Overview Articles

InGaN: An overview of the growth kinetics, physical properties and emission mechanisms - Yam

Intro

- "continuous alloy system" ranging from 0.7 eV (InN) to 3.4 eV (GaN)
    - Heterojunctions can be fabricated with band gaps from 0.7 to 3.4 eV with suitable InGaN alloy combinations
- Direct band gap
- InGaN used for LED lighting as it covers visible and part of the near UV spectral region
- InGaN still not very well understood, difficult to grow high In, determine In content
- Optical, structural and electrical characteristics of InGaN are highly affected by its growth conditions

Growth Kinetics

- Difficult to grow high quality InGaN due to a few problems:
    - Large difference in interatomic spacing between InN and GaN results in a solid phase miscibility gap
    - Relatively high vapour pressure of InN compared to GaN leads to low indium incorporation in the InGaN alloy
    - Difference in formation enthalpies for InN and GaN causes a strong indium surface segregation on the growth front
- These can be minimized by optimizing growth parameters:
    - relatively low growth temperatures
    - high V/III flux ratio
    - low growth rate
    - low growth pressure
- Indium clusters tend to form on the surface, once they reach a critical size they act as sinks for additional indium atoms and can dominate the indium incorporation process – indium droplets increase with lower growth temperatures
- Increasing nitrogen can decrease indium segregation on the surface by allowing for more nitrogen bonding sites for the indium as a result of the increased # of N radicals
- Evaporation of indium from the surface will be reduced at:
    - Lower temperatures
    - Higher growth rates (atoms get trapped under growing layer)
- Lower temperature (850C to 500C) strongly increases indium incorporation but reduces material quality (due to droplets, phase separation and composition inhomogeneity) - lowering growth rate at low T can help improve the quality (more time for atoms to move)
- Lower pressure improves indium incorporation – causes red-shift and broadening of PL spectra indicating degradation of optical properties (due to inhomogeneous indium distribution)
- MOCVD is main fabrication technique but MBE is a good alternative
- If In and Ga fluxes are increased, Ga may compete to enter the bulk and displace In atoms causing a decrease in indium incorporation

Properties of InGaN

Optical

- Samples grown at high T (>750C) show near band emission, samples grown <750C are dominated by a deep level or impurity transition – H.-C. Lin paper
- Optical quality improved with decreasing inhomogeneity of indium composition
- Optical quality tends to decrease with higher indium contents

Structural Properties

- Kim reported that with increasing thickness of the GaN (from 5.6 to 22.4 nm), the abruptness of the interface between InGaN/GaN layers deteriorated
- N-polarity GaN underlayers lead to poor crystalline quality with large FWHM values on XRD peak and no PL emission in certain cases, whereas Ga-polarity GaN underlayer leads to high quality films and a much narrower PL peak

Electrical Properties

- Activation energy, Ea, of Mg acceptors decreased as indium content increased
- Studies of Mg-doped InGaN found measured hole concentration increased with higher indium
- Extremely high resistivity found for samples grown below 620C and dropped drastically above this temperature
- Resistivity decreased with increasing In content but mobility and carrier density increase with increasing In content

Vegard's Law

- Bowing parameters ranging from 1eV to 6eV have been reported – variance due to different InGaN growth conditions and measurement techniques
- "For precise determination of the composition-dependent InGaN band gap, the band gap should be measured by photoreflection or spectroscopic ellipsometry rather than from PL. This is because the InGaN near band edge PL spectrum is Stokes shifted relative to the band edge, leading to an underestimate of the energy gap"
- "The thin InGaN layer grown on GaN was greatly strained by biaxial compressive stress which caused a blue-shift of the band gap as compared to the unstrained InGaN. Therefore, the band gap of unstrained InGaN is expected to be smaller than that determined by a similar technique. Since the sources of erroneous measurements have led to the inaccuracy of the alloy composition, at present no common agreement is established for the use of Vegard's law in determination of the indium content. Furthermore, first-principles calculations found that the bowing parameter should vary significantly with composition and the claim was confirmed by the work done by Shen et al."
- XRD good for determining composition if lattice parameters are in fact relaxed, strain will cause an overestimation of the InN content
- Still debate as to true band gap of InN

XRD

- Lattice mismatch between InN and GaN is about 10%
- If thickness of InGaN on GaN is:

  - < critical thickness, InGaN will be pseudomorphically strained (in-plane lattice constant of InGaN strains to match that of GaN)
  - > critical thickness, strain relaxation occurs due to introduction of defects
- Critical thickness is approximately 75nm

Indium Segregation and Piezoelectricity

- Large Stokes shift between absorption and emission is claimed by many groups – attributed to the effect of exciton localization caused by spatial indium fluctuations or phase segregation
  - Due the large miscibility gap between GaN and InGaN
- Other groups claim the emission mechanism is due to the quantum-confined Stark effect induced by piezoelectric field resulting from strain

Complete compositional tunability of InGaN nanowires using a combinatorial approach - Kuykendall

- Propose the tenability of InGaN nanowires is due to the low process temperature and the ability of the nanowire morphology to accommodate strain-relaxed growth which decreases the tendency towards phase separation
- Lattice mismatch between GaN and InGaN lead to threading dislocations which typically act as non-radiative recombination centres
- Hydrogen is well known to affect the incorporation of indium in InGaN alloys
- No phase separation for columns with 0-60% In
- "strain relaxed growth" for epitaxial growth (critical thickness) and nanowire growth (enhances relaxation) – leads to an improvement in indium incorporation
- Believe low T (550C) and high growth rate promote formation of the non-thermodynamically-stable product
- "It is interesting to note that the commonly observed 'valley of death' drop-off in PL efficiency observed for high-indium-concentration MOCVD samples seems to be significantly diminished for these InGaN nanowires"
- Determine bowing parameter of 1.01eV and InN band gap of 1.12eV – disparate InN value in literature due to dependence of bandgap on the free-electron concentration

InGaN Material Characterization

Effects of Substrate Temperature on Indium Gallium Nitride Nanocolumn Crystal Growth – Keating (QAS Group)

- Show XRD and PL results for a range of compositions and changing substrate temperatures

Optical characterization of $In_xGa_{1-x}N$ alloys - Gartner

- Sources for other optical studies of InGaN with disagreements in band gaps and strain dependencies
- InGaN layer quality known to benefit with a GaN layer, thickness of GaN affects optical properties
- Lattice mismatch (11-13%), higher for wurtzite, leading to compressive strain layer
- Spectroscopic ellipsometry used for analysis – advantage of sensitivity of layer thicknesses to a few nm
  - Nice tight experimental paragraph on SE
- Grew 600nm thick InGaN layers ($0<x<0.14$) on GaN buffers on sapphire using MBE
- For GaN films, optical band gaps determined from the real part of the pseudo-dielectric function <e1>
  - For InGaN, e1 was calculated using a parametric model
  - Optical gap matched PL data well
- InGaN/GaN interface could have an effect on dielectric properties

- Found linear relationship for low-In content films: Eg = 3.44 - 4.5x

***Optical band gap in Ga[sub 1–x]In[sub x]N (0<x<0.2) on GaN by photoreflection spectroscopy - Wetzel**

- Photoreflection (PR) and photoluminescence (PL) on pseudomorphically strained (biaxial compression) InGaN on GaN
- PL peak redshifted 50-120mEV wrt to band gap from PR
  - Attributed to the localization of photocarriers into the electric field induced tailstates below the DOS (density of states) band gap
- Find bowing parameter of b=2.6eV for PR data (x<0.2) and be=3.2eV from PL data
  - Estimate of b=3.8eV by removing effects of strain

  Nakamura found b=1, other b values by authors

***Small band gap bowing in In[sub 1–x]Ga[sub x]N alloys - Wu**

- 240nm InGaN films (0<x<0.5) grown on sapphire with AlN buffer layer between 470-570C
- **Discussion of early InN 1.9eV band gap determinations**
- Broadening of PL curves increases with increasing Ga content
  - Film with x=0.5 – peak is at 1.2eV, 1.75eV for absorption absorption coefficient
- Sharp rise in absorption coefficient (10^5 cm^{-1} at 0.5eV above band gap) typical of direct band gap semiconductors
  - Linear section also implies direct fundamental band gap
- InN band gap of 0.77eV
- **BOWING PARAMETER b=1.43eV**
  - Fits low and high x values
  - Compositional dependent bowing parameter proposed but b=1.43eV fits entire range
- PL Stokes shift as large as 0.56eV
  - Stokes shift reaches maximum in middle of composition range
    - Indicates inhomogeneous distribution of In and Ga atoms
    - Largest concentration fluctuation and structural disorder
    - Also seen by increasing FWHM with Ga content
  - Stokes shift indicates PL is not a reliable technique to determine bowing parameter
    - Bowing parameters from PL tend to be higher (b=2.5) (ref)
- PL spectrum indicates distribution of localized states in smaller-gap regions with larger In compositions
  - Absorption transmission largely reflects density of delocalized states

Spectroscopic ellipsometry characterization of (InGa)N on GaN - Wagner

- Spectroscopic ellipsometry and PR analysis of 15-60nm thick InGaN films (0.4<x<0.1) grown on a thick GaN layer by MOCVD
- Show real part of pseudodielectric function <e1> matching PR peaks for interband transitions
  - Fourier transform filtered out Fabry-Perot oscillations due to multiple internal reflections
- PL peak Stokes shifted by 40 meV to lower energies relative to PR band gap determination

Structural and optical properties of an $In_xGa_{1-x}N$/GaN nanostructure - Korcak

- XRD, AFM, spectroscopic ellipsometry, PL tests on GaN/InGaN/GaN MQW structure for LEDs
- Used real part of pseudodielectric function <e1> to determine band gaps and indium content
- SE done from 0.59eV – 4.7 eV, PL using 55mW He-Cd laser

- **Fabry-Perot interference destroyed sharp absorption resonance behaviour of InGaN layer – looks more like my spectra**
- Concentration estimated using Kramers-Kronig at 0.12eV using a 3.8 eV Bowing parameter (ref)
- **Sharp PL peak at 2.8eV, origin of a broad yellow-band emission attributed to deep gap states formed by Ga-impurity complex, which are trapped at side faces (ref)**

Photoluminescence measurements on cubic InGaN layers deposited on a SiC substrate - Pacheco-Salazar

- In segregation leading to In clusters would provide efficient recombination centres
- Results: In-rich clusters represent a negligible volume fraction but dominate the PL emissions with a peak around 2.5eV
    - Not detectable by typical optical techniques or x-ray diffraction
    - Recombination energy not affected significantly by In content indicating insensitivity in the cluster composition to nominal indium content
- Absorption edge is dictated by the bulk material composition so it follows the expected band gaps for InGaN with a bowing parameter of 0.4 and Eg (InN)=0.6eV

***Growth and some properties of $In_xGa_{1-x}N$ thin films by reactive evaporation - Sato**

- Growth of high InN InGaN difficult due to high dissociation pressure of InN
- Grew high-In films on A_2O_3 and GaAS substrates
- Molar fractions determined by electron probe X-ray microanalyzer (EPMA)
- Vegard's Law: composition of alloys linearly proportional to lattice constants
- Crystallinity decreases with GaN increase! – attributes to non-ideal growth T for GaN (500C) since GaN has a higher melting point than InN(1700C vs 1200C)
- GaN/InN lattice mismatch is large at 10.7% (0.318nm for GaN, 0.354nm for InN) – non-uniform strains are assumed to be present leading to crystallinity deteriorations and a large Bowing parameter
- Absorption coefficients of about 10^5 cm^{-1} near absorption edges
- Use Tauc type plots (α^2 vs hv) to get band gaps, determine Bowing parameter of 1.5 eV – Bowing parameter tends to increase with lattice mismatch

***Dielectric function and Van Hove singularities for In-rich InxGa1−xN alloys: Comparison of N- and metal-face materials - Schley**

- Lowering of InN band gap from 1.9 to 0.7eV lowered bowing parameter estimations
    - Wu found b=1.4 eV for 0.5<x<1
    - author previously reported b=1.77 eV
- Discussion of N (nitrogen)-face and M (metal)-face polarity layers
- 210nm In-rich InGaN layers grown on GaN or InN buffers with sapphire substrate
  GInN buffer
- Spectroscopic ellipsometry (SE) process explained
- **Buffers result in much sharper increase in e2 and improved structural properties**
- Criticizes Tauc method for band gap determination – analyzes e2 directly
    - Shows why extrapolation method is slightly off
- Finds bowing parameter b = 1.72eV
    - Others find b=1.51, b=1.7eV and b=1.44eV (refs)
- Extracted results apply to all bulk In-rich InGaN alloys
- PR ideal method for band gap

*Indium incorporation into InGaN and InAlN layers grown by metalorganic vapour phase epitaxy - Leszczynski

- InGaN for LEDs
- Growth of high-In difficult for 3 reasons:
    - Low growth T that slows down surface-diffusion of incoming atoms and thus stimulates 3-D growth
    - Large lattice mismatch (10%) leading to In segregation, tilting of the layer planes wrt to the misoriented substrate, and defects (dislocations, cracks, pin-holes from O2)
    - Built-in electric fields in the wurtzite structure along c-direction which separate spatially electrons and holes (applies to LED more)
- **In incorporation increases with growth rate**
    - In atoms get trapped by gallium atoms and are less likely to evaporate out
    - In adatoms much more likely to evaporate (5:1 In:Ga in vapour, 1:10 in bulk)
    - All GaN adatoms become incorporated (not affected by high T up to 1050C)
- **In incorporation decreases with GaN substrate misorientation**
- Morphology differs with In incorporation

*Band gaps and lattice parameters of 0.9 um thick $In_xGa_{1-x}N$ films for 0<x<0.14 - Beach

- Strain effects can alter band gap and composition measurements
- SEM images: scanning electron micrographs – revealed 900nm thick InGaN film
- Electron microprobe used for composition measurements at 90% confidence
- Performed Hall measurements giving carrier concentration, Hall mobility and resistance
- XRD to get lattice constants – increasing linearly with GaN content
- InGaN grown on a GaN buffer layer requires about 200nm to reach its relaxed state (Parker ref)
- Electrochemical photocurrent spectroscopy used to get band gaps
- Samples showed rectifying behaviour indicating formation of Schottky junctions
- Performed PL using pulsed laser
    - **Luminescence peaks found below band gaps determined by photocurrent spectroscopy**
    - **Similar phenomenon seen by other researchers who attribute the luminescence to excitons localized in InN quantum wells dispersed throughout InGaN film**
    - **Stokes shift increases linearly as luminescence energy peak decreases (not in this study)**
- **"Band filling" term – use to indicate emissions due to classic conduction-valence emission, also interband transitions**
- Used ND filters on laser light – as attenuation increases, spectra shift their peak toward lower energies and above-gap luminescence becomes smaller relative to the peak
    - This supports band filling as cause of above-gap luminescence and suggests illumination intensity can affect InGaN band gap determination from PL

*Determination of the critical layer thickness in the InGaN/GaN heterostructures - Parker

- InGaN layers under critical layer thickness (CLT) have mismatch accommodated by elastic strain, films above CLT accommodate by a combination of strain, dislocations and 3-D growth
- Band gap of strained films expected to be higher than relaxed films due to compressive stresses in the strained films
- Peak emission redshifts as the thickness increases and is dominated by deep level emission indicating the onset of relaxation
- Power-dependent PL shows deep level emission saturation but linear relationship with peak energy
    - Therefore, it is assumed that deep level emission is defect related and high-energy peak is band edge related

- CLT at 150nm for 5% In, 60nm for 20% In, curve flattening around 40nm
- Possible defect formation at InGaN/GaN interface that dominates deep level PL emission
- Defects affect surface morphology, smooth for thin films, more 3-D for thicker films (relaxed) 10^{10} dislocations/cm for InGaN, much more than other III-V compounds

The critical thickness of InGaN on (0001)GaN - Leyer

- CLT can be measured by redshift (relaxed) and blueshift (strained) in PL, or misfit dislocations and force
    - This paper uses in-situ SE and X-ray reciprocal mapping
- X=0.315 for relaxed film, x=0.1 for strained film**,** 2 possible reasons:
    - Roughness of relaxed layer offers more indium incorporation sites
    - Gallium on strained surface has higher chance of desorption due to strain lowering the binding energy
- Determine lower CLT critical thicknesses than Parker
- Relaxed layers encourage 3-D growth, strained limits to 2-D

***Growth temperature effects on InxGa1–xN films studied by X-ray and photoluminescence - Lin**

- In difficult to incorporate due to low In dissociation temperature and high N equilibrium pressure leading to phase separation and In droplets for In-rich InGaN films
- Performs growth temperature tests
    - In increases from 0.01 to 0.28 as T decreases from 850C to 600C
    - Films grown above 750C: show consistent In fraction (low)
    - Below 700C: near band edge emission disappears and impurity transitions (IT) dominate
        - IT unaffected by temperature changes
- Chose bowing parameter b=1 (same as Nakamura) to measure indium content

Investigation on the Correlation Between the Crystalline and Optical Properties of InGaN Using Near-Field Scanning Optical Microscopy - Lin

- Good intro on In-rich growth difficulties, LED references
- Found highly crystalline regions exhibit more intense PL and longer wavelengths of emission

Compositional dependence of the strain-free optical band gap in In[sub x]Ga[sub 1−x]N layers - Pereira

- Some authors argue phase segregation is the cause of the good light emission properties of InGaN despite the large dislocation density in the active region
- PL peaks are Stokes shifted (refs) so band edge is not at peak
- Spectral broadening from PL or optical absorption hinders a clear identification of the band energy
- InGaN layers (75-500nm) were grown on sapphire via MOCVD
- Images showing difference in x calculations with relaxed vs strained (pseudomorphic)
    - Layers above CLT (relaxed) are in good agreement with Rutherford backscattering spectrometry
    - Partial strain possible
- Urbach tails found for most absorption curves

Luminescences from localized states in InGaN epilayers - Chichibu

- Nakamura used a high growth rate to suppress re-evaporation of InGaN during growth
- EL, PL and PLE spectra for 50nm thick InGaN (0<x<0.1) films

- InGaN exhibits intense EL and PL peaks despite its large threading dislocation densities
- Recombination of excitons from segregated In-rich regions source of InGaN emission

Photoluminescence from quantum dots in cubic GaN/InGaN/GaN double heterostructures - Husberg

- Performed PL and PLE tests on InGaN (x=0.09-0.33) samples
- Observed PL peak around 2.3-2.4eV regardless of In content
    - Attributed to a pseudomorphic In rich phase with x=0.56 in the InGaN layer
    - Should have an Eg of 2.13eV, 2.3-2.4eV peak is explained as the radiative recombination of excitons localized in these In-rich quantum dot structures of about 15nm
- PL peak shifts as QDs shrink with increasing In content, high density of QDs

Photoluminescence associated with quantum dots in cubic GaN/InGaN/GaN double heterostructures - Husberg

- Luminescence from InGaN QWs is redshifted from the alloy band gap measured by absorption – attributed to excitons localized in indium-rich regions
- Same results as other Husberg paper

Refractive index and gap energy of cubic $In_xGa_{1-x}N$ - Goldhahn

- Performed spectroscopic ellipsometry analysis from 1.5 – 4eV on 70-280nm thick **c-InGaN** with $0.02<x<0.18$
- Found a bowing parameter of 1.4eV – hexagonal InGaN might be higher? 3.2 or 3.8eV

$In_xGa_{1-x}N$ refractive index calculations - Anani

- III-V semiconductors have good optoelectronic properties but III-N compounds have large direct band gaps
- Thin GaN buffer layer helps reduce problems from sapphire(Al_2O_3)-GaN lattice mismatch (16%)
- Wurtzite is thermodynamically stable structure of GaN and InN (ref)
    - Zinc-blende other structure type
- Indium incorporation strongly dependent on growth rate, temperature, pressure, carrier gas and III-V ratio
- **Great information on bowing parameter, InN band gap**
    - Mean value of bowing is 2.17eV
- Refractive index has a reverse proportional relation with the gap of a material and also expresses the ratio between light celerity in a vacuum and in the considered material
    - Wavelength reversely directly proportional to band gap: $Eg=1.24/\lambda$
    - Therefore, n is directly proportional to wavelength with a parabolic form
    - Provides refractive index as function of x for InGaN
    - Bowing equation can be used for n as well
- Decrease in index of refraction in first quarter of molar fraction likely due to lattice mismatch which disturbs first few layers of InGaN where x is not so important, as InN increases the natural tendency of decreasing band gap and thus increasing n takes over

Optical Properties of Strained AlGaN and GaInN on GaN - Takeuchi

- Nitrides have difficulty in growing large bulk-crystals, lack of substrates with matching lattice constants and thermal expansion coefficients and difficulty in obtaining p-type films
    - Use of thin GaN buffer layer helps these problems significantly
- InGaN = ternary alloy, grown using MOPVE with a thickness of 40nm and $x<0.2$, 2um GaN layer

- Used PL for band gaps and XRD for composition
    - Found a bowing parameter of 3.2eV, reasonable since lattice constant difference is 11%
- InGaN was strained by biaxial compressive stresses (under CLT), therefore PL was blueshifted wrt unstrained InGaN
    - Band gap of strained InGaN film is higher than unstrained

***Optical and microstructural properties versus indium content in In[sub x]Ga[sub 1−x]N films grown by metal organic chemical vapor deposition - Gokarna**

- 200nm-thick InGaN films (0.7<x<0.14) grown on GaN/sapphire using MOCVD
- Good introduction
- Analyze samples using SIMS, XRD, AFM, TEM, SEM and spectroscopic ellipsometry
- Thickness of InGaN film slightly changes indium content
- **SIMS: indium segregated to surface**
- Ellipsometry from 0.7eV to 4eV with a step of 0.01eV, model layers stack as series of films with different optical properties, good info on ellipsometry
    - Error: +/-0.02 and 0.01 for n and k respectively, from covariance matrix method (90% confidence)
    - n: 2.3 to 2.8, k: 0 to 0.33
- **Compare SE plots: broad hump due to alloy scattering and composition fluctuations (inhomogeneity)**
    - Urbach tail for x>0.14 – due to point defects, disordered structure, excitonic transitions or inhomogeneous strain

Time-Resolved Photoluminescence Studies of Indium-Rich InGaN Alloys - Guang-De

- Performed PL tests on 100nm In-rich InGaN alloys (x=0.32) grown on 1um GaN on sapphire by MOCVD
- Perform intensity and temperature dependent studies
    - Two emission lines (1.83eV and 2.67eV) from phase separation
    - Emission Intensity and peak position energy forms direct relationships with excitation intensity
    - Increase in peak energy attributed to week Coulomb screening of the quantum confined Stark effect induced by the weak piezoelectric field due to 100nm thickness of samples
- PL decay lifetime behaviour photo-excited carriers can be transferred within the low indium regions as well as from low indium region to high indium region

Correlation of crystalline defects with photoluminescence of InGaN layers - Faleev

- Typically epitaxially grown InGaN has a threading dislocation density between 10^{8} – 10^{10} cm^{-2}
- 50-400nm InGaN grown on 2um GaN by MOCVD, x=0.12+/ 0.005
- Claim InGaN critical thickness is 8nm (2 refs)
    - However only partial relaxation in the 200nm and 400nm thick samples
- Detailed talk about defects during growth
- PL: intensity drops after 200nm thickness due to the creation of nonradiative recombination centres in the bulk InGaN
    - PL intensity increased from 100nm to 200nm as nonradiative recombination on edge segments of dislocation loops in the volume were compensated by increased thickness of the layer
- No phase separation

MOVPE growth and Mg doping of InxGa1-xN (x<0.4) for solar cell - Horie

- XRD used to analyze InGaN and Mg-doped InGaN films

    - FWHM increases with In content
    - Metal source rate does not change composition much at high temperatures (>800C)
- Mg-doping causes phase separation more quickly

Cathodoluminescent investigations of In$_x$Ga$_{1-x}$N layers - Domracheva

- Looked at emissions of InGaN epilayers with different In contents and thicknesses
- Good info on critical layer thickness for strain relief
- High In content (>20%) layers characterized by full phase separation

High-quality In$_{0.47}$ Ga$_{0.53}$ N/GaN heterostructure on Si(111) and its application to MSM detector - Chuah

- Old paper but good general InGaN info
- "The InGaN diffraction peak is very sharp, which indicate that the In composition is of high uniformity in the layer"
- Reasons for difficulties growing high In-content InGaN
    - Interatomic spacing InN and GaN differences resulting in solid-phase miscibility gap
    - Vapour pressure differences
    - Formation enthalpy differences
    - Thermodynamic instability of InN
- High amount of defect densities due to above growth problems

Magnesium Doping of In-rich InGaN - Chang

- Grew a 200-300nm Mg-doped InGaN layer on thick GaN buffer layer at 550C via MOVPE
- Samples grown at higher than 550C exhibited lower In incorporation due to high evaporation rate of InN
    - Lower T (550C) samples showed more narrow FWHM
    - Differences between nominal and actual In composition greater at Ga-rich end
- Higher temperatures helped create p-IngGaN at up to x=0.5
- Attributed to enhanced incorporation of Mg into favourable sites for subsequent activation to occur

Optical studies on a coherent InGaN/GaN layer - Correia

- Grew a 200-300nm Mg-doped InGaN layer on thick GaN buffer layer at 550C via MOVPE
- Samples grown at higher than 550C exhibited lower In incorporation due to high evaporation rate of InN
    - Lower T (550C) samples showed more narrow FWHM
    - Differences between nominal and actual In composition greater at Ga-rich end
- Higher temperatures helped create p-IngGaN at up to x=0.5
- Attributed to enhanced incorporation of Mg into favourable sites for subsequent activation to occur

Band Gap of Hexagonal InN and InGaN Alloys - Davydov

- Found InN band gap to be 0.7eV
    - Higher InN band gaps may be due to oxynitrides forming
- Optical study (PL) of In-rich InGaN ($0.36<x<1$) on sapphire finding a Bowing parameter of about 2.5eV
- High absorption coefficient typical of interband absorption in direct-band-gap semiconductors
- at large electron concentrations the absorption edge is much higher than fundamental band gap
- PL band peak is redshifted from absorption edge by a value of about one half FWHM of PL band
    - Shift consistent with Burstein-Moss effect due to charge carrier concentrations
- **Detailed PL analysis with absorption theory**

Thermal Annealing of Cubic-InGaN/GaN Double Heterostructures - Husberg

- Evidence of In-rich clusters in c-InGaN/GaN structures increasing radiative recombination of electron-hole pairs in the form of QDs (10nm) or QWs
  - Peak at 2.3eV
- PL and Raman measurements indicate In-rich phase is stable up to about 700C, out-diffusion of In into c-InGaN found at 750C
  - Forms new layer with PL at 2.8eV (x=0.2)
- **Spontaneous formation of nm-sized compositional inhomogeneities on h-InGaN surfaces observed (ref)**

Pulse laser assisted MOVPE for InGaN with high indium content - Kawaguchi

- Grew InGaN film (x=0.53) using pulsed laser
- In-content fluctuation regions contributed to broadening of the PL peak
- Film grown without laser has different peak, attributed to high carrier concentration originating from defects

InGaN/GaN quantum-well nanocolumn crystals on pillared Si substrate with InN as interlayer - Hu

- Column crystal growth effective way to relax strain between GaN and Si substrate
  - InN and Si lattice mismatch = 9%, GaN and Si lattice mismatch = 17%, thermal expansion coefficients are also closer – helps with strain
  - Improves internal QE
- GaN columnar LEDs fabricated commercially
- **GaN thermal expansion coeff: 5.59E-6, InN: 4.0E-6,** Si: 2.59E-6
  - **InN easily evaporates above 550C¸ used GaN layer on top to suppress evaporation during 900C growth**
- Created flower-like structures
- PL and emissions analyzed

Formation of InGaN nanorods with indium mole fractions by hydride vapor phase epitaxy – Kim

- InGaN nanorods avoid threading dislocations (and subsequently non-radiative recombination) that plague typical InGaN/GaN layers
- Grew 70nm wide, 2um long hexagonal nanorods on sapphire
- SEM and CL tests

CVD growth of InGaN nanowires – Cai

- Good intro with many sources to nanorods
- In depth analysis of CVD-grown nanowires
- GaN can be grown at 950C and InN at 550C, InGaN in between – found 600C to work best
- Helical (under some conditions) and straight nanowires grown
  - Increase in Ga shortens length of wires, In does opposite**,** at same ratio higher rates shortened length
- **When In:Ga source rate ratio is 1:1, EDX determined a 10% In content, when 1:3 it's 30%, 3:1 is 20%**
  - No explanation for strange ratios
- Needed Au catalyst for nanowire growth

InGaN nanopillars grown on silicon substrate using plasma assisted molecular beam epitaxy - Vajpeyi

- Good intro with many sources to nanorods
- In depth analysis of CVD-grown nanowires

Control of electron density in InN by Si doping and optical properties of Si-doped InN - Higashiwaki

- InN band gap estimates differ due to varying crystalline qualities and background electron densities of InN
- **Estimated intrisinc InN band gap to be 0.6-0.65 eV** with conduction-band renormalization effect (20meV)

Optical properties of InN-the bandgap question - Monemar

- In depth review of InN band gap question
    - Value of 0.7eV most consistent
- Use of Tauc plots (a^2 vs eV)

GaN: from fundamentals to applications - Pankove

- Practical applications for III-nitrides (GaN): U-V detectors, x-ray detectors, LEDs/laser diodes, surface acoustic wave devices, cold cathodes (NEA), heterojunction bipolar transistors
    - Info on each
- Good for background on III-Vs

<u>InGaN Photovoltaics</u>

***Photoelectric characteristics of metal/InGaN/GaN heterojunction structure - Sun**

- Multi-junction cell references
- p/n tunnelling junction (TJ) key for full-spectrum InGaN solar cells
    - TJ must be of low impedance to get a low photogenerated electrodynamic potential and have matching lattice constant etc.
- Difficult to get high-quality p-doped InGaN
- InN and GaN heterojunction exhibits strong rectifying behaviour like a Schottky junction
- InGaN/metal junction forms Schottky contact a seen by rectifying I-V curve
- Produced photocurrent spectra
    - **Contribution of GaN to PC is two orders of magnitude higher than that of InGaN due to poorer crystalline quality due to compositional homogeneity and higher defect density**
    - Shows likely recombination at InGaN/GaN iterface
- InGaN layer of 110nm seen via XRD to be compressively strained

***Design and characterization of GaN⁄InGaN solar cells - Jani**

- Nitrides advantages for photovoltaics:
    - Wide band gaps
    - Low effective mass of carriers
    - High mobilities
    - High peak and saturation velocities
    - High absorption coefficients

    - Radiation tolerance (increases lifetime in space)
    - **Can achieve 50% MJ solar cells**
- High-band gap InGaN used as active material in absorber layer of violet and blue LEDs
- 200nm InGaN layer made between p-GaN and n-GaN layers
- Absorption coefficient at 10-5 cm-1 near band edge (3.2eV)
    - Indicating 99% of light above band gap is absorbed in first 500nm
- To maximize absorption in InGaN layer, top p-GaN layer limited to 100nm which is still enough to provide charge to the junction and top metal contacts
- Cell demonstrates Voc as high as 2.4eV and FF=78-80%, IQE=60%, resistances reported
- **III-V nitrides are highly pyroelectric meaning large polarization charges at heterojunctions significantly influence electric field and mobile carrier distributions**
    - **Due to high resistance, difficulty obtaining high p-type doping and low-resistance Ohmic contacts**
- **Phase separation reduces Voc of cell but also enhances recombination decreasing photogenerated current**

***Growth And Characterization Of Ingan For Photovoltaic Devices - Boney**

- Good intro on InGaN growth difficulties
    - Segregation partially due to higher surface mobility of indium atoms compared to gallium, difference in vapour pressures and resulting narrow window of conditions for good growth
- Besides growth, other problem is still a lack of knowledge and info on InGaN optoelectronic properties (majority carrier mobility, minority carrier lifetime and absorption coefficient)
- Grew 300-700nm thick InGaN films from x=0.15 to x=1
- Contactless electroreflectance (CER) used to get band gaps, **PL peaks were Stokes shifted by 175-250 meV**
- **PL: single peak indicates one phase, breadth of emission (similar to FWHMs of XRD) indicate small compositional variations in the layers causing localized emission phenomenon**
- Cells: current (up to 2.2mA/cm2) generally increased with indium content but other characteristics degraded
    - Degradation seemingly due to increased threading dislocation density from lattice mismatch

High internal and external quantum efficiency InGaN/GaN solar cells - Matioli

- Good intro on InGaN solar cells
- Non-radiative recombination centres (NRCs) reduce carrier lifetimes and reduce solar cell short circuit
- Grew n-GaN/InGaN/p/GaN p-i-n cells (60nm thick InGaN)
- IQE measured as ratio of EQE and light absorption curves
    - IQE up to 97% found in InGaN region
        - Indicates efficient conversion of absorbed photons into electrons and holes and efficient transport of these carriers outside the device
    - But light absorption is less than 60%
    - Making surface rough increased light absorption to 80%
        - Reduces reflection and increases optical path length by changing incident angle (Yablonovitch ref)
    - 76-78 % fill factors

***Modeling of InGaN/Si tandem solar cells - Hsu and Walukiewicz**

- Good MJ cell intro
    - Traditional III-Vs limited to bandgaps less than 2.2eV, InGaN up to 3.4eV
    - Structural defects and poor quality growth may limit InGaN from being commercial
- Theoretical modelling of tandem cell

- Current matching via thickness and InGaN band gap adjustments
- Si valence and InGaN (x=0.46) conduction bands align avoiding the need for heavy doping (tunnel junctions) to create low-resistance junctions (forms Ohmic junction)

Characteristics of InGaN designed for photovoltaic applications - Trybus

- Estimates n for InGaN: 2.3<n<2.8

Growth, fabrication, and characterization of InGaN solar cells - Chen

- GaInP /GaAs/ Ge cells have achieved over 30% efficiency
- P-type InGaN doping difficult because conduction band is 0.9eV lower than the Fermi level stabilization energy (E_{Fs})
- Made an p-i-n InGaN (x=0, 0.2, 0.3) cell
- No sign of phase separation in XRD
- Report I-V curves, resistances, FF=61% and Voc =2.5 eV (for GaN)
- Lower turn-on voltage, higher output as In content increases
- Compared to GaN cell, InGaN cells have much higher current leakage
  - **Likely due to numerous defects, strong surface electron accumulation as In content rises**

InGaN/GaN multiple quantum well solar cells with long operating wavelengths - Dahal

- Advantages of InGaN:
  - Direct band gap range
  - High carrier mobility
  - Drift velocity
  - Radiation resistance
  - Optical absorption of 10^5 cm-1 near band edge
- Phase separation mainly a problem in middle composition range
- PL: intensity at x=0.4 one hundredth of x=0.2
- Made cell with InGaN/GaN MQW layer sandwiched between p- and n-GaN layer
- Voc for x=0.3 and x=0.5 are 2.0eV and 1.8eV respectively (close to band gap)
  - FF=60%, EQE = 40% at 420nm and 10% at 450nm

Optimization of GaN Window Layer for InGaN Solar Cells Using Polarization Effect - Jani

- Window layers serve to passivate the top junction surface and generate a front-surface field to minimize front surface recombination
- Strain generates piezoelectric polarization
  - Modelled band diagrams shown
- Strained n-GaN window layers are used (opposed to normal p-GaN) which enhance tunnelling of holes from the p-InGaN junction due to the piezoelectrically induced sheet charge and strong band bending at the heterointerface
- Cells demonstrated improved Voc (2eV) and FF (68%)

Improved Conversion Efficiency of GaN/InGaN Thin-Film Solar Cells - Ray-Hua Horng

- InGaN cells show less than 2% efficiency (sources)

- InGaN crystalline defects typically include v-shaped pits, phase separation and dislocations which deteriorate PV performance by increasing leakage current and recombination
- Relaxation of InGaN layer (above critical thickness) leads to dislocations

Photovoltaic Effects of InGaN/GaN Double Heterojunctions With p-GaN Nanorod Arrays - Dong-Yan Zhang

- P-GaN(nanorods)/InGaN/n-GaN cell made
- III-V nitrides have a refractive index of about 2.5 which according to Fresnel equates to 18% reflection
- Maximum EQE is 55.5% **-** result of p-GaN nanorod array
- If grown bottom up (VLS growth), nanorods reduce material cost – 18% of planar film of same thickness

InGaN quantum dot photodetectors - Ji

- Mentions InGaN phase separation resulting in In-rich clusters which act as quantum dots (QDs)
- Ways to improve light to dark current ratios – use metal with larger Schottky barrier height on InGaN

Analytical model for the optical functions of amorphous semiconductors from the near-infrared to ultraviolet: Applications in thin film photovoltaics - Ferlauto (+Pearce)

- Fit optical properties from T+R data for a-Si films using parametric models
- Used Tauc plot method to determine band gaps
- Created database of parameters in the model used

The Effect of Grain Boundaries on Electrical Conductivity in Thin GaN Layers - Salzman

- Phenomena of electrical transport in GaN:
    - Persistent and non-exponentially decaying photoconductivity
    - Large ultra-violet photo-response gain
    - A wide range of reported electron mobility values and an increase in mobility with increasing carrier concentration
    - How can a material with so many defects exhibit large optical gain?

Photoconductivity in nanocrystalline GaN and amorphous GaON - Koo

- Absorption and photoconductivity tests
    - Photoconductivity and photocurrent on the order of nA (hundreds, tens respectively)
- Very detailed analysis

Nanocolumns/Nanowires

***InGaN nanorod arrays grown by molecular beam epitaxy: Growth mechanism structural and optical properties - Wu**

- Great nanocolumn (nanorod) paper – **columns look just like Moshe's**
- Show good SEM images of single-crystal nanocolumns as a function of time
- Nanocolumn growth: along the c-axis
- "It is well known that misfit accommodation can take place through the onset of islanding and generating surface roughness in strained epitaxial systems"

- Growth mechanism:
  - InGaN film grown pseudomorphically on sapphire until critical thickness (~30nm) is reached
  - Once at CT, 3D islands form and InGaN nanorods start to nucleate on the rough islands
  - Coalescence of a few nanorods may occur after long growth periods
- Red-shift (smaller band gap) occurs as the nanorods grow – attributed to partial release of compressive stress

***Gallium nitride nanorod arrays as low-refractive-index transparent media in the entire visible spectral region - Chen**

- Grew GaN nanorods (400-2000nm tall with 50%+ fill factor) by PE-MBE
- Reflectivity is the characterization technique employed (spectrophotometer used)
- **Great information and equations for effective refractive index and reflectivity**
- **Good information on GaN nanorod growth and properties**
  - Mean diameter and aerial density of GaN nanorods depend on growth temp and III/V ratio while nanorod height depends on growth time
  - Uniform height: optically flat interface with ambient air
  - Coalescence occurs with increasing growth time
- **Explanation of ImageJ-like analysis to determine fill factor from SEM images**
- Attribute reflectivity oscillations to Fabry-Perot microcavities
- “The effective refractive index depends not only on the lateral coverage but also on the vertical profile of GaN nanorod arrays”

$\alpha = 4\pi k_{eff} / \lambda$ – **absorption to extinction coefficient relationship**

$R = |r|^2 = [(n_{eff}-1)^2 + k^2_{eff}] / [(n_{eff}+1)^2 + k^2_{eff}]$ **- Fresnel eq with $n_{air} = 1$**

$f_{GaN}[(n^2_{GaN} - n^2_{eff}) / (n^2_{GaN} + 2n^2_{eff}) + (1-f_{GaN})[(n^2_{air} - n^2_{eff}) / (n^2_{air} + 2n^2_{eff}) = 0$ – **Bruggemann EMA**

--In-rich InGaN difficult to grow at high quality and to dope—

Formation of InGaN nanorods with indium mole fractions by hydride vapor phase epitaxy - Kim

- InGaN for LEDs
- **Threading dislocations from lattice mismatch are non-radiative recombination centres**
  - **TDs can be all but nonexistent in nanorods**
- Nanorods - average diameter: 70nm length: 2 um
- In mole fractions became saturated at x=0.2

InGaN-Based Nanorod Array Light Emitting Diodes - Hwa-Mok Kim

- Formation of dislocation-free InGaN/GaN MQWs in nanorods
  - Potential for negligible non-radiative recombination loss – higher efficiency
- Greater SA of nanorods better for emission

Rapid growth and characterization of InN nanocolumns on InGaN buffer layers at a low ratio of N/In - Pan

- Grew InN nanocolumns on InGaN substrate
- Good info on InN and nanocolumns
  - InN – smallest band gap of III-nitrides at 0.65eV, large lattice mismatch with common substrates, impurity-prone surface, tight growth range of 460C to 490C

- Nanocolumns – quantum confinement effect may yield novel functions and improve performance

Selective area metalorganic molecular-beam epitaxy of GaN and the growth of luminescent microcolumns on Si/SiO[sub 2] - Guha

- Use of metallic Ga for GaN growth leads to nonselective growth with nucleation of polycrystalline GaN on the SiO2
- Describes growth mechanism started with Ga-balling
- CL tests show the sparse nanocolumns luminesce indicating surface non-radiative recombination is not a significant issue

Periodic Si Nanopillar Arrays Fabricated by Colloidal Lithography and Catalytic Etching for Broadband and Omnidirectional Elimination of Fresnel Reflection - Wang

- NWs act as an EMA with intermediate refractive index, n, which avoids abrupt transition at the air/substrate interface
    - Reduces reflection and enhances light absorption
- Most suppressive if pillars spaced out at wavelength of incident light
- ***Equation to calculate n_{eff}* using Bruggeman EMA – requires fill ratio of pillars to total substrate and index of refraction for substrate**

Watching GaN Nanowires Grow - Stach

- Self-catalytic VLS GaN nanowire growth (12um thickness)
- Nucleation and growth of GaN nanowires from liquid Ga droplets
- Ga droplets help decompose GaN, vapour species then redissolves into the Ga liquid droplets supersaturating them and establishing a liquid-Ga/solid-GaN interface
- Also possible is a direct vapour-solid process

Direct Observation of Vapor−Liquid−Solid Nanowire Growth - Wu

- Schematic illustration of VLS growth process (use image)
    - Three stages: metal alloying, crystal nucleation and axial growth
- Ge nanowires grown using Au as catalyst
- Thickness directly related to catalyst clusters (droplets) but grow even thicker than initial droplets due to the alloying process

Three-dimensional nanopillar-array photovoltaics on low-cost and flexible substrates - Fan

- Good general intro on solar cells
- Information in nanowire benefits, VLS growth, flexibility, enhanced carrier collection efficiency

Self-catalyzed growth of GaAs nanowires on cleaved Si by molecular beam epitaxy - Jabeen

- Grows wires in two different ways
- Good paper, gives good sources on NW growth

Crystallographic alignment of high-density gallium nitride nanowire arrays - Kuykendall

- Lattice constant of GaN: 3.19A

- Useful for nanocolumn info, VLS growth

Single Nanowire Photovoltaics - Tian

- Makes radial and axial Si nanowires with p-i-n junctions
- Performs all common PV characterization tests

Thesis - First, single-crystalline materials with low defect densities, as demonstrated in the structures of Fig. 2, are beneficial for PV applications because defects can function as deleterious recombination centers that reduce open circuit voltages and short-circuit currents

Toward the Lambertian Limit of Light Trapping in Thin Nanostructured Silicon Solar Cells - Han

- Uses wave optics to maximize light absorption in array designs

Growth of InN nanocolumns by RF-MBE - Nishikawa

- Grown on sapphire substrate
- In droplets formed first at low T (200C), then InN nanocolumn growth from 380 to 500C
- SEM and XRC of the growth process
- *Proves InN nucleation with In droplet formation and the subsequent nitriding treatment of In droplets is essential for InN nanocolumn growth*

Ultradense, Deep Subwavelength Nanowire Array Photovoltaics As Engineered Optical Thin Films - Tham

- Complex modelling of Si nanowire arrays
- Uses ellipsometry and TEM
- Uses open source implementation of Moharam's formulation of the rigorous coupled wave analysis (RCWA) to get optical properties of the film and nanowires
- (not clearly useful)

Plasmon effects on infrared spectra of GaN nanocolumns - Iwanaga

- Doped Mg atoms act as compensation centres for residual donors as well as scattering centres for conduction electrons
- Mg doping on GaN nanocolumns
- Suggest nanocolumn sidewalls play a major role for scattering processes of conduction electrons

Luminescence properties and defects in GaN nanocolumns grown by molecular beam epitaxy - Calleja

- Morphology and quality of the GaN layers depends strongly on the III/V ratio
- Columnar growth more likely to occur under N-rich conditions (far from stoichiometric (Ga=N))
- PL peaks around 3.4 eV
- Detailed explanation of PL peaks to GaN morphology

Stimulated emission from GaN nanocolumns - Kikuchi

- Nanocolumn: nanocrystal with a small diameter and a large aspect ratio
- PL on GaN nanocolumns grown with plasma
- PL peak at 370nm and 360nm depending on excitation intensity
- Nanocolumns became thinner as temperature increased (best at 850C)
- Peak intensity 30x higher for GaN nanocolumns compared to MOCVD-GaN layer

- Good optical quality indicates the GaN nanocolumns are almost dislocation free and the surface non-radiative recombination rate is very low

Two-dimensional exciton behavior in GaN nanocolumns grown by molecular-beam epitaxy - Na

- Ga-balling model for nanocolumn growth
- PL on GaN nanocolumns

Structural and optical characterization of intrinsic GaN nanocolumns - Sanchez-Paramo

- Growth of III/V on Si is appealing due to the substrate's doping capability, crystal quality, thermal stability and potential integration of these inexpensive substrates – self-assembled nanocolumns could become a cheap alternative to device fabrication
- Broad, low-energy bands produced from bottom of nanocolumn, higher energy from its length – believe low-energy emissions due to defects at Ga-rich interface between columns and compact layer
- Growth carried out under N-rich conditions to get columnar growth
- Absence of strain is independent of the substrate employed and use of buffer layer
- Emissions from column much more intense than compact layer

The Controlled Growth of GaN Nanowires - Hersee

- TEM and PL data on GaN nanowires grown using a selective mask

Structural and optical properties of GaN nanocolumns grown on (0001) sapphire substrates by rf-plasma-assisted molecular-beam epitaxy - Sekiguchi

- GaN nanocolumns can significantly reduce the dislocation densities that plague the quantum efficiency of planar GaN films
- GaN columns grown on differing thickness of AlN buffer layers
- SEM and TEM images
- Obtained RT-PL spectra – much higher emission for nanocolumns compared to HVPE-grown GaN, same peak so columns can be considered freestanding and not strained

InGaN and Light Emitting Diodes (LED)

Light-Emitting Diode Extraction Efficiency - Boroditsky (+Yablonovitch)

High-power InGaN single-quantum-well-structure blue and violet light-emitting diodes - Nakamura

Origin of high oscillator strength in green-emitting InGaN/GaN nanocolumns - Kawakami

- Made for LEDs
    - Device performance rapidly degrades increasing x if wavelength is beyond blue-green
    - Likely due to quantum confinement Stark effect (QCSE) caused by strong piezoelectric and spontaneous polarization in strained InGaN/GaN quantum wells (QWs)
- Nanocolumns individually tested by PL
    - Finds range of 2.2 to 2.6 eV indicating meaning broad InGaN PL spectrum is due to compositional fluctuations of individual nanocolumns

- **Carrier localization as well as the piezoelectric polarization field is suppressed in InGaN/GaN nanocolumns**

Growth Kinetics and Microstructure

Growth and properties of InAlN nanocolumns emitting in optical communication wavelengths - Kamimura

- InAlN (x=0.71-0.92) nanocolumns grown on Si via RF-MBE
- In composition determined by XRD
- SEM images
- Obtained RT-PL spectra

Plasma ehnancement of metalorganic chemical vapor deposition and properties of Er2O3 nanostructured thin films - Giangregorio

- Two T-L oscillators used to model ellipsometry
- Index of refraction (n) increased with increasing thickness
- Tauc gaps found from ellips data

Temperature induced shape change of highly aligned ZnO nanocolumn - Park

- Nanocolumns become thinner and longer as T increases
- Lower temperature – triangular, columnar grains (as opposed to nanocolumns)

AlGaN Nanocolumns Grown by Molecular Beam Epitaxy: Optical and Structural Characterization - Ristic

- Actual Al content higher than nominal due to Ga desorption at high temperature (In desorption explains lower indium contents)
- N-rich growth regime leads to nanocolumns but also implies a drastic reduction of the growth rate
- Sources for GaN column diameters as related to III:V ratio
- Ga-balling and VLS growth suspected growth mechanisms
- SEM, CL, Raman and PL measurements taken

Optical Modelling of Thin Film Microstructures

Improved refractive index formulas for the AlxGa1-xN and InyGa1-yN alloys - Laws

- Estimates n for InGaN: 2.3<n<2.8
  - N is higher as In content increases
- Quantum confinement affects electronic structure, dielectric function and refractive index of InGaN quantum wells so they differ from the bulk
- Phase separation and pzioelectric-field induced Stark effect also increase inhomogeneities

Photovoltaic Behavior of Nanocrystalline SnS/TiO2 - Wang

- Tauc plot looks similar to InGaN films
    - Tauc's law: $(\alpha h\nu)^n = A(E_g - h\nu)$ n = ½ for indirect transmission
- Quantum confinement due to particle size (small) is considered to result in an enlargement of the band gap