MOCVD Growth and Characterization of Wide Bandgap $ZnGeN_2$ Thin Films

Md Rezaul Karim[1], Benthara Hewage Dinushi Jayatunga[2], Zixuan Feng[1], Menglin Zhu[3], Jinwoo Hwang[3], Kathleen Kash[2], and Hongping Zhao[1,3]

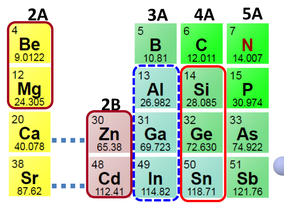
[1]Department of Electrical and Computer Engineering, The Ohio State University, Columbus, OH 43210, USA

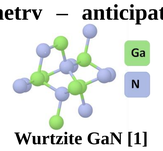
[2]Department of Physics, Case Western Reserve University, Cleveland, OH 44106, USA

[3]Department of Materials Science and Engineering, The Ohio State University, Columbus, OH 43210, USA

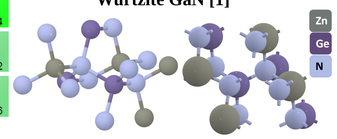
II-IV-N_2 Materials

- Group of nitride materials with cations of different valences
  - Group – II cations: Be, Mg, Zn, Cd
  - Group –IV cations: Si, Ge, Sn
- Crystal structure
  - Orthorhombic ($Pna2_1$) - perfectly ordered cations
  - Wurtzite (P3m1) - completely disordered cations
- Bandgap: < 1eV ($CdSnN_2$) - ~6 eV ($ZnSiN_2$)
- Intriguing features
  - Consists of earth abundant elements, e.g., Zn
  - Two cations – expected flexibility in doping
  - Reduced crystalline symmetrv – anticipated non-linear optical properties

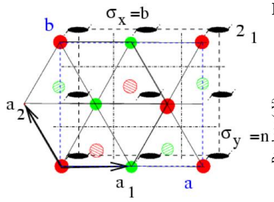




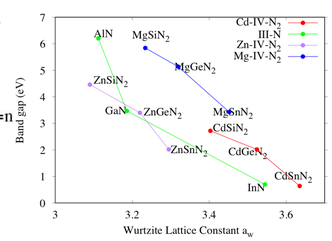
Wurtzite GaN [1]



Disordered $ZnGeN_2$ [1] Ordered $ZnGeN_2$ [1]

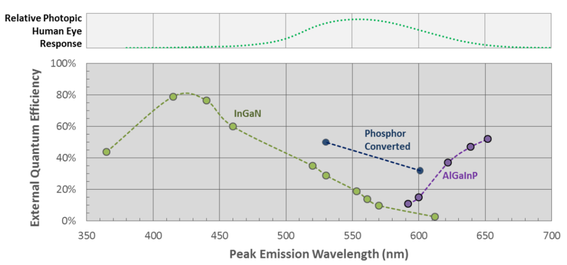


Relationship of orthorhombic structure to the wurtzite structure [2]



Bandgap vs. lattice constant plot of some II-IV-N_2 compounds [2]

Motivation



EQE of "best research" LEDs for different wavelengths [3]

- Persistent challenges in improving the efficiency of green and amber LEDs using conventional materials
- $ZnGeN_2$ – novel material for optoelectronic applications
  - Bandgap: ~3.4 eV (very close to GaN) [4]
  - Almost lattice matched with GaN (less than 0.1% lattice mismatch) [4]
  - Large band offset (ΔE_V ~ 1.4 eV) with GaN [5]
    - InGaN/$ZnGeN_2$ based high efficiency blue and green LEDs

Objective

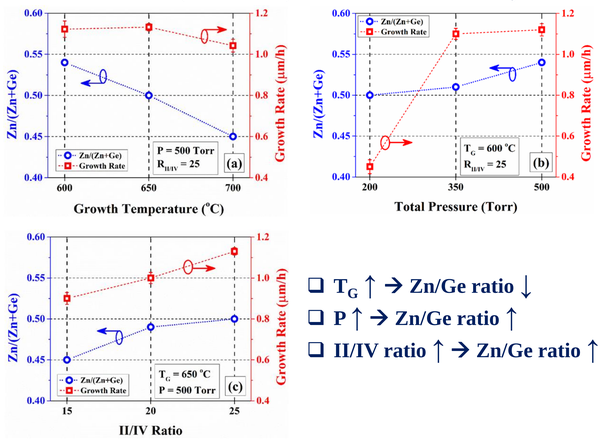
- Growth of $ZnGeN_2$ thin films by metalorganic chemical vapor deposition (MOCVD)
  - Studying the effect of growth parameters
  - Establishing the optimal MOCVD growth conditions for $ZnGeN_2$ thin films
  - Characterization of structural, electrical and optical properties of $ZnGeN_2$ thin films

Experimental details

- Substrates
  - GaN/c-sapphire templates
  - Sapphire (c-, r- and a-plane)
- Precursors
  - Diethylzinc (DEZn)
  - Germane (GeH_4)
  - Ammonia (NH_3)
- Temperature (T_G): 500 °C - 800 °C
- Pressure (P): 100 Torr – 500 Torr

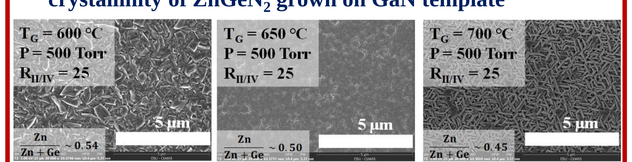
Results – $ZnGeN_2$ growth on GaN template

- Effects of growth temperature, pressure and DEZn/GeH_4 flow rate ratio (II/IV ratio) on cation stoichiometry

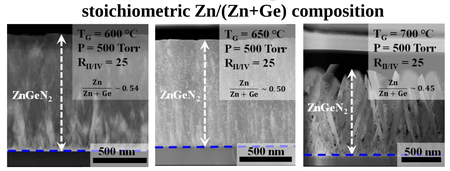


- T_G ↑ → Zn/Ge ratio ↓
- P ↑ → Zn/Ge ratio ↑
- II/IV ratio ↑ → Zn/Ge ratio ↑

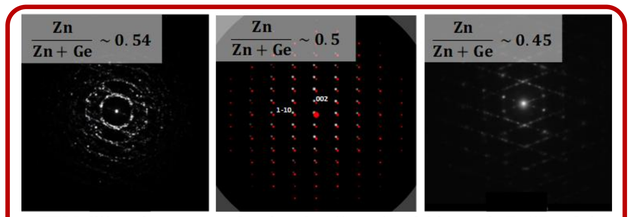
- Effects of cation compositions on morphology and crystallinity of $ZnGeN_2$ grown on GaN template



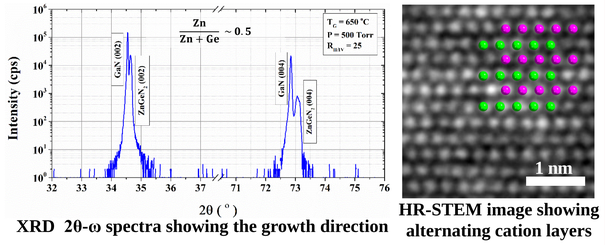
Plan-view FESEM images of $ZnGeN_2$ films showing the effect of stoichiometric Zn/(Zn+Ge) composition



STEM-LAADF images showing dramatically different cross-sectional morphology in $ZnGeN_2$ films having different cationic compositions



TEM diffraction pattern showing the effect of stoichiometric Zn/(Zn+Ge) composition on crystallinity of the film.

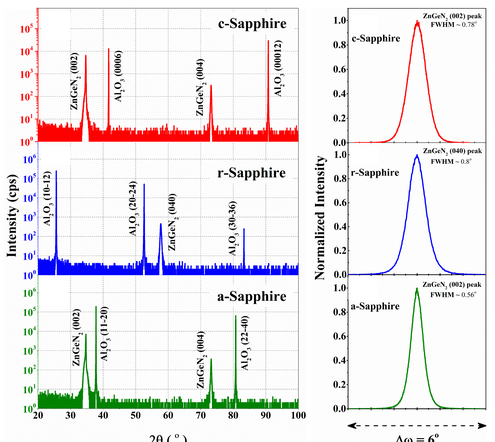


XRD 2θ-ω spectra showing the growth direction

HR-STEM image showing alternating cation layers

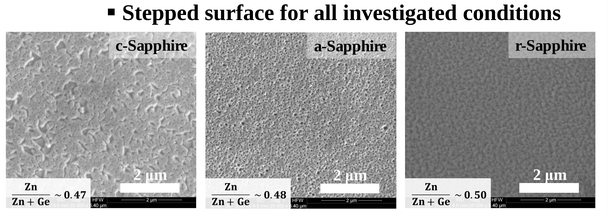
Results – $ZnGeN_2$ growth on sapphire substrates

- XRD 2θ-ω spectra
  - Growth direction
    - Along P3m1 [0001] on c- and a-sapphire
    - Along P3m1 [11-20] on r-sapphire
  - Crystallinity – affected by growth conditions
    - Small growth window on c- and a-sapphire
    - Relatively large growth window for r-sapphire



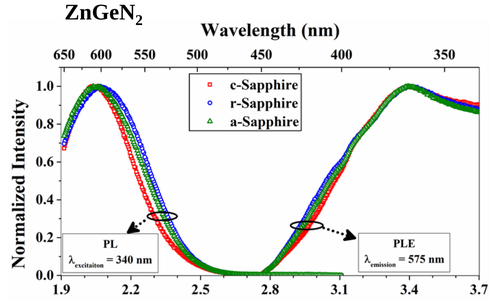
XRD 2θ-ω spectra and rocking curves

- Surface morphology from FESEM imaging
  - C- and a-sapphire substrate
    - Planar surface – near stoichiometric films
  - R-sapphire substrate
    - Stepped surface for all investigated conditions



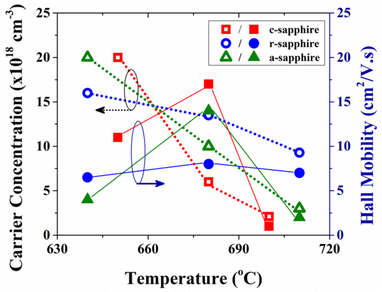
Plan-view FESEM images of $ZnGeN_2$ films grown on c-, a- and r-sapphire substrates

- Optical properties
  - Photoluminescence (PL) spectra
    - One broad peak around ~2.05 eV – deep level defect related
  - PL excitation spectra
    - Peak around 3.4 eV – close to band gap of $ZnGeN_2$



Combined PL and PLE spectra of $ZnGeN_2$ films grown on c-, r- and a-sapphire substrates

- Electrical transport properties – Hall measurements
  - N-type conductivity in as-grown films – 10^{18} -10^{19} cm^{-3}
    - Carrier concentrations decreases with T_G
  - Carrier mobility up to 17 $cm^2/V{\cdot}s$



Carrier concentrations and Hall mobility of $ZnGeN_2$ films grown at different temperature

Summary

Key accomplishments to date

- ✓Near stoichiometry $ZnGeN_2$ film
- ✓Control over stoichiometry → from Zn-rich to Zn-poor
- ✓Decent surface morphology and crystalline properties
- ✓Electrical transport property measurements

Ongoing and future work

- Thermal annealing for improving the film properties
- Use of buffer layer to address the lattice mismatch

References

[1] https://materialsproject.org/
[2] https://sites.google.com/a/case.edu/dmref/crystal-structure-confusions
[3] Department of Energy Solid State Lighting R&D Plan, June (2016).
[4] A. Punya, T. R. Paudel, and W. R. L. Lambrecht, Phys. Status Solidi C, 8, 2492 (2011) .
[5] A. P. Jaroenjittichai, S. Lyu, W. R. L. Lambrecht, Phys. Rev. B, 97, 079907 (2017).
[6] M. R. Karim, B. H. D. Jayatunga, Z. Feng, K. Kash, H. Zhao, Cryst. Growth Des., 19, 4661(2019)

Acknowledgement

This project is funded by NSF (SusChEM:DMREF-1533957), and DOE (DE-EE0008718).