Neutral-donor–bound-exciton complexes in ZnO crystals

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Neutral-donor–bound-exciton transitions have been observed in ZnO. The isolated neutral donors are made up of defect pair complexes. The neutral-donor nature of these pair complexes was determined from magnetic-field measurements and from two-electron transitions. Excited states of the neutral-donor bound excitons were observed in the form of rotator states analogous to rotational states of the H_2 molecule.
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INTRODUCTION

Defect pair spectra have been extensively studied in GaAs.[1–11] A large number of photoluminescent (PL) lines were observed resulting from excitons being bound to the defect pairs (the term ''defect'' can include both foreign impurities as well as native defects). Several of the lines were observed to be strongly polarized.[7] The polarization of the lines suggests that during growth, defect complexes are preferentially incorporated in certain crystallographic orientations. The crystal will be strained in the vicinity of the defect pairs with the strain being oriented in the direction of the pair. This results in the electric vector being parallel to the strain direction. Similar polarization properties were reported by Langer *et al.*[12] from uniaxial pressure measurements on ZnO crystals.

In this paper we report a number of PL lines in ZnO crystals which are associated with defect pairs. The defect pairs have the properties of neutral donors and the emission lines result from the collapse of excitons bound to the neutral-donor complexes. The chemical makeup of the defect pair is not known, but from the PL analysis, it must simulate a neutral donor. One would speculate that in the growth process the first component of the pair would be incorporated, perhaps at a lattice site. This would then be conducive to the incorporation of the second component, which would occupy a nearest-neighbor lattice, or interstitial, or more distant site. The pair would then be crystallographically oriented. Annealing studies show that as the annealing temperature is increased, the higher energy PL lines disappear and, at an annealing temperature of 800 °C, essentially all of the emission intensity goes into the lowest-energy emission line, which is believed to be the near-neighbor alignment. It would appear that annealing results in defect diffusion, which ultimately produces nearest-neighbor defect pairs. The PL spectrum of this final pair also shows polarization properties that are consistent with defect pair structure.

On the high-energy side of the neutral-donor–bound-exciton complex lines is a similar set of lines, which are believed to be excited states of the lower-energy complex structure. Similar emission lines have been observed in many other materials, CdTe,[14] GaAs,[15,16] CdS,[17] and ZnSe.[13] These transitions were first interpreted as excited states of the neutral-donor–bound-exciton D^0,X but with very little detail as to their nature. Later, Guillaume and Lavallard[18] proposed a rigid rotation model to explain these excited states in CdTe. In this model the hole is excited to rotate around the fixed donor, analogous to rotation of diatomic molecules. This model had difficulty in predicting the observed energies for the excited-state transitions. A non-rigid-rotator model was subsequently proposed by Ruhle and Klingenstein,[19] which was successful in predicting the excited-state energies in InP and GaAs. A more sophisticated model was applied to the D^0,X ground and excited states by Herbert,[20] this model predicts the energy ordering of the excited states.

A final model was proposed by Rorison *et al.*[21] to explain their high-magnetic-field results in InP. In this model D^0,X is considered to be a free exciton orbiting a neutral donor; one electron was considered to be strongly correlated with the hole and the other with the donor. This model was capable of explaining the relative intensities of the PL transition in the ground- and excited-state regions of InP.

In the current investigation, the problem is more complicated since the neutral donor is a complex rather than an electron bound to a positively charged ion. Here it is observed that some of the transitions in the excited-state region occur only in the presence of an applied magnetic field. These are believed to be due to the Γ_6 exciton, which is an unallowed transition, in the absence of a magnetic field. This may support the model of Rorison,[21] in which the exciton is excited to rotate.

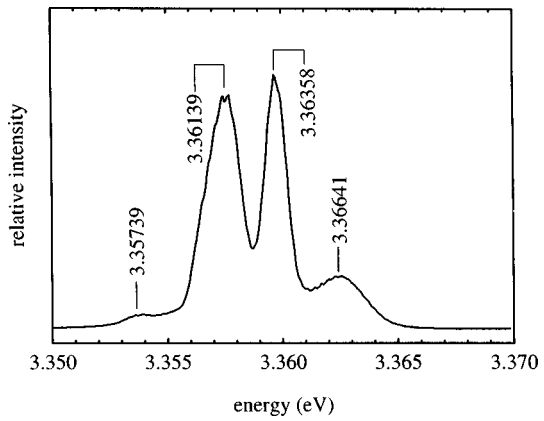

FIG. 1. Neutral-donor defect pair spectra in ZnO, first-order spectrum.

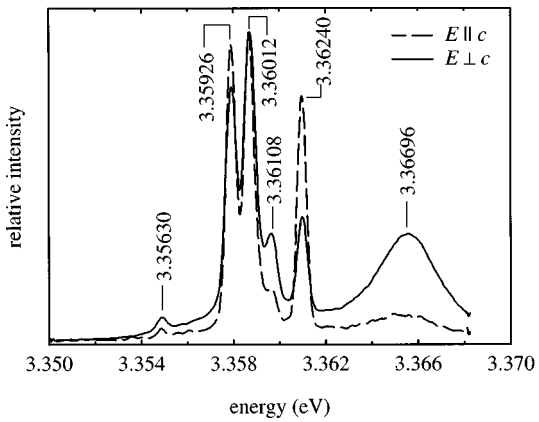

FIG. 3. Polarized spectra of Fig. 2.

EXPERIMENTAL RESULTS

The neutral donor defect pair spectra are shown in Fig. 1. The spectra are recorded in first order and result from excitons bound to the neutral-donor defect pairs. The same spectra recorded in second order are shown in Fig. 2. In these spectra more lines are resolved. Defect pair spectra would be expected to show polarization effects. Local strains oriented in the direction of the pair will result, and the electric vector will orient in the direction of the strain. Polarization effects are shown in Fig. 3. The solid line shows the spectra with the electric vector perpendicular to the ''c'' axis of the crystal, $E\perp c$. The dashed line shows the spectra with the electric vector parallel to the ''c'' axis of the crystal, $E\|c$. Some of the lines show strong polarization, indicating the direction of the pairs. This evidence supports the contention that these emission lines are associated with defect pair complexes. The emission results from the collapse of excitons bound to the defect pair complexes that simulate neutral donors. These complexes are shown to have the electronic character of neutral donors. The magnetic field splitting of the lines is consistent with neutral-donor bound excitons in the wurtzite structure. Plotted in Fig. 4 is the splitting as a function of magnetic field, with the crystalline ''c'' axis oriented perpendicular to the magnetic field ($c\perp H$). The magnetic field data are for the line at 3.36012 eV. One would expect a doublet splitting (with $c\perp H$) to arise from an exciton bound to a neutral donor or acceptor in the wurtzite symmetry. In this orientation the hole g value in the upper state goes to zero ($g_h = g_{h11}\cos\theta$), so the magnetic-field splitting results from the electron-spin splitting in the final state. From these data, the electron g value is measured, giving a value $g_e = 1.85$ in good agreement with the previously measured $g_e = 1.95$.[22] A magnetic-field splitting for the orientation $c\|H$ was not observed. In this orientation, a contribution from both the electron and hole spins is expected. The spin-up, spin-down transitions leading to a sum of the g values ($g_e + g_h$) are not allowed. The transitions leading to a difference of the g values ($g_e - g_h$) are the spin-conserving transitions. These transitions are allowed but the resulting g value is small so that the splitting is not resolved. The other D^0,X transitions showed similar magnetic-field splitting.

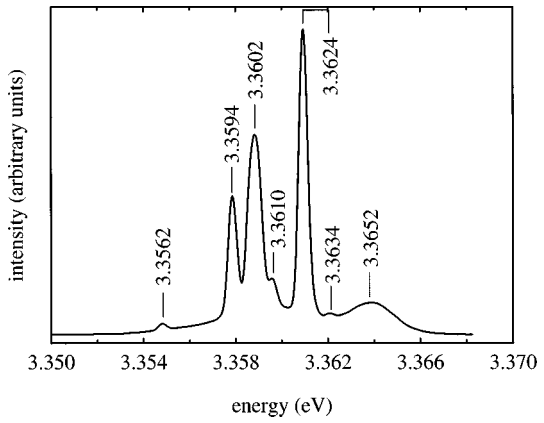

FIG. 2. Second-order spectrum of defect pair spectra in Fig. 1. Except for the first-order spectrum of Fig. 1, it should be noted that all other spectra (Figs. 2, 3, 4, 5, 6, 8, and 9) are recorded in the higher dispersion, second-order diffraction pattern of the grating spectrometer whose first-order blaze center (peak intensity) falls at a wavelength of 5000 A (2.478 eV) and whose second-order blaze center falls at 2500 A (4.956 eV).

Another characteristic of neutral-donor–bound-exciton transitions is the two-electron transitions.[23] For this case the exciton collapses and the neutral donor returns to the ground state, or it may pick up energy from the exciton, leaving the electron on the donor in an excited state, in the final state. The energy of the transition is

$$E_T = E_{FX} - E_b - \Delta E, \tag{1}$$

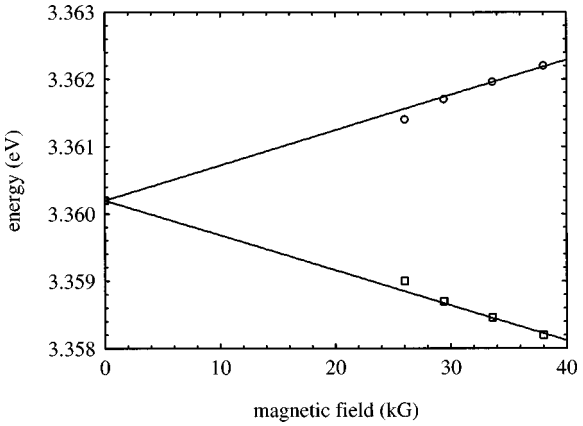

FIG. 4. Magnetic-field splitting of the 3.36012-eV defect-donor–bound-exciton line in the orientation $c\perp H$.

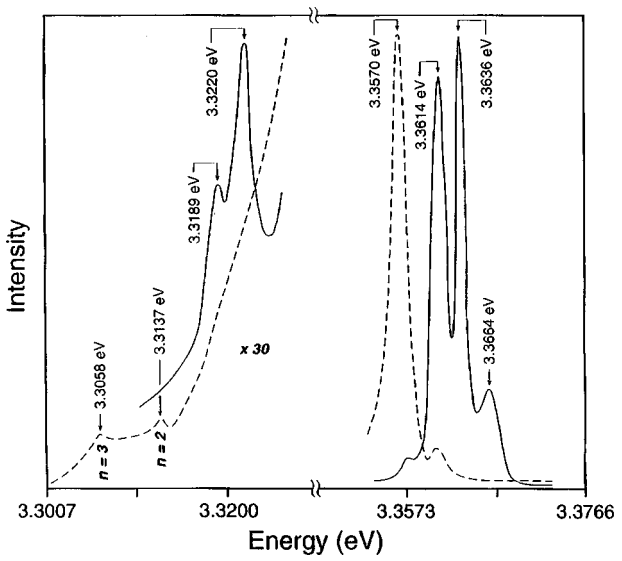

FIG. 5. Two electron transitions associated with the ground-state defect-donor bound excitons.

where E_T is the transition energy, E_{FX} is the free exciton energy, E_b is the energy with which the exciton is bound to the donor, and ΔE is the energy necessary to put the donor into an excited state. Transitions of this type are shown in Fig. 5. The solid curve shows the donor–bound-exciton transitions (D^0,X) at 3.3636 and 3.3614 eV and the respective two-electron transitions at 3.3220 and 3.3189 eV. From these energies, the donor binding energies can be calculated, assuming the excited states are hydrogenic. The donor at 3.3636 has a binding energy of 55.5 meV, the donor at 3.3614 eV has a binding energy of 56.7 meV. The dashed curve shows the sample after annealing at 800 °C. The D^0,X emission essentially goes into the line at 3.3570 eV, for which the two-electron transitions are $n=2$, $E=3.3137$ and $n=3$, $E=3.3058$ eV. The $n=2$ state gives a donor binding energy of 57.7 meV and the $n=3$ state gives a donor binding energy of 57.6 meV. It is believed that the defect pairs at lower energies are moving closer together. It also appears that the donor binding energy is increasing as the pairs move closer together.

As alluded to above, sample annealing moves all of the D^0,X emission into the lowest-energy line. It appears that the more distant pairs are the first to break up and move to closer spacing. There is a near conservation of the total emission intensity, suggesting that the pairs are not eliminated, but simply reconfigure. The total integrated intensity of all of the lines as a function of annealing temperature is shown in the inset of Fig. 6. It is noted that the total intensity of all of the D^0,X lines is conserved within less than a factor of two. The shift of the emission intensity to the lowest energy line with annealing temperature occurs rather dramatically between 700 °C and 800 °C. It is also noted that the lowest-energy line broadens dramatically as the total intensity is culminated in that line. This may be a strain broadening as all of the pairs move to near-neighbor distances. From the annealing temperatures, an activation energy can be obtained. Using the expression for first-order annealing,

$$PL_{i+1}=PL_i e^{-\nu t e^{-E/kT_i}} \tag{2}$$

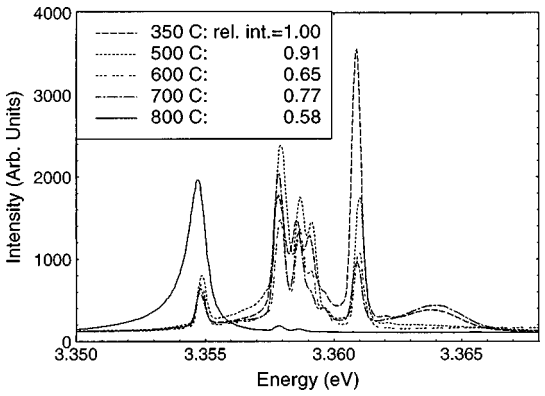

FIG. 6. Integrated intensity of the defect-donor–bound-exciton lines as a function of annealing temperature.

where the prefactor $\nu=1.744\times10^{13}$ (optical phonon frequency), t is the annealing time, E is the activation energy, and T_i is the annealing temperature, the curve in Fig. 7 is obtained. This gives a value $E=3.6$ eV for the activation energy. The activation energies for the diffusion of Zn in ZnO have been previously determined.[24–27] These activation energies fall within the range 3.0–3.3 eV. Thus, an activation energy of 3.6 eV would appear to be a reasonable value for promoting the motion of the defect pairs.

Excited states associated with the D^0,X ground-state transitions are observed. These are observed at high resolution in second order, on the high-energy side of the ground-state transitions and are analogous to the excited-state transitions described in the Introduction. The transitions 3.3662 eV (Γ_6) and 3.3670 eV (Γ_5) in Fig. 8 are excited states analogous to rotational states of the H_2 molecule. These states are rotational states associated with the 3.3564-eV ground state, and are not electronic excited states. To our knowledge, this is the first time these transitions have been observed when the neutral donor itself is a complex center. As observed from Fig. 8, these transitions are on the low-energy side of the 3.3772-eV (Γ_5) and 3.3750-eV (Γ_6) free exciton (FE) transitions. The solid curve in the figure represents spectra with an applied magnetic field of 18 kG. The Γ_6 exciton is an unallowed transition that becomes allowed in the presence of an applied magnetic field. The dashed curve shows the same transition in zero magnetic field. Note that the rotator state associated with the Γ_6 exciton is observed. The two lowest-

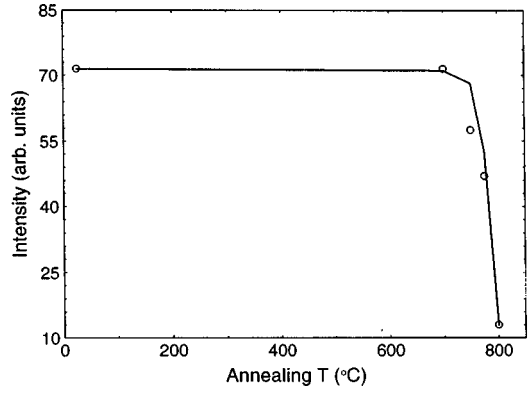

FIG. 7. First-order annealing curve for the defect-donor bound excitons.

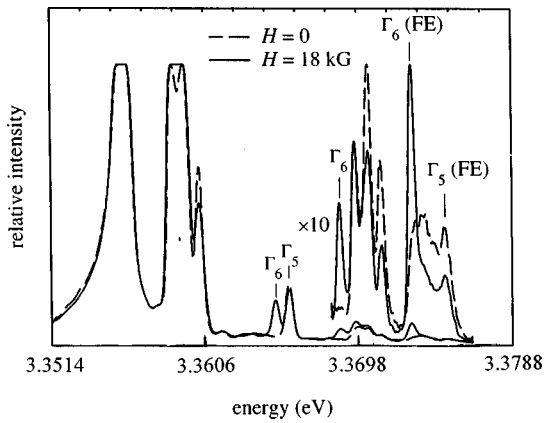

FIG. 8. Excited rotational states associated with the defect-donor bound excitons. Note that Γ_6 rotational excitons are observed. These are second order spectra.

energy rotation states are associated with the lowest-energy 3.3564-eV D^0,X transition. The next two lowest-energy rotator states, 3.3714 eV (Γ_5) and 3.3702 eV (Γ_6), are associated with the next-lowest-energy 3.3594 eV D^0,X transition. It is noted that again one of the rotator states is associated with the Γ_6 exciton. Other rotator states associated with the Γ_6 exciton are most likely not resolved since they would come in the energy region where they would not be resolved from other Γ_5 rotator states. We observe that rotator states are associated with the Γ_6 unallowed exciton, which lends support to the model that the exciton itself rather than the hole is rotating.[21]

Following the arguments of Ref. 18, using the Hellmann-Feynman theorem, one derives the energy difference:

$$\Delta E \approx J(J+1)\sigma E_D/r^2 \tag{3}$$

for the rotator states. J is the rotational quantum number, E_D is the binding energy of the donor, $\sigma = m_e/m_h$, and r is the radius of the excitonic molecule. According to Akimoto and Hanamura[28] r is between 1.44 and 3.47 times the Bohr radius of the free exciton.

From the data of this paper, one obtains an average value of $E_D = 56.9$ meV. Assuming r to be twice the Bohr radius one obtains $\Delta E \approx 6$ meV. This agrees satisfactorily with the experimental value of 10.6 meV. Taking the experimental value of 10.6 meV, and inserting it into Eq. (3), a value of 1.5 is obtained for the Bohr radius, which is in the same range 1.44–3.47 given in Ref. 28. One would expect the Bohr radius to be reduced in ZnO due to the greater binding energy.

The energy-level diagram of the transitions shown in Fig. 5 and Fig. 8 is shown in Fig. 9, for the as-grown sample and for the sample after an 800 °C anneal. The fourteen transitions in the as-grown sample reduce to five after annealing. The left-hand scale gives the energies of the transitions. It is noted that after annealing, all of the higher energy, D^0,X transitions disappear and only the lowest-energy D^0,X transition remains. If one assumes that the higher-energy excited rotator transitions result from the rotation of the exciton, the Γ_5 and Γ_6 excitons are labeled. For the two lowest energy

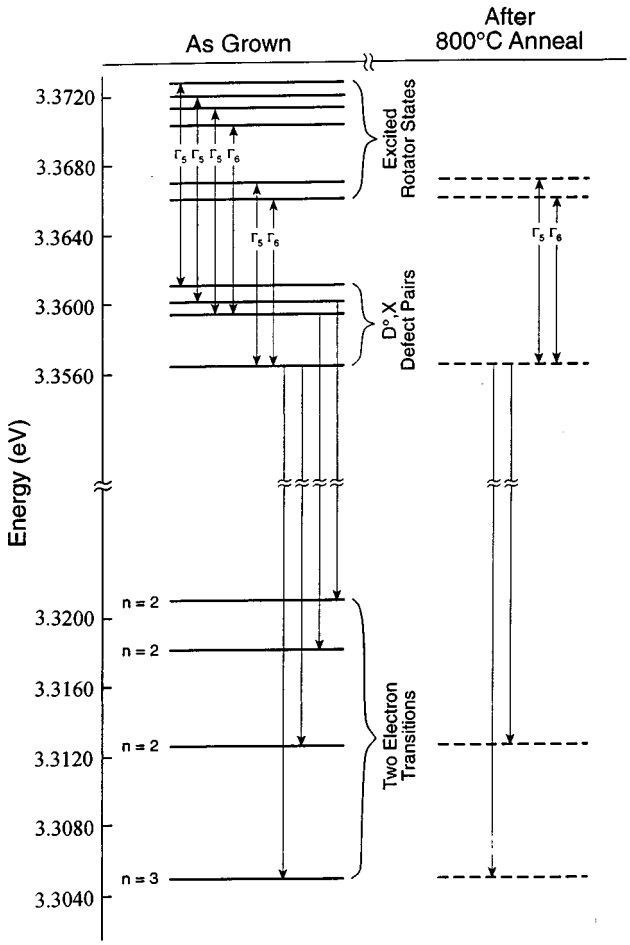

FIG. 9. Energy-level diagram showing the transitions in Fig. 5 and Fig. 8. The energies of the transitions as well as their identities are given for the as-grown sample and for the sample after an 800 °C anneal.

D^0,X states, the Γ_5 and Γ_6 rotator states are clear, but for the two highest energy D^0,X states the Γ_6 rotator states will not be resolved from the Γ_5 rotator states. After annealing, only two excited rotator states remain and they are clearly identified with the application of a magnetic field.

CONCLUSIONS

We have shown the presence of neutral-donor–bound-exciton transitions in ZnO where the neutral donors are pair-type complexes. Magnetic field measurements and two electron transitions show that the pair complexes have the properties of neutral donors and the optical transitions result from the collapse of excitors bound to the neutral donors. Annealing experiments show that the higher-energy emission lines disappear, and at annealing temperatures nearing 800 °C all of the emission intensity appears in the lowest-energy donor–bound-exciton transition. Integrated intensity measurements reveal that the total emission intensity is roughly conserved. This suggests that the higher-energy emission lines are due to neutral-donor–bound-exciton transitions in which the pairs making up the neutral donors are more distantly spaced. These are the ones that are first to

break up with annealing. The conservation of emission intensity suggests that the pairs are not eliminated but do in fact move to closer pair spacing. The measured activation energy of 3.6 eV is consistent with this motion. The observation of excited rotator states would be expected to be associated with neutral-donor bound excitons. The existence of Γ_6 rotator states may lend support to the model that predicts that the exciton rather than the hole is rotating.

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