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Development of indium-rich InGaN epilayers for integrated tandem solar cells

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ABSTRACT

InGaN epilayers have been investigated for use in photovoltaic solar cells for the past years. At present, almost all photovoltaic device structures reported have exhibited very low short circuit currents and thus very low solar conversion efficiency. This phenomenon has been attributed to point and extended defect chemistry in InGaN epilayers (e.g. vacancies, misfit dislocations, and V-defects), as well as to spinodal decomposition of the strained InGaN wurtzite lattice system. These defects become more dominant for higher indium concentration InGaN epilayers needed for multijunction photovoltaic device structures. In this work, we will report on the growth and characterization of indium-rich InGaN epilayers that have been grown by novel MOCVD growth technology, including the growth at superatmospheric reactor pressures.

INTRODUCTION

The ternary InGaN material system offers a superior potential for the development of high performance photovoltaic (PV) devices with reduced cost for terrestrial applications. The primary advantage of this material system is a direct-band gap, high absorption coefficient, and the ability to tailor bandgaps ranging from 0.7 eV to 3.4 eV, covering the majority of the solar spectrum. A continuum of bandgaps can be obtained by varying the indium and gallium ratio in this ternary InGaN material system, compared to the current use of multiple group III-V materials (e.g. group III-phosphide/arsenide alloys) to achieve the same end [1]. Moreover, InGaN is one of the few material systems that provide band gaps greater than 2.4 eV, which is required for tandem solar cells with high photovoltaic conversion efficiencies. However, presently encountered scientific and technological challenges obstruct the fabrication of efficient solar cells with $E_G < 2.0$ eV necessary for >50% conversion efficiencies [2].

InGaN solar cells have not yet realized their full transformative potential despite a significant research effort over the past 7-8 years. The reason lays in the numerous materials challenges that have to be solved in order to achieve useful efficiencies and to increase the indium incorporation in InGaN alloys so that devices with bandgaps below 2.0 eV can be produced. While high peak internal and external quantum efficiencies (IQE and EQE) have been reported, InGaN solar cell efficiencies have never exceeded 3%. High V_{OC}'s have been reported, but J_{SC}'s have remained very low. This is most likely due to the many crystal defects commonly observed in InGaN epilayers and poor device design such as not properly optimizing the internal field caused by polarization effects. While it is possible to manipulate Metal Organic Chemical Vapor Deposition (MOCVD) process parameters to produce high quality gallium-rich InGaN solar material, low-pressure MOCVD growth has been shown to be limited to ~30% indium incorporation [3]. The present growth process limitations in the integration of dissimilar ternary

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and quaternary group III-nitride compound semiconductor alloys govern the pursuit of new approaches to stabilize the growth surface in order to reduce the point defect concentrations as well as the formation of extended defects such as misfit dislocations, surface V-defects and phase separation. One such approach is superatmospheric Metal Organic Chemical Vapor Deposition (also denoted as high-pressure CVD or HPCVD) [4]. We will show that HPCVD will likely reduce/supress crystal defects, which currently limit the performance of indium-rich InGaN materials structures that are needed for solar cells devices with $E_G < 2.0$ eV.

STATE-OF-THE-ART INGAN SOLAR CELLS

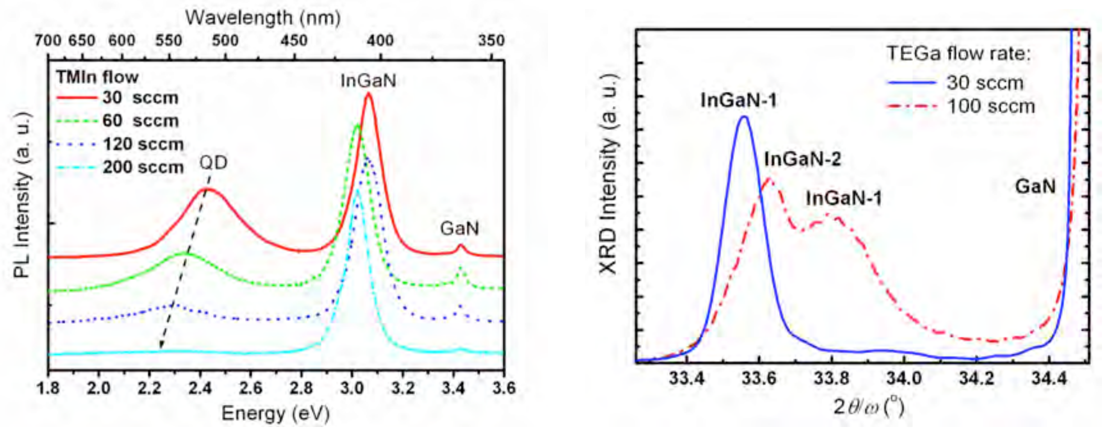
The potential for using InGaN alloys for solar cells was formulated by Wu et al. in 2003 [1] but there were no reports of actual devices until the work of this group in 2005 [5], which stimulated the still ongoing interest in InGaN based solar cells. Like most group III-Nitride based devices, InGaN solar cells are typically epitaxially grown by MOCVD, a epitaxial growth technology of great commercial relevance for the fabrication of optoelectronic devices due to the high achievable growth rates, superior optical material quality, and low point defect densities compared to other growth techniques. These first InGaN p-i-n solar cells had an IQE of 19%. However, phase segregation in indium-rich InGaN alloys resulted in lower bandgap InGaN alloys and reduced the V_{OC} to about 2 V instead of the expected 2.6 V, showing the importance of indium uniformity in this material [5]. This work was expanded to include InGaN quantum well solar cells, and these devices had open circuit voltages of 2.1 V and estimated EQE of >30%. The correlation of physical properties with extended crystalline defects opened the way for optimized designs of InGaN solar cells with controlled types and dislocation densities in the InGaN epilayers. This allowed the development of solar cells with open circuit voltages up to 2.4 V and IQE as high as 60% [6] and with the control of phase separation for 28% indium compositions a band gap of 2.5 eV with an open circuit voltage of 2.1 eV [7].

Zheng *et al.* [8] studied high quality p-GaN/i-$In_{0.1}Ga_{0.9}N$/n-GaN heterojunction epilayers grown by MOCVD with no observable phase separation. High performance photovoltaic cells with open circuit voltage of around 2.1 V and fill factor up to 81% under standard AM 1.5 conditions were obtained. Cai *et al.* [9] reported InGaN p-i-n homojunction solar cells with different In content (x=0.02, 0.12, 0.15) with V_{OC}'s 2.34 V, 1.34 V and 0.96 V respectively. Their results also indicated that reduction of defects is a key factor in the fabrication of nitride solar cell. Jeng *et al.* [10] experimentally measured $In_{0.2}Ga_{0.8}N$ and $In_{0.28}Ga_{0.72}N$ multiple quantum well solar cells (MQWs) open circuit voltages as 2.2 V and 1.8 V respectively. The higher quantum well energy barrier exhibited a low fill factor of 0.52 possibly due to the loss of electric field and the higher energy barrier. Dahal *et al.* [11] also reported on the fabrication and photovoltaic characteristics of solar cells based on $In_{0.3}Ga_{0.7}N$/GaN MQWs. They exhibited an open circuit voltage of about 2 V, fill factor of about 60%, and an external efficiency of 40% (10%) at 420 nm (450 nm). Trap-filling due to the high dislocation density of bulk, 5.5×10^{8} cm^{-2}, and surface traps in GaN/ InGaN PV devices has been postulated as reducing of the collection efficiency of the photo-generated carriers [12]. This trapping mechanism would increase the series resistance (R_S) and reduce the shunt resistance (R_{sh}), reducing J_{SC}.

MATERIAL RELATED ISSUES WITH INGAN SOLAR CELLS

In order to achieve a solely InGaN based multi-tandem solar cell, junctions with InGaN at >40% indium ($E_G \approx 2.00$ eV) and InN ($E_G = 0.70$ eV) are required. However, the quantum efficiency of present devices with indium content of greater than 30% ($E_G \approx 2.37$ eV) remains very poor, due to various crystal defects and alloy instabilities that occur in indium-rich InGaN films, which adversely affect the optical and electrical device performance. Understanding and reducing these alloy instabilities and crystal defects is critical for advancing towards high efficiency InGaN tandem solar cells.

It is well known that the structural, optical, and electrical properties of InGaN epilayers are all affected by MOCVD growth conditions such as growth rate, chamber pressure, substrate temperature, precursor ratio, and carrier gas. The indium content of InGaN epilayers is primarily controlled by the substrate temperature during growth. This is due to the evaporation rate of indium from the growth surface, which varies greatly with temperature in the range of 850 °C (low indium) to 500 °C (high indium). For this reason, low growth temperatures must be used to achieve films with high indium content. However, the low growth temperature reduces the cracking efficiency of ammonia, resulting in an increase in nitrogen vacancies. Nitrogen vacancies are the cause of the high unintentional n-type doping in InGaN films [13], Moreover, the equivalent group-V vacancies in arsenide semiconductors are known to be non-radiative recombination centers and this typically reduces carrier lifetimes in solar cells.



(a) (b)

Figure 1: (a) PL spectra correlating micro-/nano-scale phase separation with TMIn flow. (b) XRD scans correlating macroscopic phase separation with TEGa flow [3].

Another crystal defect in InGaN films is the formation of micro-/nano-scale regions of higher indium material within the crystal. These regions have a lower bandgap than the surrounding material and confine electrons and holes; behaving effectively as quantum dots. This research group performed initial studies on phase separation in InGaN epilayers grown by low pressure MOCVD under varying conditions [3]. Two types of phase separation were observed during growth of the InGaN layers. One was caused by In-rich InGaN micro-/nano-structures, and was observed through photoluminescence (PL) measurements. The other type of phase separation observed was macroscopic as observed in X-ray diffraction (XRD) measurements. Figure 1(a) shows correlation of the two types of phase separation with InGaN precursor flow rates. In addition, Figure 1(b) shows the ability to suppress the phase separation by carefully optimizing the growth process.

The charge carrier confinement caused by phase separation is beneficial to the operation of InGaN-based light emitting diodes [3]. However, the occurrence of phase separation is detrimental to InGaN solar cell performance, because it results in the trapping of the photo-generated carriers and thus reduces the carrier lifetime and ultimately reduces J_{SC}. In addition, the V_{OC} typically collapses towards the lowest effective bandgap in the material. While it is possible to suppress phase separation for some compositions of InGaN using standard low-pressure MOCVD growth applications, a rapid material degradation still occurs in films with >30% indium and cannot be controlled, Figure 2. After ~30%, the FWHM for both PL and XRD rise rapidly, indicating a rapid degradation of crystal quality and the reoccurrence of clustering or phase separation.

Increased incorporation of indium results in an increase in the lattice size of the InGaN crystal which causes a lattice mismatch with surrounding layers. If the InGaN epilayer is kept thin enough, below the critical thickness for the particular alloy composition, then the film will be pseudomorphically strained to conform to the crystal lattice size of the underlying layer. Experimentally observed values for the critical thickness of InGaN epilayers on GaN vary greatly from the expected critical thickness models for traditional III-V heterostructures [14]. InGaN epilayers grown beyond the critical thickness relax and form threading dislocations which terminate at the surface as V-defects. V-defects are inverted hexagonal pyramids nucleating at a threading dislocation and evolve in the form of a thin six-walled structure with {1011} layers [15]. These inverted pyramids have angles with respect to the device surface sufficient to channel incident light through reflection to threading dislocations. V-defects absorb photons above and below the InGaN bandgap and effectively result in shadowing of the devices.

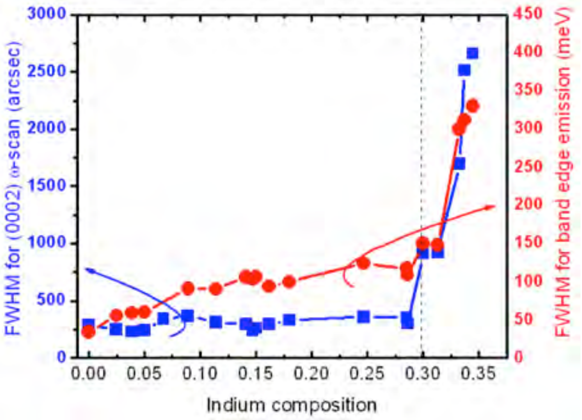


Figure 2: FWHM for XRD (blue squares) and PL (red circles) of InGaN films.

SUPERATMOSPHERIC GROWTH OF INGAN FOR SOLAR CELLS

The recent developed thin film growth technology, superatmospheric MOCVD –or HPCVD - has the potential to address these material issues and achieve high quality, high-indium InGaN material for solar cells with a bandgap of <2.0 eV, typically 60% indium [4]. Compound stoichiometry related materials instabilities and related crystal defects can be controlled by the partial pressures as well as the different growth chemistries of In- or Ga-dominated growth surfaces. For indium-rich ternary group III-Nitrides, the vastly different partial pressures between group III-elements and nitrogen, becomes more pronounced [16], suggesting the stabilization of these compounds that high nitrogen pressures [17] even though there still remains a great deal of uncertainty in the p-T-x relations [16]. The extended parameter space of HPCVD growth

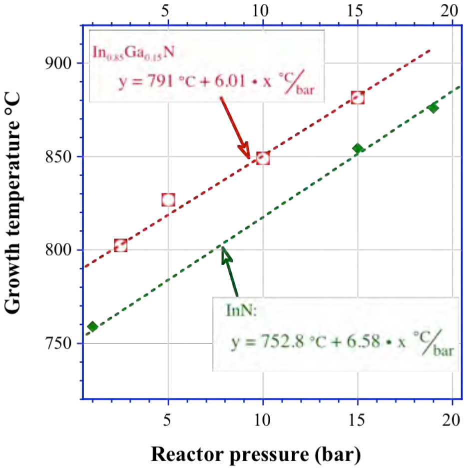


Figure 3: Growth temperature vs. reactor pressure for the growth of InGaN at elevated reactor pressures.

conditions accesses an extended process parameter space to stabilize InGaN growth surfaces using temperature- and pressure- regimes, not accessible by traditional low-pressure (LP-) MOCVD. However, the low cracking efficiency of ammonia at InGaN growth temperatures and the different surface chemistries for TMG and TMI necessitate an adjustment of the precursor injection timing in the reaction zone for different Ga/In precursor ratios, in order to obtain optimum, single phase InGaN alloys.

One of the first observations with HPCVD is the ability to stabilize the growth of InGaN at higher growth temperatures compared to conventional LP- MOCVD. For example, the growth temperatures of InN can be increased by more than 120 °C in the pressure regime between 1 and 20 bar, compared to LP-MOCVD, where the growth temperatures is below 650 °C, Figure 3. This advantage is maintained, in part, for $In_{0.85}Ga_{0.15}N$ although the increase of growth temperature as function of reactor pressure decreases due to the reduced temperature gap between InN and GaN. Therefore the MOCVD reactor pressure (high-pressure versus low-pressure) is a critical balance between the partial pressures of the alloy compositions that have to be stabilized at a specific growth temperature. If the growth process itself does not provide sufficient surface stabilization, the growth temperature difference between the two binaries still provides a significant driving force for the structural degradation of the layer quality and a similar miscibility gap seen in the low concentration InGaN alloys [3]. In addition, compositional induced lattice strain, interfacial piezoelectric polarization effects, and extended defect related effects will also dominate.

A major drawback of the high-pressure CVD approach lies in the significant reduction in growth rates with increasing reactor pressure. In the investigated pressure range of 20 bars, the growth rate falls almost by one order of magnitude, suggesting that even if this approach is feasible to stabilize and integrate thin layers with vastly different partial pressures, it might not be viable for thick material layer growth. However, the stabilization of indium-rich InGaN can be addressed in HPCVD by using a pulsed injection of the precursor scheme, which minimizes gas phase reactions and allows for a precise engineered surface chemistry to prevent growth surface induced phase instabilities. The thermal stability process window of indium-rich InGaN alloys studied in this work focused on growth temperatures in the range of 850 – 950 °C, with reactor pressures from 1 to 18 bar, and a simultaneous group-III precursor injection approach. The XRD analysis for various indium-rich InGaN shows that a macroscopic single-phase material can be obtained, Figure 4. The broadening of the InGaN (0002) Bragg reflection and the rocking curve with FWHM's around 3000 arcsec for x = 0.31 indicate a potentially high density of point- and extended defects in these layers but this requires further investigation. The structural degradation with increasing gallium incorporation is currently being addressed by exploring a sequential group-III precursor injection approach, adjusting the surface chemistry to each group III element (Ga and In) separately. However, these initial results still show that high-pressure MOCVD is a feasible approach to address the challenges in the growth and stabilization of indium-rich InGaN alloys for solar cell applications.

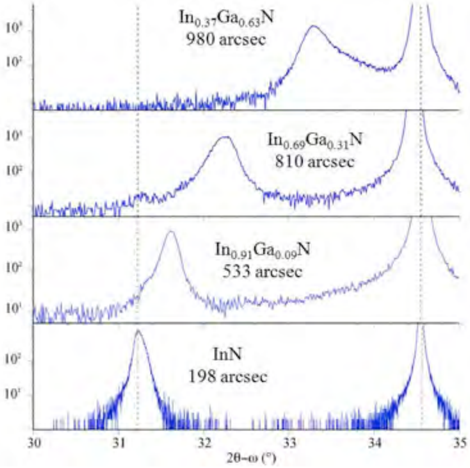


Figure 4: Structural quality of InN and indium-rich InGaN alloys grown by HPCVD.

CONCLUSIONS

The growth and integration of high-quality ternary InGaN epilayers over a wide range of composition has many challenges to overcome. The successful integration of InGaN alloys with Eg < 2.0 eV, typically 60% indium, is required for PV solar cell structures. In this paper we have shown that superatmospheric growth MOCVD provides one such approach. However, while this HPCVD has shown an improvement in the quality high indium concentration InGaN the integration of highly dissimilar group III-Nitride alloys will remain an ongoing research challenge.

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