AlN Base Material Development for High Temperature Application

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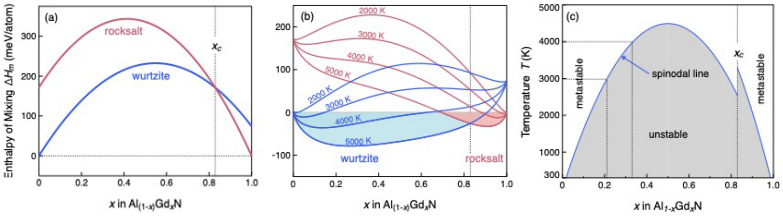
Motivation

Polar wurtzite AlN-based alloy materials have exceptional optoelectronic and charge transport properties (e.g., $Al_{1-x}Ga_xN$ in LEDs and $Al_{1-x}Sc_xN$ as a promising new ferroelectric[1]). Other cation substitutions include Ta^{3+}, Cr^{3+}, Er^{3+}, Yb^{3+}, and small amounts of Gd^{3+},[2-6] but **ionic size** effects are a serious issue, and **other variables affecting solubility are underexplored** in this family, hampering development of new functional AlN-based alloys.

Thermodynamics of $Al_{1-x}Gd_xN$

- The ground state is wurtzite up to x_c=0.82, and rocksalt is the ground state for $x > x_c$
- Calculated T_{eff}–composition phase diagram reveals a large miscibility gap at low T_{eff}
- Higher T_{eff} stabilizes higher Gd^{3+} solubility in wurtzite AlN

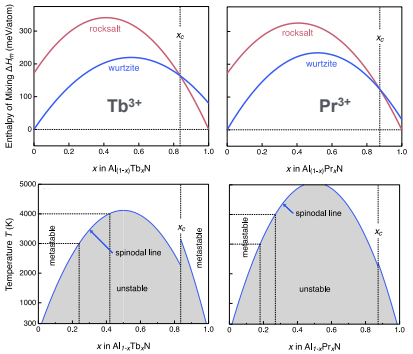


DFT-computed (a) mixing enthalpies, (b) free energies, and (c) T_{eff}–composition phase diagram

Other $Al_{1-x}M_xN$ alloys

Ion	Radius	χ	x_c
Sc^{3+}	0.75 Å	1.36	0.55-0.64[1,3]
Y^{3+}	0.9 Å	1.22	0.75[3]
La^{3+}	1.03 Å	1.1	0.95[7]
Pr^{3+}	**0.99 Å**	**1.13**	**0.87**
Gd^{3+}	**0.94 Å**	**1.2**	**0.82**
Tb^{3+}	**0.92 Å**	**1.1**	**0.84**
Yb^{3+}	0.87 Å	1.1	0.75[5]
Al^{3+}	0.39 Å	1.61	–

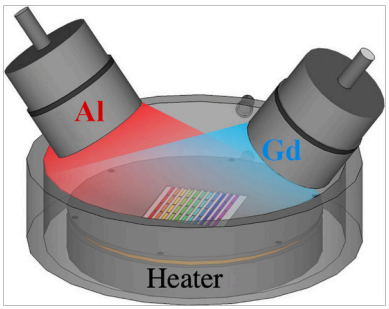
- Trends in x_c due to both **size effects** and ***M*–N bond ionicity**
  - Al–N more polar/covalent
  - More ionic *M*–N bonds allow easier incorporation



Calculated mixing enthalpies and T_{eff}–composition phase diagrams of $Al_{1-x}Tb_xN$ and $Al_{1-x}Pr_xN$ alloys

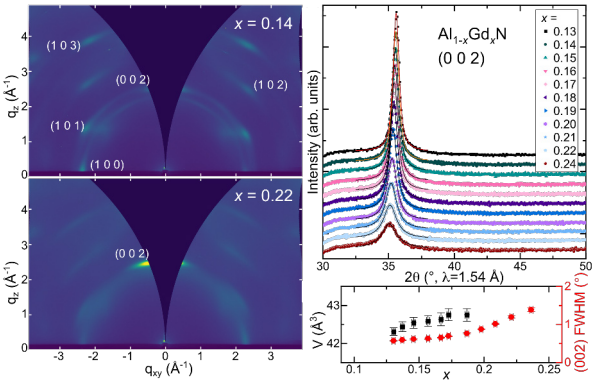
Combinatorial thin film growth and structure

- RF co-sputtering yields a composition gradient roughly $Al_{0.87}Gd_{0.13}N$ – $Al_{0.76}Gd_{0.24}N$
- Highest previous via sputtering was x≈0.06, with phase separation to Gd above x≈0.1[6]



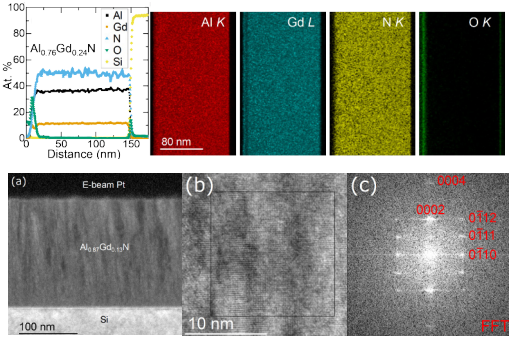
Combinatorial RF sputtering setup

- GIWAXS (SSRL 11-3) reveals phase-pure wurtzite crystal structure across the composition gradient
- Unit cell volume and *c* extracted from lab XRD of the (0 0 2) peak are consistent with Vegard's law



GIWAXS patterns and lab XRD at the wurtzite (0 0 2) peak

- TEM-EDS shows homogeneous Gd incorporation and negligible oxygen in both x=0.13 and x=0.24
- SAED confirms wurtzite structure
- Semi-oriented sample with columnar grains



TEM EDS on $Al_{0.76}Gd_{0.22}N$ and SAED analysis on $Al_{0.87}Gd_{0.13}N$

Conclusions

- The key to synthesizing Gd-rich wurtzite $Al_{1-x}Gd_xN$ alloys is accessing high T_{eff} (3000–4000 K) under non-equilibrium conditions
- Using RF co-sputtering at T_{eff} ≈ 4000 K, we have experimentally incorporated Gd^{3+} into wurtzite AlN up to x ≈ 0.25
- Universal trends: calculations reveal that bond ionicity is a key determinant of the solubility of large M^{3+} cations in wurtzite AlN

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References

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