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## Fine structure on the green band in ZnO

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An emission band at 2.4 eV, called the green band, is observed in most ZnO samples, no matter what growth technique is used. Sometimes this band includes fine structure, which consists mainly of doublets, repeated with a longitudinal-optical-phonon-energy spacing (72 meV). We have developed a vibronic model for the green band, based on transitions from two separate shallow donors to a deep acceptor. The donors, at energies 30 and 60 meV from the conduction-band edge, respectively, are also found from Hall-effect measurements. © 2001 American Institute of Physics. [DOI: 10.1063/1.1356432]

### I. INTRODUCTION

Wurtzitic ZnO is a wide band gap (3.437 eV at 2 K) semiconductor which has many applications, such as piezoelectric transducers, varistors, phosphors, and transparent conducting films. Most of these applications require only polycrystalline material; however, recent successes in producing large-area single crystals have opened up the possibility of producing blue and UV light emitters, and high-temperature, high-power transistors. The main advantages of ZnO as a light emitter are its large exciton binding energy (60 meV), and the existence of well-developed bulk and epitaxial growth processes; for electronic applications, its attractiveness lies in having high breakdown strength and high saturation velocity. Optical UV lasing, at both low and high temperatures, has already been demonstrated, although efficient electrical lasing must await the further development of good, *p*-type material. ZnO is also much more resistant to radiation damage than are other common semiconductor materials, such as Si, GaAs, CdS, and even GaN; thus, it should be useful for space applications.

Low-temperature photoluminescence (PL) measurements in ZnO are typically dominated by emission from donor-bound excitons ( $D^0, X$ ), near 3.36 eV, and a deep center near 2.4 eV, called the green band.<sup>1,2</sup> Emission from the  $D^0, X$  transitions generally leaves the donor in its ground state ( $n=1$ ), but sometimes, in good material, excited terminal states ( $n=2,3,\dots$ ) are also evident. If transitions involving both  $n=1$  and  $n=2$  can be seen, then the hydrogenic model can be applied<sup>3</sup> to give the donor ground-state energy  $E_D$ ; i.e.,  $E_D = E(n=1) = 4/3[E(n=1) - E(n=2)]$ . In bulk ZnO, grown by the vapor-phase technique,<sup>1,4</sup> at least three of the  $D^0, X$  lines can be analyzed in this way, and they all turn out to have energies  $E_D = 57 \pm 2$  meV.<sup>3</sup> An earlier study, involving ZnO platelets, found a similar value of  $E_D$ .<sup>5</sup> Indeed, such a value is expected from a simple effective-mass calculation:  $E_D = 13.6 m^*/\epsilon_0^2 = 65$  meV. What is surprising, however, is that temperature-dependent Hall measurements find two donors,<sup>4</sup> designated  $D1$  and  $D2$ , at about 30

and 60 meV below the conduction band edge, respectively, while PL spectra do not seem to reveal  $D1$ . Several reasons for the missing PL data are possible: (1) the concentration of  $D1$  is usually much lower than that of  $D2$ ; (2) excitons might be expected to preferentially bind to the deeper donor,  $D2$ ; and (3) the  $D^0, X$  transition for  $D1$  would fall among the excited-state (“rotator-state”) transition energies of  $D2$ , and thus might be masked.

The green band (GB), on the other hand, may also involve donors, in that it probably consists of a transition from a shallow donor to a deep acceptor. The reason for such an assignment arises from the close similarities between the GB in ZnO, and the yellow band (YB) in GaN<sup>6</sup> the latter being likely due to a shallow-donor/deep-acceptor transition, in which the acceptor involves the Ga vacancy  $V_{Ga}$ . That is, if the YB can be assigned to  $D-V_{Ga}$ , then the GB would be associated with  $D-V_{Zn}$ . Several groups<sup>2,7</sup> have conjectured that the GB involves substitutional  $Cu^{2+}$ , but our material contains less than 50 ppb Cu, as measured by glow-discharge mass spectroscopy. In fact, it is possible that there is more than one source of the GB, since the peak emission energy is not always the same in all samples. In any case, if we designate the appropriate deep acceptor by “ $A_{GB}$ ”, then the generic GB transition would be  $D-A_{GB}$ . If there are two dominant donors, as in our situation, then we might expect two transitions (or sets of transitions),  $D1-A_{GB}$  and  $D2-A_{GB}$ . Indeed, we see GB structure that can be explained by the participation of two donors.

### II. EXPERIMENTAL DETAILS

The ZnO sample investigated in this work was grown by a vapor-phase technique, such as that described in Ref. 4. However, the same GB structure as that seen for this sample (i.e., Fig. 1), has been observed by us in several other ZnO samples, including those grown as platelets, by vapor transport down a quartz tube. Also, other workers have reported very similar structures, with clear doublet features.<sup>2</sup> Many of the samples grown by the vapor-phase method are quite pure, with most impurity elements in the ppb level, or lower. Hall-effect measurements on similar samples typically have donor concentrations in the mid-to-high  $10^{16} \text{ cm}^{-3}$  range,

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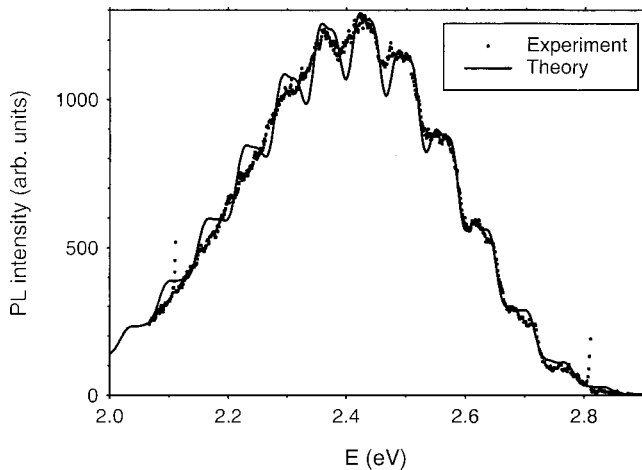


FIG. 1. PL spectrum of the GB in ZnO (small squares) and a fit to a vibronic model (solid line).

and acceptor concentrations in the low  $10^{15} \text{ cm}^{-3}$  range.<sup>4</sup> The 2 K photoluminescence spectra, shown in Fig. 1, were excited with a 45 mW HeCd laser, and analyzed with a high-resolution 4 m spectrometer equipped with a Radio Corporation of America C31034A photomultiplier tube for detection.

### III. MODEL AND DISCUSSION

Transitions from the conduction band or a shallow-donor level D to a deep level A can often be described in terms of the so-called “vibronic,” or “configuration-coordinate” model.<sup>8</sup> That is, the deep center can have its own set of vibrational states, characterized by a local phonon energy  $E_{loc}$ . In the simplest form, the energies of these states are given by  $E_0 + \eta E_{loc}$ , where  $E_0$  is the ground-state energy and  $\eta$  is an integer. A broad emission band will result from the series of possible D–A transitions:  $E_{\eta} = E_D - (E_0 + \eta E_{loc})$ , where all states are referred to the valence band, for convenience. The zero-phonon line (ZPL), will have an energy  $E_{ZPL} = E_D - E_0$ ; however, although this line is normally quite sharp, it is not the most intense peak in the spectrum, because the spatial wave function overlap between the shallow-donor state and the deep-center ground state may be small, due to displacement of the deep center. In fact, the maximum of the emission will typically occur at an excited state  $E_{\eta}$  for which  $\eta \sim S$ , the Huang–Rhys factor. Now, a further complication arises because the various transitions may involve not only local phonons, but also lattice phonons, in particular the longitudinal-optical (LO) phonon. In this case, the transition energy will be  $E_{\eta, \eta'} = E_D - (E_0 + \eta E_{loc}) - \eta' E_{LO}$ , where  $E_{LO} = 72 \text{ meV}$  in ZnO. Typically,  $E_{loc}$  will represent a breathing mode of the deep center, with  $E_{loc} \ll E_{LO}$ . The final complication to our model will be the addition of a second donor, giving a whole new series of lines, displaced by  $E_{D2} - E_{D1} \approx 60 - 30 \approx 30 \text{ meV}$ . We will give evidence of all these effects in the spectra shown as follows.

Each individual emission line in the spectrum is modeled by a Gaussian function with linewidth  $\sigma$ . The probability of a given phonon emission is proportional to  $(S_{loc}^{\eta} / \eta_{loc}!)$   $\times (S_{LO}^{\eta'} / \eta_{LO}!)$ , where  $S_{loc}$  and  $S_{LO}$  are the Huang–Rhys fac-

tors for the local and lattice phonons, respectively, and  $\eta_{loc}$  and  $\eta_{LO}$  are the numbers of each type of phonon emitted in a particular transition. The solid line in Fig. 1 results from the sum of all of the emission lines, using the following parameters:  $E_{D1} = 30 \text{ MeV}$ ;  $E_{D2} = 60 \text{ MeV}$ ;  $E_{LO} = 72 \text{ MeV}$ ;  $E_{loc} = 64 \text{ MeV}$ ;  $E_0 = 2.93 \text{ eV}$ ;  $S_{LO} = 0.9$ ;  $S_{loc} = 6.9$ ; and  $\sigma = 1.35 \text{ meV}$ . As can be seen, the fit to the data is quite good for  $E \approx 2.3 - 2.9 \text{ eV}$ , but poorer for  $E \approx 2.0 - 2.3 \text{ eV}$ . Note that this lower energy portion involves highly excited phonon states, where some anharmonicity in the deep-center potential might be expected. The important conclusion from this fit is that the fine-structure doublets on the high-energy side of the GB can be explained by the presence of two donors, with activation energies of 30 and 60 meV, respectively, as also seen by Hall-effect analysis.<sup>4</sup> There may also be other potential explanations, but the 30 meV separation of each doublet pair is easily accounted for in our model. Earlier, Kuhnert, and Helbig observed very similar structure in the GB of a vapor-phase-grown ZnO sample.<sup>2</sup> Although they did not carry out detailed fitting, they did obtain a local-phonon Huang–Rhys factor of 6.5, in good agreement with our value. Their spectra also included two sharp lines in the highest-energy portion of the band, and these were interpreted as zero-phonon lines of substitutional Cu. The doublet structure observed by us was also clearly evident in their data, and it was noted that the 30 meV splitting did not correspond to any expected phonon replicas. Although we have no evidence for Cu contamination in our samples, and see no clear zero-phonon lines, we cannot rule out the participation of Cu in the GB, either directly or indirectly. However, we note that several other defects and/or impurities have also been invoked to explain the green band, in particular,  $V_{Zn}$  and  $V_O$ . Again, the important point of our study is that a two-donor, deep-acceptor vibronic model can quantitatively explain the spectra.

### IV. CONCLUSIONS

The ubiquitous GB in ZnO can be explained as phonon-assisted transitions between two different shallow donors, of energies 30 and 60 meV, respectively, and a deep acceptor. In particular, the energies of the two donors agree well with those found from Hall-effect measurements. The identities of the two donors and the acceptor are not yet clear.

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