REMOTE PLASMA ENHANCED CHEMICAL VAPOUR DEPOSITION GROWTH AND CHARACTERISATION OF POLYCRYSTALLINE INDIUM NITRIDE THIN FILMS

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Abstract

This thesis investigates the growth temperature dependent apparent band-gap shift in polycrystalline indium nitride (InN) thin-films that were grown using the remote-plasma-enhanced chemical vapour deposition (RPECVD) method.

The polycrystalline InN thin-films were grown between 200 and 570 °C on various types of substrates, including *c*-plane sapphire, n-type silicon, gallium nitride template, borosilicate glass, Schott glass, and cover glass (microscope glass slide cover slip). Trimethylindium and nitrogen gas were used as the precursors for indium and nitrogen, respectively. Nitrogen gas was also used as the carrier gas for the indium precursor vapour. Reactive nitrogen radicals were produced by a remote nitrogen-plasma discharge, which was induced by a microwave electromagnetic field with a frequency of 2.45 GHz.

A comprehensive range of sample characterisation analyses was conducted. The sample optical properties were examined by optical transmission measurements. The electronic characteristics were determined by Hall effect measurements. The physical and morphological characteristics were analysed by scanning electron microscopy (SEM), X-ray diffraction (XRD) and electron-backscattered diffraction (EBSD). Compositional characterisation was carried out using X-ray photoelectron spectroscopy (XPS), low-energy electron-induced X-ray emission spectrometry (LEXES), elastic recoil detection analysis (ERDA), and secondary ion mass spectroscopy (SIMS). Finally, electronic structure characterisation was performed using synchrotron soft X-ray absorption (SXA) and soft X-ray emission (SXE) techniques.

The research outcomes are presented in six parts and include eleven publication works, which were either published or submitted for publication.

The growth kinetics of these polycrystalline InN thin-films were found to be sensitive to the growth conditions used, indicating a reaction limited process. This resulted in a regime where the thin-film characteristics had a strong dependency on growth temperature. The measured apparent band-gap was between ~ 0.9 and ~ 2.3 eV. This phenomenon was hypothesised to originate from the combined effects of changes in the In-N bonding characteristics and the presence of an increased free electron density in the material. The InN films with apparent band-gaps < ~ 1.7 eV appeared to have an ionic-like bonding characteristic, while the samples with > ~ 1.8 eV were suggested to have a more covalent-like bonding characteristic. Thus, they should be treated as two different electronic materials.

Declaration

This thesis is submitted according to the regulations for the degree of Doctor of Philosophy by Research in the Department of Physics and Astronomy, Faculty of Science at Macquarie University. The thesis contains original work performed by me. Several parts of this thesis represent a collaborative work with my supervisors and other research institutions. They have been acknowledged and their contribution is recognised in the section where their assistance was received. I declare that the research work described herein has not, either in whole or in part, been submitted for a higher degree to any other university or institution.

Patrick P Chen

24 October 2011

Declaration of Collaborations

I declare that the PhD candidate, Patrick P. Chen, whom I have co-supervised during his PhD candidature, has truthfully represented his contribution to the papers that he has authored and co-authored as described in this thesis. Patrick Chen's thesis therefore provides a true representation of his work towards the Doctor of Philosophy by Research in the Department of Physics and Astronomy, Faculty of Science at Macquarie University.

Professor K. Scott A. Butcher

Honorary Associate, Macquarie University

Publications

The following publications listed in Roman numerals are presented in their published form in this thesis, and were either published or submitted for publication during the period of candidature for the degree. These relevant papers are part of the distinct contribution to the knowledge of the thesis. A United States Patent Publication on method and apparatus for growing group (III) metal nitrides by RPECVD is presented in Appendix A. Several works conducted prior to the commencement of this research have also been published during the period of candidature, and are presented in Appendix B.

Publication I (primary author):

P. P.-T. Chen, K. S. A. Butcher, M. Wintrebert-Fouquet, and K. E. Prince, "***Properties of InN grown by remote plasma enhanced chemical vapour deposition***", 2004 Conference on Optoelectronic and Microelectronic Materials and Devices (COMMAD 2004), Brisbane, Australia, 8-10 December 2004, IEEE COMMAD 2004 Proceedings, pp. 85-88.

Publication II (co-author):

K. S. A. Butcher, M. Wintrebert-Fouquet, **P. P.-T. Chen**, K. E. Prince, H. Timmers, S. K. Shrestha, T. V. Shubina, S. V. Ivanov, R. Wuhrer, M. R. Phillips, and B. Monemar, "***Non-stoichiometry and Non-homogeneity in InN***", physica status solidi (c), 2 (2005) 2263-2266.

Publication III (co-author):

K. S. A. Butcher, M. Wintrebert-Fouquet, **P. P.-T. Chen**, R. Wuhrer, and Matthew R. Phillips, "***Revisiting electrochromism in InN***", physica status solidi (c), 2 (2005) 2293-2296.

Publication IV (co-author):

S. K. Shrestha, H. Timmers, K. S. A. Butcher, M. Wintrebert-Fouquet, and **P. P.-T. Chen**, "***Nitrogen depletion of indium nitride films during Elastic Recoil Detection analysis***", Nuclear Instruments and Methods in Physics Research B, 234 (2005) 291-307.

Publication V (co-author):

K. S. A. Butcher, H. Hirshy, R. M. Perks, M. Wintrebert-Fouquet, and **P. P-T. Chen**, "***Stoichiometry effects and the Moss-Burstein effect for InN***", physica status solidi (a), 203 (2006) 66-74.

Publication VI (co-author):

H. Timmers, K. Scott A. Butcher, S. K. Shrestha, **P. P.-T. Chen**, M. Wintrebert-Fouquet, and R. Dogr, "***Compositional and structural characterization of indium nitride using swift ions***", Journal of Crystal Growth, 288 (2006) 236-240.

Publication VII (primary author):

P. P.-T. Chen, K. S. A. Butcher, M. Wintrebert-Fouquet, R. Wuhrer, M. R. Phillips, K. E. Prince, H. Timmers, S. K. Shrestha, and B. F. Usher, "***Apparent band-gap shift in InN films grown by remote-plasma-enhanced CVD***", Journal of Crystal Growth, 288 (2006) 241-246.

Publication VIII (co-author):

K. S. A. Butcher, A. J. Fernandes, **P. P.-T. Chen**, M. Wintrebert-Fouquet, H. Timmers, S. K. Shrestha, H. Hirshy, R. M. Perks, and Brian F. Usher, "***The nature of nitrogen related point defects in common forms of InN***", Journal of Applied Physics, 101 (2007) 123702.

Publication IX (co-author):

M. Wintrebert-Fouquet, K. S. A. Butcher, **P. P-T. Chen**, and R. Wuhrer, "***Nitride film growth morphology using remote plasma enhanced chemical vapor deposition***", physica status solidi (c), 4 (2007) 2285-2288.

Publication X (primary author):

P. P.-T. Chen, J. E. Downes, A. J. Fernandes, K. S. A. Butcher, M. Wintrebert-Fouquet, R. Wuhrer, and M. R. Phillips, "***Effects of crystallinity and chemical variation on apparent band-gap shift in polycrystalline indium nitride***", Thin Solid Films, 519 (2011), 1831-1836.

Publication XI (primary author):

Patrick P.-T. Chen, James E. Downes, K. Scott A. Butcher, Marie Wintrebert-Fouquet, Yufeng Zhang, Kevin E. Smith, and Brian F. Usher, "***X-ray studies of the electronic structure of nitrogen-rich polycrystalline indium nitride thin-films grown by RPECVD***", submitted for publication.

Publication XII (co-author):

Kenneth Scott Alexander Butcher, Marie-Pierre Francoise Wintrebert ep Fouquet, **Patrick Po-Tsang Chen**, John Leo Paul Ten Have, and David Ian Johnson, ***Method and apparatus for growing a group (III) metal nitride film and a group (III) metal nitride film***, United States Patent Publication, Publication Number: US2008/0272463 A1, November 6, 2008.

Symbols Used in This Work

Some of the symbols have been assigned more than one meaning in this thesis, and are redefined in the relevant chapters and sections.

a	edge length of the basal hexagon in the wurtzite structure (Å)
AC	alternating current
$Area_{bulk}$	area under the SIMS MCs^+/Cs^+ curve contributed from the bulk of the material
$Area_{surace}$	area under the SIMS MCs^+/Cs^+ curve contributed from the near-surface layers
$Area_{total}$	total area under the SIMS MCs^+/Cs^+ curve
AT	atomic percentage
B	magnetic field
c	height of the hexagon prism in the wurtzite structure, or speed of light
CB	conduction band
CBM	conduction band minimum
C_{MO}	molar content of metalorganic
$C_{standard}$	standard molar concentration of the Ideal gas law
d	interplanar spacing between successive atomic planes in the crystal, or film thickness
DC	direct current
DI	deionised water
e	electron, or electron charge
E	electric field, or photon energy
EBSD	electron backscatter diffraction
E_F	Fermi level
E_g	band-gap energy (eV)
E_{Hall}	Hall field
ERDA	elastic recoil detection analysis
g	gas physical state

GaN	gallium nitride
h	Planck's constant
HT	high temperature
$h\nu$	photon energy (eV)
I	electric current, or transmitted light intensity through the film
III	group three elements of the periodic table
In	indium
In^*	excited indium state
In^+	indium ion
In_N	indium on nitrogen antisite substitution
InN	indium nitride
I_o	incident monochromatic light intensity
l	liquid physical state
LEXES	low-energy electron-induced X-ray emission spectrometry
LI-CVD	laser-induced chemical vapour deposition
LI-RPE-CVD	laser-induced remote-plasma-enhanced chemical vapour deposition
LT	low temperature
M	element of interest
MFC	mass flow controller
MO	metalorganic
n	number of moles, or order of diffraction, or refractive index
N	neutral ground state nitrogen atom
N^-	nitrogen anion
$N(^4S)$	neutral nitrogen ground state atom
N^+	nitrogen ion
N_2	neutral nitrogen molecule
$N_2(^5\Sigma_g^+)$	excited nitrogen precursor molecule
$N_2(a^1\Pi_g)$	excited metastable nitrogen molecule of 8.54 eV
$N_2(A^3\Sigma_u^+)$	excited nitrogen molecule of 6.2 eV
$N_2(B^3\Pi_g)$	excited nitrogen molecule of 7.4 eV
N_2^*	excited nitrogen molecule
N_2^+	molecular nitrogen ion
N_2^M	excited metastable states of nitrogen molecule
n_a	refractive index of air

N_c	effective conduction band density of states (cm^{-3})
n_e	electron carrier concentration (cm^{-3})
N_{In}	nitrogen on indium antisite substitution
n_m	refractive index of medium
ODS	optical density squared
O_N	oxygen on nitrogen lattice site substitution
P	pressure
$P(N_2)$	nitrogen carrier gas line pressure
PBN	pyrolytic boron nitride
$P_{carrier}$	carrier gas pressure
P_{MO}	metalorganic partial pressure
PL	photoluminescence
psi	pounds per square inch
$P_{standard}$	standard pressure of the Ideal gas law
P_{total}	equilibrium vapour pressure
RF	radio frequency
R_H	Hall constant
RPE-CVD (RPECVD)	remote-plasma-enhanced chemical vapour deposition
RT	room temperature
s	solid physical state
S	uncorrected percentage transmission data point
S_{bulk}	bulk segment of SIMS depth profile
sccm	stand cubic centimetre per minute
SEM	scanning electron microscopy
SIMS	secondary ion mass spectroscopy
$S_{surface}$	initial decreasing segment of SIMS depth profile
SXA	soft X-ray absorption
SXE	soft X-ray emission
T	temperature
T_G	growth temperature
T_M	melting temperature
TMG	trimethylgallium
TMI	trimethylindium

TMI^*	excited states of trimethylindium molecule
$T_{standard}$	standard temperature of the Ideal gas law
v	frequency, or vapour physical state
V	group five elements of the periodic table, or voltage, or volume
Va_{In}	indium-site vacancy
Va_N	nitrogen-site vacancy
VB	valence band
VBM	valence band maximum
V_{Hall}	Hall voltage
VPE	vapour phase epitaxy
$V_{standard}$	standard molar volume of the Ideal gas law
x	x-axis
x_b	reference depth below the surface of sample
XPS	X-ray photoelectron spectroscopy
XRC	X-ray rocking curve
XRD	X-ray diffraction
y	y-axis
y_b	intensity of the SIMS MCs^+/Cs^+ depth profile at a reference depth x_b
z	z-axis
%T	percentage transmission
$\%T_c$	corrected percentage transmission
α	absorption coefficient
Γ	centre of the first Brillouin zone
ψ	psi-axis, or polar angle
ω	omega-axis, or Bragg angle with respect to the incident and correction angles
ϕ	phi-axis
λ	wavelength
θ	Bragg angle
θ_c	correction angle
μ_H	Hall mobility ($cm^2 \cdot V^{-1} s^{-1}$)
θ_i	incident angle
Γ_1^c	bottom of conduction states at the centre of Brillouin zone for InN
Γ_6^v	top of valence band states at the centre of Brillouin zone for InN

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