Extended Abstracts of the 2002 International Conference on Solid State Devices and Materials, Nagoya, 2002, pp. 360-361

G-6-1 (Invited)

Growth and Characterization of p-type ZnO thin films by MBE

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1. Introduction

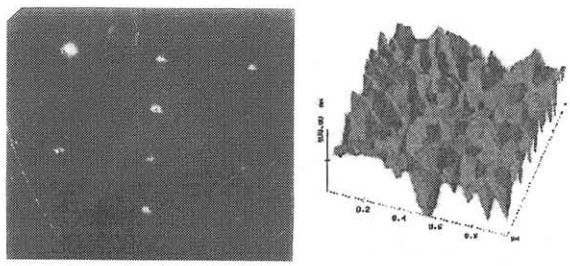
It has been known for some time that ZnO has one of the greatest potentials as a wide bandgap light emitter. It has a bandgap of 3.35 eV and a 60 meV binding energy for its excitons.[1] This exciton binding energy is nearly three times stronger than GaN or ZnSe, so it promises strong and efficient light emission at room temperature. ZnO is also more radiation resistant than other wide bandgap materials, making it a good candidate for space and military applications.[2] UV light emitters are possible, and of particular interest is the solar blind region of the UV spectrum, which can be reached with the addition of Cd and Mg for lattice-matched bandgap engineering, similar to that used in the Zn(Mg)STeSe light emitting alloys[3]. The possibility of lattice-matched structures does not easily exist in the GaN system.

2. Experimental Procedures and Results

Homoepitaxial ZnO thin-film growths were performed in a custom-built MBE system that includes extensive cryogenic shrouding and additional cryopumping. The substrates were 10-mm x 10-mm x 0.5-mm pieces cut from c-plane wafers, which themselves were sliced from bulk, 2-inch-diameter ZnO ingots grown in-house using a Seeded Chemical Vapor Transport (SCVT) process. This process is similar to the Seeded Physical Vapor Transport (SPVT)[4], used in ZnSe, CdS, and ZnTe bulk single crystal growths. In SCVT, a carrier gas is added that is reactive with the charge to increase the transport and growth rates, in this case hydrogen was used. Typical donor and acceptor concentrations in the bulk ZnO are 1 x 10^{17} and 2 x 10^{15} cm^{-3}, respectively.[5]

For the MBE growth of the ZnO films, pure (99.99995%) 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. Most of the films were grown on chemo-mechanically polished Zn (0001) faces.

The ZnO substrates were first cleaned in-situ with an H_2 + O_2 (10:1) plasma mixture in an attempt to remove hydroxyl compounds that are thought to form on the bare surface when exposed to air. During this clean, the substrate was heated to ~600-800 C. The substrate was then cooled to growth temperature and growth was initiated. Growths were carried out from 400 °C to 700 °C as measured by a thermocouple in the substrate heater block. The Zn flux was ~ 1-3 x 10^{-7} Torr as measured in the beam path with an ionization gauge. O_2 flow rates were not calibrated, but the chamber pressure during growth was maintained at ~ 5-9 x 10^{-5} Torr. During the growth, a Reflection High-Energy Electron Diffraction (RHEED) system was used to monitor the crystalline quality and roughness of the films. A streaky (i.e. 2D single-crystal) RHEED pattern was seen before and shortly after growth nucleation. As the growth progressed, the pattern remained single crystal, but started to exhibit broken lines and eventually a spotted pattern (Fig. 1a) was seen, indicating a roughening of the surface morphology. The true nature of this roughening is still being studied and is likely caused by a stoichiometry imbalance. An AFM image of the rough surface is shown in Figure 1b. Growth rates of ~40-70 nm/hr were achieved with the growth rate being Zn flux limited.



(a) (b)

Fig. 1 (a) RHEED Pattern for ZnO thin film, (b) AFM image of film surface.

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 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,[6] and it has also been employed in some of the other attempts to grow p-type ZnO.[7,8,9]

Hall-effect measurements were carried out in the van der Pauw configuration, by using a direct current of 3 μA, and a magnetic field of 15 kG. Data were compiled employing

both positive and negative currents and magnetic fields, and the results were averaged.[10] 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 $\rho = 4 \times 10^1$ Ω-cm; hole mobility $\mu_p = 2$ cm^2/V-s; and hole concentration $p = 9 \times 10^{16}$ cm^{-3}. Two other growths have given similar results, and attempts to get larger p and μ_p are now in progress. Secondary Ion Mass Spectroscopy (SIMS) was also used to verify the Nitrogen incorporation.[10]

Low-temperature (2 K) photoluminescence results for bulk, undoped samples, and MBE-grown, N-doped layers, are compared in Fig. 2. As is commonly seen,[11] the bulk sample is dominated by a series of sharp lines, probably due to neutral-donor-bound-excitons (D^0Xs); the strongest of these lines is at 3.366 eV, with an LO-phonon replica at 3.293 eV. Another group of lines, probably associated with neutral-acceptor-bound excitons (A^0Xs), falls at 3.333 eV, with replicas at 3.260 eV. Finally, the line at 3.221 eV, with a replica at 3.148 eV, is likely due to neutral-donor-acceptor (D^0A^0) pairs. When comparing the undoped and N-doped samples, the most obvious difference is that the N-doped film has a huge line in the A^0X region and a small line in the D^0X region. This is consistent with N being a shallow acceptor. Thus, in this case, most of the excitons formed in the exciting light attach to neutral acceptors, not neutral donors. It is probable that the donors 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 somewhat below that in the undoped samples, but, interestingly, this is exactly what is seen in both ZnSe and ZnS doped with N.[12]

The broad line centered at 3.245 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. In spite of 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.[13] 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.

3. Conclusions

For the first time, thin films of homoepitaxial p-type single crystal ZnO were grown by MBE and tested by Hall effect, SIMS, and photoluminescence for verification. Insulating substrates, doped with lithium, were used to provide electrically accurate test results.

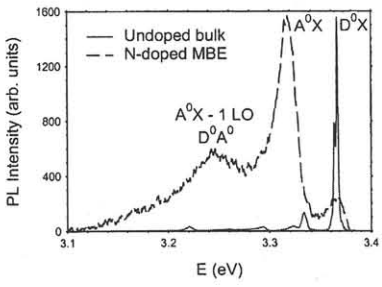


Fig. 2 Photoluminescence spectra (2 K), for an undoped bulk sample and an N-doped, MBE-grown epitaxial layer.

Acknowledgments

We would like to thank David Look, Don Reynolds, and Cole Litton at Wright State University and Wright Patterson Air Base, Ohio for their electrical and optical tests on our wafers. Also, thanks to Matt Klopfstein and Prof. Don Lucca from Oklahoma State University for AFM images.

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