9-7-2016

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

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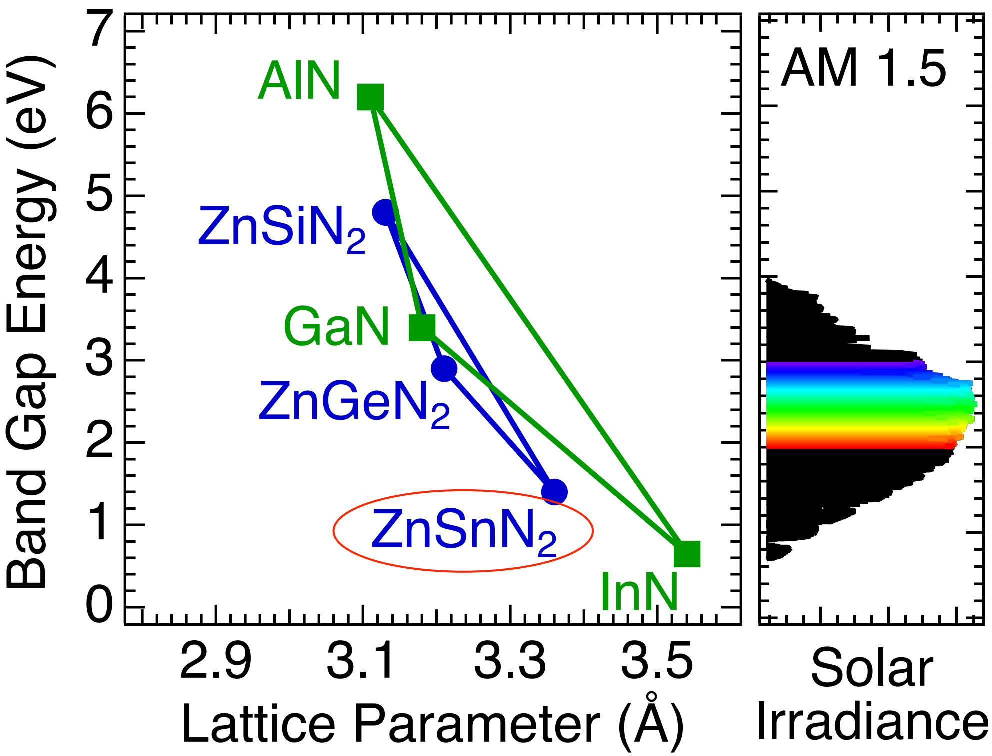
Leveraging Off-Stoichiometry to Defeat N-Type Degeneracy in Zinc Tin Nitride

Angela N. Fioretti, Andriy Zakutayev, Eric S. Toberer, Stephan Lany, and Adele C. Tamboli

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

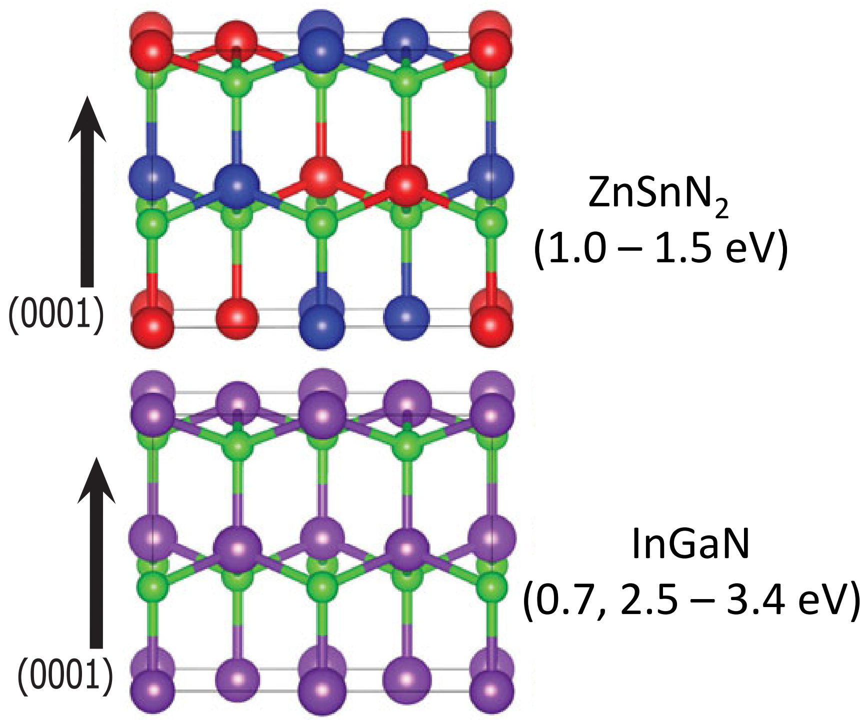
$ZnSnN_2$ in particular is a promising candidate for solar absorber applications

Prior work on $ZnSnN_2$:

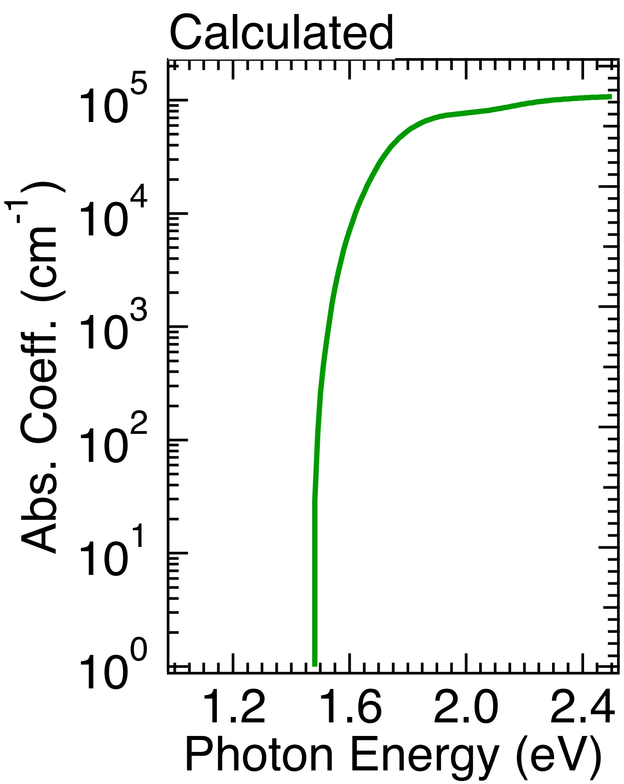
2008: First computational work on $ZnSnN_2$ [Paudel *et al., PRB,* 2008]

2013: First synthesis of $ZnSnN_2$ – degenerate doping [Lahourcade *et al., Adv. Mat.*, 2013]

Introduction: $ZnSnN_2$



Narang *et al.*, *Materials Views*, 2014



The Challenge:

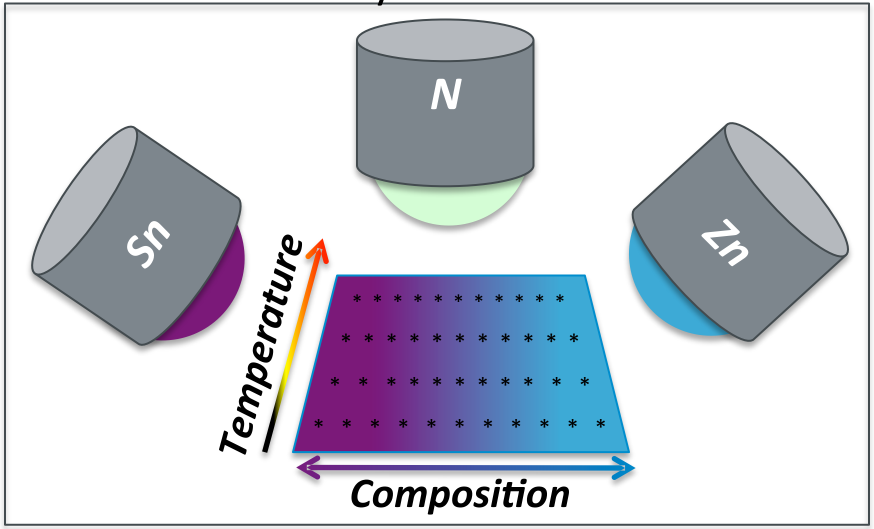
Degenerate n-type carrier density ~ 10^{20} cm^{-3}

Must suppress donor defect formation: **V_N and O_N**

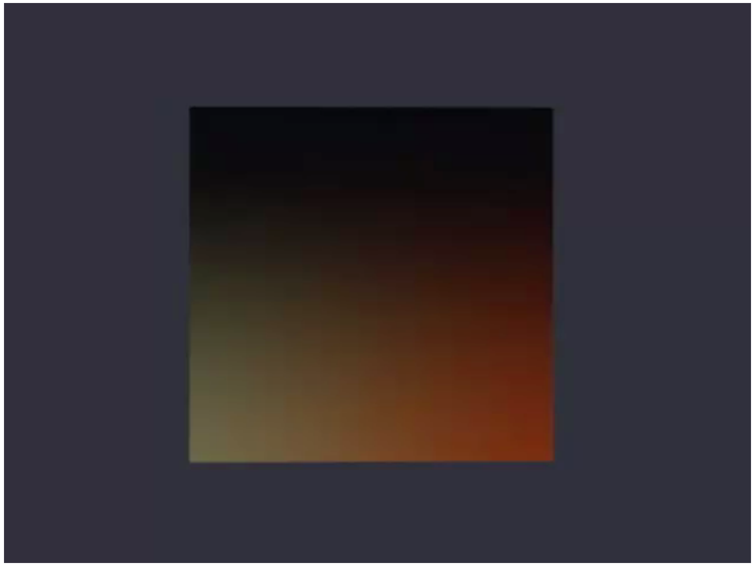
Combinatorial RF Co-Sputtering

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

Chamber Geometry

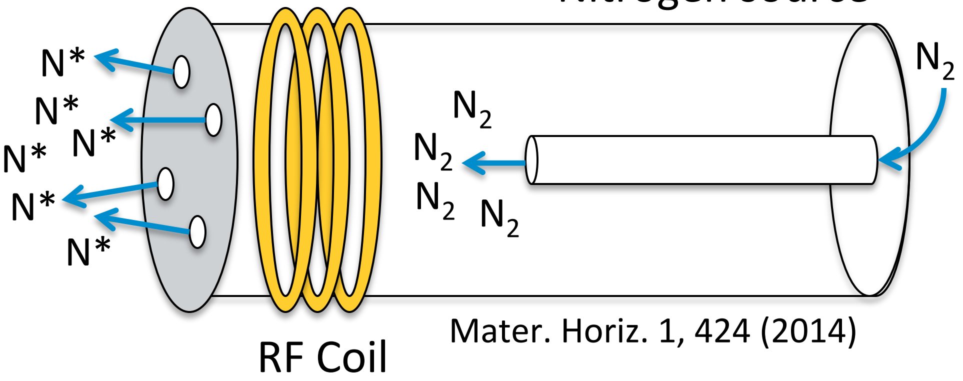


J. Mater. Chem. C, 3, 11017 (2015)



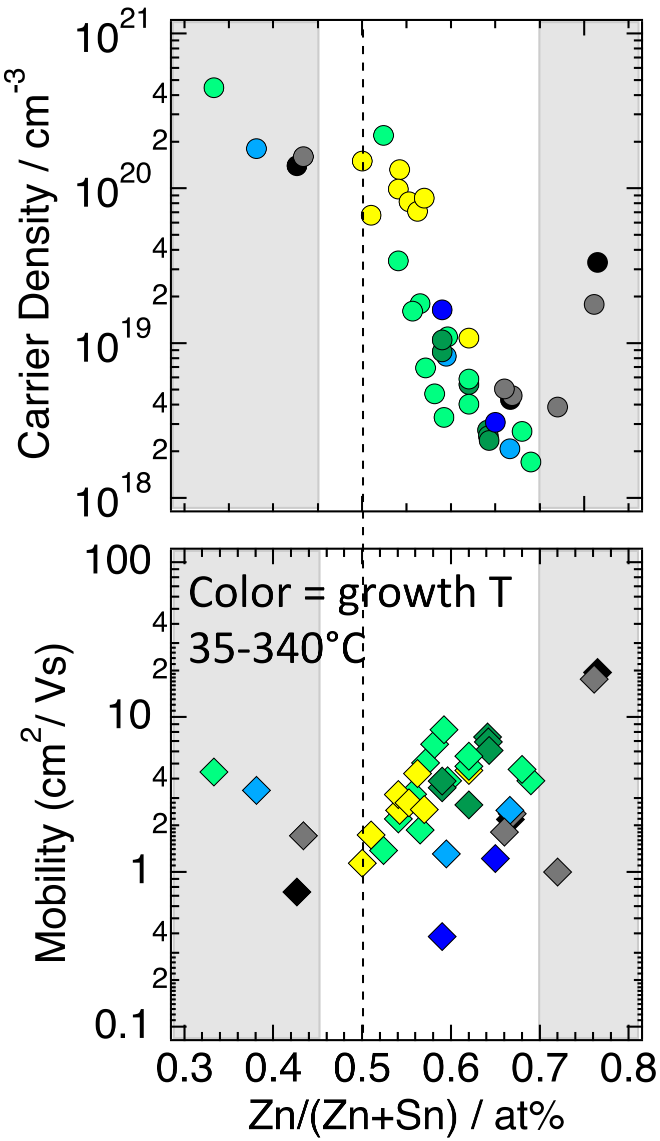
Courtesy of Chris Caskey, PhD

Nitrogen source



Mater. Horiz. 1, 424 (2014)

Doping Control with Off-stoichiometry



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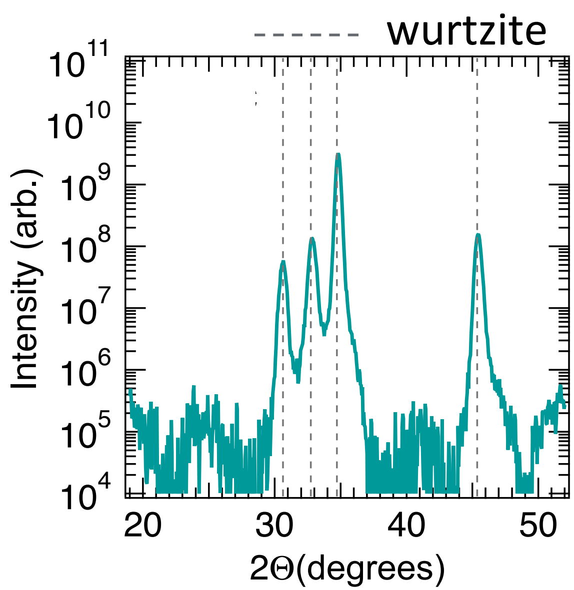
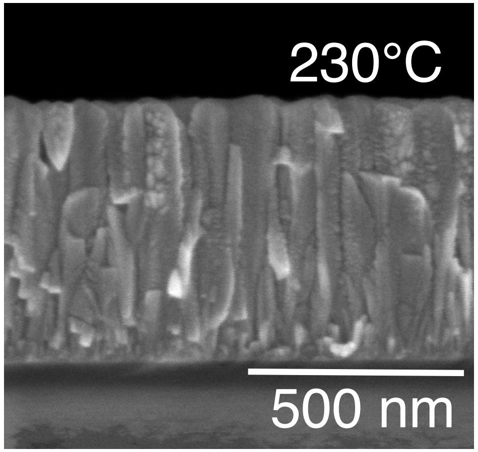


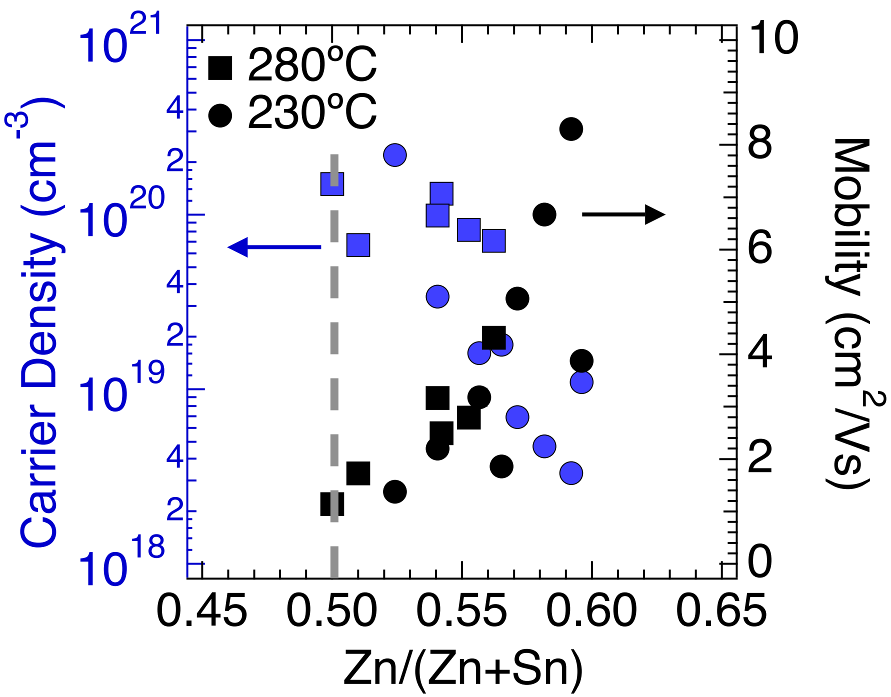


Doping control: off-stoichiometry

- 15-20% excess zinc = 2×10^{18} electrons/cm^3
  - Mobility > 1 cm^2/Vs for T_G > 200°C
- Dense, columnar growth with wurtzite XRD

Doping control achieved via off-stoichiometry while maintaining crystal structure

$Zn_{1+x}Sn_{1-x}N_2$: Defect Compensation



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- 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

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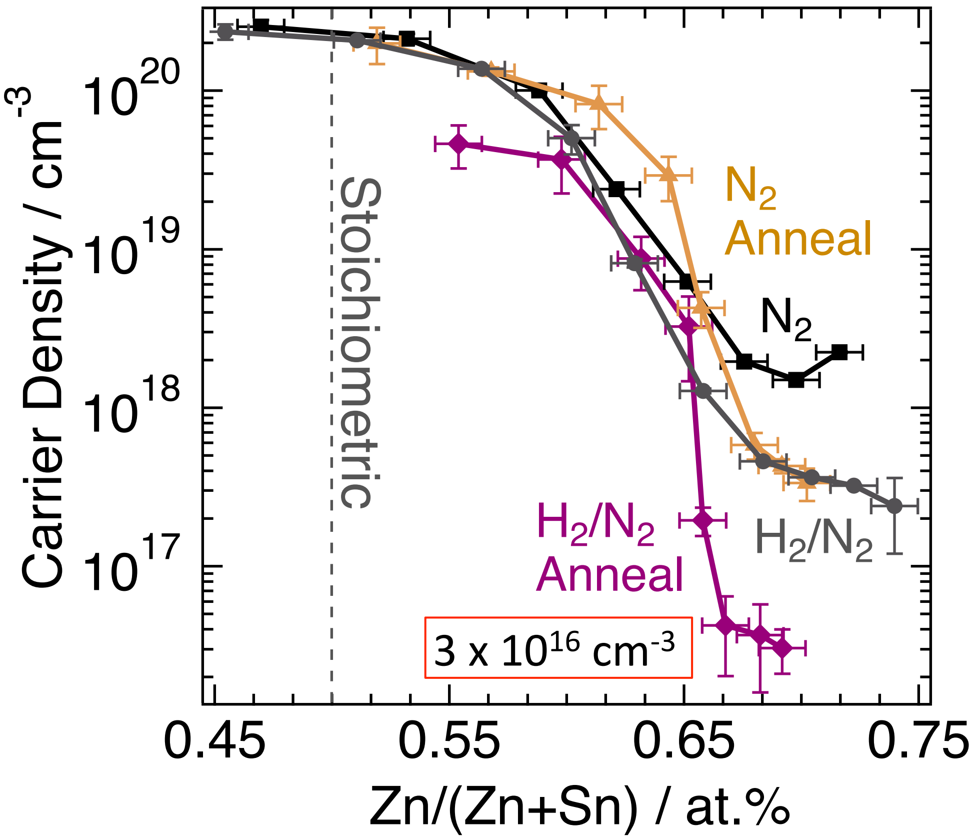

Defeating Compensation in Wide Gap Semiconductors by Growing in H that is Removed

James A. Van VECHTEN*, J. David ZOOK[1], Robert D. HORNING[1] and Barbara GOLDENBERG[1]
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(Received April 27, 1992; accepted for publication July 18, 1992)

Role of hydrogen in doping of GaN

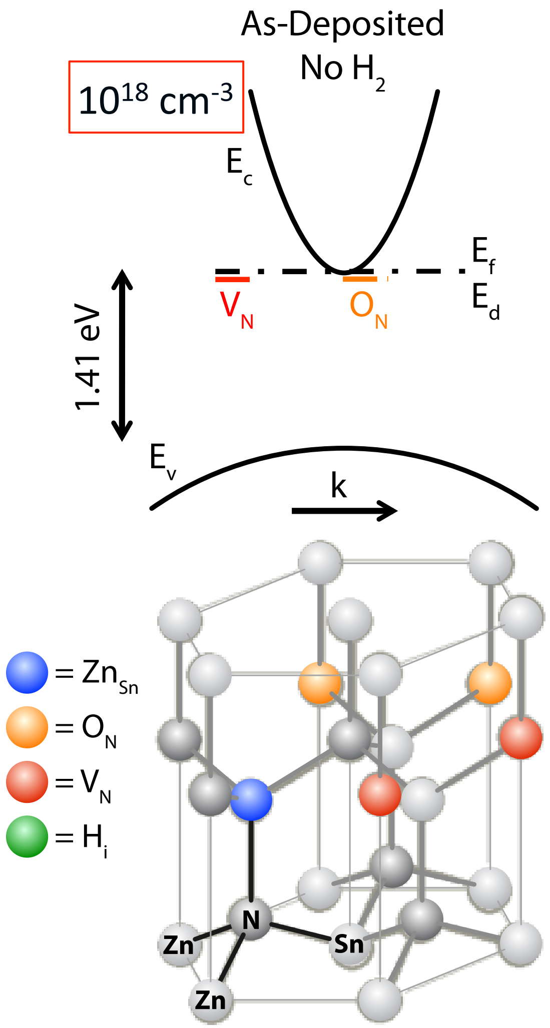
Jörg Neugebauer[a)] and Chris G. Van de Walle[b)]
Xerox Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto, California 94304
(Received 30 November 1995; accepted for publication 23 January 1996)

Hole Compensation Mechanism of P-Type GaN Films

Shuji NAKAMURA, Naruhito IWASA, Masayuki SENOH and Takashi 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



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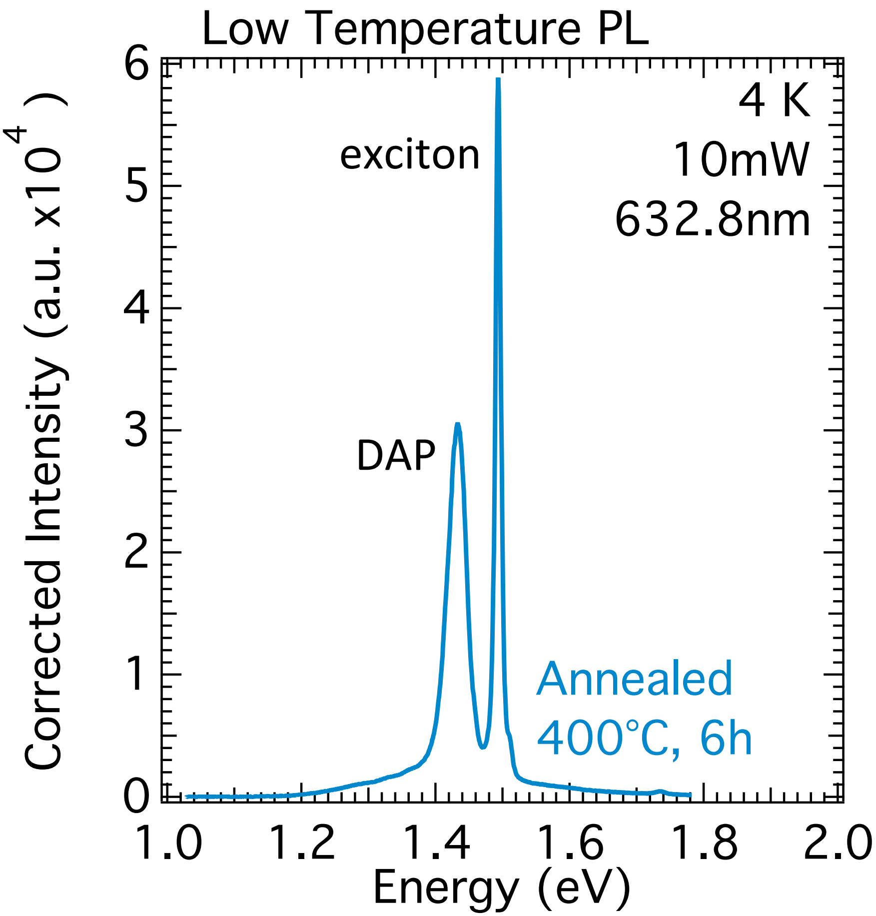
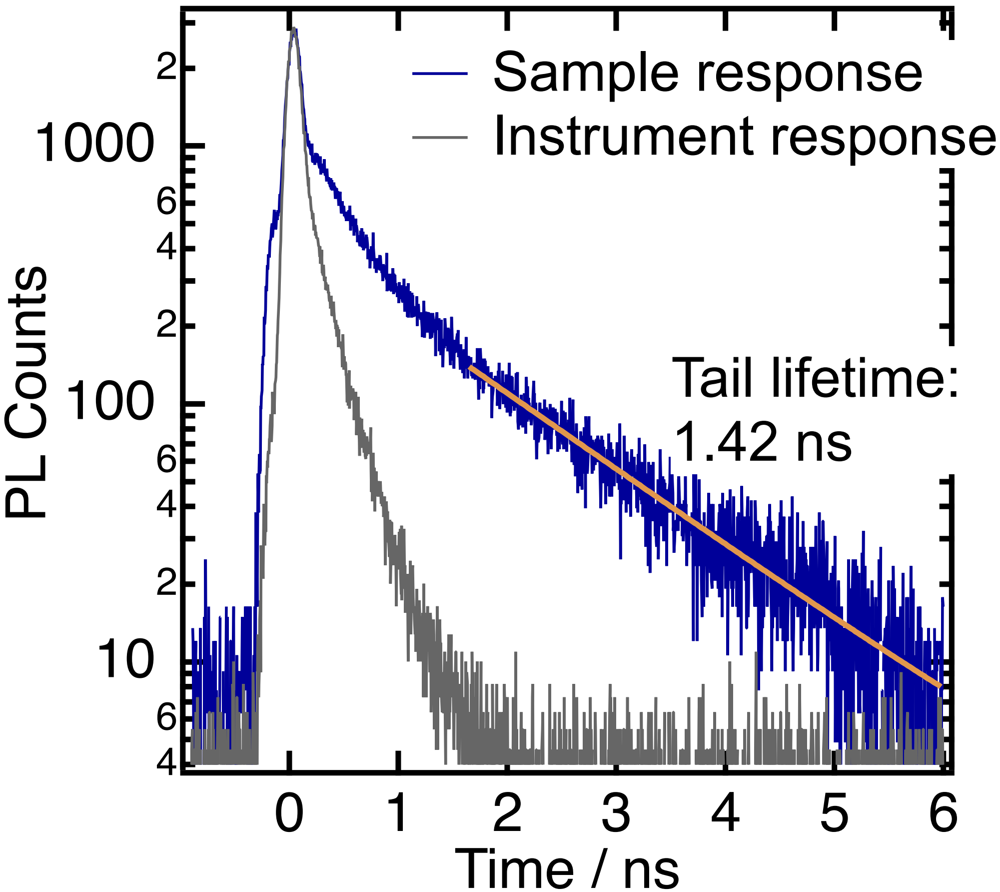
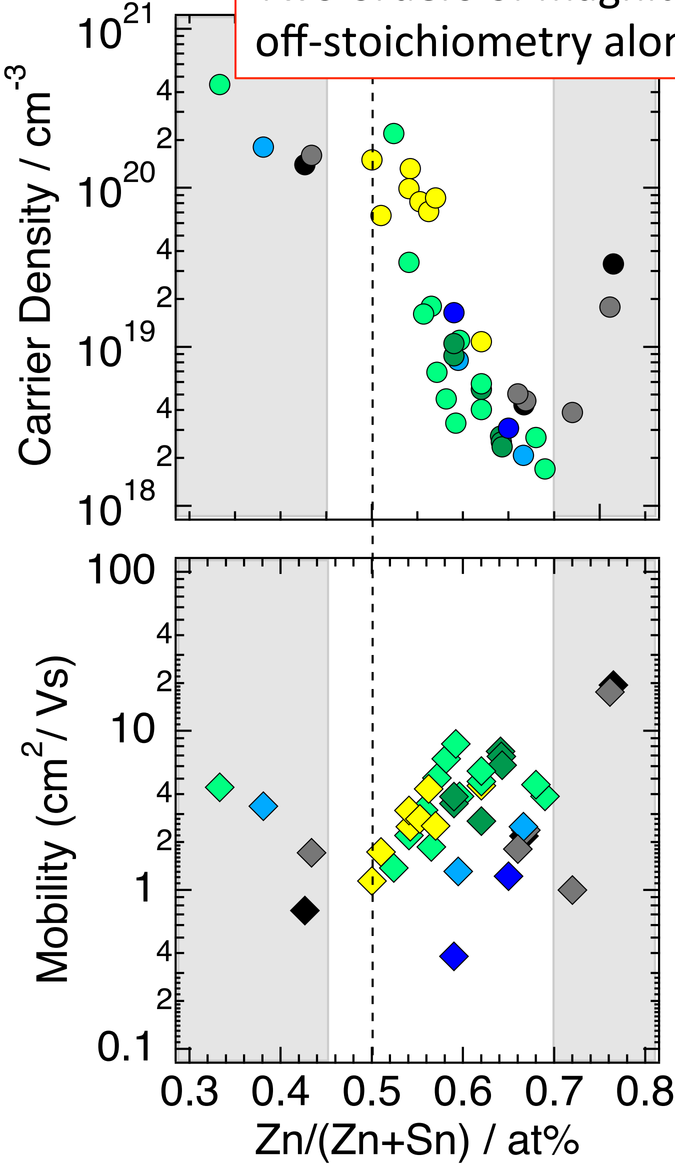
$Zn_{1+x}Sn_{1-x}N_2$: Minority Carrier Lifetime



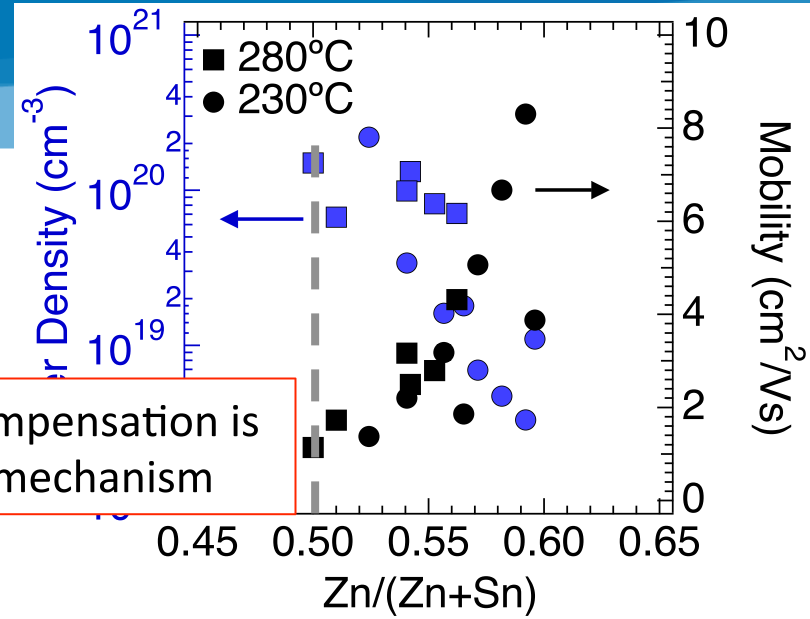


Minority carrier lifetime > 1 ns measured by TRPL.

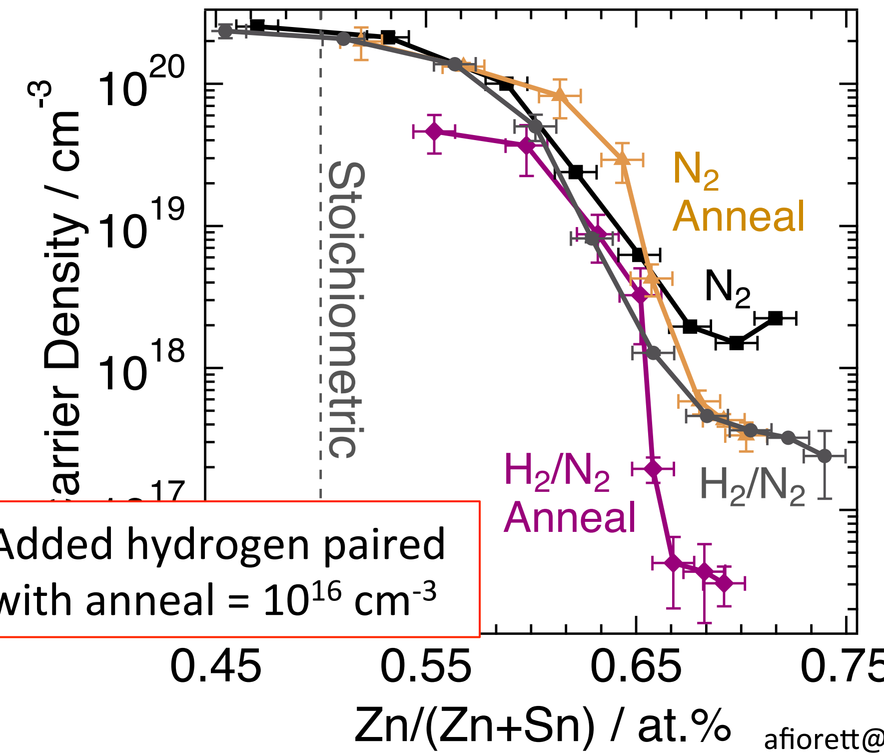
Summary



Two orders of magnitude with off-stoichiometry alone



Defect compensation is the likely mechanism



Added hydrogen paired with anneal = 10^{16} cm^{-3}

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Acknowledgements

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Thank you!

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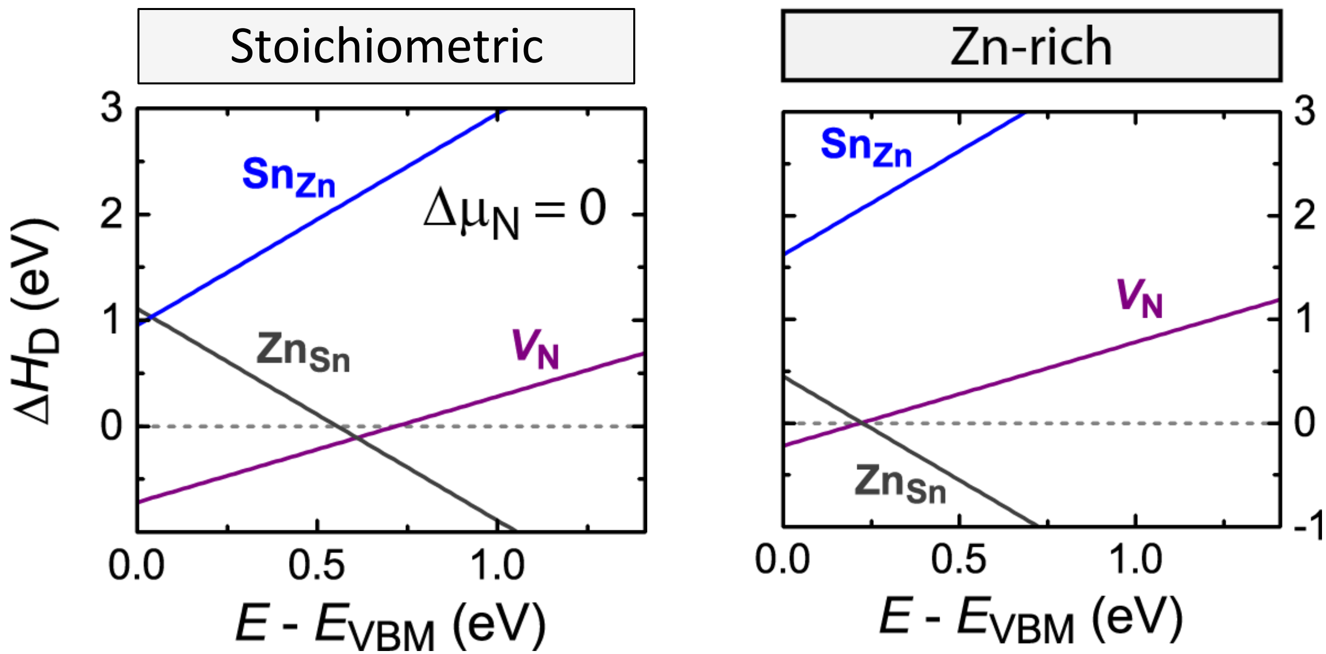
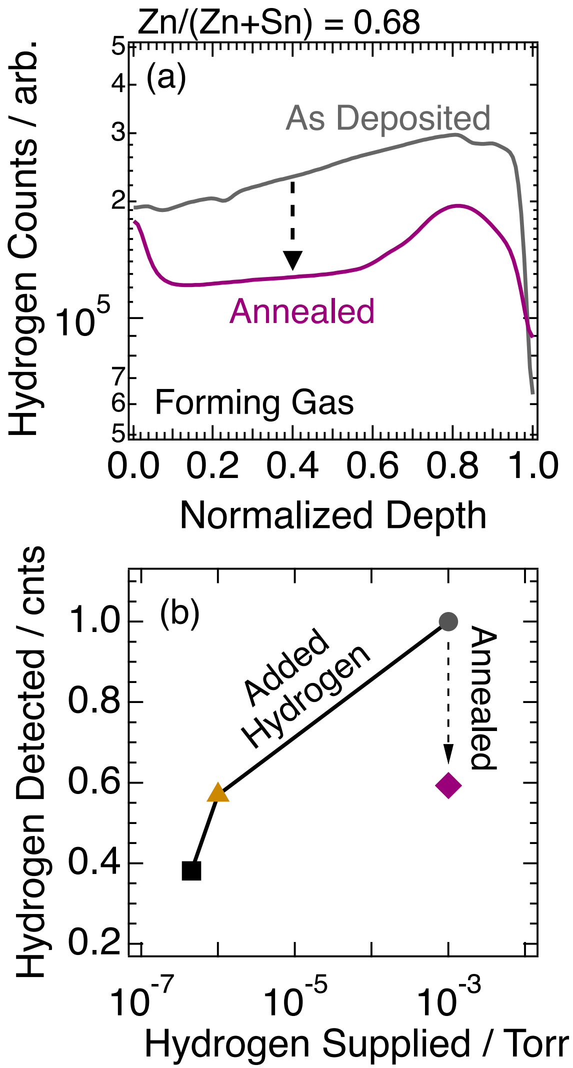
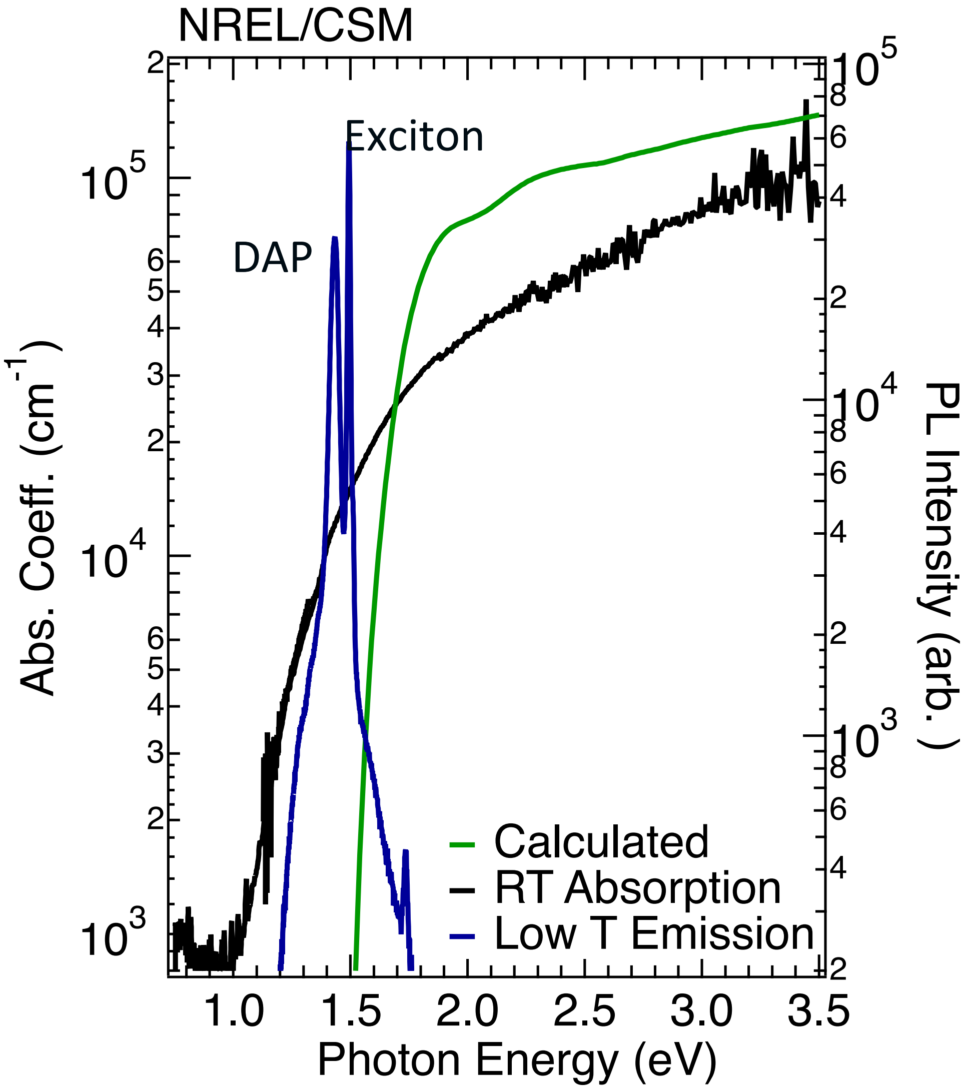


Stoichiometric
Zn-rich
$\Delta\mu_N = 0$
Sn_{Zn}
Zn_{Sn}
V_N
ΔH_D (eV)
$E - E_{VBM}$ (eV)
0.0
0.5
1.0
3
2
1
0
-1



Zn/(Zn+Sn) = 0.68
(a)
As Deposited
Annealed
Forming Gas
Hydrogen Counts / arb.
Normalized Depth
0.0 0.2 0.4 0.6 0.8 1.0
10^5
(b)
Added Hydrogen
Annealed
Hydrogen Detected / cnts
1.0 0.8 0.6 0.4 0.2
10^-7 10^-5 10^-3
Hydrogen Supplied / Torr



NREL/CSM
Exciton
DAP
Abs. Coeff. (cm^{-1})
PL Intensity (arb.)
Photon Energy (eV)
Calculated
RT Absorption
Low T Emission