Etching of ZnO towards the Development of ZnO Homostructure LEDs

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ABSTRACT

Although ZnO has recently gained much interest as an alternative to the III-Nitride material system, the development of ZnO based optoelectonic devices is still in its infancy. Significant material breakthroughs in p-type doping of ZnO thin films and improvements in crystal growth techniques have recently been achieved, making the development of optoelectonic devices possible. ZnO is known to be an efficient UV-emitting material (~380 nm) at room temperature, optical UV lasing of ZnO has been achieved, and both homojunction and hybrid heterojunction LEDs have been demonstrated.

In this paper, processing techniques are explored towards the achievement of a homo-junction ZnO LED. First, a survey of current ZnO processing methods is presented, followed by the results of our processing research. Specifically, we have examined etching through an n-ZnO layer to expose and make contact to a p-ZnO layer.

Keywords: Ultraviolet, ZnO, Light-emitting diode, Etching, Processing

1. INTRODUCTION

ZnO has attracted much attention for its potential applications in blue and UV optoelectronics and high temperature transparent electronics.[1] ZnO is similar to III-Nitride material in that it has a wide, direct band gap that is tunable when alloyed with CdO and MgO. It also has wurtzite structure and a high bond strength. However, it has many distinctive properties when compared with III-Nitride materials. In particular, ZnO has a much higher exciton binding energy than GaN (60meV), which gives it the potential for higher brightness excitonic emission, laser diodes with lower threshold currents and better high temperature performance. ZnO material is also less expensive to grow compared to III-Nitrides, due to its lower required growth temperatures, lower cost, higher quality native substrates and lower cost growth equipment. ZnO also exhibits a higher radiation resistance than GaN. Finally, ZnO is readily wet-etched, which gives it a processing advantage over the III-Nitrides that are limited to dry etching.

Despite these advantages, ZnO opto-emitter technologies lag far behind that of the III-Nitride material system. Reliable, high conductivity, p-type material is not readily available. There have only been a few publications on ZnO homojunction LEDs,[2,3] and only a few more on heterojunction LEDs.[4,5] Device fabrication techniques are still under development, and much research still needs to be done before ZnO will be in a position to compete with III-Nitride technology.

Ideally, a controlled wet etch that results in a suitable profile with smooth etched surfaces is desired. Dry etching induces etch damage and adds expense to device processing. However, although ZnO is readily wet etched by acids and bases, it is very difficult to use this process for device fabrication.

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There have been many reports on ZnO etching using dilute HCl, H_3PO_4, H_3PO_4 + Acetic acid, HNO_3, and buffered oxide etch solutions.[6,7,8] In practice, these solutions tend to lead to roughened surfaces and a discontinuity at the mesa edges, causing an open circuit for practical devices, and suffer from a lack of precise control over the etch depth.[9,3] However, Lee et. al. refer to using a H_3PO_4 / HCl / H_2O solution for fabricating a ZnO p-n homojunction diode.[10] Zheng et. al. report on using $FeCl_3$•6H2O to obtain a "U" shaped etching profile, while Pan et. al. used a NH_4Cl solution for a controlled etch rate in order to fabricate ZnO based LEDs.[9,3] These isolated reports of success, however, still leave room for alternative solutions to the etching problem.

2. FABRICATION OF A HYBRID LED

2.1. Material Growth

The growth of the III-Nitride material was first carried out at the Center for Quantum Devices in a horizontal flow metalorganic chemical vapor deposition reactor on a c-plane sapphire substrate, similar to our previous reports.[11,12] After the top p-GaN layer was grown, the sample was then transferred to Nanovation, SARL, where the top n-ZnO layer was deposited via pulsed laser deposition, as described elsewhere.[13] The device structure, with metallic contacts, is shown in Figure 1.

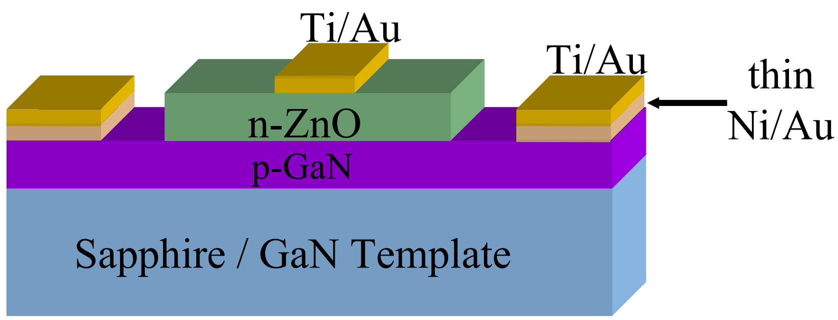
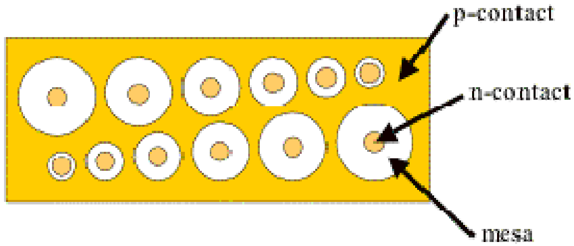


Figure 1: Schematic diagram of device structure with metallic contacts.

2.2. Device Fabrication

The mask used for the processing is composed of six different sized circular LED mesas with a common ring type contact surrounding them. The mesas range in size from 0.05 mm^2 to 0.30 mm^2, in increments of 0.05 mm^2. Each mesa has a circular metal contact in its center of approximately 0.01 mm^2.

The sample was first annealed to activate the acceptors in the p-GaN at 1000°C in nitrogen ambient. Since ZnO is easily wet-etched by most acids while GaN is not, the photolithographically defined mesas were etched down to the p-GaN material via wet-etching with a weak Acid solution. The photoresist was then removed and the sample was cleaned. The thin Ni/Au p-type contact was deposited using the ring contact mask for lift-off, followed by the standard anneal for the p-GaN contact. Next, a Ti/Au n-contact was deposited using the wire bonding contact mask, which was then annealed at 350°C in nitrogen ambient. Finally a thick Ti/Au contact was deposited directly over the thin p-contact for wire bonding purposes, again using the ring contact mask for lift-off. Since ZnO is slowly etched in developer solutions and even very slowly etched by DI water, special care was taken in order to avoid damage to the ZnO whenever possible by minimizing its exposure to harmful chemicals.



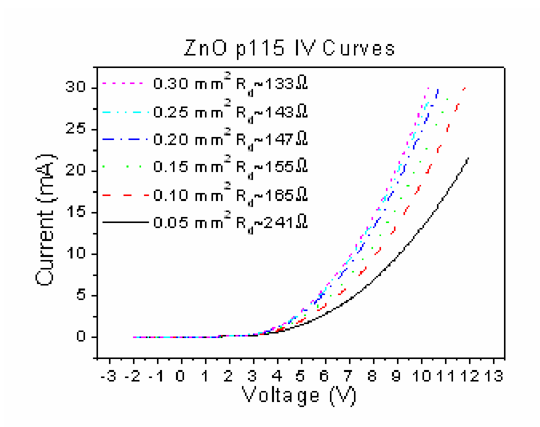
(a)

(b)

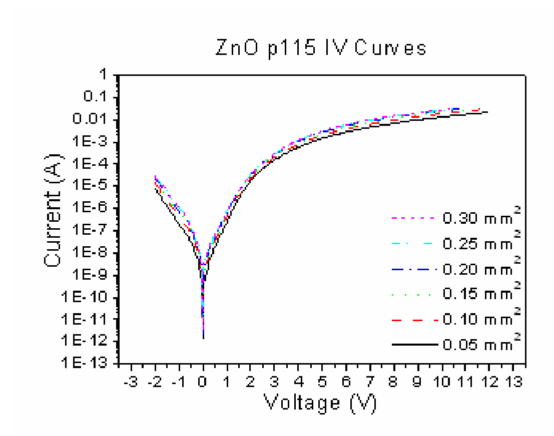
Figure 2: (a) Schematic planar view and (b) actual image of processed ZnO LEDs.

2.3. Device Results

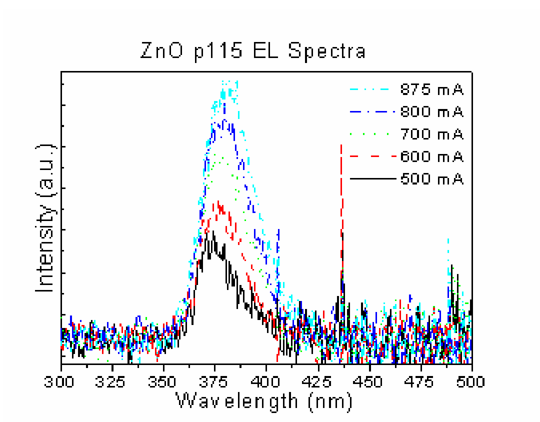
The device results from this hybrid LED are shown below in Figure 3 (a), (b), (c), and (d).



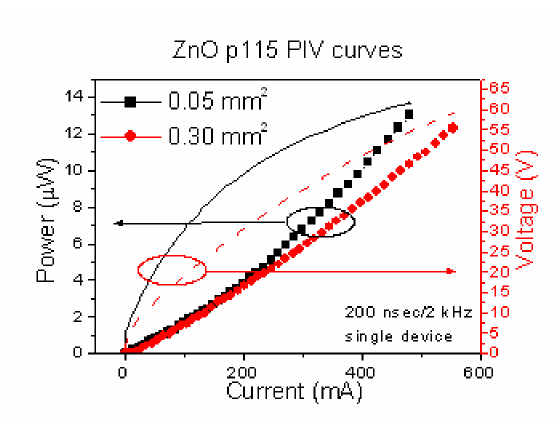
(a)



(b)



(c)



(d)

Figure 3: (a) linear I-V curve of various sized mesas, (b) semi-logarithmic I-V curve of various sized mesas, (c) EL spectra at various currents, and (d) P-I-V measurements of the smallest and largest mesa sizes.

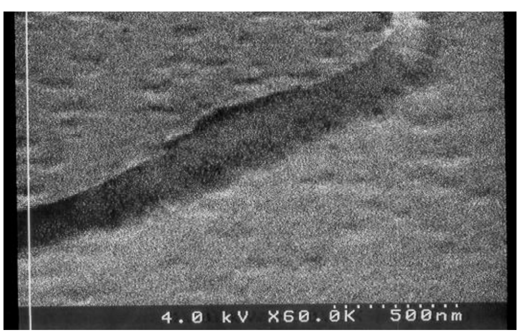
The I-V curves demonstrate a fairly constant turn-on voltage of approximately 5 V independent of mesa size, as well as a decrease in differential resistance with an increase in size. The reverse leakage current shows a slight increase with an increase in size as expected due to the increase of both area (possible bulk leakage) and circumference (possible edge leakage). The reverse leakages range from -7.06 μA at -2 V for the smallest sized LED to -28.2 μA at -2 V for the largest sized LED, which are fairly high values as compared to our non-hybrid LEDs. The EL demonstrates emission at a peak wavelength of approximately 374 nm at 500 mA and redshifts slightly with increasing current, approximately linearly, to about 382 nm at an injection current of 875 mA, attributed to device heating. This peak wavelength agrees with the photoluminescence spectrum, which had a peak wavelength of ~375 nm, and is characteristic of near-band-edge emission from ZnO. The P-I-V demonstrates ~12 μW peak power emission from both the largest and the smallest sized devices, which indicates that there is a good lateral homogeneity of the layer / device properties. For a more thorough discussion of this device, please see reference 4.

4. FABRICATION TECHNIQUES FOR A HOMOJUNCTION LED

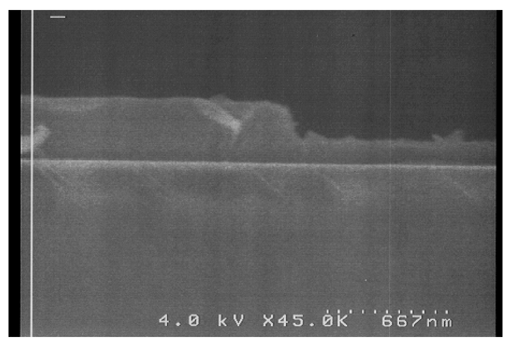
The success of the hybrid n-ZnO / p-GaN LED demonstrates that the processing techniques used are viable for processing of ZnO material. The biggest obstacle, given a good ZnO p-n junction, then remains to be the controlled etching of the ZnO through the top layer, just deep enough to expose the underlying layer, without causing significant damage to that underlying layer.

After exploring wet etching using dilute acids, it was found that control of the etch rate, achieving good surface morphology, and retaining a continuous n-type layer at the edges of the photoresist is extremely difficult. Therefore, the approach was changed in order to use a combination of wet and dry etching.

First, a BCl_3 ECR etch was explored. It was found to have an etch rate of ~45 nm/min, and the etched surface displayed similar morphology as the un-etched surface, as shown in Figure 4(a). Figure 4(b) shows the etch profile obtained from the dry etch.



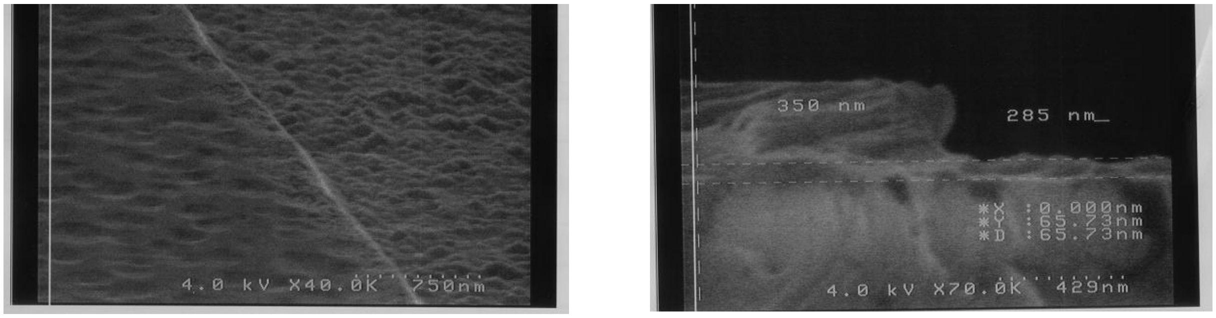
(a)



(b)

Figure 4: SEM images after dry etching of ZnO film in BCl_3 chemistry; (a) demonstrates that the etched surface has similar morphology to the unetched surface, while (b) shows the etch profile.

After using this dry etch recipe to approach the underlying ZnO layer, a very brief wet etch in a dilute acetic acid solution was used to completely etch into the underlying layer, and attempt to remove etch damage that may have occurred due to the dry etch. This short etch removed approximately 80 nm more of the material, exposing the underlying layer. A continuity between the mesa and the exposed material was successfully obtained, as shown in Figure 5(b). The etch also slightly roughened the exposed material as compared to the dry etch alone, which was expected, as shown in Figure 5(a).



(a) **(b)**

Figure 5: SEM images after combination dry and wet etch. (a) shows the surface morphology change in the wet etched layer as compared to that of the un-etched surface, while (b) demonstrates continuity between the mesa and the underlying layer was achieved.

5. CONCLUSION

In conclusion, we reported on the successful fabrication of a heterojunction p-GaN / n-ZnO LED, and explored etching techniques towards achieving a homojunction ZnO LED. A dry etch process with a low and predictable etch rate was achieved for ZnO. This dry etch followed by a brief wet etch was able to expose a buried layer of ZnO material without breaking the continuity of the buried material as is typical with wet etching alone. This is therefore a viable approach for the fabrication of a homojunction ZnO LED.

6. ACKNOWLEDGEMENT

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