to the usual intrinsic free-exciton processes.[15] Since our detector is not tuned to either the LO peak of donor-bound-exciton transitions or their two-electron satellites, we do not observe D^+ and D^- peaks in PLE. The PLE spectrum with the detector tuned at 1 LO below the B line (B_{LO}) is shown in the upper curve of Fig. 2. The important point to note is that we observe a very strong enhancement of PL at the A^+ peak.

Finally, in Fig. 3, we present PL in the excitonic region as a function of the sample temperature. We note that increasing the temperature from 2 to 25 K, the B line becomes weaker much more rapidly than the A^+ line. At the same time, the A^- line grows stronger relative to the A^+ line. Of course, we also observe the usual thermalization effects between the donor-bound-exciton and free-exciton strain-split components.[10] The most important point is that the B line thermalizes out at a much faster rate than the D^+ or FX^+ lines. For example, at 40 K, the B line is hardly observable, whereas the other two lines can be clearly seen.

We will now discuss the implications of the data presented in Figs. 1–3. First of all, since the lines A^+ and B are observed only in those samples which are implanted with oxygen ions, we conclude that they originate as a result of recombination of an excitation trapped to

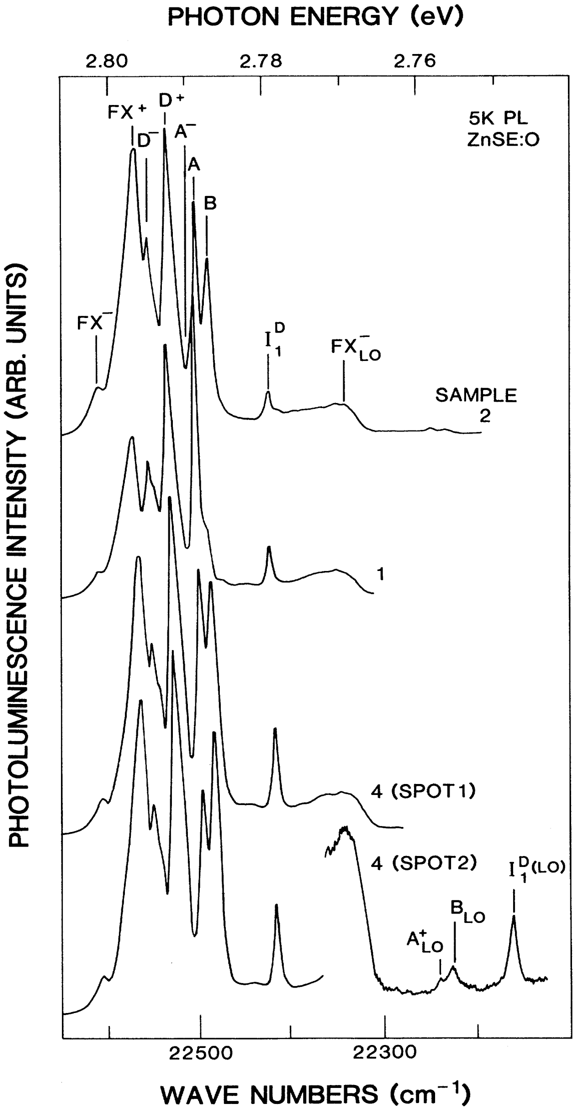

FIG. 1. Photoluminescence from three oxygen-implanted ZnSe epitaxial layers. Sample 1 had a dose of 7×10^{12} cm^{-2} and annealed at 700 °C for 5 sec. Samples 2 and 4 had a dose of 7×10^{13} cm^{-2}; the latter was annealed at 700 °C while the former at 750 °C for 5 sec. A^+, A^-, and B transitions are identified with the isoelectronic oxygen impurity. D^+,D^- and FX^+,FX^- are the strain-split donor-bound-exciton- and free-exciton-related transitions. Note the varying intensity of B from sample to sample and within a sample.

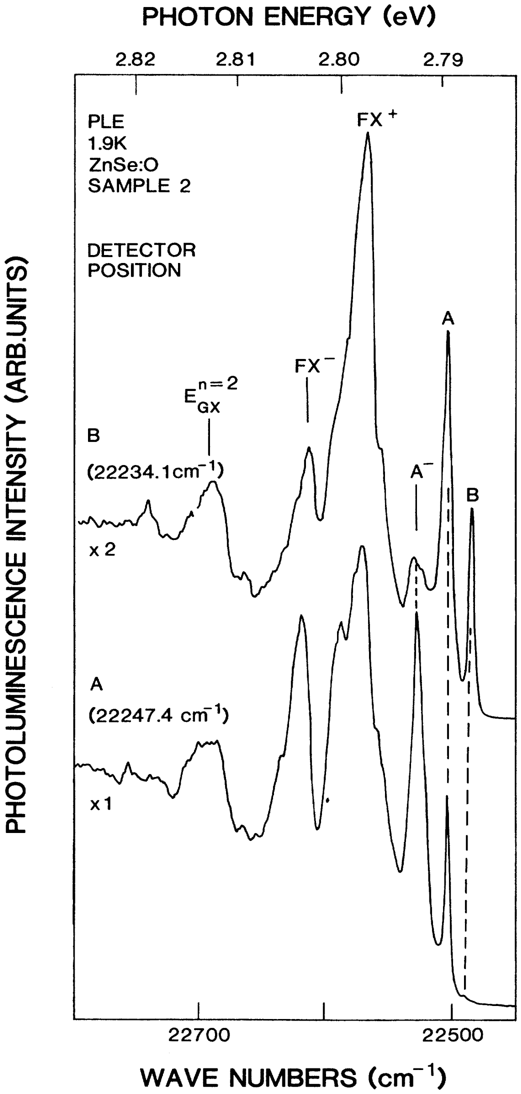

FIG. 2. Photoluminescence-excitation data for the oxygen-implanted ZnSe epilayer 2. With the detector at A^+_{LO}, a strong resonance at A^- is observe. With the detector at B_{LO}, a strong resonance at A^+ is observed.

this isoelectronic impurity. It is clear, from the varying intensity ratio of A^+ to B, that these two lines are not a strain-split doublet. The cases of strain-split doublets can be seen for the D^+ and D^- lines and FX^+ and FX^- lines where the higher-energy components are much weaker than their lower-energy counterparts at 5 K and grow in intensity as the sample temperature is raised. This is further reaffirmed by noticing that as the anneal temperature is raised from 700 °C to 750 °C , the splitting D^+-D^-, for sample, *increases* from 2.66 to 2.76 meV, as a consequence of the increasing tensile strain between the epilayer and the substrate. On the contrary, the energy separation between A^+ and B *decreases* from 1.80 to 1.67 meV for the same anneal temperatures. With an increase in the lattice temperature of the sample, the *rapid* disappearance of the B line compared with the D^+ and FX^+ lines again points to the fact that A^+ and B are not a strain-split doublet.

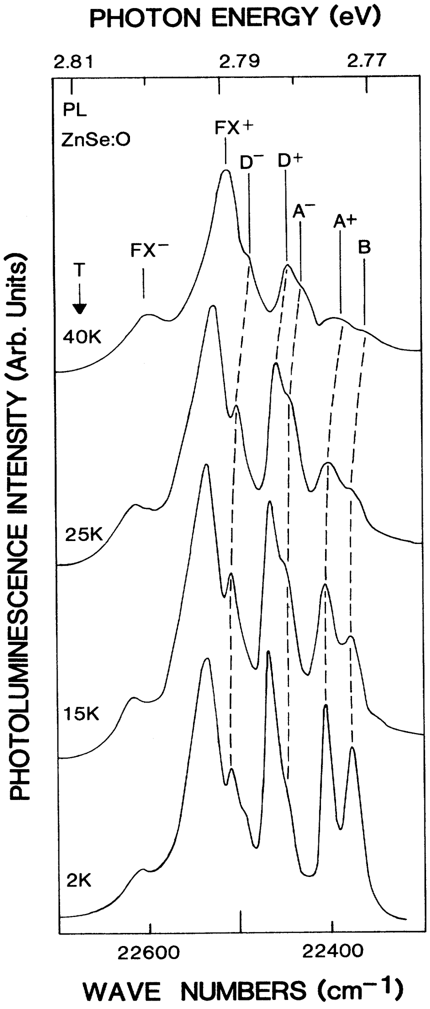

FIG. 3. Temperature-dependent photoluminescence from oxygen-implanted ZnSe epilayer 2. Note the relatively fast disappearance of the B line compared with the D^+ and FX^+ lines and increase in the intensity of A^- line relative to A^+ line.

However, the splitting between A^+ and A^- increases with increasing anneal temperature from 2.42 and 2.60 meV. Also, the intensity of the A^- line is much weaker than A^+ at 5 K but becomes stronger as the temperature is raised. In addition, PLE of A^{+}_{LO} shows a strong resonant enhancement at the A^- line. These data strongly suggest that A^+ and A^- are a strain-split doublet.

Although A^+ and B are not strain-split components and their ratio of intensities varies from sample to sample and even within a sample, they appear to be related to the oxygen impurity. This is clear from the PLE data which shows strong enhancement of the A^+ line when the PL is detected at the B_{LO} position. We will now discuss a possible origin of the A^+ and B lines.

Oxygen in ZnSe forms an isoelectronic trap by replacing the selenium atom. We postulate that the lines A^+ and B arise from the recombination of direct excitons at the center of the zone, bound to the oxygen impurity. The mechanism of binding an electron-hole pair can be understood in the following way.[16] Oxygen, being more electronegative than selenium, would bind an electron by a strong short-range interaction.[16,17] The resulting charged center then binds a hole through long-range Coulomb interaction, producing a center which behaves like an isoelectronic acceptor.[18–21] The angular momentum of the trapped electron and hole, $j=\frac{1}{2}$ and $\frac{3}{2}$, combine to form states with total angular momentum $J=1$ and 2, which are split by the Coulomb interaction. Theoretically the state with the highest degeneracy ($J=2$) will be the lowest. The transitions from the upper level ($J=1$) to the $J=0$ ground states are electric dipole allowed, whereas transitions from the $J=2$ are electric dipole forbidden. In the present case, the $J=1$ transition corresponds to the A^+ line, whereas the $J=2$ transition corresponds to the B line. The varying intensity of the B line is simply a manifestation of the breakdown of this ideal selection rule. This is expected to be particularly evident in the cases of samples which have varying degrees of implantation damage not fully annealed out. Furthermore, O-doped MBE layers (Ref. 7) show only the A line pointing to more homogeneous quality of the samples. Thus the variation in the structural quality from sample to sample or inhomogeneities within a sample would lead to varying degrees of the relaxation of the selection rule and, hence, varying intensities of the B line.

The fact that the A^+ line is found to be homogeneously broadened is consistent with the fact that this transition, being an excited state, is expected to suffer strong lifetime broadening effects.[22] The inhomogeneous broadening in the B line is understood in the following way. The electron and hole belong to representation Γ_6 and Γ_8. The direct product $\Gamma_6 \times \Gamma_8$ gives $\Gamma_4+\Gamma_3+\Gamma_5$. The $J=1$ corresponds to Γ_4 representation while $J=2$ belongs to a reducible representation $\Gamma_3+\Gamma_5$. Hence the $J=2$ level is further split by the crystal field into Γ_3 and Γ_5 with the latter lying lowest in energy.[17,22] In zero external magnetic field this splitting is expected to be very small. Instead it gives rise to an inhomogeneously broadened B line. When the temperature of the sample is increased, the B level, being lower in energy, depopulates. This, coupled with the fact that this transition is electric dipole forbidden, causes much more rapid disappearance of the B line compared with the D^+ or FX^+ lines.

The coupling of the A^+ and B lines to LO phonons is found to be almost identical and the PL and PLE spectra are found to be almost mirror images of each other. This is consistent with what is expected for an isoelectronic acceptor.[18] For the case of a trapped electron (i.e., isoelectronic acceptor), coupling to only Γ_1 phonons is important. These phonons do not mix different electron or hole spin states, and the entire PL spectrum from B will be the same as that from A^+ except shifted by the splitting A^+-B. In this case LO coupling is expected to be Γ_1 type and to be strong. This is exactly what is observed for the present case, i.e., a Huang-Rhys coupling factor of ~ 0.03 for the A^+ and B lines is strong compared with typical values expected for donor-bound-exciton transitions. This is clearly evident from the bottom spectrum of Fig. 1 where LO-phonon replicas of D^+ or D^- are not visible on this magnification. This is to be contrasted with the case of an isoelectronic donor (i.e., a trapped hole).[18] In this case Γ_1, Γ_{12}, and Γ_{15} phonons can strongly couple. This leads to cross coupling between A^+ and B states which, in turn, causes very different coupling of the A^+ and B lines to the lattice modes. Such cases have been observed, for example, for Bi and GaP (Ref. 23) and Te in CdS.[24]

In summary and conclusion, we showed that oxygen forms an isoelectronic trap giving rise to a pair of transitions A^+ and B. The former is attributed to $J=1$ and the Γ_4 representation and is electric dipole allowed while the latter is assigned to $J=2$ with the $\Gamma_3+\Gamma_5$ representation and is electric dipole forbidden. Based on this model, we explained all the experimental data presented here. For example, the varying intensity of the B line is attributed to the relaxation of this selection rule as a consequence of inhomogeneities in the implanted samples and also explains why mainly the A^+ line is observed in MBE *in situ*–doped layers. Strong and comparable couplings of the A^+ and B lines to LO phonons is shown to be consistent with the case of an isoelectronic acceptor where only Γ_1 phonons strongly couple to this state.[19] However, we did not find any evidence of acceptorlike behavior from the electrical measurements or any clear indication of donor-acceptor pair bands pointing to oxygen as a shallow acceptor.

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[11] In order to compare our value of A^+ (2.7895 eV) for the epilayer with that of the oxygen-doped layer in Ref. 7, we must add a 3.7-meV correction factor to take into account the shift due to increased thermal mismatch as a result of higher-temperature annealing. This factor can be readily obtained from subtracting the measured value of I_1^D (2.7794 eV) from the bulk (unstrained) value (2.7831 eV). We find that, to a first order, FX^+, D^+, and A^+ are shifted by this amount from their bulk values.

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[19] The term isoelectronic acceptor was originally coined to describe a model in which a hole is bound to the resulting negative ion through Coulomb potential in an acceptorlike wave function. Likewise, an isoelectronic hole trap (Ref. 20) will produce an isoelectronic donor. With the exception of a claim made in Ref. 8, the donor and acceptor nature of the isoelectronic impurity has not been substantiated by electrical measurements. However, they may provide trapping states as, for example, has been reported by Aten *et al.* (Ref. 21), who showed that CdS:Te acts as a hole trap resulting in *n*-type photoconductivity. In all the implanted samples that we studied, we did not find any evidence of acceptorlike behavior from the electrical measurements. In addition, we did not observe any clear indication of donor-acceptor pair bands pointing to oxygen behaving like a typical acceptor in ZnSe.

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