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David C. Look
Wright State University - Main Campus, david.look@wright.edu

D. C. Reynolds

C. W. Litton

R. L. Jones

D. B. Eason

See next page for additional authors

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D. C. Look[a] and D. C. Reynolds
Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio 45433 and Semiconductor Research Center, Wright State University, Dayton, Ohio 45435

C. W. Litton and R. L. Jones
Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio 45433

D. B. Eason and G. Cantwell
Eagle-Picher Technologies, L.L.C., 200 BJ Tunnell Boulevard, Miami, Oklahoma 74354

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An N-doped, *p*-type ZnO layer has been grown by molecular beam epitaxy on an Li-diffused, bulk, semi-insulating ZnO substrate. Hall-effect and conductivity measurements on the layer give: resistivity $=4\times10^{1}\ \Omega$ cm; hole mobility $=2\ \mathrm{cm}^2/\mathrm{V\,s}$; and hole concentration $=9\times10^{16}\ \mathrm{cm}^{-3}$. Photoluminescence measurements in this N-doped layer show a much stronger peak near 3.32 eV (probably due to neutral *acceptor* bound excitons), than at 3.36 eV (neutral *donor* bound excitons), whereas the opposite is true in undoped ZnO. Calibrated, secondary-ion mass spectroscopy measurements show an N surface concentration of about $10^{19}\ \mathrm{cm}^{-3}$ in the N-doped sample, but only about $10^{17}\ \mathrm{cm}^{-3}$ in the undoped sample. © *2002 American Institute of Physics.*
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The need for blue and UV solid-state emitters and detectors has propelled the investigation of several wide-band-gap semiconducting materials in recent years. Commercial applications include blue lasers for CD-ROM and DVD memories, and laser printers, while military applications include blue light-emitting diodes for non-line-of-sight communication transceivers. Most of the materials development for these applications has centered around GaN (band gap: 3.5 eV at 2 K), ZnSe (2.9 eV), and 6H-SiC (3.0 eV), with GaN and GaN-based alloys emerging as the clear winners, because SiC does not produce a very bright emitter, and ZnSe is subject to defect formation under high current drive. However, another II-VI compound, ZnO, is known to be the brightest emitter of all, because its excitons have a 60 meV binding energy, as compared with 26 meV for GaN, and 20 meV for ZnSe. ZnO also has other major advantages, such as the availability of large-area substrates, the amenability to wet chemical etching, a high radiation resistance, and relatively low materials costs.[1,2] However, ZnO has suffered from one major disadvantage: the lack of good, reproducible, *p*-type material. There are several papers on the growth of *p*-type ZnO in the recent literature;[3–7] however, many of them report unrealistically high hole mobilities and hole concentrations. Theoretical treatments of this important subject have also appeared.[8–12]

In this work, we show that reproducible, N-doped, *p*-type ZnO can be grown by molecular beam epitaxy (MBE) on ZnO substrates,[13,14] and that the electrical properties are consistent with modeling and with photoluminescence data. This advancement immediately opens the door to $p-n$ homojunctions based on ZnO materials. Heterojunctions and quantum wells can also be fabricated by using MgZnO and CdZnO as the wide-gap and narrow-gap materials, respectively.[15–17]

The homoepitaxial ZnO thin films were grown by Eagle-Picher Technologies, LLC (Miami, OK) in a custom-built MBE system that includes extensive cryogenic shrouding and additional cryopumping. The substrates were 10 mm $\times$ 10 mm $\times$ 0.5 mm pieces cut from *c*-plane wafers, which themselves were sliced from bulk, 2-inch-diam ZnO ingots grown by Eagle-Picher using a seeded chemical vapor transport (SCVT) process.[18] Typical donor and acceptor concentrations were 1×10^{17} and $2\times10^{15}\ \mathrm{cm}^{-3}$, respectively.[19] Pure (99.99 995%) Zn was supplied by means of a solid-source dual-zone effusion cell, and O and N were obtained from research-grade O_2 and N_2, respectively, flowing through an Oxford Applied Research rf plasma source, operated at a power of 350 W. Most of the films were grown on chemomechanically polished Zn (0001) faces. The substrate temperature during growth was varied from 450 to 700 °C, with 525 °C being used for the layer discussed in this paper.

For *p*-type doping of the films, a flux of N_2 gas was added to the O_2 gas flow in the rf plasma source. The level of N_2 was approximately 10–100 times less than the level of O_2. The *p*-type films were grown on Li-doped, semi-insulating ZnO substrates[20] in order to be able to perform Hall-effect measurements without influence from substrate conduction. It is well known that N acts as a shallow acceptor in ZnSe and ZnS,[21] and it has also been employed in some of the other attempts to grow *p*-type ZnO.[3,5,6] Typical film thicknesses were 1–2 μm, with the sample discussed here having a value of 1.9 μm.

Hall-effect measurements were carried out in the van der Pauw configuration, by using a direct current of 3 μA, and a

[a]Author to whom correspondence should be addressed; corresponding address: Semiconductor Research Center, Wright State University, Dayton, OH 45435; electronic mail: david.look@wpafb.af.mil

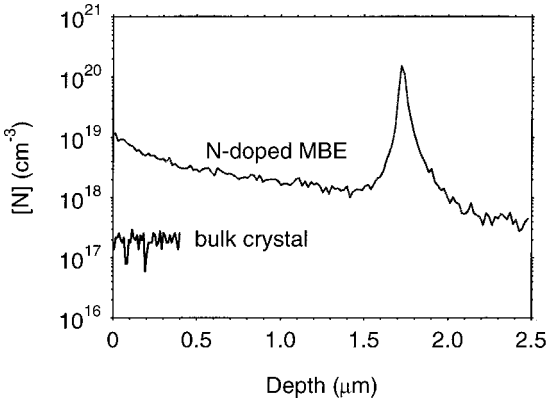

FIG. 1. Secondary ion mass spectroscopy measurements of the N concentration in two ZnO samples, one undoped, and the other, N-doped.

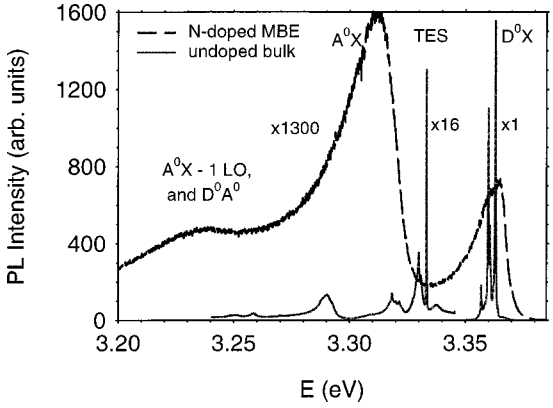

FIG. 2. PL spectra, at 2 K, for two ZnO samples, an undoped bulk sample, and an N-doped, MBE-grown epitaxial layer.

magnetic field of 15 kG. Data were compiled employing both positive and negative currents and magnetic fields, and the results were averaged in order to compensate for various electromagnetic effects.[22] Significantly, the Hall coefficient was positive (*p*-type) for all four current/field combinations, which gives confidence that the layer is truly *p*-type. The averaged results were: resistivity $\rho = 4 \times 10^1\ \Omega$ cm; hole mobility $\mu_p = 2\ \mathrm{cm}^2/\mathrm{V\,s}$; and hole concentration $p = 9 \times 10^{16}\ \mathrm{cm}^{-3}$. Several other growths have given similar results, and attempts to get larger p and μ_p are now in progress. Below, we demonstrate that the Hall results are quantitatively compatible with analytical and optical data.

Secondary-ion mass spectroscopy (SIMS) determinations of the N concentrations in similar undoped and N-doped samples are shown in Fig. 1.[23] The N concentrations were referenced to an N-implanted ZnO sample in order to get quantitative information. Absolute accuracy is estimated to be about a factor of 2 but the relative concentrations of the two samples should be more accurate. The bulk sample referred to in Fig. 1 was a substrate similar to the one used for these experiments, except without the Li diffusion. Note that the N concentration in the bulk sample is about $1 \times 10^{17}\ \mathrm{cm}^{-3}$, while the surface concentration of N in the epitaxial layer is about two orders of magnitude higher. Also, there appears to be a large N segregation at the substrate/epilayer interface, with the caveat that SIMS measurements sometimes are subject to artifacts at surfaces and interfaces. In any case, it is clear that the layer is doped with N, as intended. Of course, SIMS cannot distinguish between the various possible lattice locations for the impurity, but the Hall-effect results are consistent only with N occupying O sites, as acceptors.

Low-temperature (4 K) photoluminescence (PL) results for bulk, undoped samples, and MBE-grown, N-doped layers, are compared in Fig. 2. High-quality bulk ZnO is typically dominated by a series of sharp lines, probably due to bound excitons associated with neutral donors[24] or very shallow neutral acceptors.[25] In the present case, the strongest of these lines is at 3.3629 eV, with somewhat weaker lines at 3.3598, 3.3606, and 3.3568, in order of intensity. Phonon replicas of these lines are seen near 3.29 eV. The 3.3629 eV line has a two-electron satellite (TES) feature at 3.3332 eV, and thus is unambiguously a donor-bound exciton (D^0X),[26,27] associated with a donor at 40 meV. The 3.3568 eV line has earlier been classified as an acceptor-bound exciton (A^0X), associated with an acceptor at 79 meV.[25] This acceptor is thought to be a complex center because it seems too shallow for a simple, substitutional acceptor.[25] Another sharp, excitonic-type line falls at 3.318 eV, and if we compare with the 3.3568 eV line (evidently due to a 79 meV acceptor[25]), and apply Haynes' Rule, the 3.318 eV line should correspond to an acceptor at about 240 meV. However, there is no strong evidence that Haynes' Rule even applies in ZnO, expecially for acceptors. Note that the weaker nature of the A^0X lines in undoped SVCT ZnO is expected, because donor and acceptor concentrations in this material are about 1×10^{17} and $2 \times 10^{15}\ \mathrm{cm}^{-3}$, respectively.[19]

In comparing the undoped and N-doped samples (Fig. 2), the most obvious difference is that the latter has a huge line at 3.315 eV, near the "deep" A^0X line at 3.318 eV in the undoped sample, and a small line in the D^0X region. The simplest explanation for the 3.315 eV feature is that it is an A^0X line associated with $\mathrm{N_O}$. Its dominance over the D^0X feature is expected from the large number of $\mathrm{N_O}$ centers (Fig. 1), and the fact that there are fewer neutral donors (none, in the dark) if the Fermi level is near the acceptor level. Of course, it is also possible that the donor concentration itself has somehow been reduced during the MBE growth, but we have no evidence for this. In fact, it is probable that the only change in the donors is that they are more likely to be close to acceptors, because of the high N concentration, and thus will contribute to emission through a D^0A^0 process, rather than an excitonic process. The position of the A^0X line in the N-doped sample is a little below that in the undoped sample, but, interestingly, this is exactly what is seen in both ZnSe and ZnS doped with N.[21]

The broad line centered at 3.238 eV in the N-doped sample is probably composed of two emissions: (1) an LO-phonon replica of A^0X and (2) D^0A^0 recombination. The D^0A^0 energy for a given pair will be given by $E_{DA} = E_G - E_D - E_A + e^2/4\pi\varepsilon r$, where E_G, E_D, and E_A are the band gap, donor, and acceptor energies, respectively, ε is the dielectric constant, and r is the pair separation. The average coulomb energy $\Delta E = e^2/4\pi\varepsilon\langle r\rangle$ can be very roughly estimated by letting $\langle r\rangle \sim (3/4\pi N_A)^{1/3}$, with $N_A \sim 10^{18}$–$10^{19}\ \mathrm{cm}^{-3}$, giving $\Delta E \sim 0.03$–0.06 eV. At 2 K, the band gap is 3.437 eV, and the donor energy is known to be

about 60 meV.[2,24] Thus, $E_A = 3.437 - 3.238 - 0.060 + \Delta E \approx 0.17 - 0.20$ eV. The high end of this range is comparable to the optical (PL) value of 224 meV found for the acceptor in lightly Mg-doped GaN.[28] This is not unexpected, since the band structures of GaN and ZnO are very similar. Interestingly, the low end of our range, 0.17 eV, is comparable to the electrical (Hall) value of E_A in *p*-type GaN.[29] Along with the similarities in the PL spectra of *p*-type ZnO and *p*-type GaN, there is an interesting difference: the A^0X emission is much stronger than the D^0A^0 emission in heavily N-doped ZnO (Fig. 2), but the opposite is true in heavily Mg-doped GaN.[30] This fact supports the contention that the emission in ZnO-based photonic devices is more likely to be driven by excitonic processes than that in GaN-based devices.

To compare the electrical properties of *p*-type ZnO and GaN, we note that, for Mg-doped, *p*-type GaN, typical values of μ_p and p are about 5 $\mathrm{cm^2/V\,s}$ and 1×10^{17} $\mathrm{cm^{-3}}$, respectively,[29,31] close to our measured values for N-doped, *p*-type ZnO. Moreover, any reported values of μ_p and p much higher than these in GaN should be viewed with some caution, as will be discussed later. To be more quantitative, the hole concentration, in a nondegenerate, single-donor/single-acceptor model, will be given by[22]

$$p = \frac{1}{2}(\phi_A + N_D)\left\{\left[1 + \frac{4\phi_A(N_A - N_D)}{(\phi_A + N_D)^2}\right]^{1/2} - 1\right\} \qquad (1)$$

where N_A and N_D are the acceptor and donor concentrations, respectively, and $\phi_A = (g_{A1}/g_{A0})N_V' T^{3/2} \exp(\alpha_A/k) \times \exp(-E_{A0}/kT)$. Here, g_{A0} and g_{A1} are the unoccupied and occupied state degeneracies, respectively, N_V' is the effective density of states at 1 K, T is the absolute temperature, and α_A is a linear temperature coefficient defined by $E_A = E_{A0} - \alpha_A T$. For N on an O site, we would expect that $g_{A0} = 4$ and $g_{A1} = 1$. If we assume an effective hole mass of $m_p = 1m_0$, then $N_V' = 4.94\times10^{15}$ $\mathrm{cm^{-3}\,K^{-3/2}}$, and if we assume that $E_A = 170$ meV, as estimated above, then $\phi_A = 9\times10^{15}$ $\mathrm{cm^{-3}}$. Since, from the SIMS data, $[N] \approx N_A \geqslant 5\times10^{18}$ $\mathrm{cm^{-3}} \gg \phi_A$, we can approximate Eq. (1) by $p = (N_A/N_D - 1)\phi_A$. Then, our value of $p = 9\times10^{16}$ $\mathrm{cm^{-3}}$ would be consistent with a compensation ratio $N_D/N_A \approx 0.1$, a reasonable value, and within the range of compensation ratios determined in Mg-doped *p*-type GaN.[29,31] It is interesting that, for ZnO in this concentration regime, the *ratio* N_A/N_D is more important than N_A itself for obtaining a high value of p. Of course, for high mobility, both N_A and N_D should be small.

There have been several reports of *p*-type ZnO recently. Minegishi *et al.*[3] obtained $\mu_p = 12$ $\mathrm{cm^2/V\,s}$ and $p = 1.5\times10^{16}$ $\mathrm{cm^{-3}}$, and Butkhuzi *et al.*[7] obtained $\mu_p = 23$ $\mathrm{cm^2/V\,s}$ and $p = 4\times10^{14}$ $\mathrm{cm^{-3}}$; these values seem reasonable, according to the above arguments. However, most of the other workers[4–6] have obtained values of p in the 10^{18}–10^{21} $\mathrm{cm^{-3}}$ range. It is difficult to understand how such high hole concentrations could result from a >150 meV acceptor. In this regard, it should be pointed out that an artificially low Hall voltage, which can result from a number of causes, will lead to artificially high values of p, and low values of μ_p. Thus, great care must be taken in the Hall-effect measurements and their interpretation.

In summary, we have produced homoepitaxial N-doped, *p*-type ZnO by MBE. The values of μ_p and p from Hall-effect measurements are reasonable and quantitatively consistent with modeling, with SIMS results, with PL spectra, and with Hall and PL results for *p*-type GaN and other *p*-type II-VI compounds. These results suggest that a $p-n$ homojunction can be produced in ZnO.

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