EFFECT OF PHASE SEPARATION ON PERFORMANCE OF III-V NITRIDE SOLAR CELLS

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ABSTRACT: The III-nitride material system provides a wide direct-band gap range of 0.65eV (InN) to 6.2eV (AlN) making it crucial for high-efficiency photovoltaics. Phase separation of material in solar cells not only tends to reduce the short circuit current by forming low band gap recombination centers, but also tends to pin down the open circuit voltage. Phase separation is controlled during MOCVD epitaxial growth by increasing the indium carrier gas flow rate, increasing the growth rate and limiting the thickness of the epitaxy. A high n-type defect density in thick InGaN test structures compensates the p-type doping, which prevents junction formation in the device, and thus, is detrimental for the solar cell. P-type doping is confirmed for thin InGaN test structures with indium compositions as high as 28%, and the resultant test structures demonstrate expected photovoltaic effect. Test structures of band gap 2.5eV measure an open circuit voltage of 2.1V. Test results indicated the significance of epitaxial thickness optimization for high performance InGaN solar cells.

Keywords: III-V semiconductors, Epitaxy, Defects, Phase separation

1 INTRODUCTION

One of the requirements to achieve 50% photovoltaic conversion efficiencies using the multi-junction conversion concept is to have a component junction of band gap 2.4eV or greater as indicated by detailed-balance modeling [1, 2]. The III-nitride material system, which consists of InN (0.65eV), GaN (3.4eV), AlN (6.2eV) and their alloys, is offers substantial potential to develop ultra high-efficiency solar cells. This material system has an apparent insensitivity to high dislocation densities as the polarization and piezoelectric properties [3, 4] of the material introduce electric fields and surface diploes that may counter the effect of dislocations. Additional advantages include low effective mass of electrons and holes, high mobilities, high peak and saturation velocities [5], high absorption coefficients and radiation tolerance. Moreover, a continuum of band gaps can be obtained by changing the compositions of indium and gallium making it relatively easier for molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD) to grow a multi-junction device limiting the number of material sources. This material system has undergone remarkable development due to the use of GaN and InGaN in blue LEDs and laser diodes [6].

A major challenge in the epitaxy of III-nitrides is the high defect density due to the lack of a suitable lattice-matched substrate. Although sapphire is the substrate of choice for growth of GaN, the lattice mismatch of 16% between the two materials gives rise to a high dislocation density in the 10^7-10^{10}cm^{-2} range [7, 8]. A dominant mechanism for relaxation of this strain arising due to lattice mismatch in thick InGaN layers is phase separation.

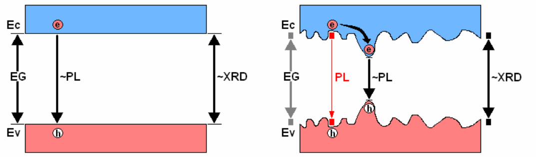

Figure 1: Schematic comparison of (a) stoichiometrically perfect material to (b) phase-separated material.

2 PHASE SEPARATION IN InGaN

2.1 Cause of phase separation

Phase separation is the formation of microscopic or macroscopic domains of variable constituent composition in a material. This phenomenon occurs in InGaN primarily due to the low miscibility of InN in GaN. Theoretical calculations [9] based on a valence-force-field (VFF) model [10, 11] predict that phase separation in InGaN strongly depends not only on the temperature and In composition, but also on the strain state of the InGaN films. Figure 1 (a) and (b) schematically compares the band diagram of a stoichiometrically perfect InGaN, and a phase-separated InGaN, where the variable indium and gallium compositions lead to formation of variable band gap domains in the material. Phase separation is identified in photoluminescence (PL) and X-ray diffraction (XRD) through broader or secondary peaks in addition to the main luminescence or crystallographic peak corresponding to the expected material.

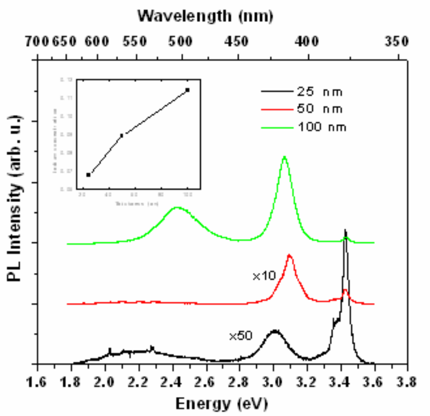

Figure 2: Photoluminescence data indicating increasing emission from phase separated InGaN with increasing thickness.

2.2 Control of phase separation

A systematic study of MOCVD epitaxy of InGaN with indium composition ranging from 0 to 30% indicates the increasing tendency of phase separation with increasing indium composition [12]. The study also suggests an increase in phase separation corresponding to relaxation of the material at higher thicknesses as shown in Figure 2. Phase separation in InGaN bulk layers can be suppressed by increasing the epitaxial growth rate, increasing the indium carrier gas (TMIn – trimethyl-indium) flow rate, and limiting the thickness of the material to the minimum requirement. The control of phase separation by increasing the TMIn flow rate during InGaN epitaxial growth is evident with the suppression of the secondary PL emission peak as seen in Figure 3.

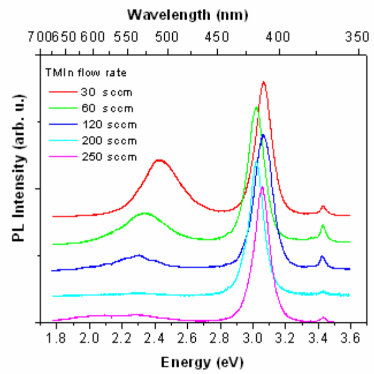

Figure 3: PL data summary of InGaN growth with variable TMIn flow rate.

2.3 Implications of phase separation on solar cell performance

Although phase separation incorporates lower band gap domains within the material that absorbs corresponding low energy light, its effect is opposite to that of intermediate bands or quantum dots. As the size and distribution of the lower-band gap phase-separated domains are not optimal, they act as recombination centers decreasing the short circuit current of the solar cell. It is also evident from the theory of quantum well solar cells [13] that the lower band gap material tends to dominate by pinning down the open circuit voltage of the device. Thus, phase separation may hinder the performance of a solar cell in a twofold manner.

3 DEVICE GROWTH AND FABRICATION

We have previously demonstrated p-i-n GaN/InGaN solar cells with indium composition up to 7% and measured V_{OC}s as high as 2.4V [14]. These devices consisted of u-InGaN test layers sandwiched between p-type and n-type GaN layers. These structures were used as a transition design from the III-nitride LED and photodetector technology to ensure successful fabrication. Non-optimal ohmic contacts were identified as a important area of improvement in device design and fabrication. Phase separation was identified as a major loss mechanism on the epitaxial growth front, which lowered the band gap of a 3.2eV solar cell to 2.4V. In the present work, we design homojunction InGaN solar cells to test the implications of material quality, including phase separation, on photovoltaic performance.

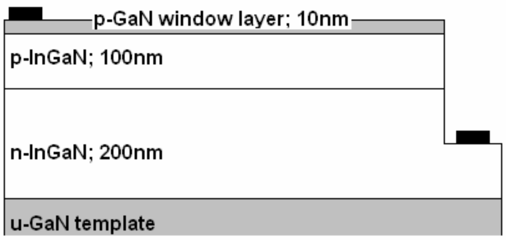

Figure 4: Schematic of the InGaN epitaxial structure fabricated into a solar cell.

3.1 Epitaxial growth and characterization

The test InGaN solar cells are epitaxially grown in an Emcore MOCVD D-125 rotating disk reactor with a short jar configuration. The active device layers are grown on 2μm GaN nucleation layers over commercial 2-inch sapphire substrates. Indium compositions are in the 10-20% range for 300nm thick InGaN epitaxy.

The schematic of a typical epitaxial-grown test structure is shown in Figure 4. The n-type and p-type InGaN layers measure a thickness of 200nm and 100nm, respectively. Si is used as the n-type dopant and measures a carrier concentration in the high $10^{18}cm^{-3}$, while Mg is used as the p-type dopant and is calibrated for a carrier concentration in the low $10^{18}cm^{-3}$. The net thickness of the solar cell is limited to 300nm as this thickness absorbs more than 95% of the light with energy greater than its band gap. A 10nm p-GaN window layer is used as the capping layer for surface passivation and to protect the InGaN from oxidation. The epitaxial structures are then annealed for thirty minutes at 625˚C in a N_2 ambient to activate the Mg acceptors by breaking the Mg-H bond formed during growth.

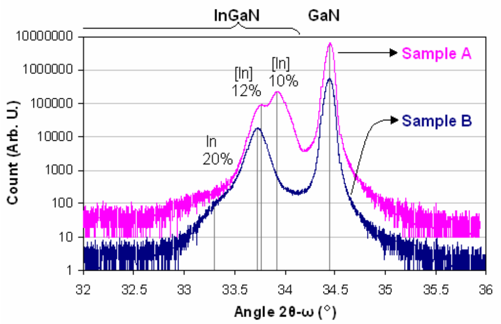

Figure 5: XRD of preliminary test InGaN solar cells indicting phase separation. (Plots offseted for clarity.)

The preliminary epitaxial structures are grown with varying degrees of intentional phase separation. The XRD of two of the epitaxial structures with intended indium composition of 10% are shown in Figure 5. In addition to the GaN peak, InGaN peaks corresponding to indium composition of 10%/12% and 12%/20% are seen for Samples A and B, respectively. The FWHMs of primary InGaN peaks are in the range of 450-500 arcsec, while that of the 20% InGaN peak is about 5200 arcsec.

Phase separation in these samples is also evident from PL data as seen in Figure 6. In addition to 10% and 12% indium peaks, sample A also indicates a broad PL peak at an indium composition of 16%. Sample B shows

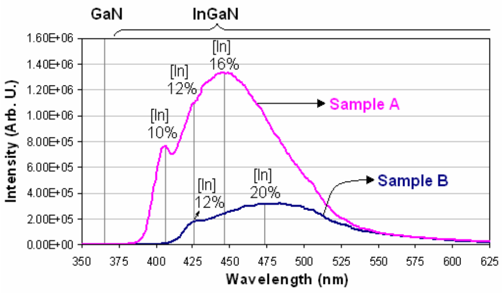

Figure 6: PL of preliminary test InGaN devices indicting phase separation.

PL peaks at 12% and 20% indium compositions, but they are of lower intensity, and hence, lower optical quality. The broad secondary peaks of both the samples indicate the presence of multiple phases of InGaN within the material.

Additional InGaN devices of superior quality with indium compositions as high as 30% but with lower thickness are also grown for comparison. The thickness of InGaN in these devices is limited to 100nm to suppress phase separation and ensure high structural quality. P-InGaN is grown on thick n-GaN templates to ensure successful fabrication of the device. XRD of one such epitaxial structure, Sample C, is given in Figure 7, which clearly shows the presence of a single phase in the epitaxy.

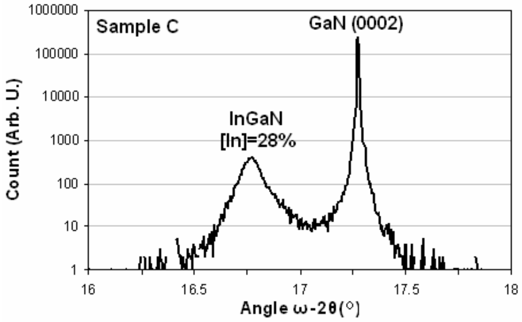

Figure 7: XRD of InGaN sample with high indium composition and no phase separation.

3.2 Device fabrication

A 5nm-Ni/5nm-Au layer is deposited on p-InGaN and annealed for one minute at 525°C in an O_2 ambient to form NiO along with Au islands. The annealing yields low specific contact resistivity in the order of $10^{-6}\Omega$-cm^2 and also increase the transparency of the layer [15]. 50nm-Ni/100nm-Au is then deposited to form contact pads to externally probe the layer. Recessed trenches are etched to access the n-InGaN layer using inductively coupled chlorine plasma. The n-InGaN contact is formed by e-beam evaporation of 10nm-Ti/30nm-Al/10nm-Ti/100nm-Au. The p-contact and n-contact grid lines are 5μm wide and are spaced 50μm and 100μm apart (Figure 8). The area of the fabricated devices range from 1mm x 1mm to 5mm x 5mm.

4 RESULTS AND DISCUSSION

4.1 Photovoltaic response

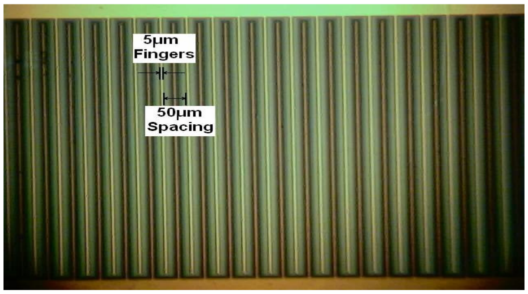

Figure 8: Top view of an InGaN solar cell with interdigitated grid contacts.

The performance of the solar cells is tested through their I-V characteristics. An additional UV bias is added to the 6000K spectrum during testing to enhance the photoresponse of the test structures. No photoresponse is observed for cells of thickness around 300nm. This result hold true for all the devices irrespective of the degree of phase separation. Moreover, the current tends to vary linearly with voltage indicating a non-diode-like behavior.

The devices with 100nm thick InGaN, with structures similar to Sample C, demonstrate a strong photoresponse. Sample C measures a V_{OC} of 2.1V as shown in Figure 9. This voltage is in accordance to the band gap of the material at 2.5eV. This is the first report of a photovoltaic response obtained from InGaN at such high indium compositions.

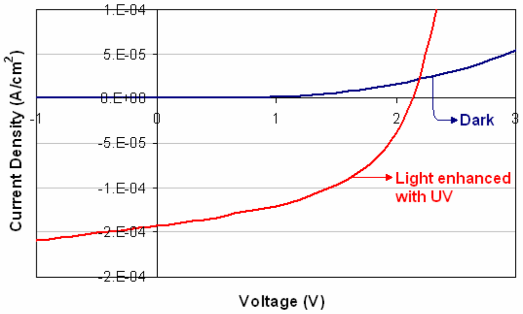

Figure 9: I-V characteristics of Sample C under dark and illuminated conditions.

4.2 Discussion

The results are unexpected as at least some photovoltaic effect was expected from the phase separated test structures. It is speculated that due to the high degree of phase separation and dislocations for thick InGaN layers, the resultant defects, which are inherently n-type, overcome the p-type doping in the material. As a result, an n-n junction is obtained instead of a p-n junction and the test structures demonstrate a resistor-like behavior. Hence, no photovoltage is obtained from these samples.

For the thin devices, p-type doping is successfully achieved in spite of the high indium composition. Moreover, epitaxial characterization reveals high crystalline quality of the material. As a result, the test structures demonstrate the expected V_{OC} of 2.1V for a 2.5eV material.

It becomes clear from these results that it is imperative to control phase separation within the solar cell, which in turn corresponds to the thickness of the test structure. This effect is particularly crucial in InGaN as phase separation increases the defect density of the material that negates the effect of p-type doping.

5 CONCLUSION

The implication of phase separation on performance of InGaN solar cells is studied. Effective ways of controlling phase separation during epitaxial MOCVD growth of InGaN are by increasing the indium carrier gas flow rates and the net growth rate. However, it becomes difficult to control phase separation at the present state of technology for InGaN epitaxial thicknesses greater than 200nm. On the other hand, p-type doping is successfully achieved for InGaN with indium compositions as high as 28%, and the resultant test structures measure a V_{OC} of 2.1V, which successfully corresponds to its band gap of 2.5eV. The p-type doping in test structures exceeding this thickness is compensated by the n-type nature of the resulting defects. Thus, it is crucial to optimize the thickness of epitaxy to fabricate a successful InGaN solar cell.

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