Optically Active Dilute-Antimonide Ga(In,Sb)N Nanostructures for Deep-visible Optoelectronics and Solar Fuel Applications

<u>Faqrul A. Chowdhury</u>[1], Qing Shi[2], Hong Guo[2] and Zetian Mi[1,3 +]

[1]*Department of Electrical and Computer Engineering, McGill University, Montreal, QC, Canada.* [2]*Department of Physics, McGill University, Montreal, QC, Canada.*

[3]*Department of Electrical Engineering and Computer Science, University of Michigan, Ann Arbor, MI, United States*

The bandgap of GaN alloy can be reduced to ~2 eV by introducing very small amount (1-5%) of antimony (Sb). This is equivalent to incorporation of >30% of In in GaN, however, with substantially reduced lattice mismatch between GaSbN and GaN, compared to that between InGaN and GaN. The reduction of GaN energy bandgap with Sb incorporation is primarily due to upward shift of the valence band-edge [1], which is in direct contrast to downward shift of the conduction band-edge by alloying with In [2]. Therefore, precise tuning of the band-edges can be obtained with simultaneous incorporation of In and Sb in GaN, and the energy bandgap can be drastically reduced to deep visible and near-infrared spectral range, while maintaining a relatively small lattice mismatch to the underlying GaN template/substrate. We have recently shown [3-4], both theoretically and experimentally, that MBE grown GaSbN nanostructures are optically active, exhibiting strong, tunable photoluminescence (PL) emission at room temperature from UV to deep visible range in dilute Sb limit (<1%). Subsequently, we have demonstrated GaSbN dot-in-nanowire devices as an archetype for In-free visible LEDs. Herein, we have successfully synthesized InGaSbN nanowire heterostructures and explored their properties using X-ray diffraction, micro-Raman, and X-ray photoelectron spectroscopy. We have demonstrated that the emission wavelengths can be readily varied from blue, green to red spectral range with very small amount of Sb into InGaN. For example, the emission wavelength of InGaN (with ~28.9% of In) can be extended from 574 nm to 630 nm by incorporating only ~0.3% of Sb in InGaSbN under identical growth condition, which would otherwise require ~39% of In incorporation in InGaN. The outcomes of this study can have a profound impact on the development of high-efficiency, phosphor-free LEDs and a broad impact on solar energy conversion, including solar cells, solar fuels, and various electrochemical devices and systems [5].

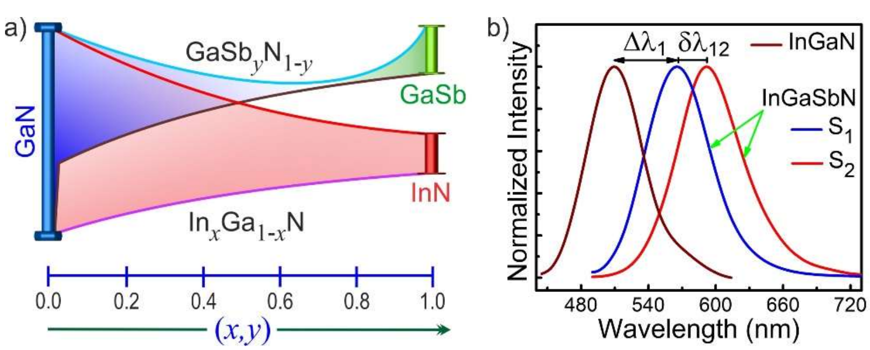

Figure 1: a) The bandgap energy of GaSbN alloys calculated using BAC model, and that of the InGaN over the whole composition range of Sb and In incorporation, respectively. b) Room-temperature PL spectra of InGaN and InGaSbN, showing the tuning of optical bandgap by varying In and Sb compositions. Here Δλ and δλ denotes the change in emission wavelength due to the change in Sb and In composition, respectively.

+ Author for correspondence: ztmi@umich.edu

[1] R. M. Sheetz *et al.*, *Phys. Rev. B* **84** (7), 075304 (2011). [2] P. G. Moses *et al.*, *Appl. Phys. Lett.* **96** (2), 021908 (2010). [3] F. A. Chowdhury *et al.*, *Appl. Phys. Lett.* **111**, 061101 (2017). [4] Q. Shi *et al.*, *Phys. Rev. Mater.* **1**, 034602 (2017). [5] A. Martinez-Garcia *et al.*, *Adv. Energy Mater.* 1703247 (2018).

Supplementary Information:

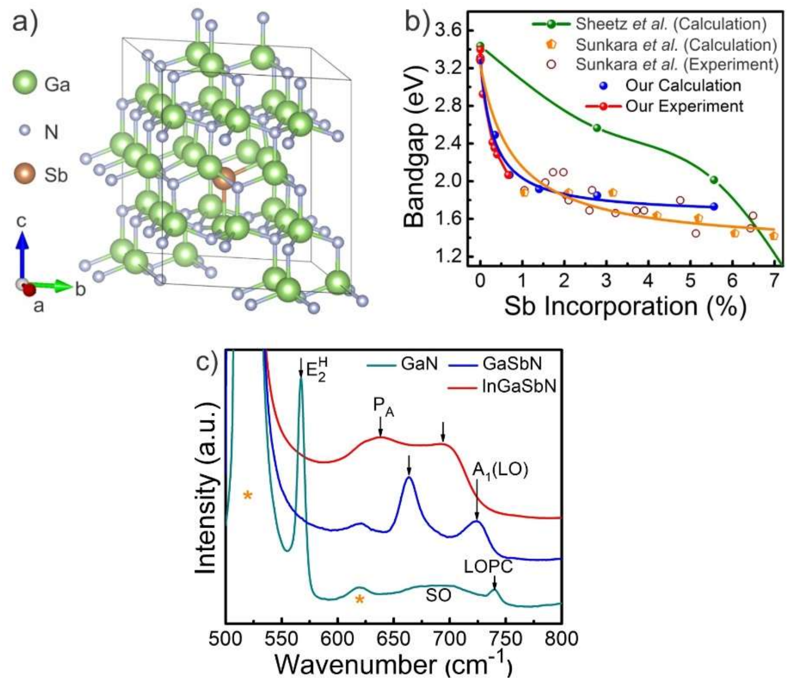

Figure 2: a) A ball and stick model of $GaSb_xN_{1-x}$ supercell with x = 2.7% of Sb incorporation, optimized using DFT simulations. The perturbation of Ga atoms near the Sb atom can clearly be observed in a unit cell. b) Energy Band gap of GaSbN vs. Sb concentration. There have been no studies, either theoretical or experimental, for GaSbN with Sb composition <1%. Our calculations herein (blue dots) demonstrate controllable tuning of the energy bandgap from 3.4 eV to 2eV in the dilute limit (<1%). Our experiments (red dots) also show excellent agreement with the theoretical calculation. c) Room-temperature micro-Raman spectra obtained from the GaN, GaSbN and InGaSbN on Si substrate, clearly depicting the evolution of the prominent modes. The contributions from the Si substrate are marked with '*'.

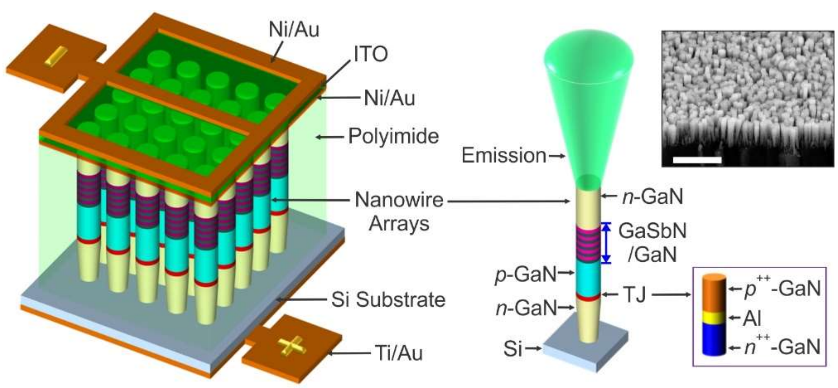

Figure 3: Schematic representation of GaSbN/GaN dot-in-wire tunnel junction (TJ) light emitting diode (LED) structure. Schematic view of different layers incorporated in the nanowire arrays of GaSbN LED is also presented. The inset on the top-right shows 45° tilted SEM image of as-grown GaSbN dot-in-nanowire arrays. Scale bar 1 μm. The schematic of the TJ is also illustrated in the inset (bottom-right).