Leveraging off-stoichiometry to defeat n-type degeneracy in zinc tin nitride

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Non-Stoichiometric Compounds VI
September 7th, 2016
Introduction: Zn-IV-N$_2$ Materials

- Part of II-IV-V$_2$ class
  - Analogs of III-Vs
- Could fill gaps in III-N functionality
  - Bandgaps convenient for visible light applications (solar, three-color LEDs)
  - Small lattice mismatch between members = opportunity for alloys
- Properties similar to III-Ns
  - Wurtzite structure
  - Ionic character = possible defect tolerance

Prior work on ZnSnN$_2$:
2008: First computational work on ZnSnN$_2$ [Paudel et al., PRB, 2008]
2013: First synthesis of ZnSnN$_2$ – degenerate doping [Lahourcade et al., Adv. Mat., 2013]
Introduction: ZnSnN$_2$

The Challenge:
Degenerate n-type carrier density $\sim 10^{20}$ cm$^{-3}$
Must suppress donor defect formation: $V_N$ and $O_N$
Combinatorial RF Co-Sputtering

- High throughput synthesis and characterization
- $V_N \rightarrow$ nitrogen plasma source
- $O_N \rightarrow$ fast deposition rate and reactive nitrogen
- Off-Stoichiometric $\rightarrow$ defect compensation

Chamber Geometry


Courtesy of Chris Caskey, PhD
Doping Control with Off-stoichiometry

- **Doping control** achieved via off-stoichiometry while maintaining crystal structure

- **Doping control**: off-stoichiometry
  - 15-20% excess zinc = $2 \times 10^{18}$ electrons/cm$^3$
  - Mobility > 1 cm$^2$/Vs for $T_G > 200^\circ$C
  - Dense, columnar growth with wurtzite XRD

- ** Carrier Density / cm$^3$**
  - $10^{18}$ to $10^{21}$

- **Mobility (cm$^2$/Vs)**
  - 0.1 to 10

- **Zn/(Zn+Sn) / at%**
  - 0.3 to 0.8

- **Color = growth T**
  - 35-340$^\circ$C

- **Intensity (arb.)**
  - 200ºC, 0.50
  - 230ºC, 0.60
  - 230ºC, 0.40
  - 230ºC, 0.50

- **A. Fioretti et al J. Mater. Chem. C, 2015, 3, 11017**
Zn\(_{1+x}\)Sn\(_{1-x}\)N\(_2\) : Defect Compensation

- Disordered Zn\(_{1+x}\)Sn\(_{1-x}\)N\(_2\) mobility increases with increased off-stoichiometry
- Mobility and carrier density inversely proportional as a function of zinc at%
- Suggests defect compensation or complexing leads to carrier density reduction


Reduction in carrier density with higher zinc content likely due to defect compensation
Going Further
Playing Tricks with Hydrogen...

Defeating Compensation in Wide Gap Semiconductors by Growing in H that is Removed
James A. Van Vechten*, J. David Zook1, Robert D. Horning1 and Barbara Goldenberg1
Center for Advanced Materials Research, Oregon State University, Corvallis, Oregon 97331-3211, USA
1Sensor and System Development Center, Honeywell Inc., Bloomington, Minnesota 55420, USA
(Received April 27, 1992; accepted for publication July 18, 1992)

Role of hydrogen in doping of GaN
Jörg Neugebauera) and Chris G. Van de Walleb)
Xerox Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto, California 94304
(Received 30 November 1995; accepted for publication 23 January 1996)

Hole Compensation Mechanism of P-Type GaN Films
Shuji Nakamura, Naruhiro Iwasa, Masayuki Senoh and Takeshi Mukai
Nichia Chemical Industries, Ltd., 491 Oka, Kaminaka, Anan, Tokushima 774
(Received January 13, 1992; accepted for publication February 15, 1992)

Lowest carrier density yet reported for zinc tin nitride films
Hydrogen in ZTN: Proposed Mechanism

A. N. Fioretti et al, submitted to Advanced Materials
Zn$_{1+x}$Sn$_{1-x}$N$_2$ : Minority Carrier Lifetime

Low Temperature PL

Corrected Intensity (a.u. x10$^4$)

- Exciton
- DAP

Annealed 400°C, 6h

Energy (eV)

PL Counts

Time / ns

Sample response
Instrument response

Tail lifetime: 1.42 ns

Minority carrier lifetime > 1 ns measured by TRPL.

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Summary

Two orders of magnitude with off-stoichiometry alone

Defect compensation is the likely mechanism

Added hydrogen paired with anneal = $10^{16}$ cm$^{-3}$
Acknowledgements
Thank you!

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The diagrams illustrate the relationship between stoichiometric and Zn-rich conditions with respect to the difference in Fermi level ($\Delta \mu_N$) and the energy difference ($E - E_{VBM}$). The graphs show the changes in $\Delta H_D$ as a function of $E - E_{VBM}$, with distinct lines representing $\text{Sn}_\text{Zn}$, $\text{Zn}_\text{Sn}$, and $V_N$ in both stoichiometric and Zn-rich conditions.

Stoichiometric:
- $\Delta \mu_N = 0$

Zn-rich:
- $V_N$

The diagrams suggest that the behavior of $\Delta H_D$ changes significantly between the two conditions, with different slopes and intercepts for the lines representing the different compounds.
Hydrogen Counts / arb.

Normalized Depth

Hydrogen Detected / cnts

Hydrogen Supplied / Torr

Zn/(Zn+Sn) = 0.68

As Deposited

Annealed

Hydrogen Detected / cnts

Hydrogen Supplied / Torr

Hydrogen Counts / arb.

Normalized Depth

(a)

(b)
Abs. Coeff. (cm$^{-1}$)

Photon Energy (eV)

PL Intensity (arb.)

NREL/CSM

Exciton

DAP

Calculated
RT Absorption
Low T Emission

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