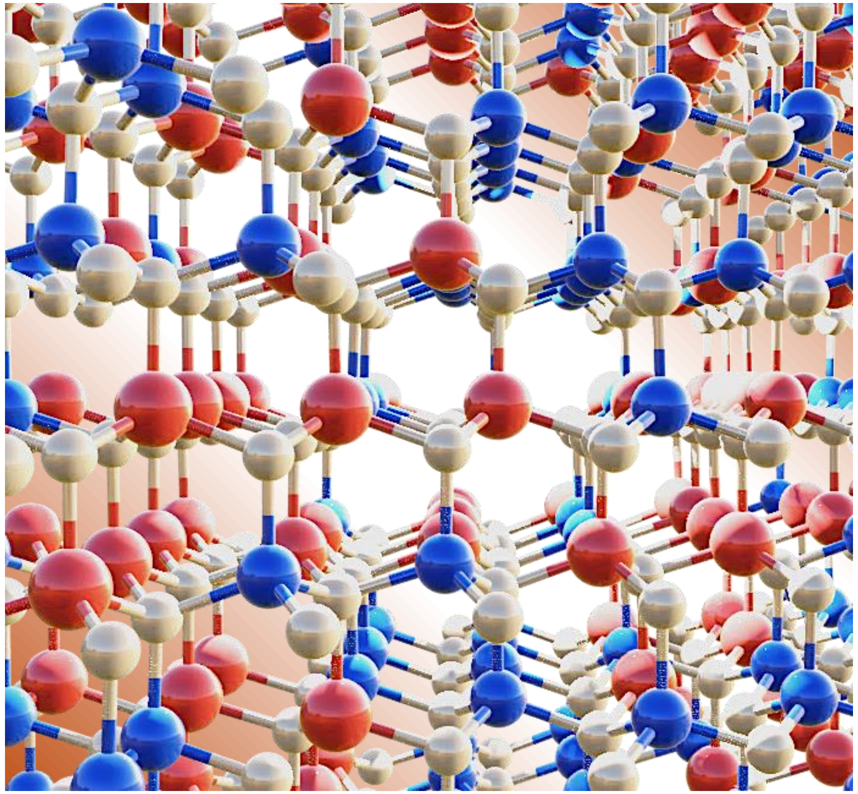
Summer School on the physics and Applications of Nitrides

Defects and dopants



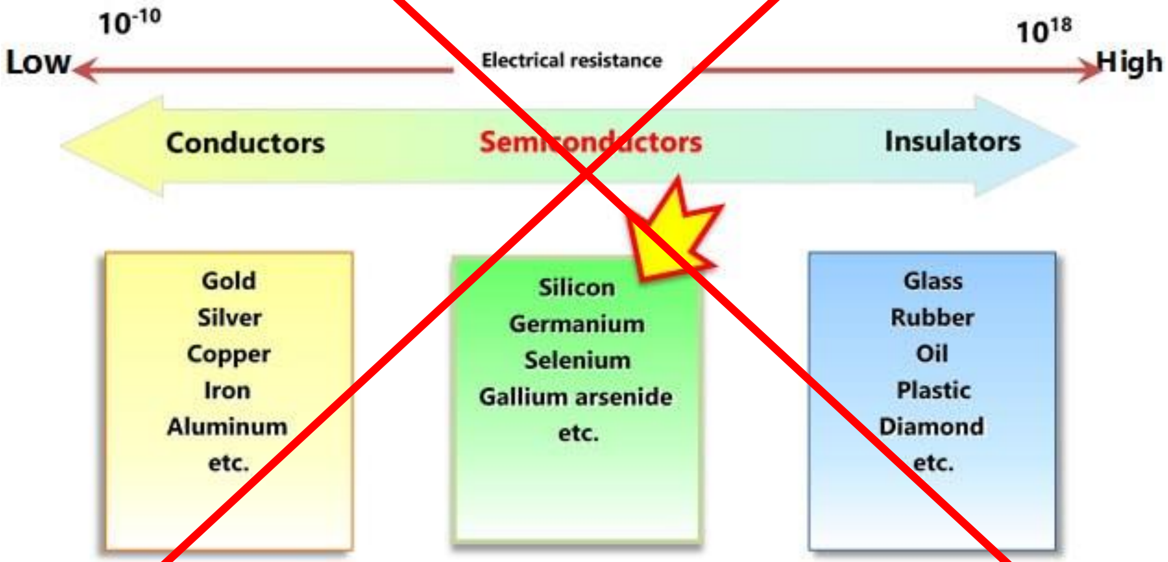
Emmanouil (Manos) Kioupakis[1,2]

[1] Professor, Materials Science and Engineering, University of Michigan

[2] Visiting Professor, IMX and IEM, STI, EPFL

Definition: what is a semiconductor?

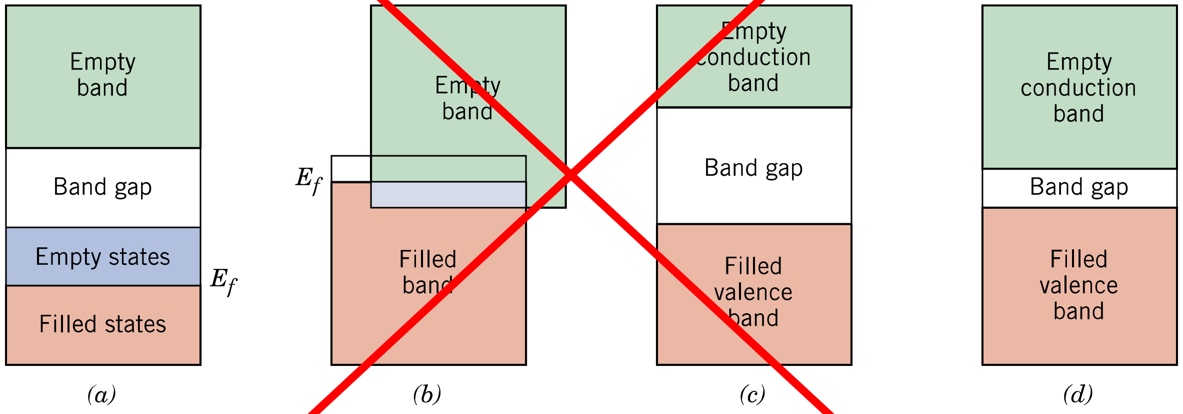
(a) Classification based on magnitude of **electrical conductivity**: “Semiconductors have an electrical resistivity value between those of conductors and insulators”



https://toshiba.semicon-storage.com/

But: semiconductors are much more than just bad conductors.

(b) Classification based on magnitude of the **band gap**: “Semiconductors have narrow band gaps”, typically defined as less than ~3 eV.



Callister, *Materials Science and Engineering: An Introduction*

Metal Semimetal Insulator Semiconductor

But: materials with wider gaps (e.g., GaN, Ga_2O_3, diamond) behave as semiconductors and are used for devices.

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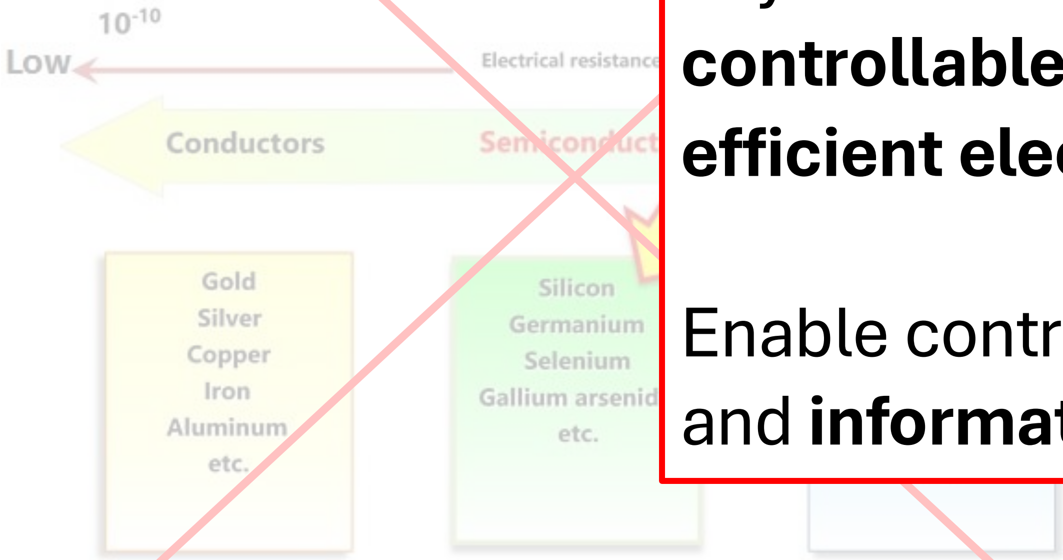

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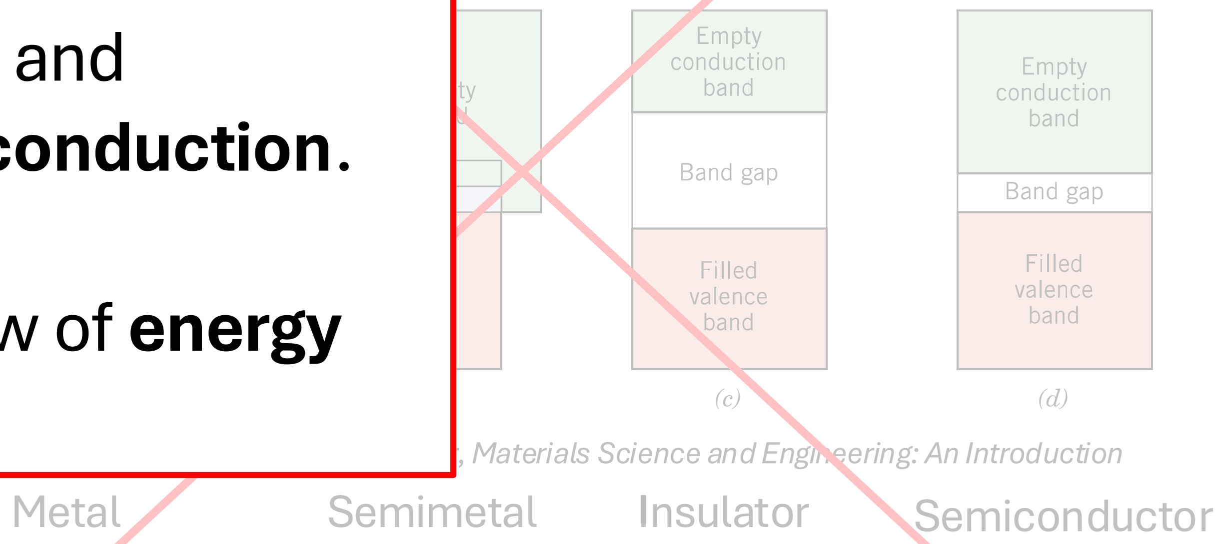
Classification based on magnitude of the **band gap**: "Semiconductors have narrow band gaps", typically defined as less than ~3 eV.



, *Materials Science and Engineering: An Introduction*

Key features of semiconductors: **controllable doping** and **efficient electrical conduction**.

Enable control of flow of **energy** and **information**.

But: semiconductors are much more than just bad conductors.

But: materials with wider gaps (e.g., GaN, Ga_2O_3, diamond) behave as semiconductors and are used for devices.

Common point defects in semiconductors

What types of defects exist in materials?

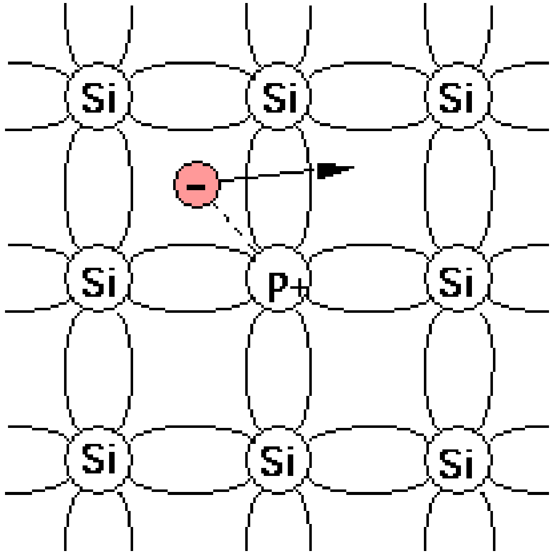
- Point defects vs. line defects
- Point defects:
  - Vacancies
  - Interstitials
  - Substitutional
  - Antisite, antisite pairs
  - Frenkel pair: vacancy-interstitial
  - Schotky pair: cation-anion vacancies

- Defect formation energy E_{form} on the order of 1 eV (chemical reaction)
- How it affects defect concentration?
- $\frac{N_{defect}}{N} = \exp(-\frac{E_{form}}{k_B T})$

Doping in semiconductors

Control the conductivity of semiconductors by **doping**: intentional addition of foreign atoms with one more or one less electrons than the host atoms.

The **dopants** provide **free electrons** or **free holes** and enable conductivity.

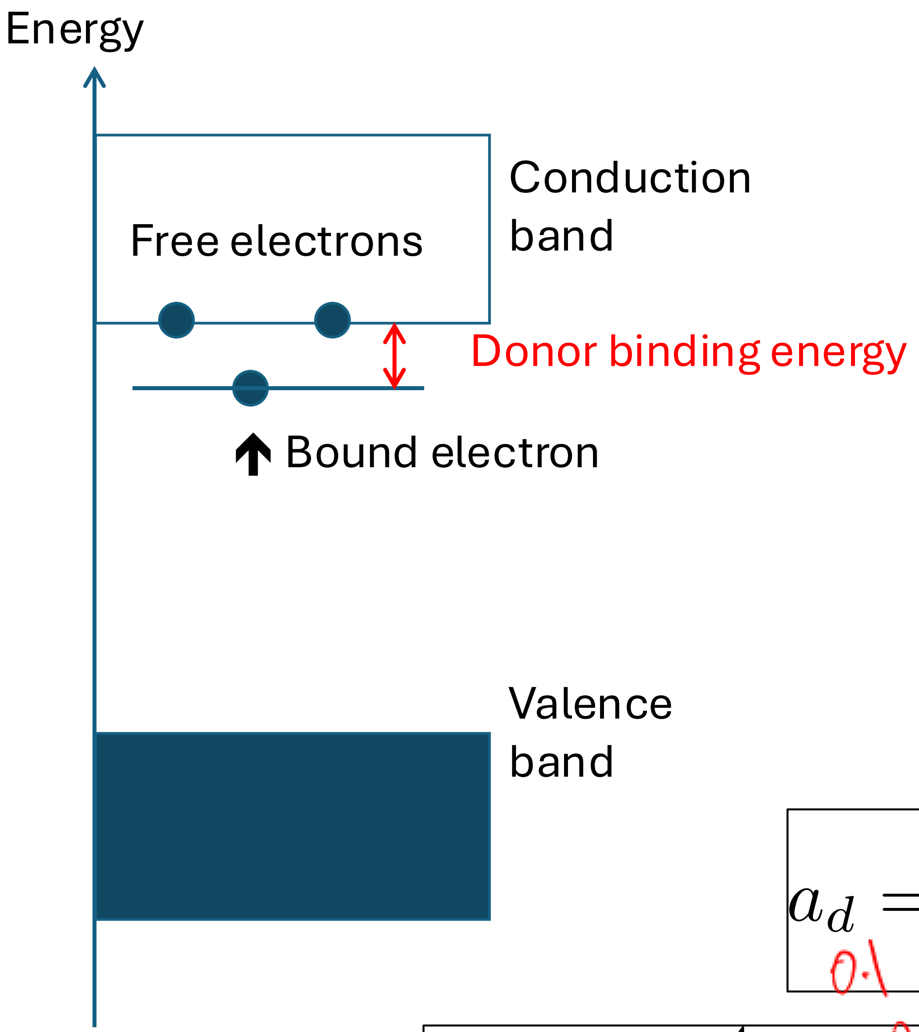


Donor atoms have one more electron than host, provide free electrons in the conduction band.

E.g., P in Si

➔ **n-type** semiconductor.

Shallow donor levels (e.g., P in Si) or Si in GaN



Question: how to calculate the donor binding energy (= energy needed to overcome the attraction of the electron to the positively charged P$^+$ ion) and the radius of the donor wave function?

Answer: modified Bohr model.
Effective mass: m → m*
Dielectric constant: $\varepsilon_0 \rightarrow \varepsilon\varepsilon_0$

$$\boxed{a_d = \frac{4\pi\overset{\sim 10}{\varepsilon}\varepsilon_0\hbar^2}{\underset{0.1}{m_e^*}e^2} = \frac{a_B\varepsilon}{m_e^*/m_e}} \sim 100\,a_B$$

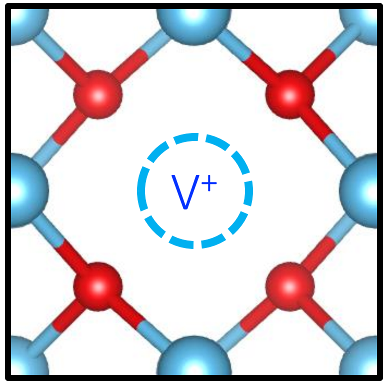
$$\boxed{E_d = \frac{e^4\overset{\sim 0.1}{m_e^*}}{2(4\pi\underset{\sim 10}{\varepsilon}\varepsilon_0\hbar)^2} = \frac{13.6\ \text{eV}}{\varepsilon^2}\frac{m_e^*}{m_e}} \sim \frac{13.6\,\text{eV}}{1000} \sim 10\ \text{meV}$$

Methodology: formation and ionization of defects and dopants

Chemical potential

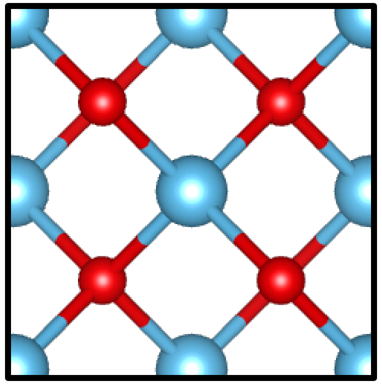
[1]Formation energy of isolated point defect D in charge state q

$$E^f(D^q) = E_{tot}(D^q) - E_{tot}(\text{bulk}) - \underline{\sum n_i \cdot \mu_i} + \underline{q}(\boxed{E_F} + E_V) + E_{corr}(D^q)$$



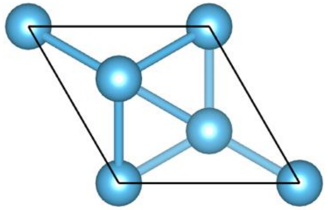
Defect (e.g., metal vacancy)

–



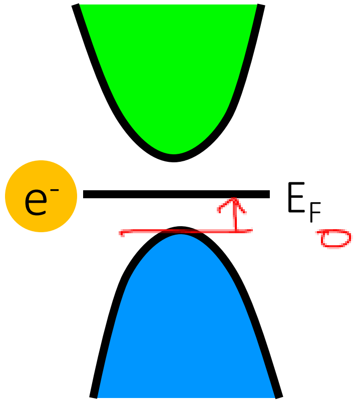
Bulk

+



Metal bulk / atom

+



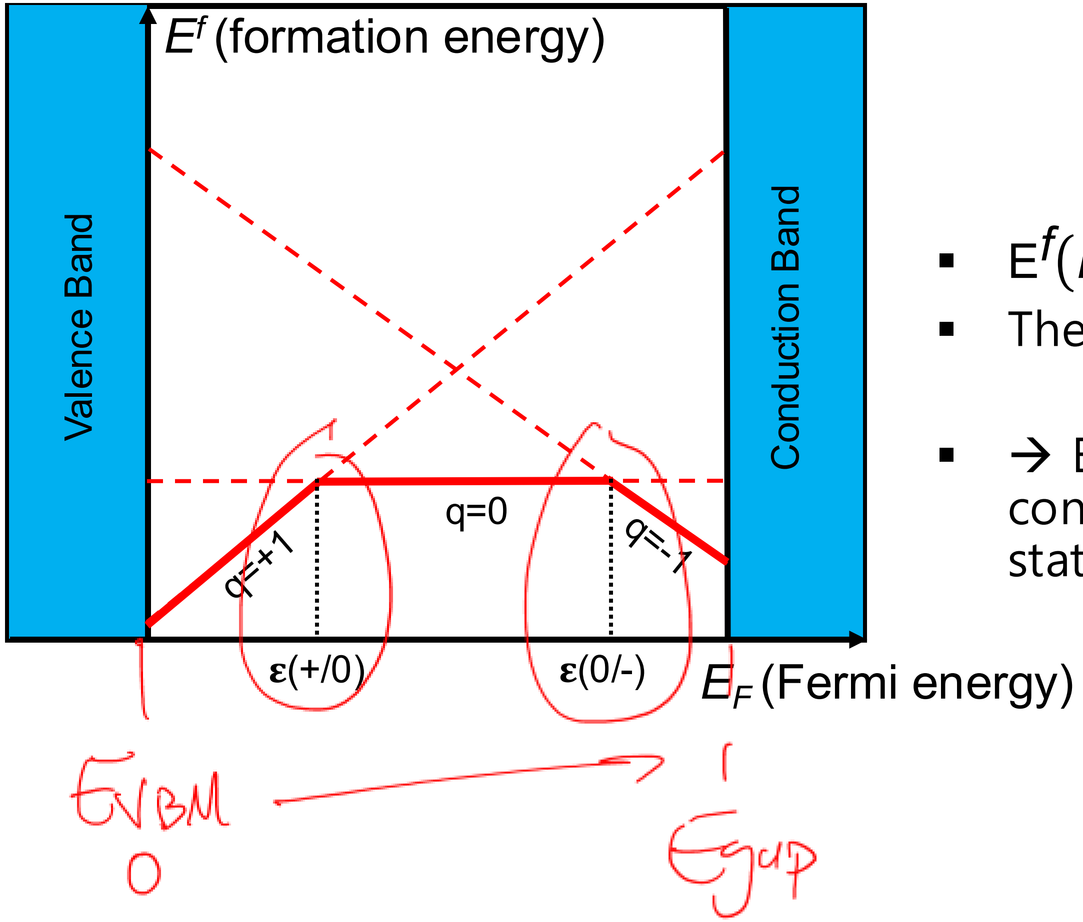
e^- @ E_F

n_i: the number of defect atoms removed or added
μ_i: chemical potential per i atom in its elemental phase
E_F: the Fermi level
E_V: valence band maximum
$E_{corr}(Dq)$: correction energy calculated with SXDEFECTALIGN code[2]

[1] C. Freysoldt et al. Rev. Mod. Phys. 86, 253 (2014).
[2] C. Freysoldt et al. Phys. Rev. Lett. 84, 016402 (2009).

Methodology: formation and ionization of defects and dopants

$$E^f(D^q) = E_{tot}(D^q) - E_{tot}(\text{bulk}) - \sum n_i \cdot \mu_i + \boxed{q(E_F + E_V)} + E_{corr}(D^q)$$

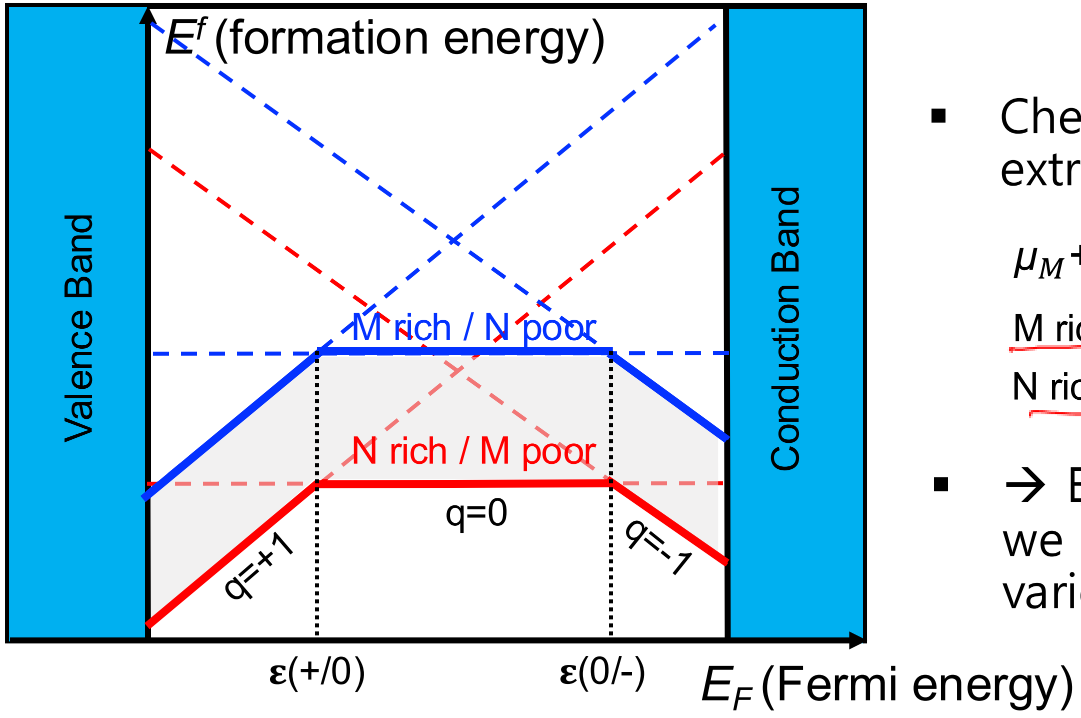


- $E^f(D^q)$ is considered as a function of E_F
- Thermodynamic transition energy, **ε**(q/q′)

- → By varying the Fermi level, we can control formation energy and charge state

Methodology: formation and ionization of defects and dopants

$$E^f(D^q) = E_{tot}(D^q) - E_{tot}(\text{bulk}) - \sum n_i \cdot \boxed{\mu_i} + q(E_F + E_V) + E_{corr}(D^q)$$



- Chemical potentials are defined at two extreme growth conditions

  $\mu_M + \mu_N = \Delta H^f(MN)$

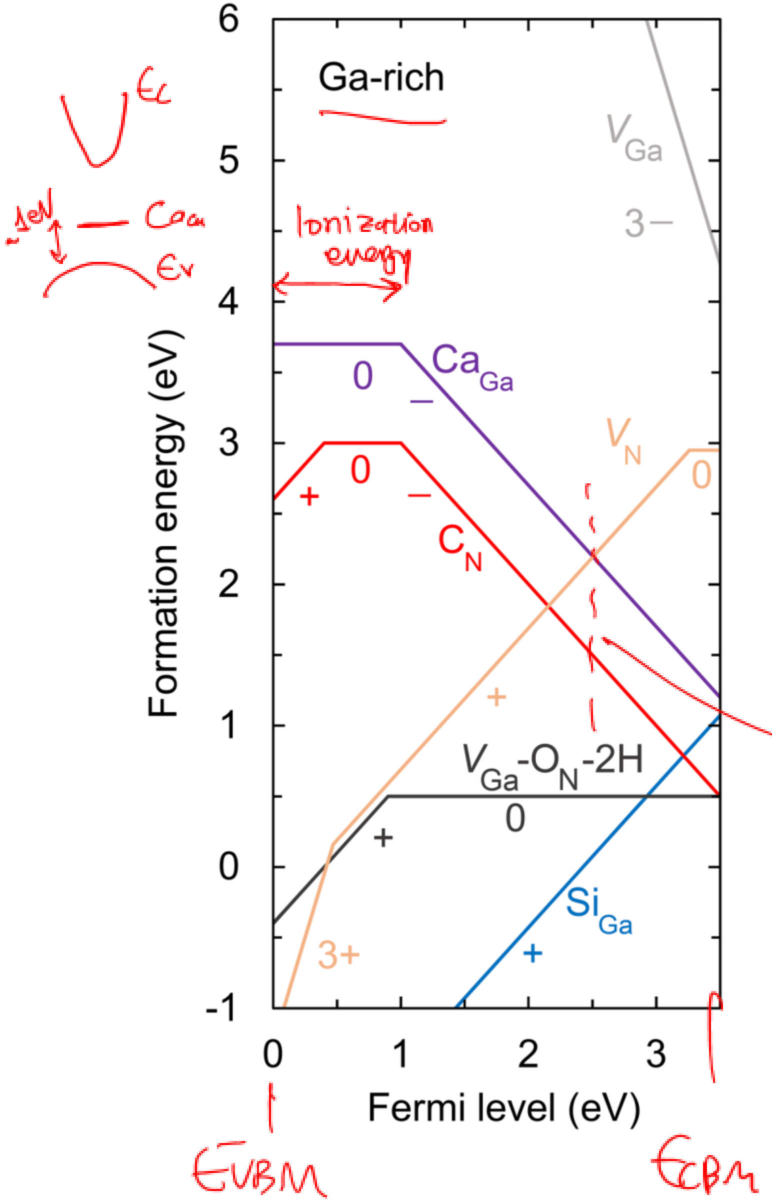
  M rich / N poor: $\mu_M = 0, \mu_N = \Delta H^f(MN)$

  N rich / M poor: $\mu_M = \Delta H^f(MN)\ \mu_N = 0$

- → By varying the growth conditions, we can control formation energy of various defects

Defects and dopants in GaN

e^{-E_{form}/k_BT}



What can you comment about the formation and ionization of the various defects in GaN listed in the figure?

V^{3+}: donor : Eform can be negative

V_{Ga}? not so much

~V_N? Yes!

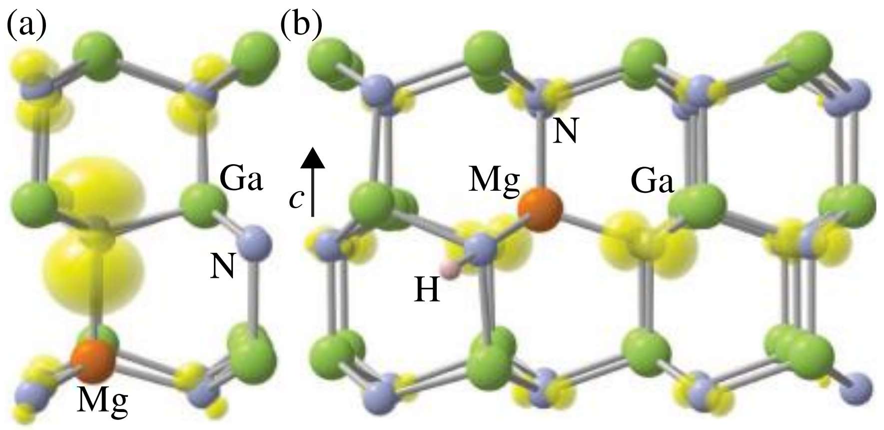
Si excellent donor

Ca acceptor?

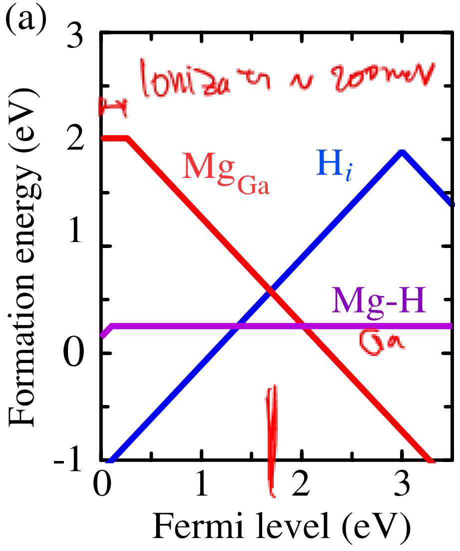
→ Fermi level pinning competition between Ca_{Ga} & V_N

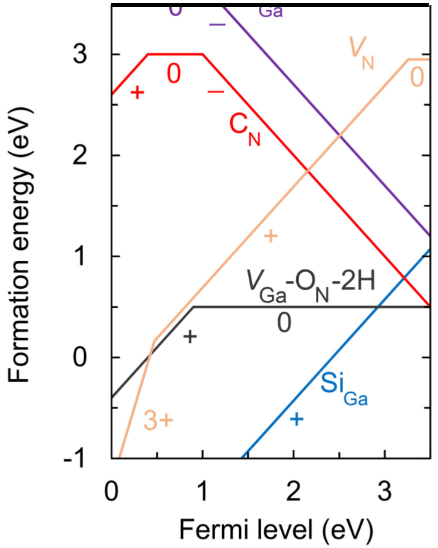
Tutorial on defects and dopants in GaN by Van de Walle and collaborators:
J. Appl. Phys. 129, 111101 (2021)
https://doi.org/10.1063/5.0041506

P-type doping of GaN



Van de Walle and team, Phys. Rev. Lett. **108**, 156403 (2012)





Acceptors in GaN: Mg, Be. Ionization energy is large (~200 meV) but workable.

Bigger problem: **compensation**. As the Fermi level moves towards top of valence band (i.e., zero in these plots), it inhibits the incorporation of Mg and promotes the formation of compensating defects.

Solution: **co-dope with hydrogen**, form neutral Mg-H complexes that incorporate Mg without shifting Fermi level. Subsequently, remove H by annealing to activate acceptors, enable p-type doping. → LEDs, Nobel prize

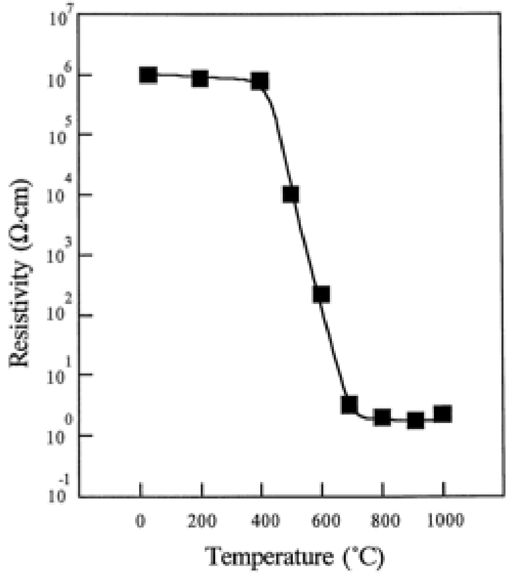
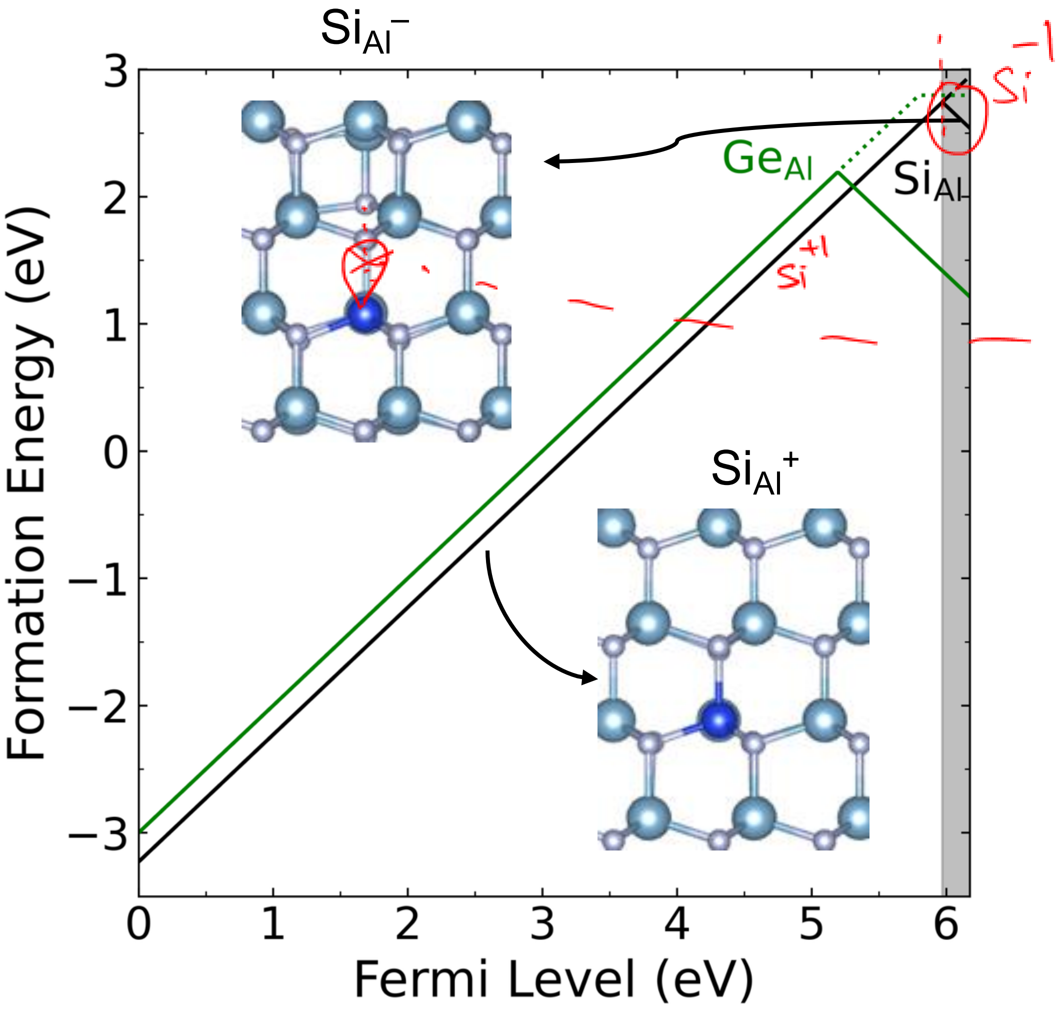


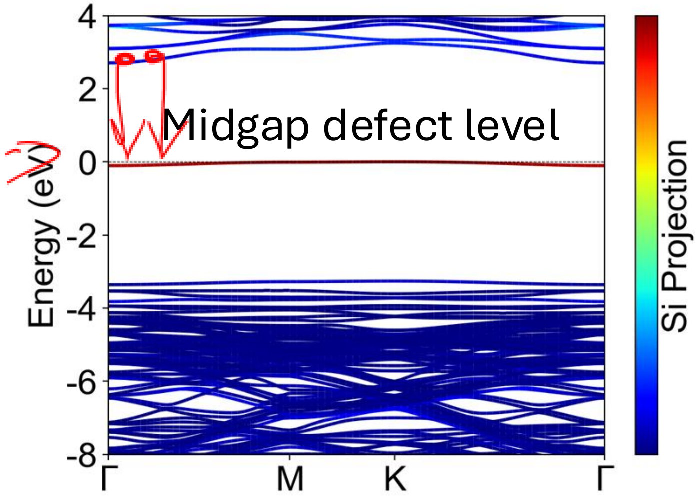
Fig. 1. Resistivity of Mg-doped GaN films as a function of annealing temperature.

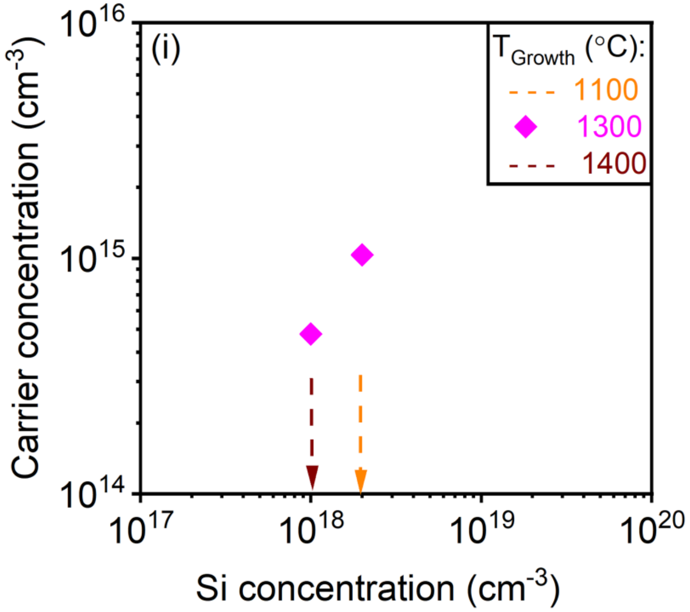
Shuji Nakamura *et al* 1992
Jpn. J. Appl. Phys. **31** L139

Doping of AlN: Si_{Al} and Ge_{Al} DX centers.



Extra electron in Si-doped AlN has enough energy to break an Al-N bond and lower its energy by forming mid-gap states





J. Appl. Phys. 132, 185703 (2022)
https://doi.org/10.1063/5.0124589

Fermi-level pinning due to competition between Si_{Al}^{+} and Si_{Al}^{-}: ε(+/–) = 0.210 eV

→ **Ionization of Si donors in AlN is poor**.

Defects and functional properties

What effects do you know (beneficial or detrimental) of defects in nitrides?

− non-radiative recombination ⇒ lose efficiency

− PL emission

− Fermi level pinning ⇒ can't dope

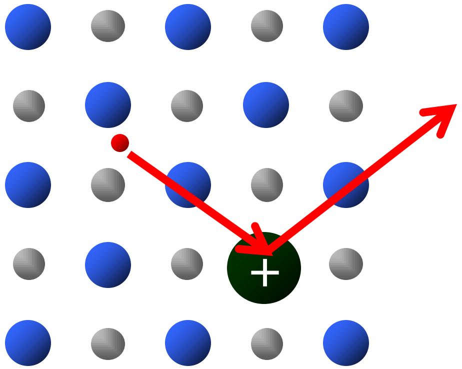
+ 2DEG doping + dopants

− Mobility ↓

+/− release strain

What scatters electrons? Ionized impurities

Dopants become ionized → Charged impurities interact with and scatter electrons through the Coulomb interaction

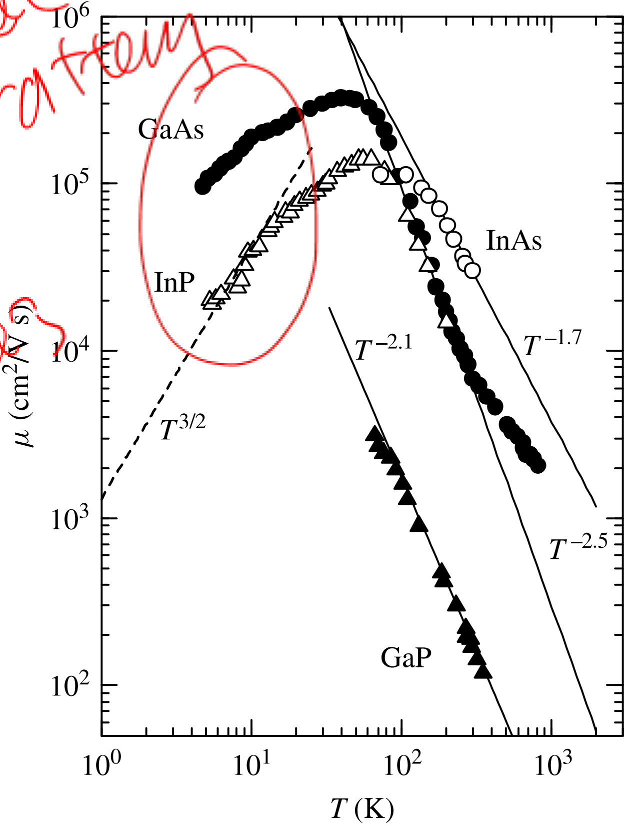


$$\Delta V_{\mathrm{defect}} = \frac{4\pi Z e^2}{\varepsilon(q)(q^2 + \lambda^2)}.$$

Z = charge of defect
ε = dielectric constant
λ = accounts for screening of Coulomb interaction by free carriers.

Important at low temperatures or high doping concentrations

Typical data for semiconductors



due to Scattering

by defects

Figure 12.4 Electron Hall mobility μ versus temperature T for relatively pure n-type GaP, GaAs, InP and InAs. The experimental data are gathered from various sources (see text)

Adachi book

Table 12.3 300 K (μ_{300K}) and peak Hall mobilities (μ_{peak}) for electrons in some cubic, hexagonal and rhombohedral semiconductors. The conductivity electron mass m_c^α in the lowest conduction band is also presented in the third column

System	Material	m_c^α/m_0	μ_{300K} (cm^2/V s)	μ_{peak} (cm^2/V s)
IV	Diamond	0.48	2800	9000 ($T \sim 80$ K)
	Si	0.259	1750[a]	500000 ($T \sim 8$ K)[a]
	Ge	0.119	2300	530000 ($T \sim 11$ K)
	α-Sn	0.029[b]		80800 ($T = 4.2$ K)
	3C-SiC	0.32	980	3000 ($T \sim 66$ K)
	6H-SiC		375	10940 ($T = 50$ K)
	15R-SiC		500	1700 ($T \sim 90$ K)
III–V	c-BN	0.31		4 ($T = 900$ K)
	BP	0.28	190	190 ($T = 300$ K)
	AlP	0.31	80	80 ($T = 300$ K)
	AlAs	0.26	294	294 ($T = 300$ K)
	AlSb	0.29	200	700 ($T = 77$ K)
	α-GaN	0.21	1245	7400 ($T \sim 60$ K)
	β-GaN	0.15	760	11000 ($T \sim 50$ K)
	GaP	0.37	189	3100 ($T \sim 70$ K)
	GaAs	0.067	9340	400000 ($T = 28-40$ K)
	GaSb	0.039	12040	12700 ($T = 77$ K)
	InN	0.12	3100	5000 ($T \sim 150$ K)
	InP	0.07927	6460	400000 ($T \sim 45$ K)
	InAs	0.024	30000	170000 ($T = 77$ K)
	InSb	0.013	77000	1100000 ($T \sim 50$ K)
II–VI	ZnO	0.234	226	2400 ($T = 40$ K)
	α-ZnS	0.28	140	300 ($T = 185$ K)
	β-ZnS	0.2	107	
	ZnSe	0.137	1500	13600 ($T = 55.6$ K)
	ZnTe	0.117	600	
	c-CdS	0.14	70–85	
	w-CdS	0.151	390	70000 ($T = 1.8$ K)
	w-CdSe	0.125	900	20000 ($T \sim 23$ K)
	CdTe	0.09	1050	100000 ($T \sim 30$ K)
	β-HgS	0.012[b]	230	580 ($T \sim 4.2$ K)
	HgSe	0.019[b]	22000	170000 ($T \sim 20-30$ K)
	HgTe	0.030[b]	26500	1400000 ($T = 4.2$ K)

[a] Drift (conductivity) mobility

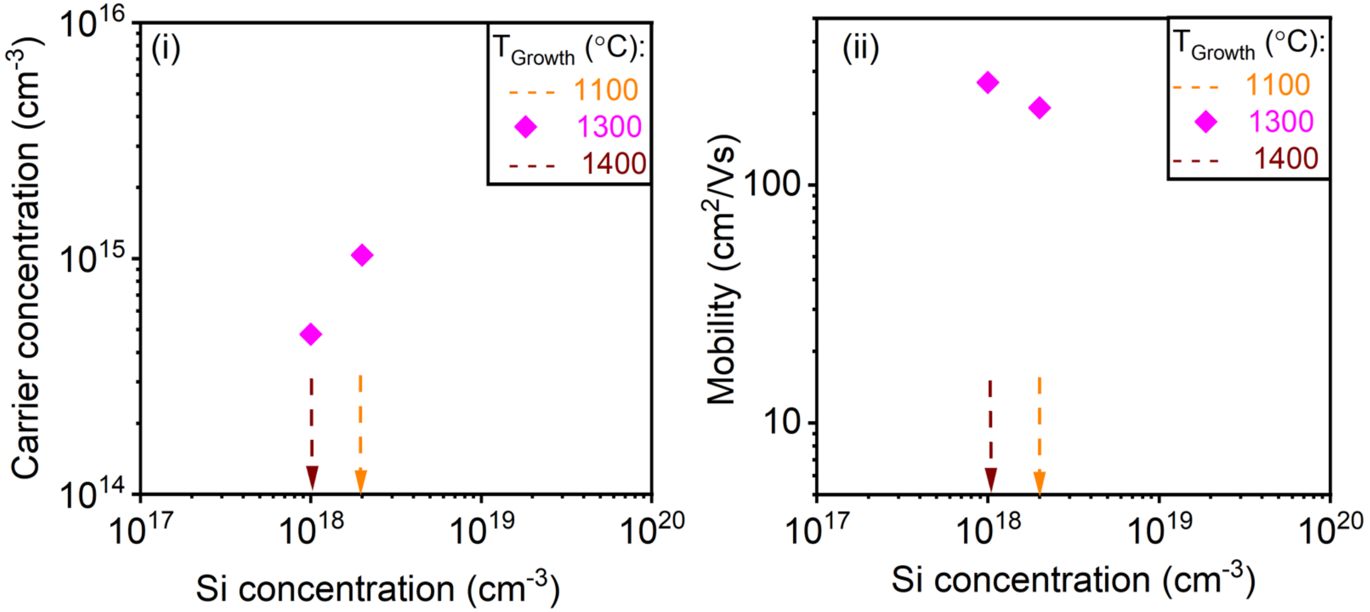
[b] Showing negative band-gap (semimetalic) nature

Electron mobility of doped AlN

AlN: the widest-gap III-nitride, important for power-electronic applications.

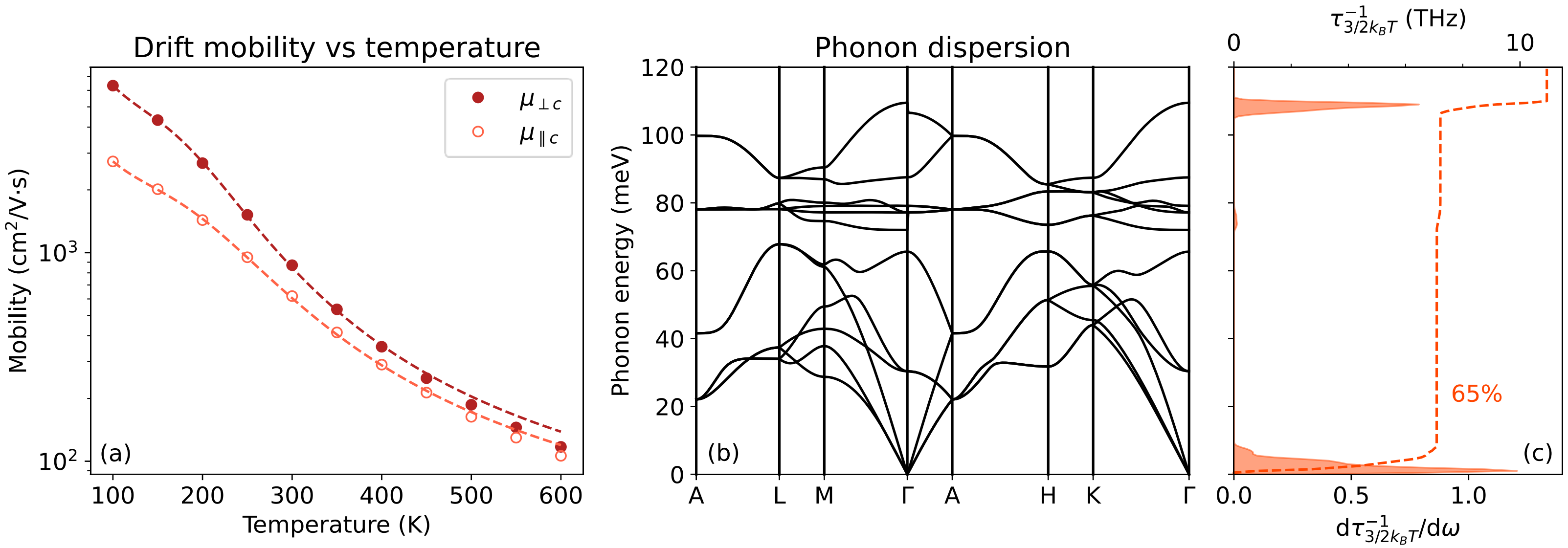
Challenges with doping remain, but high mobility (~300-400 cm^2/Vs) achieved through optimized growth on AlN substrates.

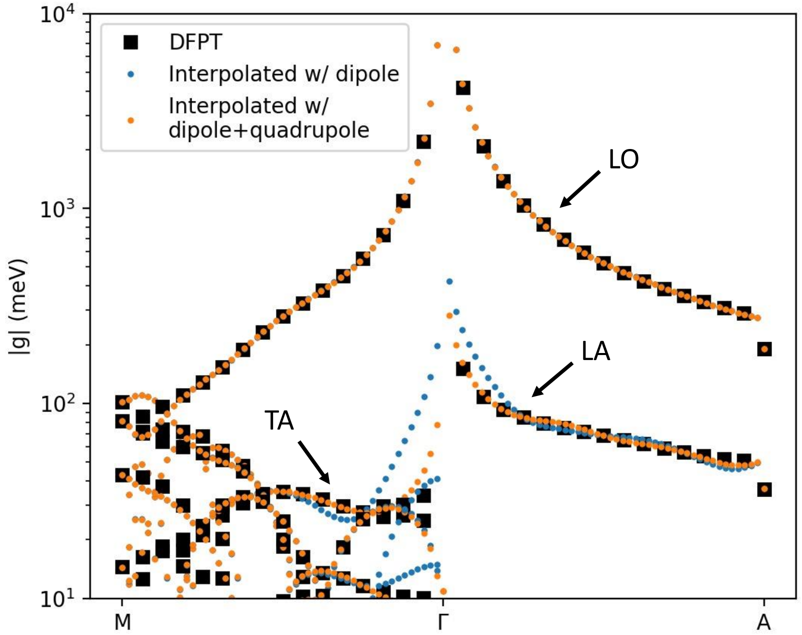
Goal: understand the fundamental limits of the electron mobility in AlN as a function of doping and temperature.



Sitar and Collazo groups at North Carolina:
J. Appl. Phys. 132, 185703 (2022)
https://doi.org/10.1063/5.0124589

Electron mobility vs. temperature: which phonon dominate scattering?





$$\mu_{\text{ph}}(T) = \left(\frac{1}{\mu_{\text{low}}} e^{-T_{\text{low}}/T} + \frac{1}{\mu_{\text{high}}} e^{-T_{\text{high}}/T}\right)^{-1}$$

$$kT_{\text{low}} = 7\text{-}8 \text{ meV}$$
$$kT_{\text{high}} = 104\text{-}106 \text{ meV}$$

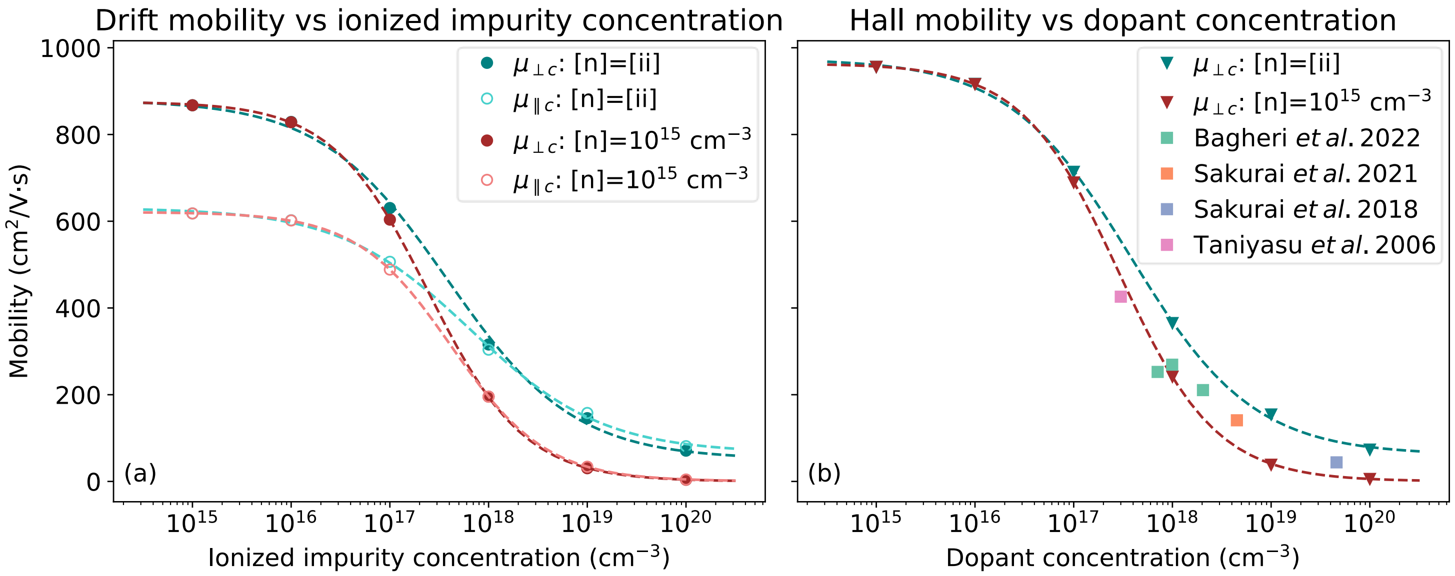
Acoustic phonons dominate: Even though LO phonons couple strongest with electrons:

→ Electrons do not have enough energy (kT~25 meV) to emit LO phonon

→ LO phonon occupation is small (~1%), not many LO phonons to absorb.

Electron mobility vs. doping, and comparison to experiment

$$\mu_{\text{total}}(n) = \mu_{\text{min}} + \frac{\mu_{\text{max}} - \mu_{\text{min}}}{1 + \left(n/n_{\text{ref}}\right)^{\beta}}.$$



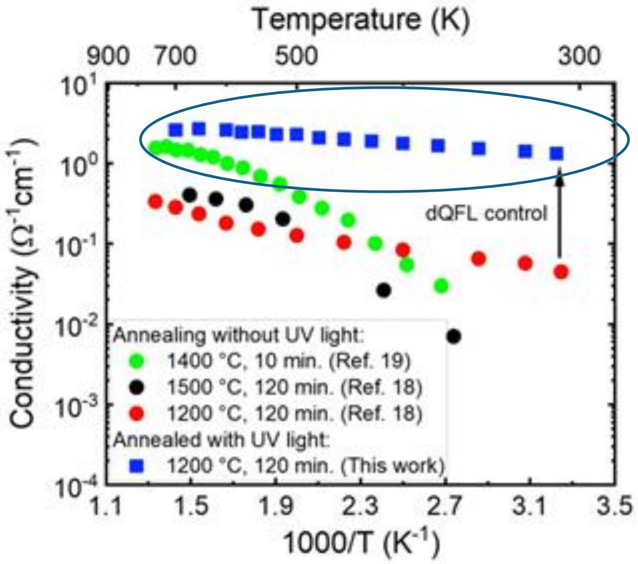
Although Si DX centers (Si⁻) compensate donors and do not provide free electrons (they even consume one free electron), they still scatter the free carriers, reducing the mobility.

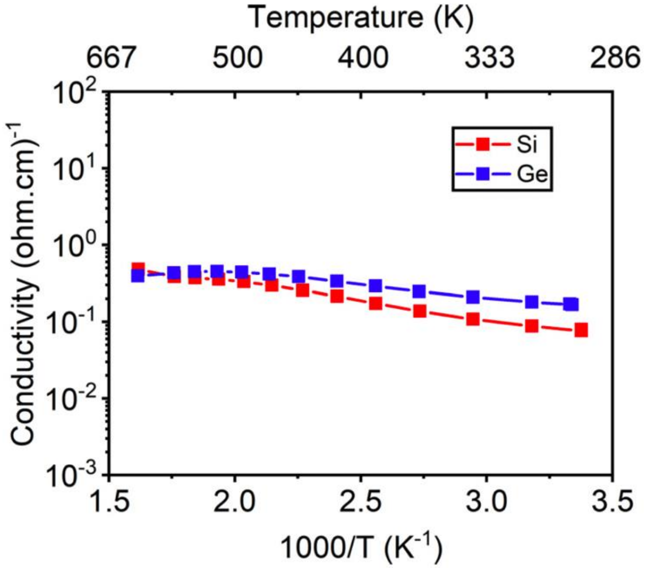
Solution: improve material quality so that lower Si concentrations can enable doping.

Amanda Wang et al., Electron mobility in AlN from first principles, submitted. Posted on arXiv on 10/06/2025

Shallow donor observation for Si- and Ge- implanted AlN

- Shallow donor observations in Si- and Ge-implanted AlN (annealed under illumination), or in AlN grown at low temperature under Al-rich conditions: **$E_{activate}$ ~75 meV**, donors in AlN are **shallow**, no DX centers.

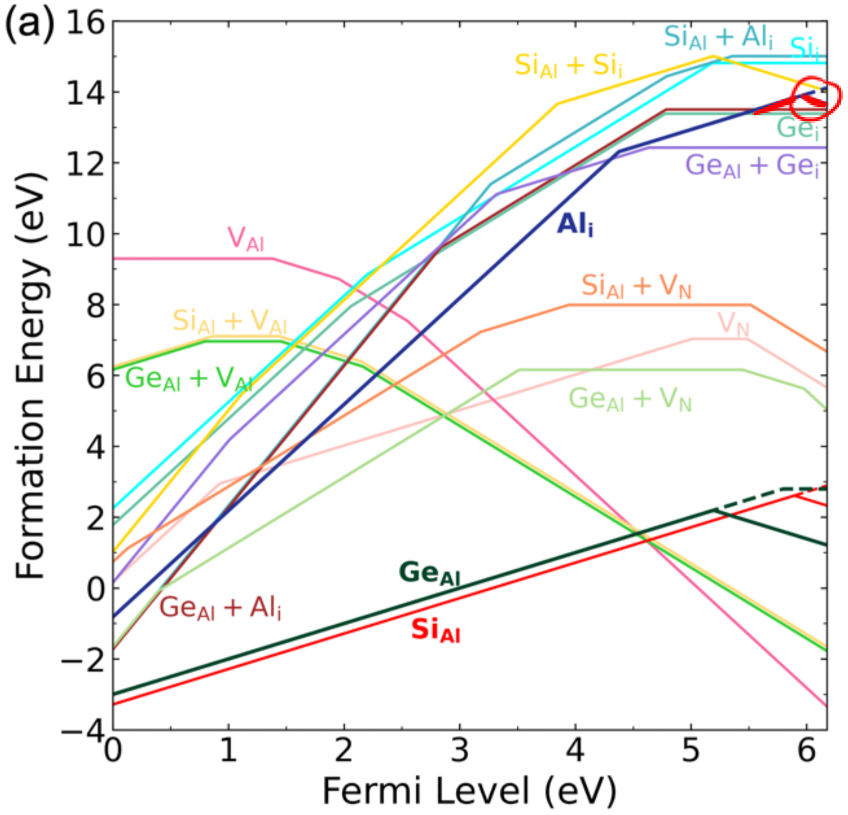


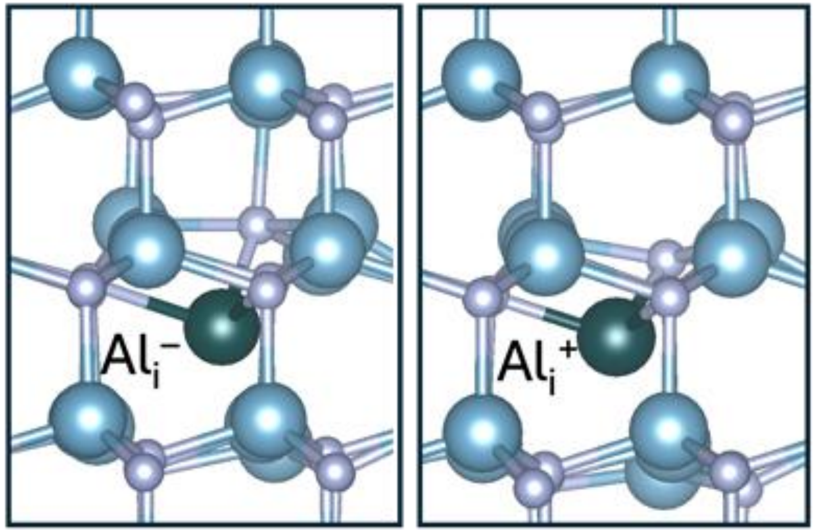


Breckenridge *et al. Appl. Phys. Lett.* (2021)

- What is the origin of the shallow donors in AlN?

Al interstitials as a source of shallow doping in AlN?

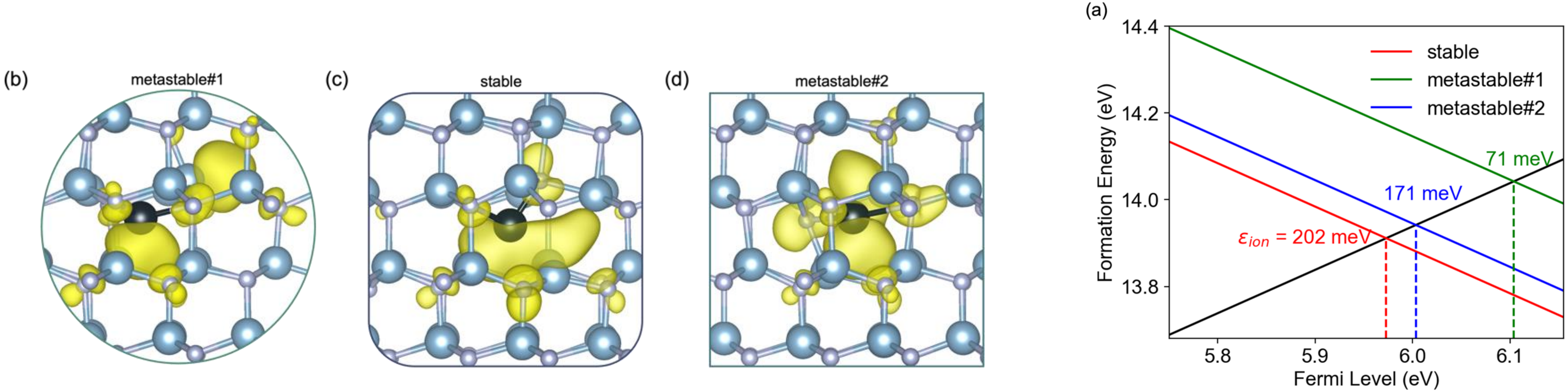




Also form DX centers, with a shallower ionization energy of 200 meV.

Still can’t explain shallow donors (75 meV)

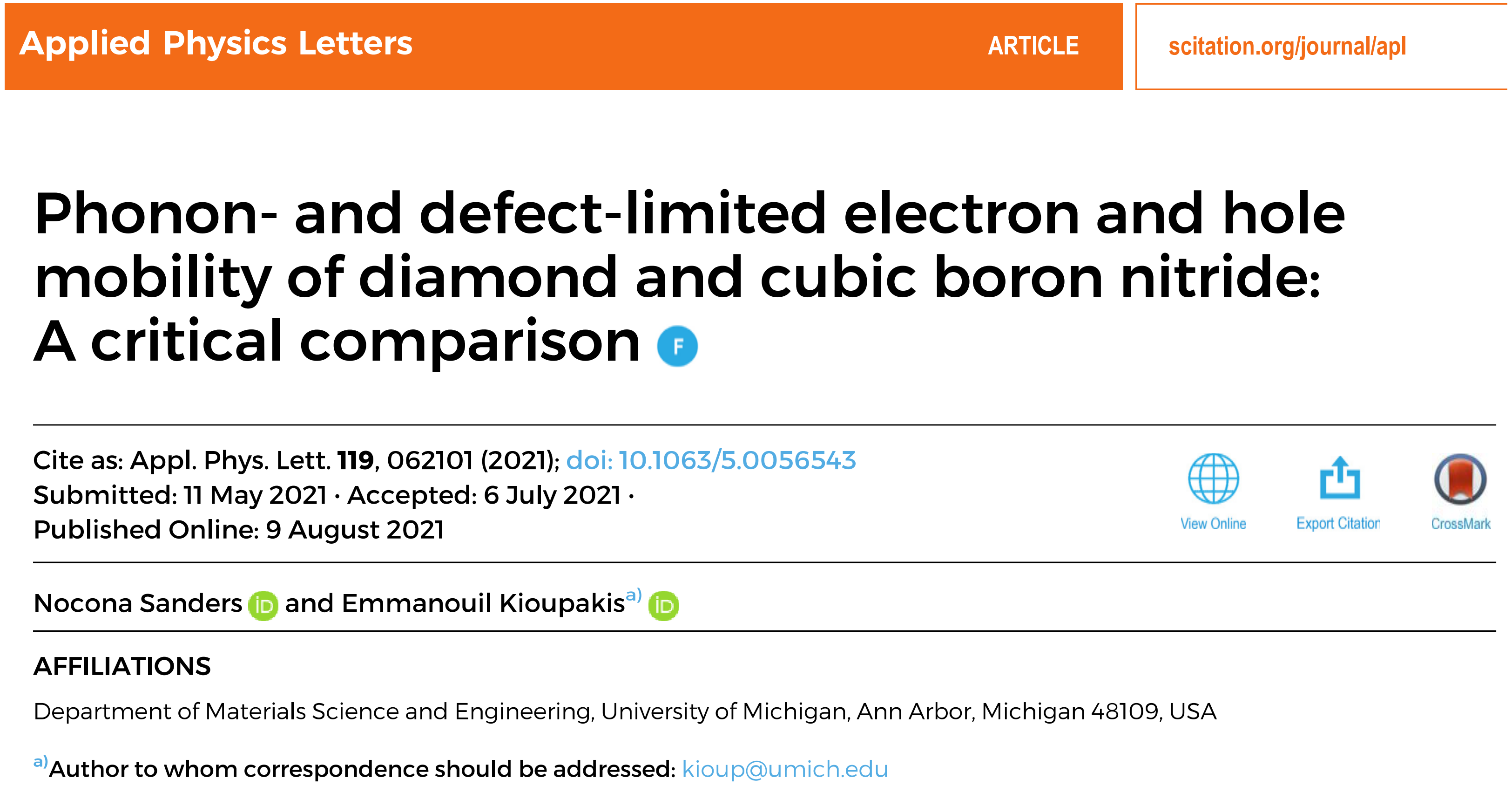
Metastable Al interstitials are shallow donors in AlN!



Can explain shallow donors observed in implanted AlN, and in AlN grown under low-T Al-rich conditions.

Yujie Liu et al, unpublished

Results for diamond and cubic BN



Applied Physics Letters ARTICLE scitation.org/journal/apl

Phonon- and defect-limited electron and hole mobility of diamond and cubic boron nitride: A critical comparison

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Nocona Sanders and Emmanouil Kioupakis[a)]

AFFILIATIONS

Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109, USA

[a)] Author to whom correspondence should be addressed: kioup@umich.edu

Data

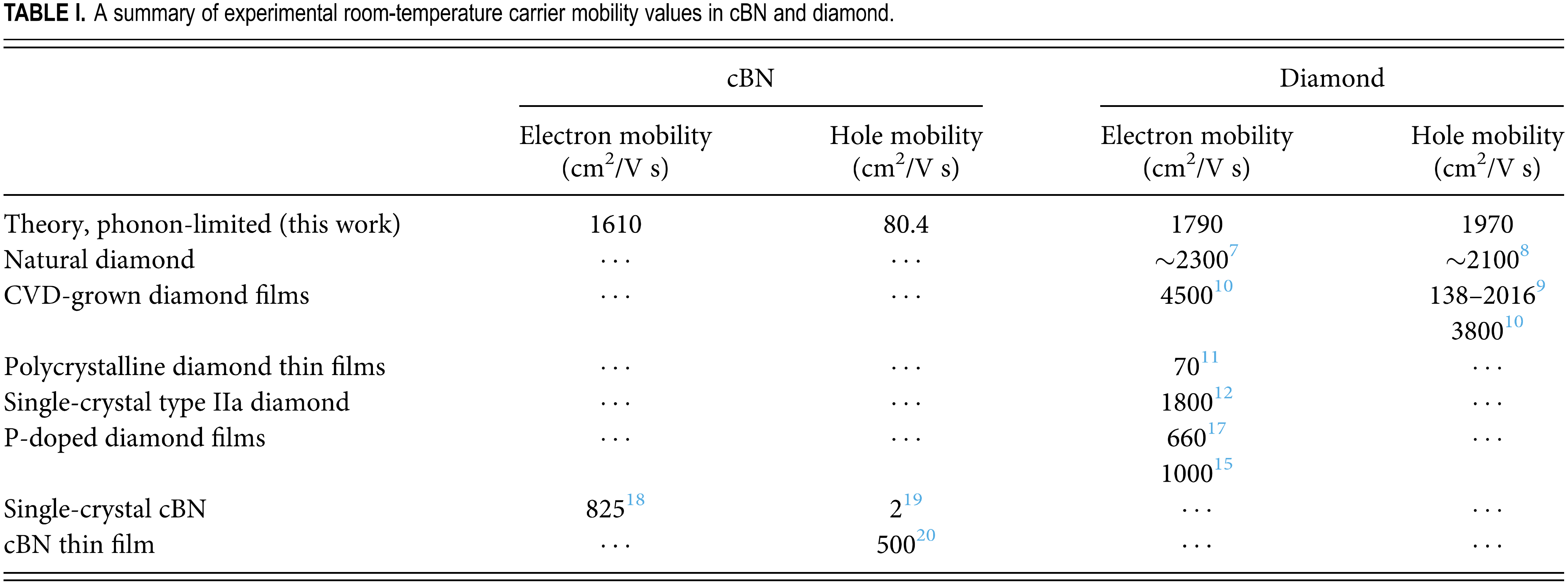


TABLE I. A summary of experimental room-temperature carrier mobility values in cBN and diamond.

	cBN		Diamond	
	Electron mobility ($cm^2/V\ s$)	Hole mobility ($cm^2/V\ s$)	Electron mobility ($cm^2/V\ s$)	Hole mobility ($cm^2/V\ s$)
Theory, phonon-limited (this work)	1610	80.4	1790	1970
Natural diamond	⋯	⋯	∼2300[7]	∼2100[8]
CVD-grown diamond films	⋯	⋯	4500[10]	138–2016[9] 3800[10]
Polycrystalline diamond thin films	⋯	⋯	70[11]	⋯
Single-crystal type IIa diamond	⋯	⋯	1800[12]	⋯
P-doped diamond films	⋯	⋯	660[17] 1000[15]	⋯
Single-crystal cBN	825[18]	2[19]	⋯	⋯
cBN thin film	⋯	500[20]	⋯	⋯

Band structure and phonons

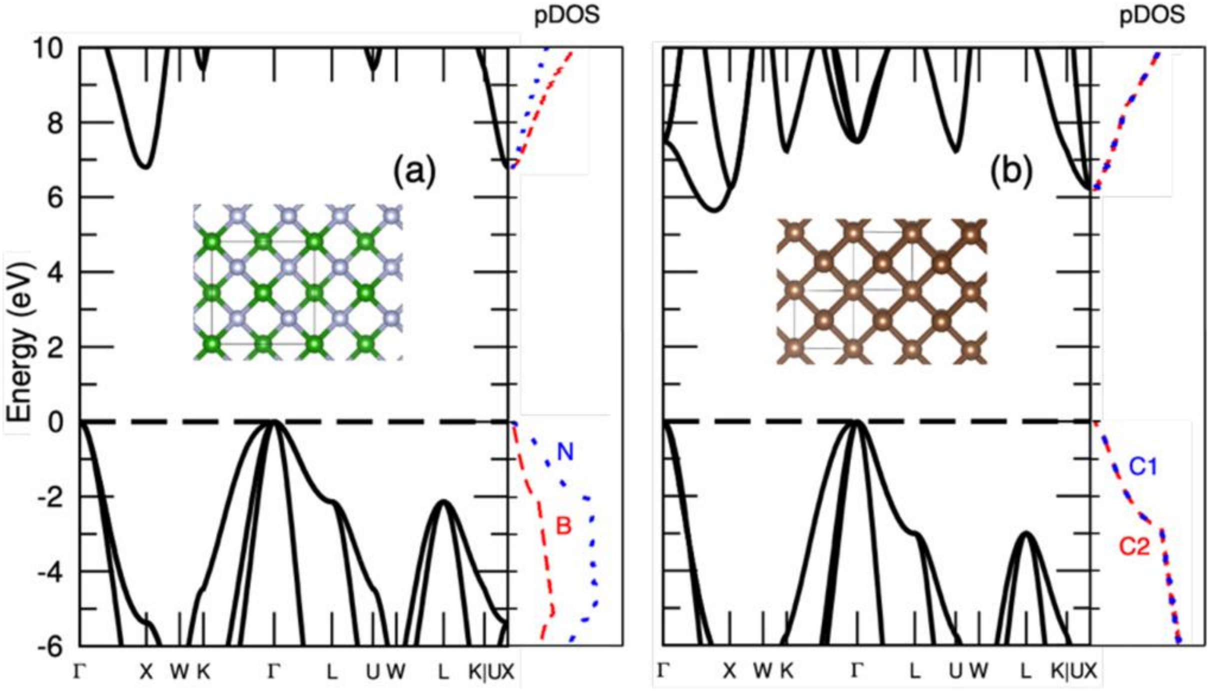


FIG. 1. The band structure and atom-projected density of states of (a) cBN and (b) diamond, shown with their crystal structures. While the bandgaps are similar, the hole effective masses are heavier in cBN. This is because the cBN valence bands consist primarily of second-nearest-neighbor N orbitals, while the diamond valence band is formed by nearest-neighbor C orbitals.

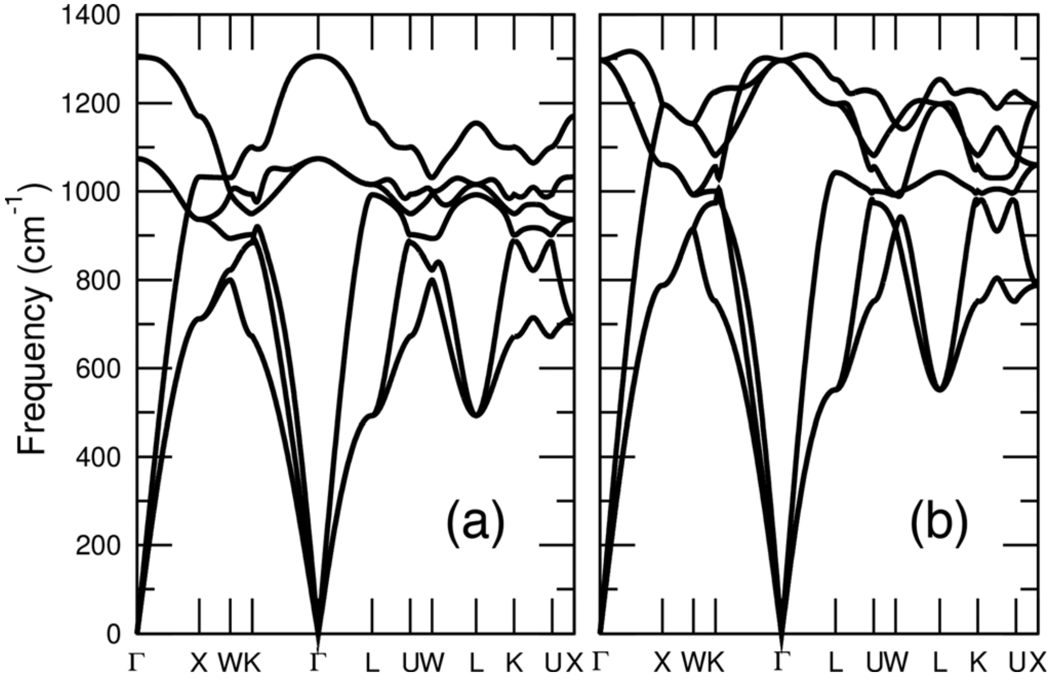
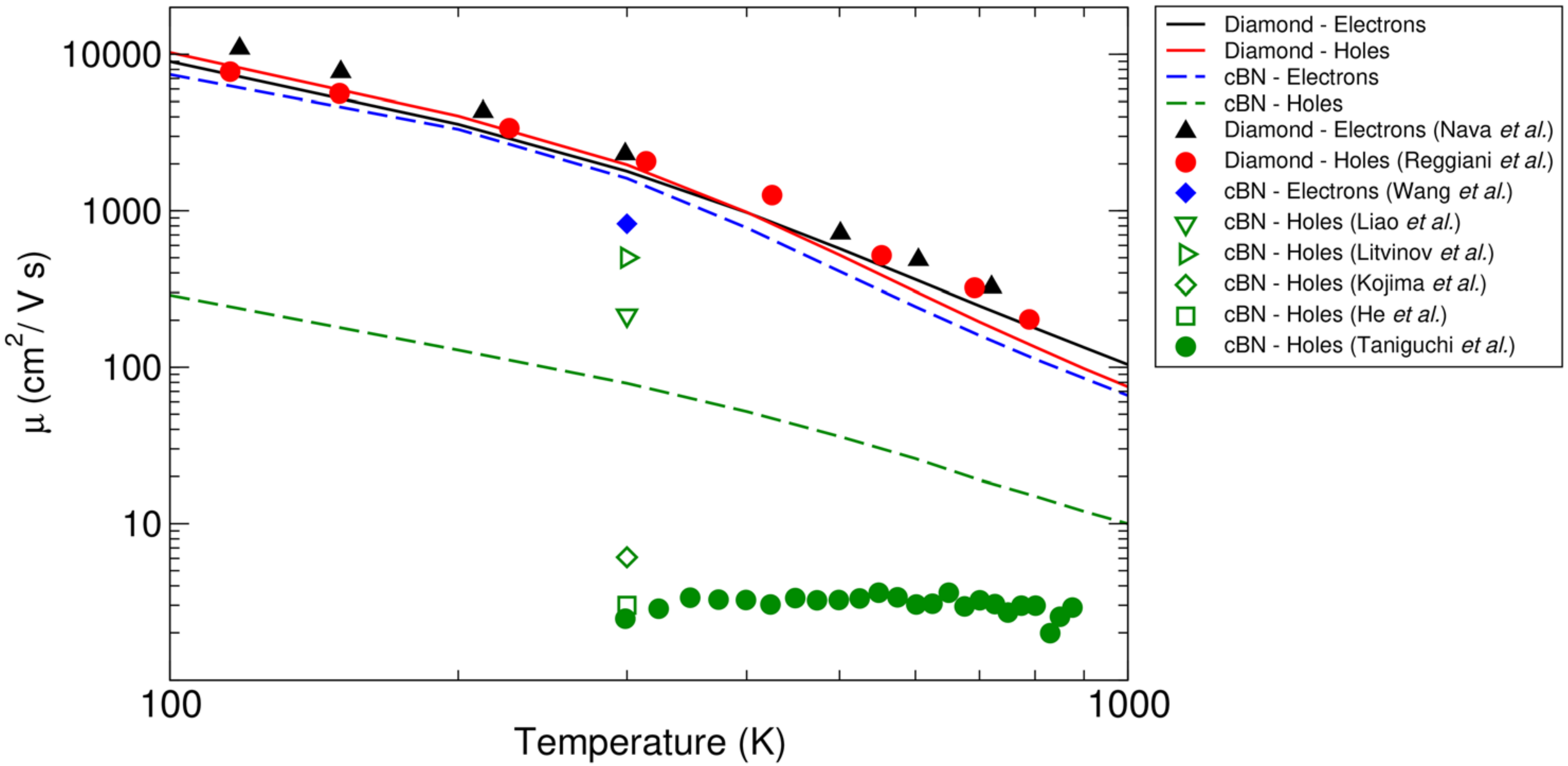


FIG. 2. Phonon dispersions of (a) cBN and (b) diamond. Apart from the LO–TO splitting at Γ in polar c-BN, both structures exhibit similar maximum phonon frequencies, sound velocities, and overall band characteristics.

Mobilities versus Temperature



Mobilities vs. doping

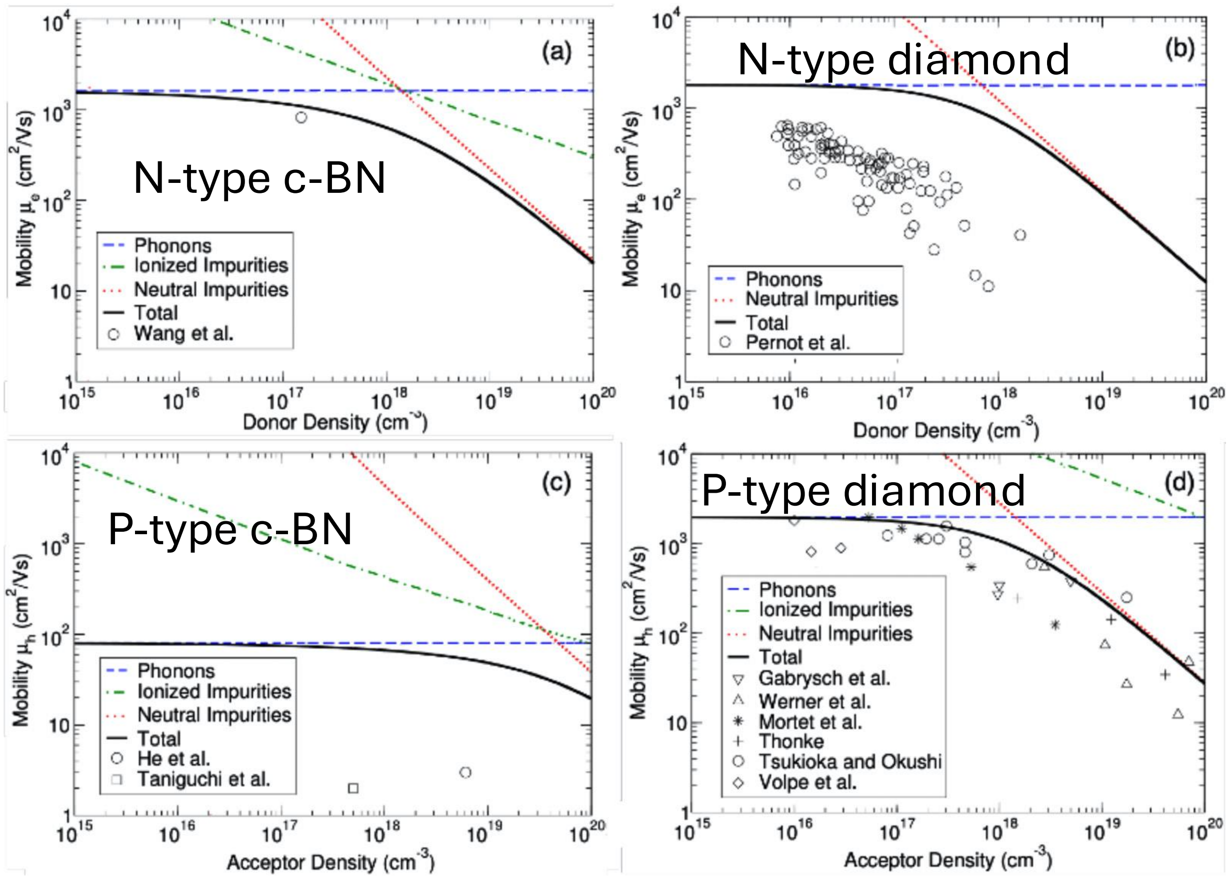
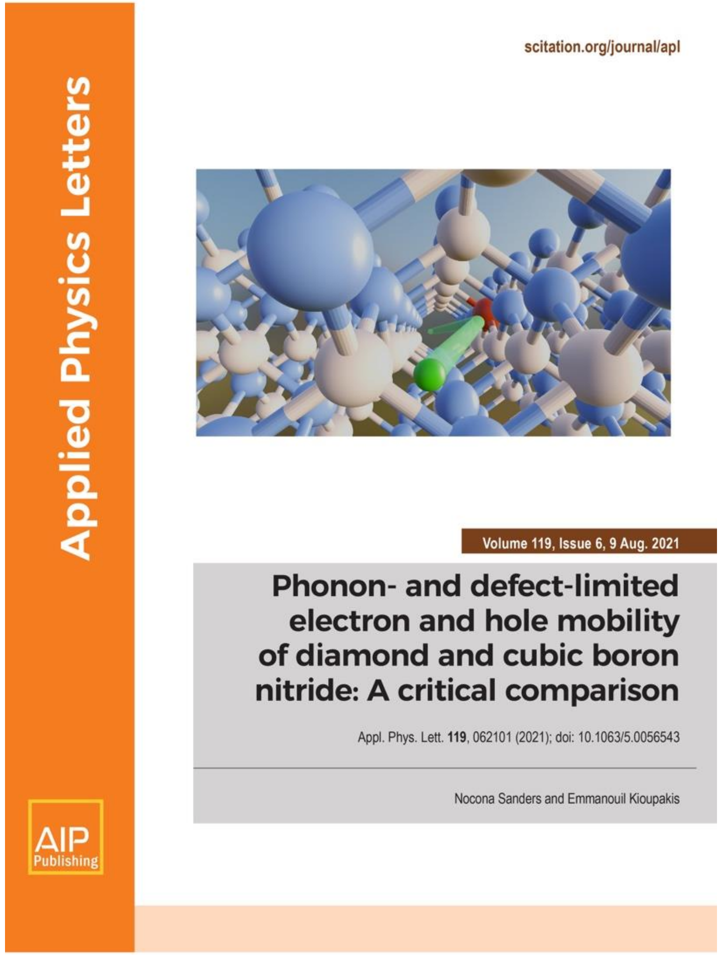


FIG. 7. Carrier mobility at 300 K as a function of dopant density in (a) n-type, Si-doped cBN, (b) n-type, P-doped diamond, (c) p-type, Be-doped cBN, and (d) p-type, B-doped diamond. Dashed, dotted, and dashed-dotted lines show the theoretical contributions from phonon scattering, neutral impurities, and ionized impurities, respectively. Experimental data points are from experimental work by Wang *et al.*,[18] He *et al.*,[49] Taniguchi *et al.*,[19] Pernot *et al.*,[57] Gabrysch *et al.*,[58] Werner *et al.*,[59] Mortet *et al.*,[16] Thonke,[60] Tsukioka and Okushi,[61] and Volpe *et al.*[62]


scitation.org/journal/apl

Applied Physics Letters

Volume 119, Issue 6, 9 Aug. 2021

Phonon- and defect-limited electron and hole mobility of diamond and cubic boron nitride: A critical comparison

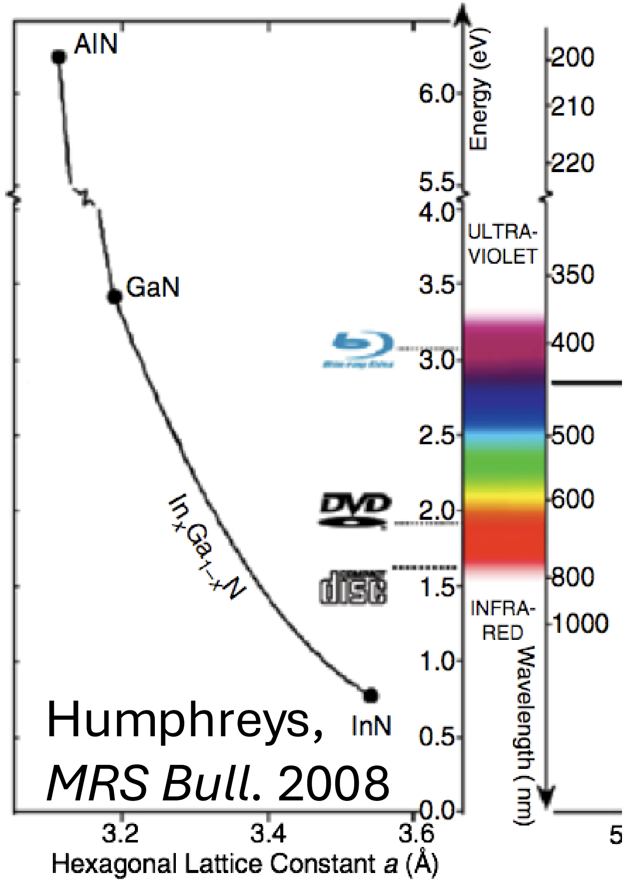
Appl. Phys. Lett. **119**, 062101 (2021); doi: 10.1063/5.0056543

Nocona Sanders and Emmanouil Kioupakis

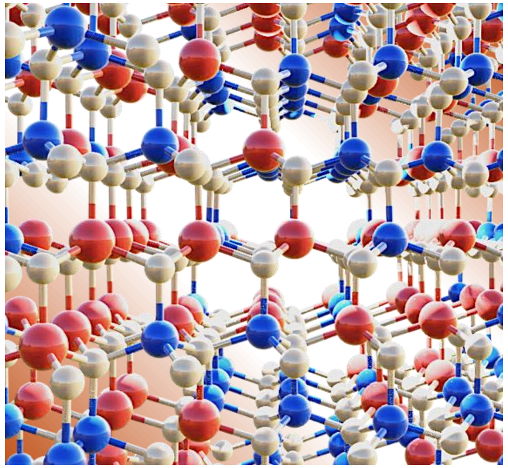
AIP Publishing

Alloys: a way to tune properties

- Mixing, e.g., *x* moles of AlN and (*1–x*) moles of GaN to form $Al_xGa_{1-x}N$
  → tune lattice constant and band gap to intermediate values.



Humphreys, *MRS Bull.* 2008

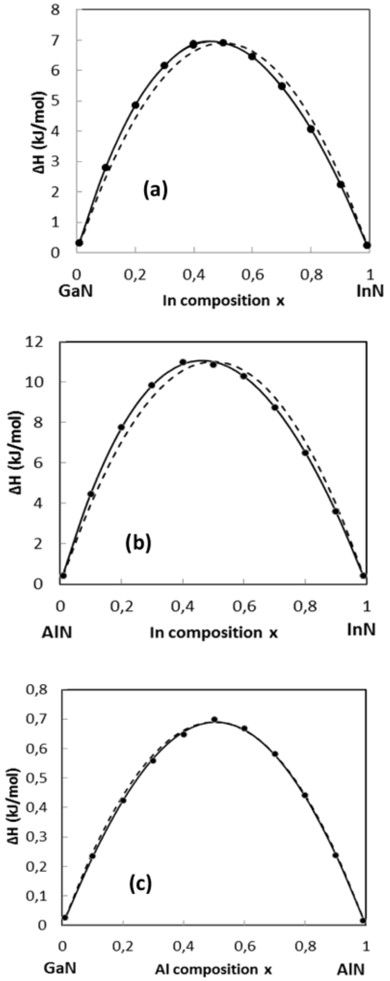


What do we expect to happen based on thermodynamics?

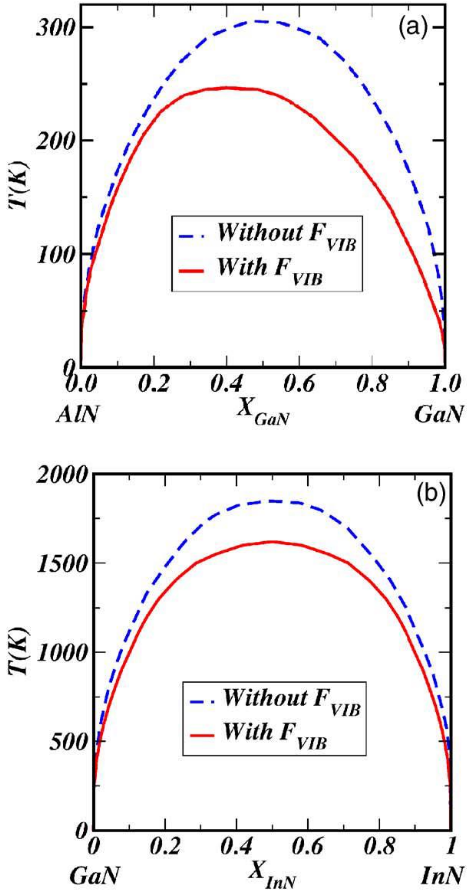
Answer: Gibbs free energy of mixing: **ΔG = ΔH – TΔS**
ΔH = enthalpy of mixing
ΔS = entropy of mixing = Σ x ln(x) for ideal solutions

- If **ΔH < 0** → intermixing is favored → **ordered compounds.**
- If **ΔH > 0** → mixing is unfavored, but:
  - If **TΔS > ΔH**: entropy of disordered material overcomes energy penalty → **random solid solutions.**
  - If **TΔS > ΔH**: entropy of disorder not enough to overcome energy penalty → **phase segregation**.

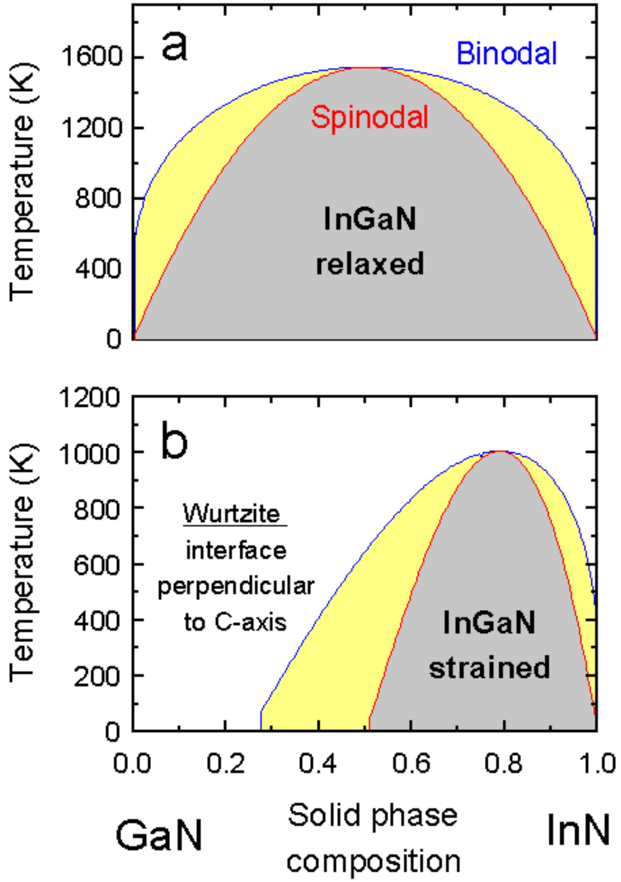
For nitrides:



ΔH > 0 → phase segregation or solid solution
ΔH large for InGaN and InAlN, small for AlGaN
https://doi.org/10.1002/pssa.201600752

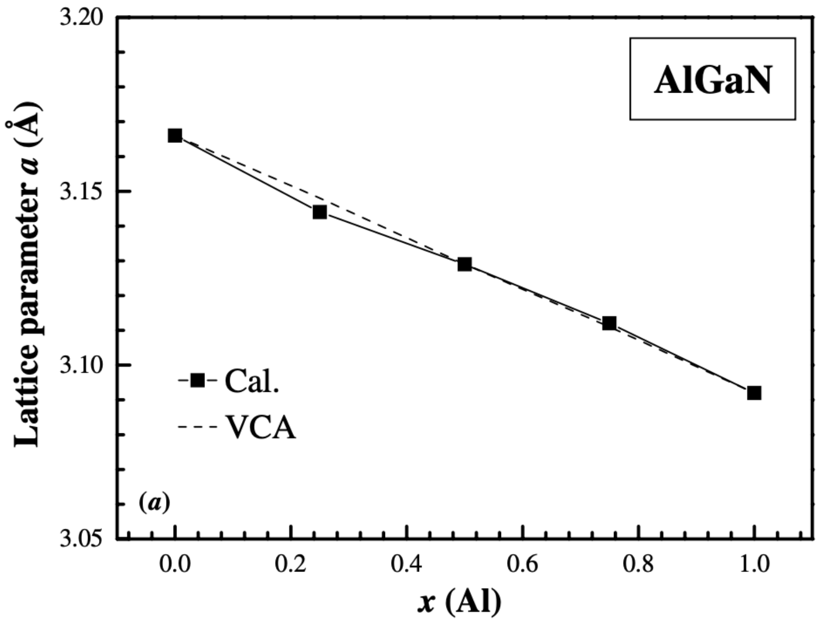


AlGaN: complete solubility even at room temperature
J. Appl. Phys. 100, 113528 (2006)



InGaN: expect phase segregation, but alloys stabilized in thin-film form, kinetics and strain play a role. 10.1557/S1092578300000880

Lattice constants of alloys: Vegard's law

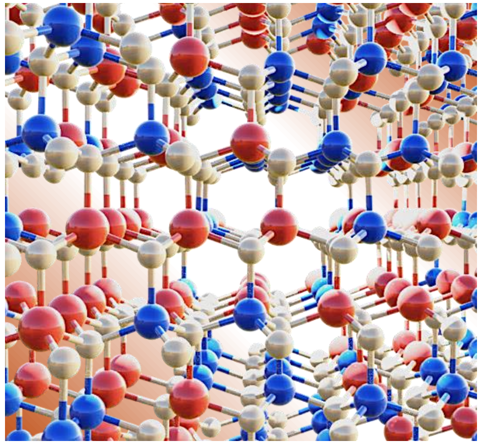


Dridi *et al* 2003 *Semicond. Sci. Technol.* 18 850

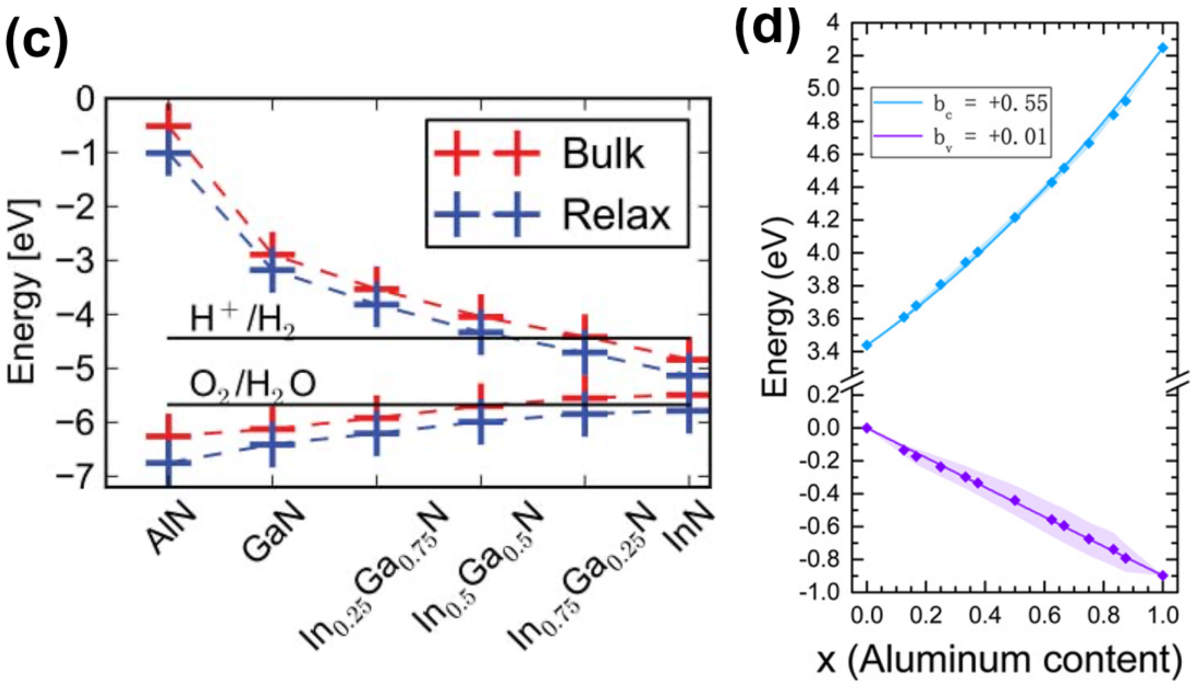
Lattice constant varies linearly with composition (Vegard's law).

$a(Al_xGa_{1-x}N) = x * a(AlN) + (1-x) * a(GaN)$

Reason: alloy contains a random distribution of Al-N and Ga-N bonds, but on a large scale the bond length is the weighted average of the bond lengths of the two materials.



Band gap and conduction/valence bands: bowing



10.1557/s43578-021-00437-6

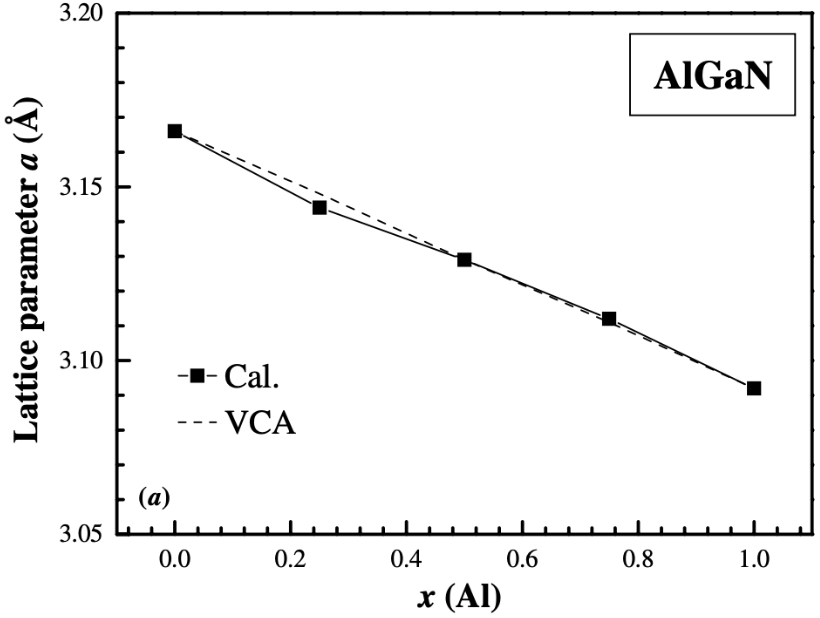
Bowing equation: modification to Vegard's law:

E(AlGaN) = x*E(AlN) + (1–x)*E(GaN) –x(1–x)*b
b = bowing parameter

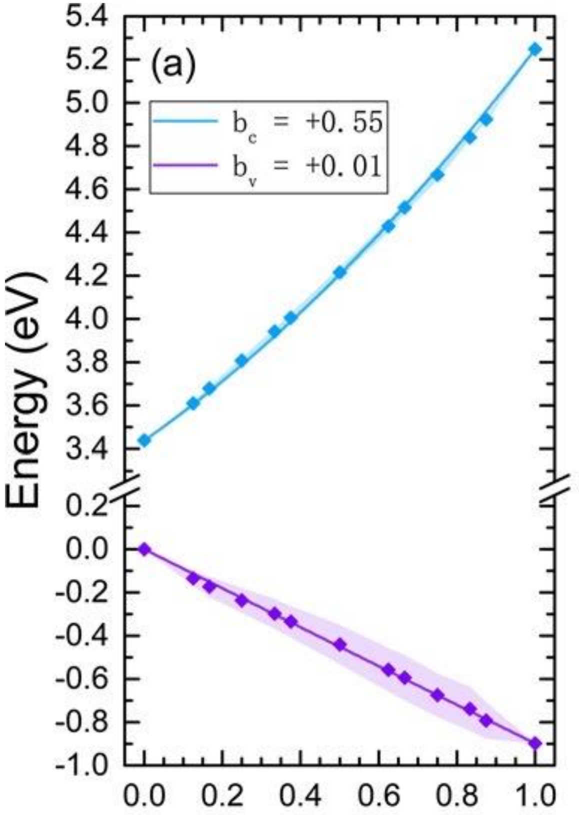
Reason: x(1–x) is a measure of fluctuations of alloy composition. Large fluctuations of composition → large fluctuations of electron and hole energies → reduction of the band gap.

Effect of alloying on mobility

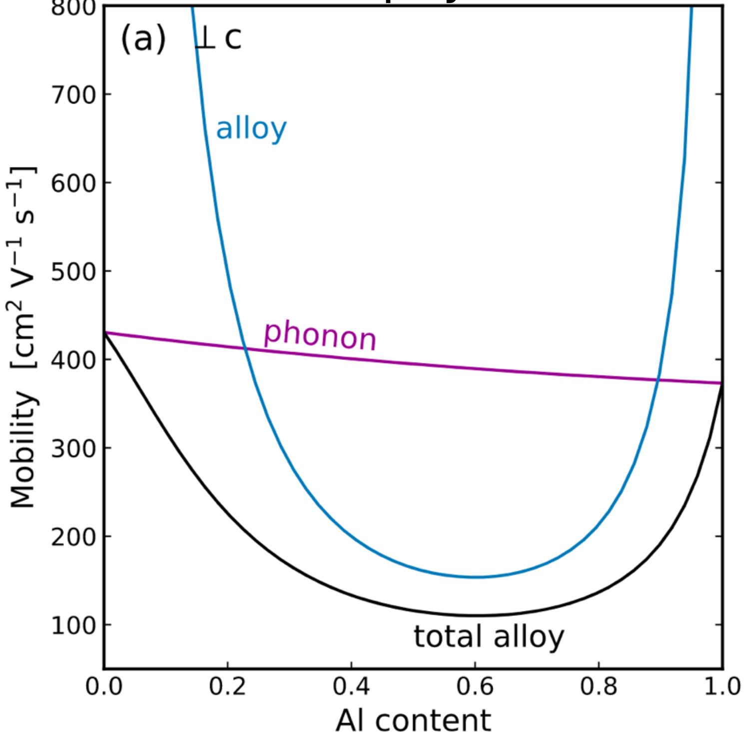
Lattice constants vary linearly with composition[1]…



band gap shows slight bowing[2]…



but mobility drops abruptly[3]

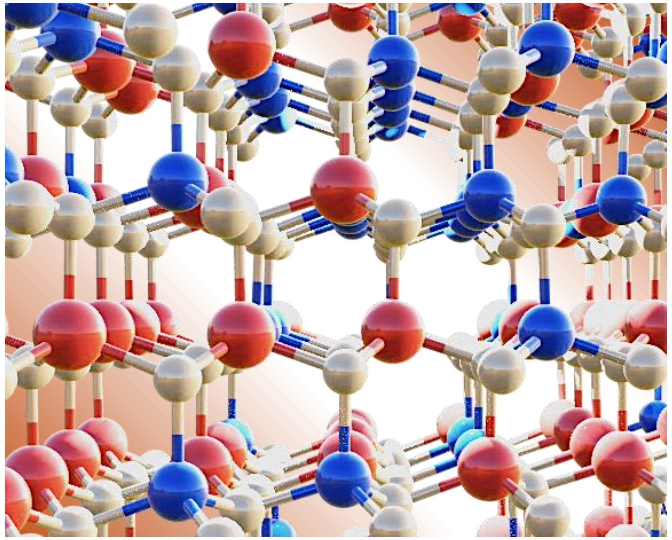


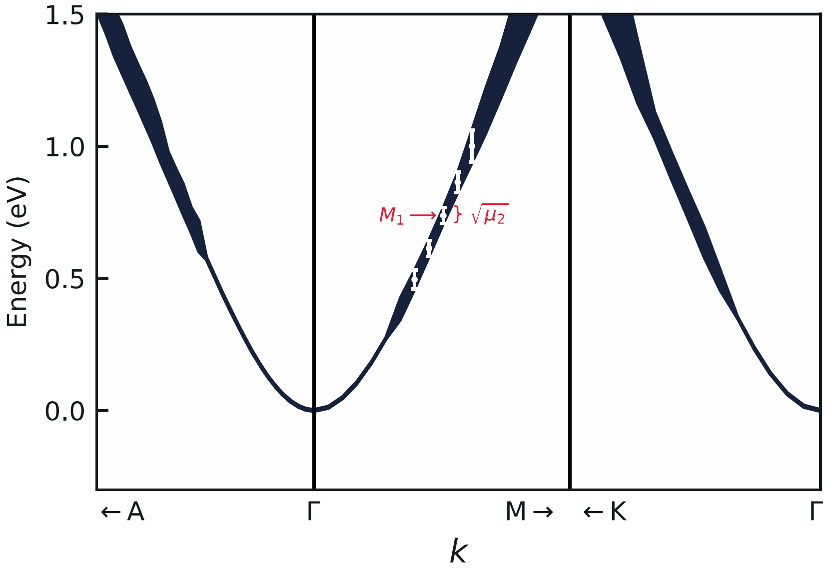
[1] Dridi *et al* 2003 *Semicond. Sci. Technol.* 18 850

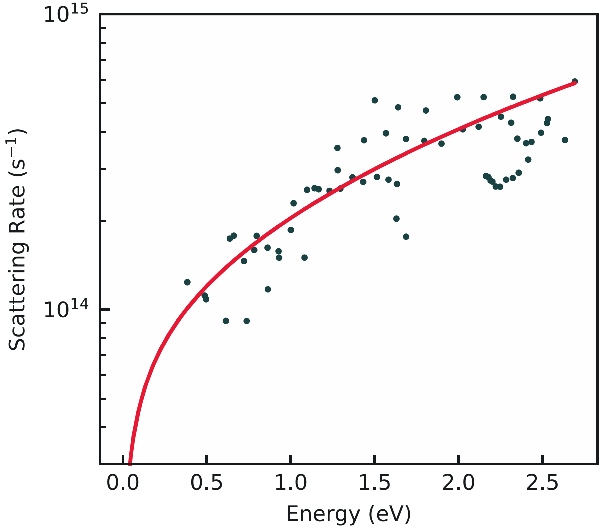
[2] Kyrtsos *et al* 2020 *J. Phys.: Condens. Matter* 32 365504

[3] Pant *et al* 2022 *Appl. Phys. Lett.* 121, 032105

Challenges with AlGaN: alloy-disorder scattering





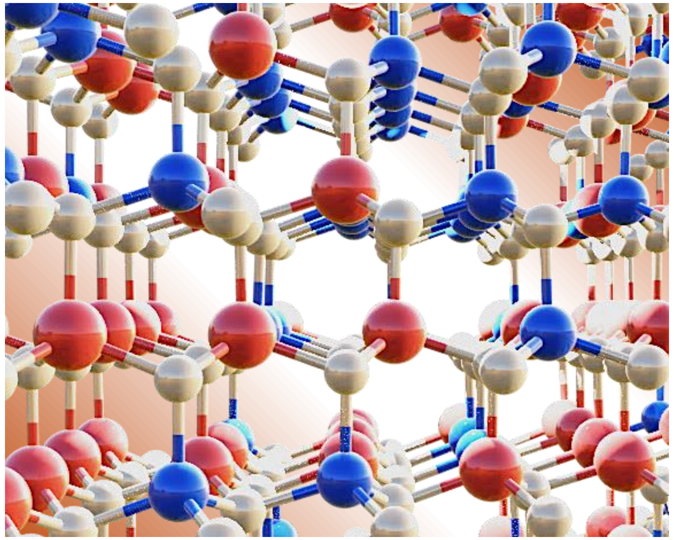


Random composition fluctuations in AlGaN scatter electrons and limit the mobility.
The scattering rate is proportional to statistical fluctuations, i.e., x(1–x).
We have applied calculations to evaluate it through the statistical broadening of the energy bands in alloys: finite broadening → finite electron lifetime: ΔE Δτ = h

$$\frac{1}{\tau} = \frac{2\pi}{\hbar} U_0^2 x(1-x)\Omega_0 \frac{m^{*3/2}}{\sqrt{2}\pi^2\hbar^3} \times (1+2\alpha\varepsilon)\sqrt{\varepsilon(1+\alpha\varepsilon)} I(\alpha,\varepsilon)$$

Pant, Deng, and Kioupakis, *Appl. Phys. Lett.* **117**, 242105 (2020)

What is the alloy scattering parameter U_0 for electrons?



$$\frac{1}{\tau} = \frac{2\pi}{\hbar} U_0^2 x(1-x)\Omega_0 \frac{m^{*3/2}}{\sqrt{2}\pi^2\hbar^3} \times (1+2\alpha\varepsilon)\sqrt{\varepsilon(1+\alpha\varepsilon)}I(\alpha,\varepsilon)$$

Many models proposed in the literature:

- Is it the difference of the conduction band energies of GaN and AlN?
- Is it the derivative of the band energy with respect to composition?

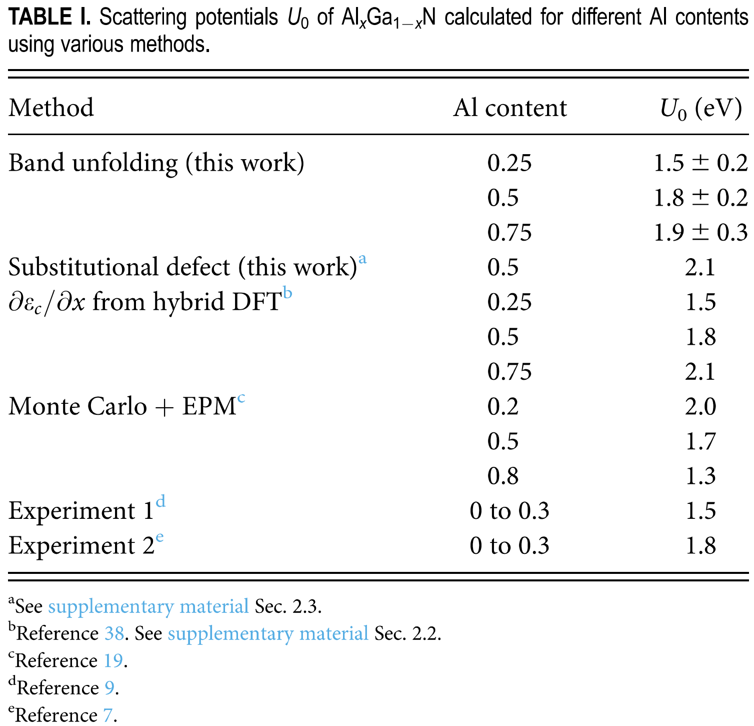


TABLE I. Scattering potentials U_0 of $Al_xGa_{1-x}N$ calculated for different Al contents using various methods.

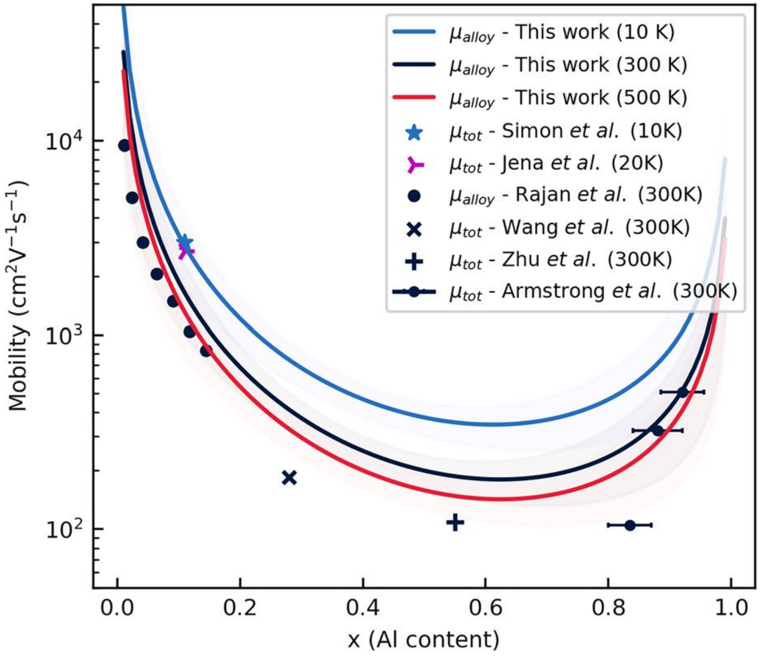
Method	Al content	U_0 (eV)
Band unfolding (this work)	0.25	1.5 ± 0.2
	0.5	1.8 ± 0.2
	0.75	1.9 ± 0.3
Substitutional defect (this work)[a]	0.5	2.1
$\partial\varepsilon_c/\partial x$ from hybrid DFT[b]	0.25	1.5
	0.5	1.8
	0.75	2.1
Monte Carlo + EPM[c]	0.2	2.0
	0.5	1.7
	0.8	1.3
Experiment 1[d]	0 to 0.3	1.5
Experiment 2[e]	0 to 0.3	1.8

[a] See supplementary material Sec. 2.3.
[b] Reference 38. See supplementary material Sec. 2.2.
[c] Reference 19.
[d] Reference 9.
[e] Reference 7.

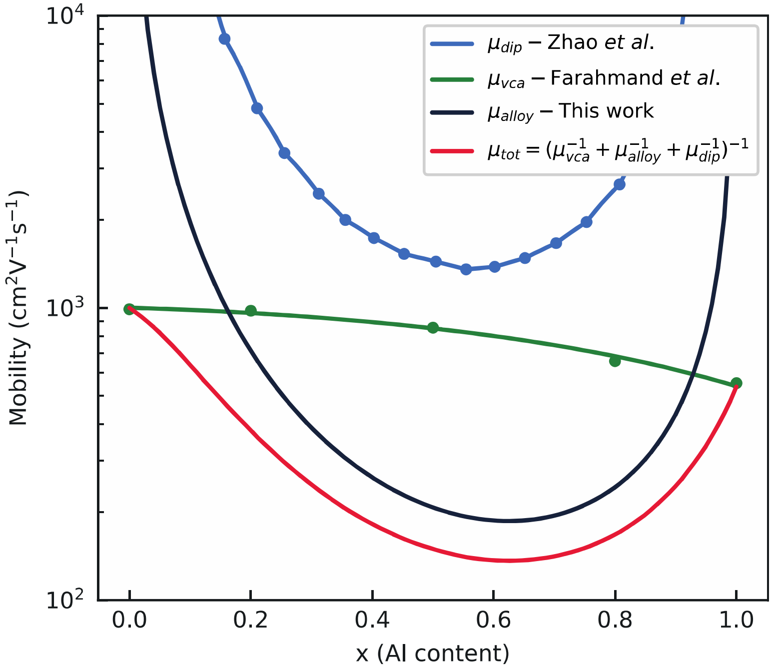
A: derivative of the band energy with respect to composition.
Wave function of electrons in AlGaN extended over several atoms →
energy determined by average composition in the wave function volume.

Alloy disorder limits the mobility of AlGaN

Alloy-limited mobility:



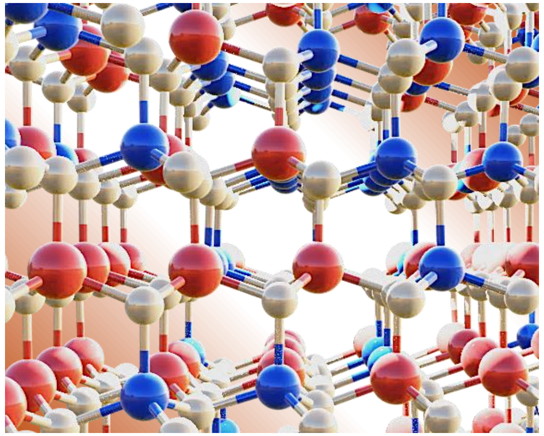
Total mobility:

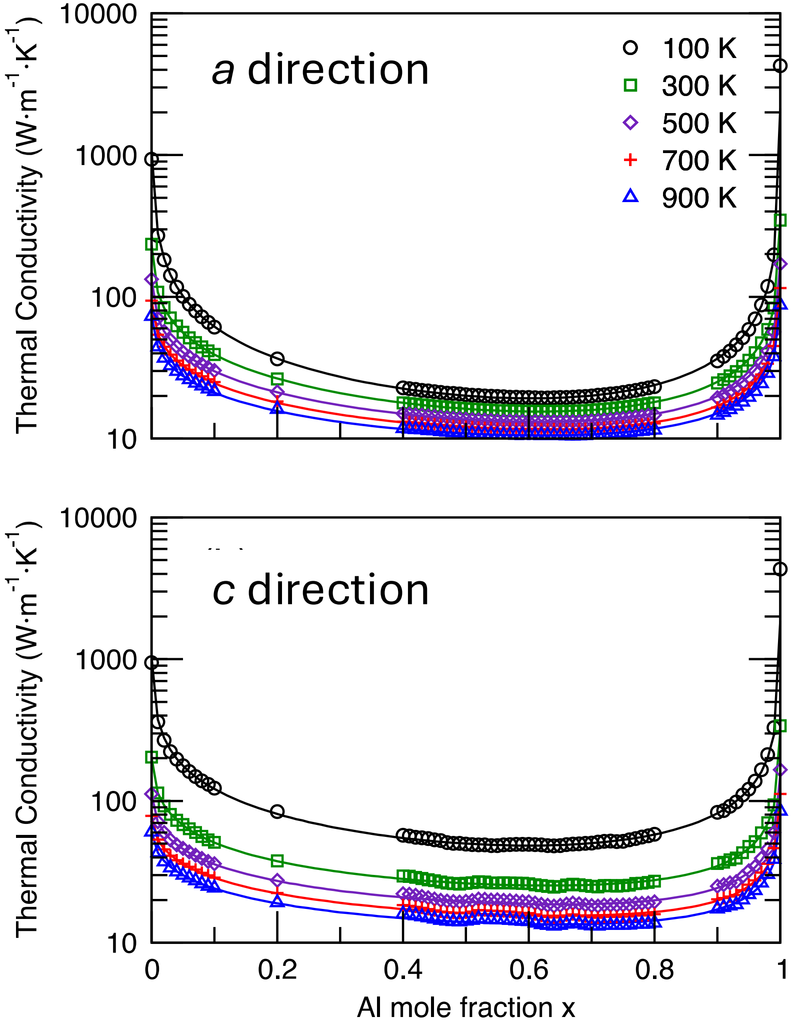


Alloy-disorder scattering is the dominant electron scattering mechanism at intermediate AlGaN alloy compositions.
At high Al composition the mobility is high, but doping and electrical contacts become difficult.

Pant, Deng, and Kioupakis,
Appl. Phys. Lett. **117**, 242105 (2020)

Effect of alloy disorder on thermal conductivity



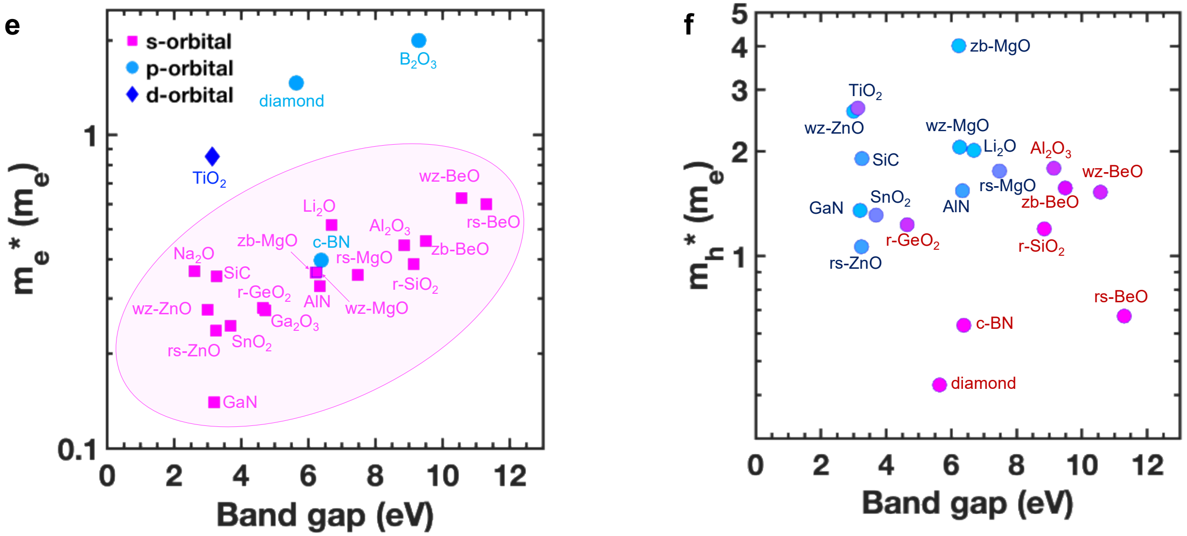


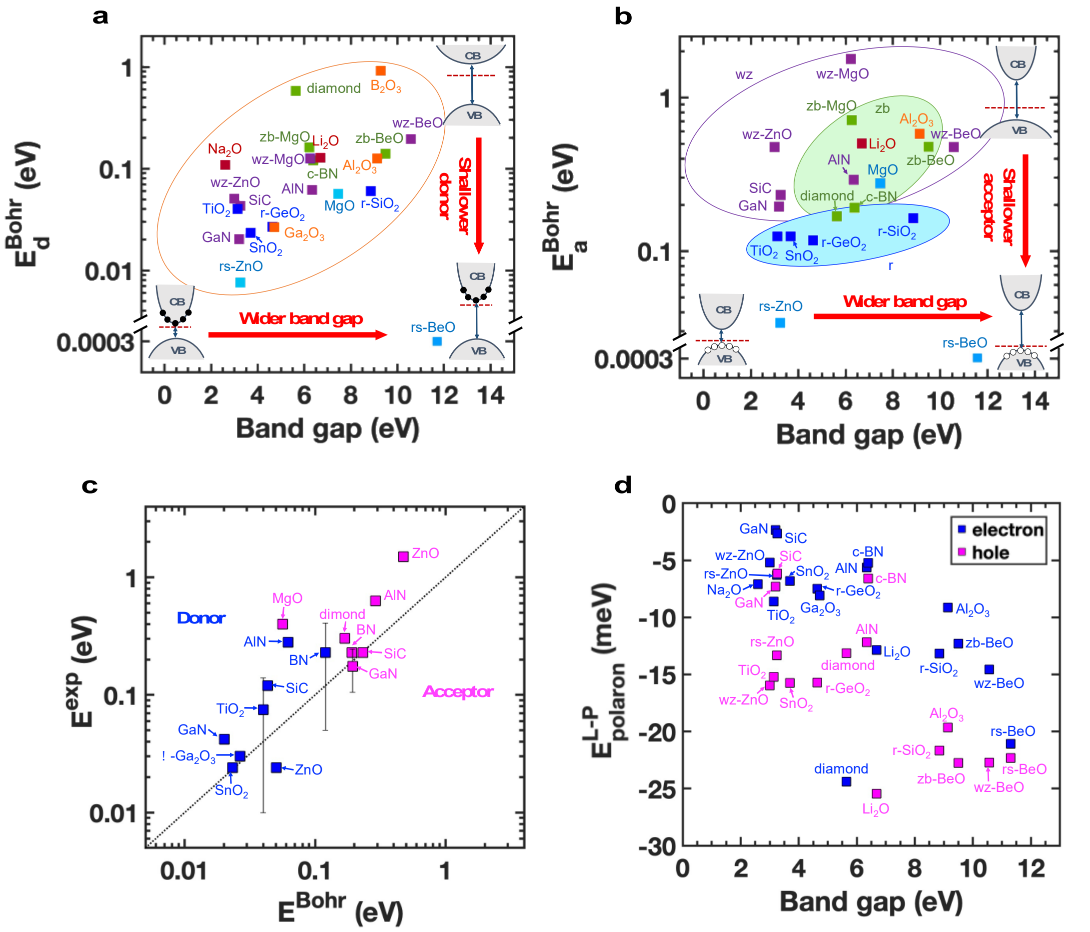
Composition fluctuations in alloys also induce fluctuations of the atomic masses, and therefore scatter vibrational waves (phonons).

→ Alloy disorder is also detrimental to the thermal conductivity of AlGaN alloys, especially at intermediate compositions.

https://arxiv.org/abs/1910.05440

Extreme-gap semiconductors: doping for E_{gap} ~ 9.5 eV





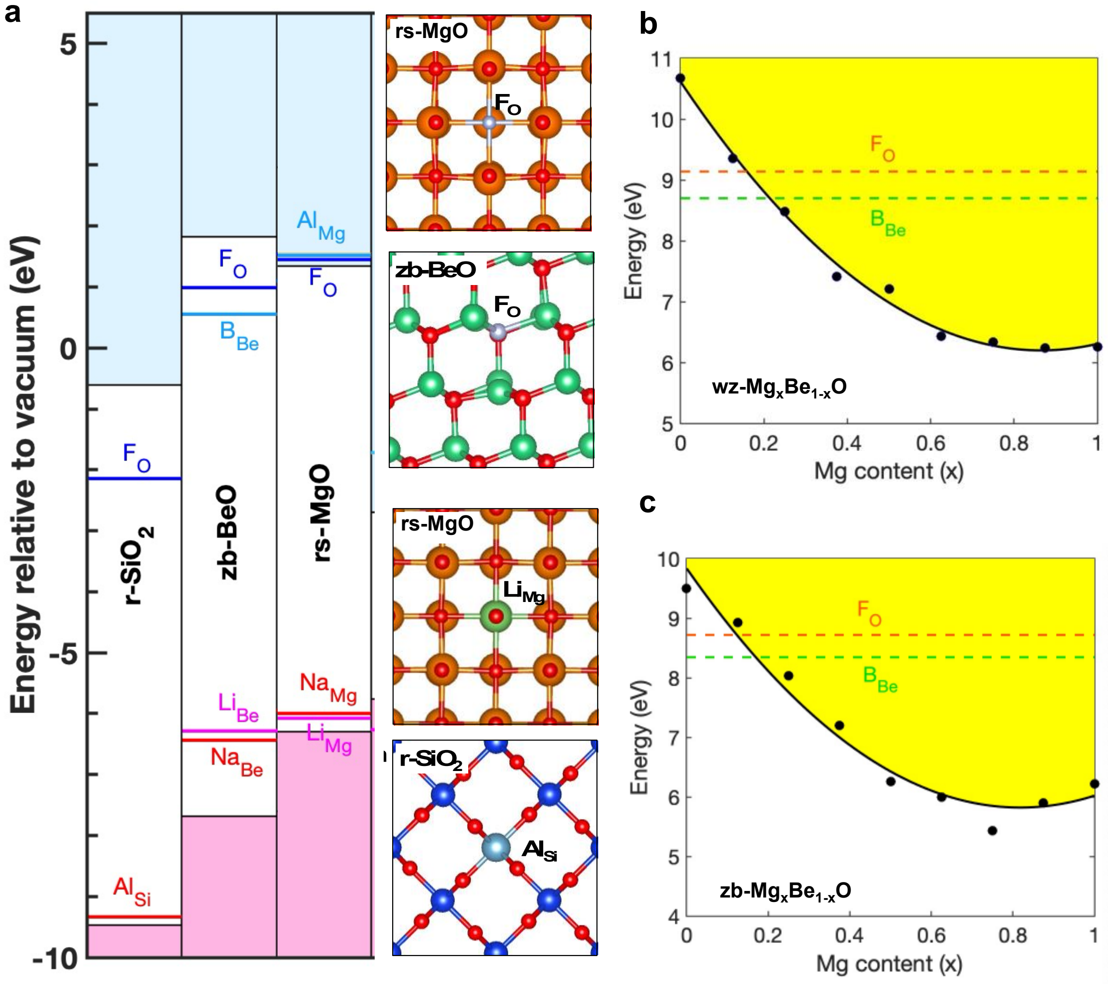
Claim: materials composed of light elements and packed in dense, symmetric crystal structures combine ultra-wide gap with relatively light effective mass, can potentially be dopable.

$$\boxed{E_d = \frac{e^4 m_e^*}{2(4\pi\varepsilon\varepsilon_0\hbar)^2} = \frac{13.6\ \text{eV}}{\varepsilon^2}\frac{m_e^*}{m_e}}$$

arXiv:2506.07284

High-throughput study for binary materials: findings agree with experiments, predicted several new candidate dopable semiconductors.

Extreme-gap semiconductors: doping for E_{gap} ~ 9.5 eV



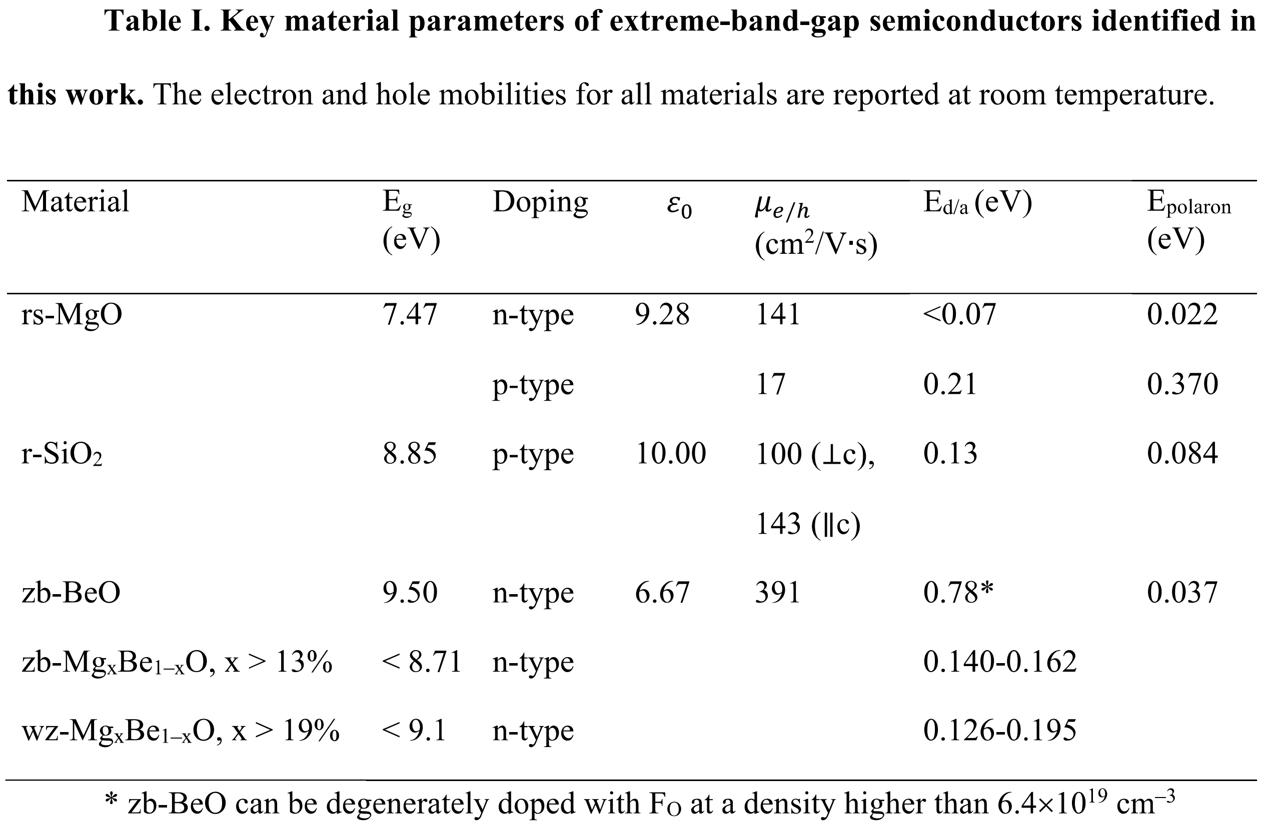


Table I. Key material parameters of extreme-band-gap semiconductors identified in this work. The electron and hole mobilities for all materials are reported at room temperature.

Material	E_g (eV)	Doping	ε_0	$\mu_{e/h}$ ($cm^2/V{\cdot}s$)	$E_{d/a}$ (eV)	$E_{polaron}$ (eV)
rs-MgO	7.47	n-type	9.28	141	<0.07	0.022
		p-type		17	0.21	0.370
r-SiO$_2$	8.85	p-type	10.00	100 (⊥c), 143 (∥c)	0.13	0.084
zb-BeO	9.50	n-type	6.67	391	0.78*	0.037
zb-Mg$_x$Be$_{1-x}$O, x > 13%	< 8.71	n-type			0.140-0.162	
wz-Mg$_x$Be$_{1-x}$O, x > 19%	< 9.1	n-type			0.126-0.195	

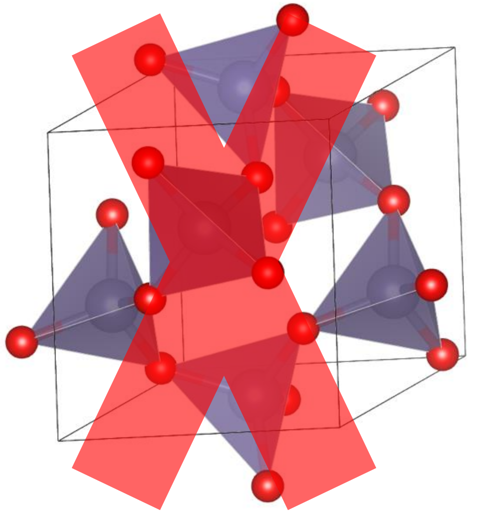
* zb-BeO can be degenerately doped with F$_O$ at a density higher than 6.4×10^{19} cm^{-3}

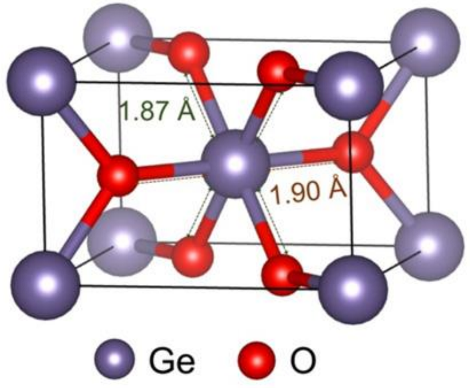
Predicted several new materials with band gaps as wide as 9.5 eV that can be doped with donors or acceptors (but need out-of-equilibrium doping)

arXiv:2506.07284

Computational discovery of rutile GeO_2 as a new ultra-wide gap semiconductor

Rutile GeO_2: a higher-symmetry ultra-wide gap oxide



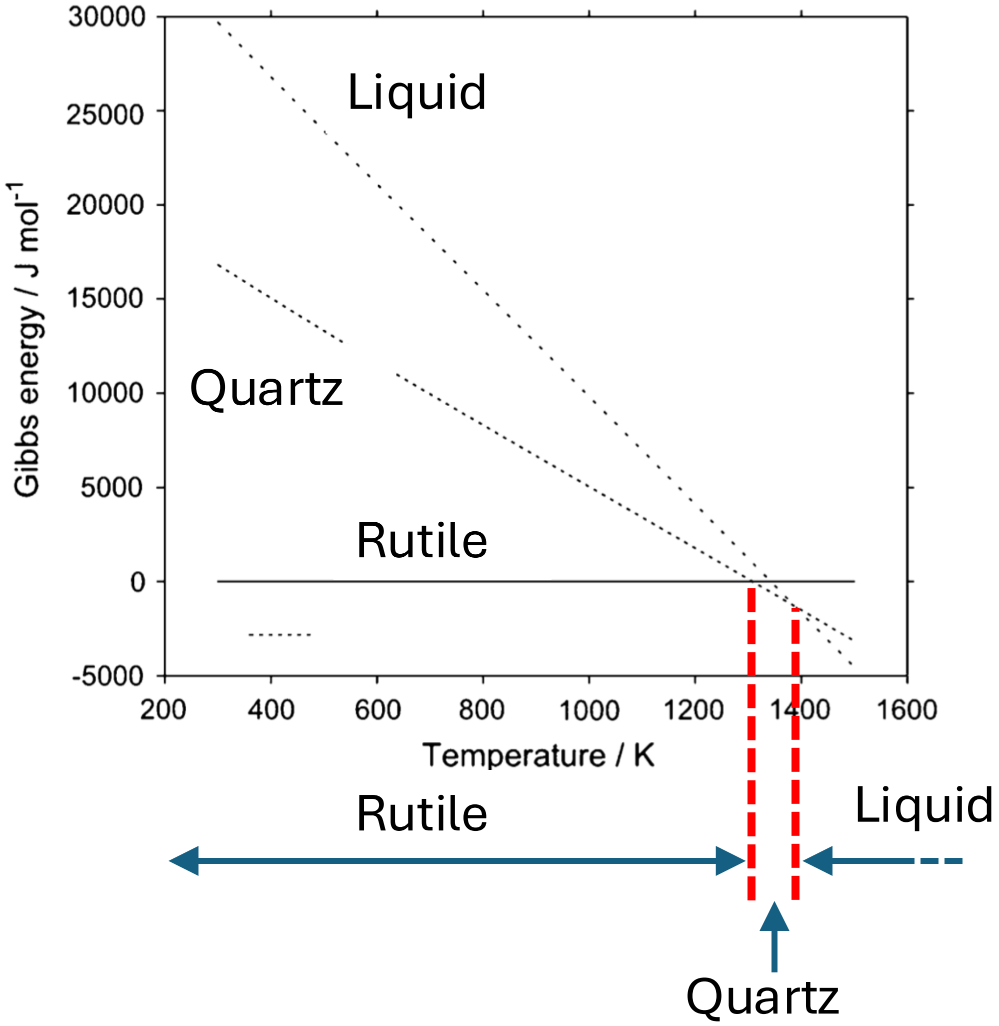


Quartz GeO_2

- Tetrahedral
- Low density
- Water soluble
- Most stable in powder form

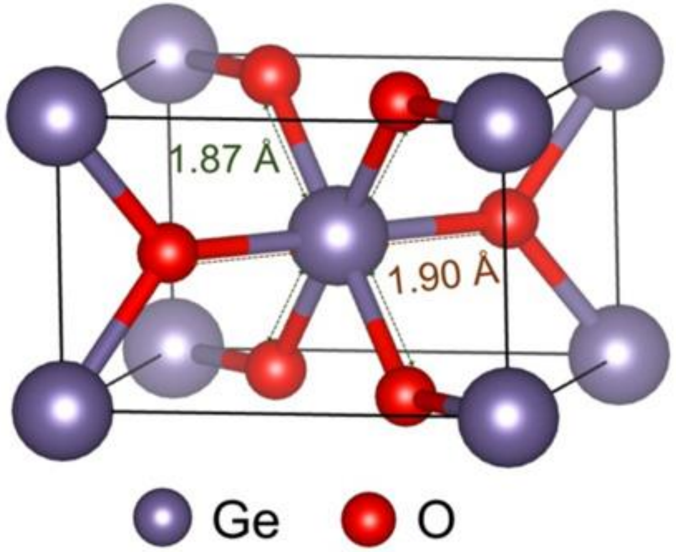
Rutile GeO_2

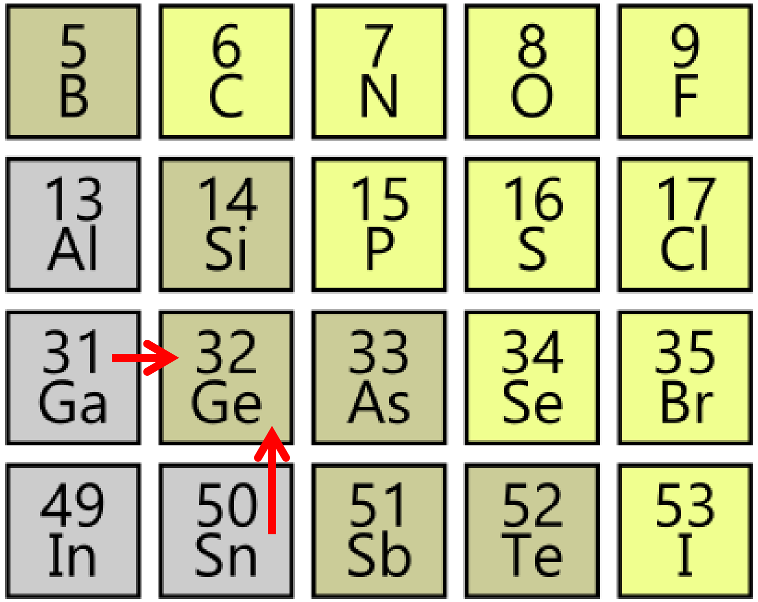
- Octahedral
- High density
- Insoluble in water
- Most stable bulk phase in ambient conditions



J. Phase Equilib. Diffus. **36**, 254–261 (2015)

Why is rutile GeO_2 an alternative for Ga_2O_3?



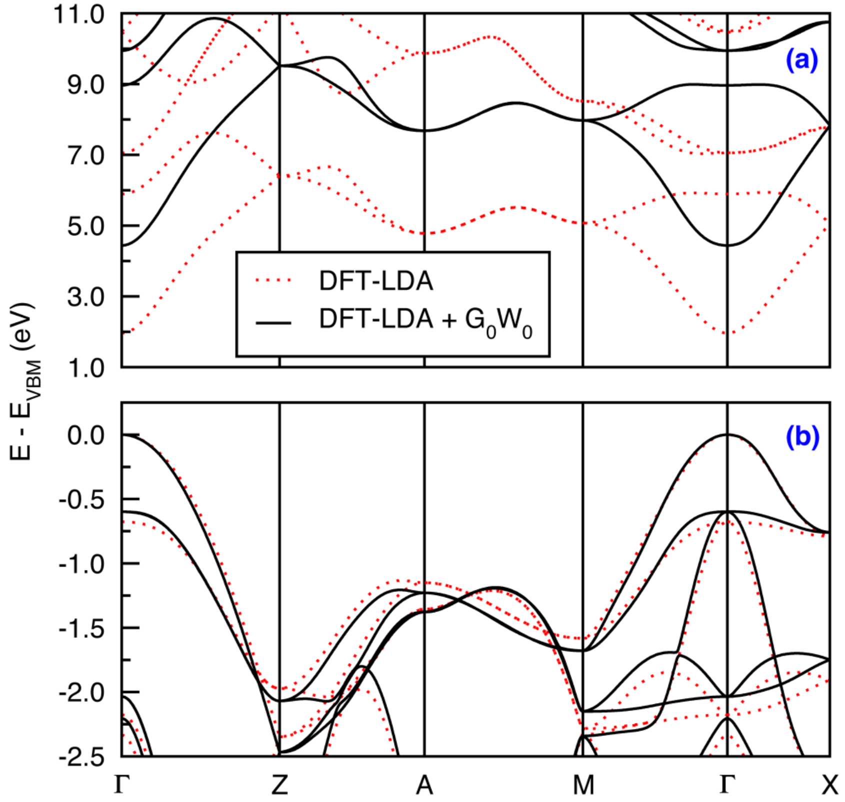


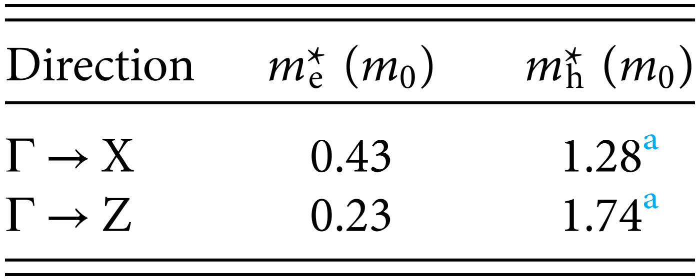
5 B	6 C	7 N	8 O	9 F
13 Al	14 Si	15 P	16 S	17 Cl
31 Ga	32 Ge	33 As	34 Se	35 Br
49 In	50 Sn	51 Sb	52 Te	53 I

- Similar to n-type semiconducting oxides **Ga_2O_3** and **rutile SnO_2**.
- Higher symmetry crystal structure → we expect higher thermal conductivity and higher carrier mobility.
- High density of O atoms: easier for holes to hop between O 2*p* orbitals, possibility of p–type conductivity.

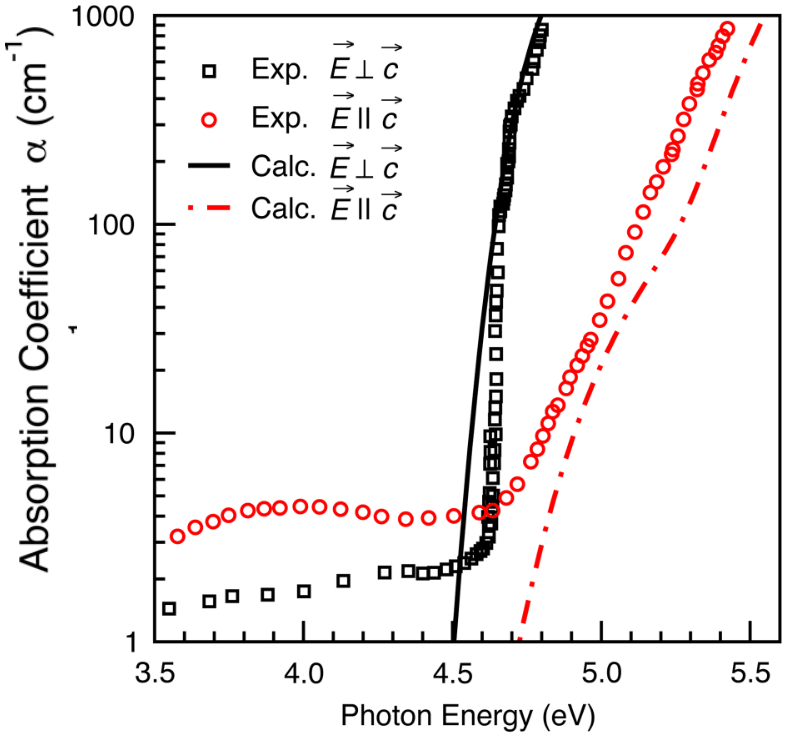
Previously unexplored as a semiconductor, but **can it be doped?**

Band structure and effective masses of rutile GeO$_2$





Direction	m_e^* (m_0)	m_h^* (m_0)
$\Gamma \rightarrow X$	0.43	1.28[a]
$\Gamma \rightarrow Z$	0.23	1.74[a]



Dipole-forbidden gap at 4.6 eV, agreement with optical spectra. *Solid State Commun*. **25**, 959 (1978).

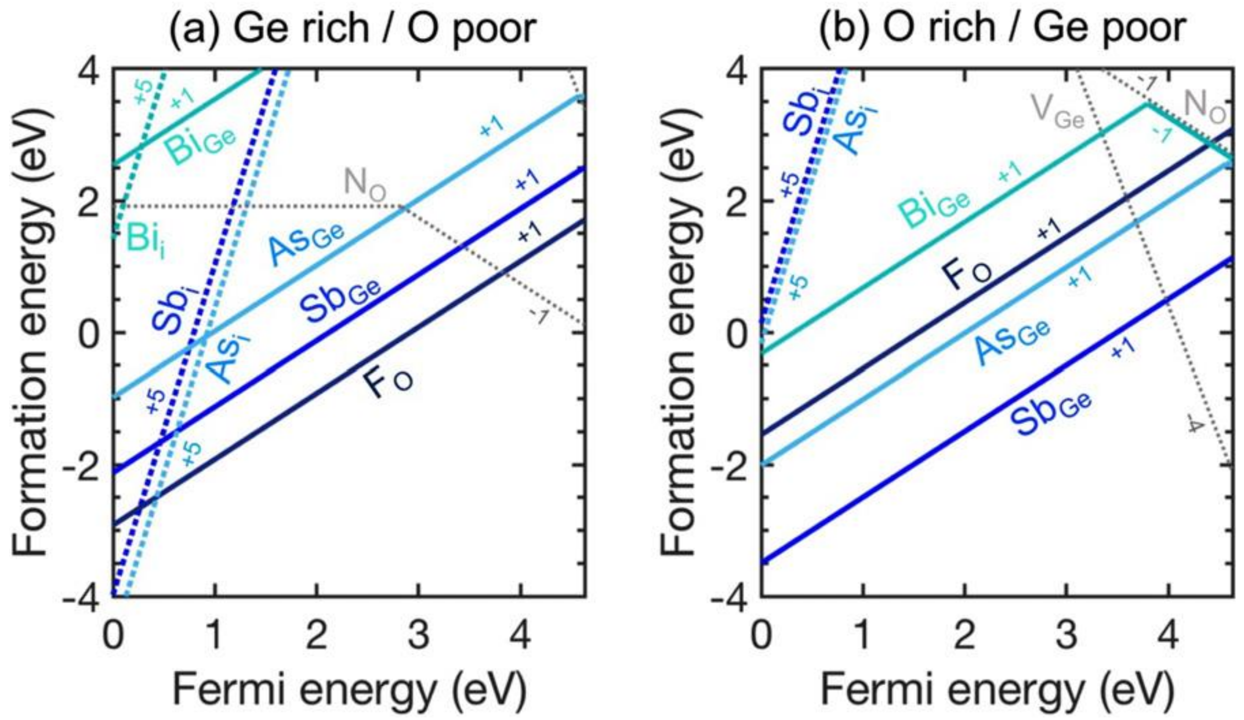
Dispersive valence and conduction bands, light electron and hole effective masses.

→ Promising for ambipolar doping and high carrier mobilities

Kelsey Mengle, Chae, and Kioupakis, *J. Appl. Phys*. **126**, 085703 (2019)

But is rutile GeO$_2$ dopable?

Shallow donors of rutile GeO_2

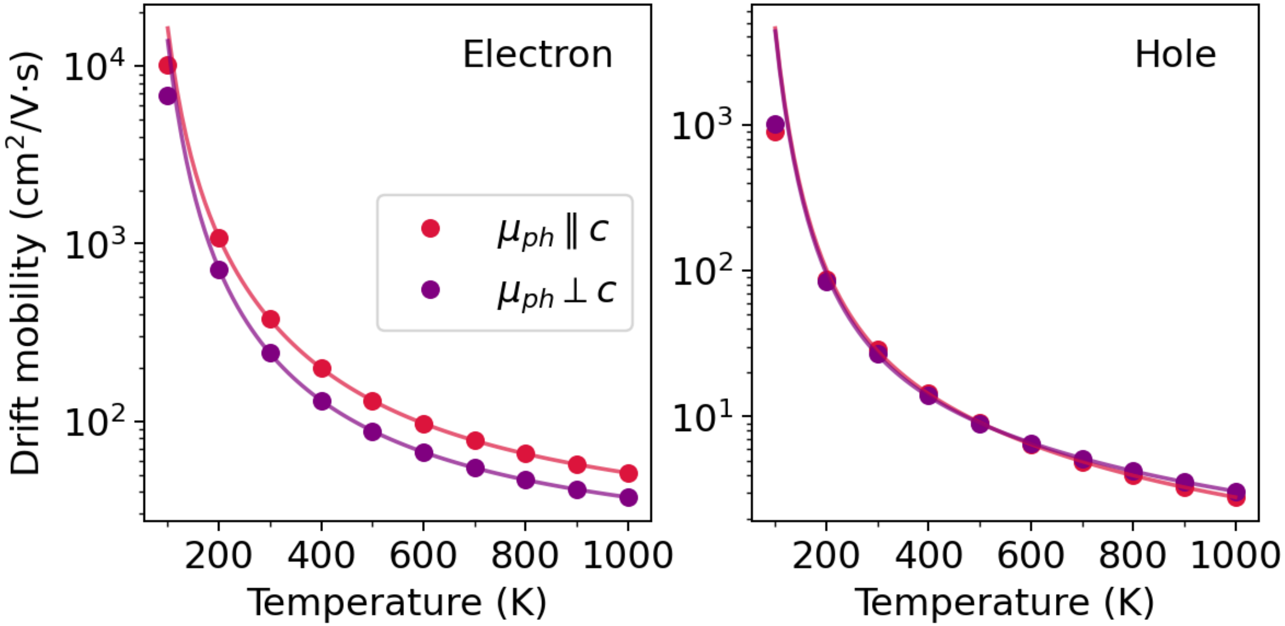


- O-poor growth: F_O is best, but need to avoid nitrogen during growth/annealing.
- O-rich growth: Sb_{Ge} is best, but it is compensated by Ge vacancies.
- Hydrogen interstitials also act as shallow donors

→ Predicted **ease of n-type doping** of rutile GeO_2 with Sb_{Ge}, As_{Ge}, F_O, and H_i

Sieun Chae, Lee, Mengle, Heron, and Kioupakis, *Applied Physics Letters* **114**, 102104 (2019)

Carrier mobility of rutile GeO_2

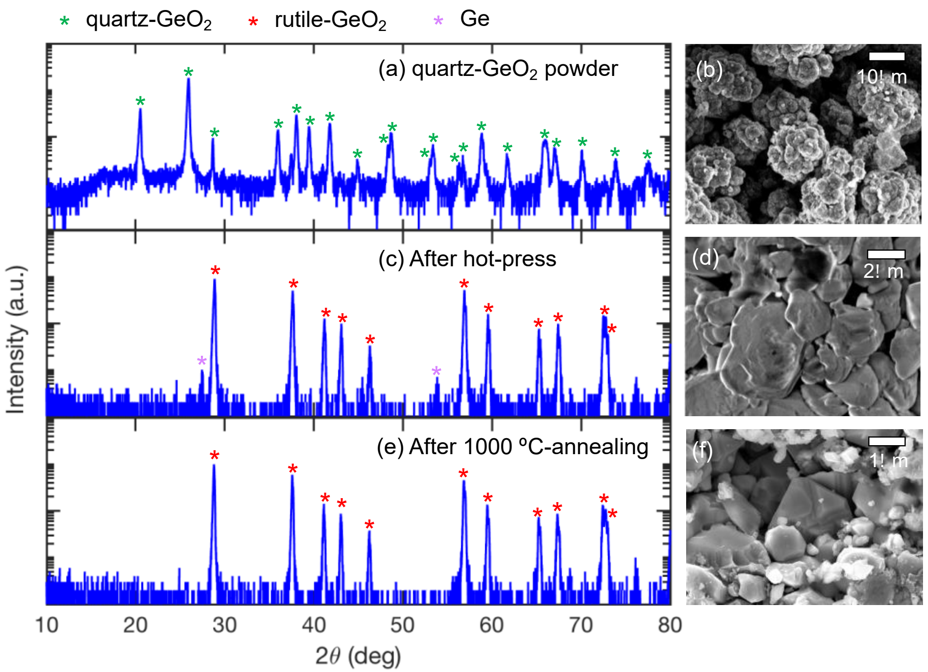


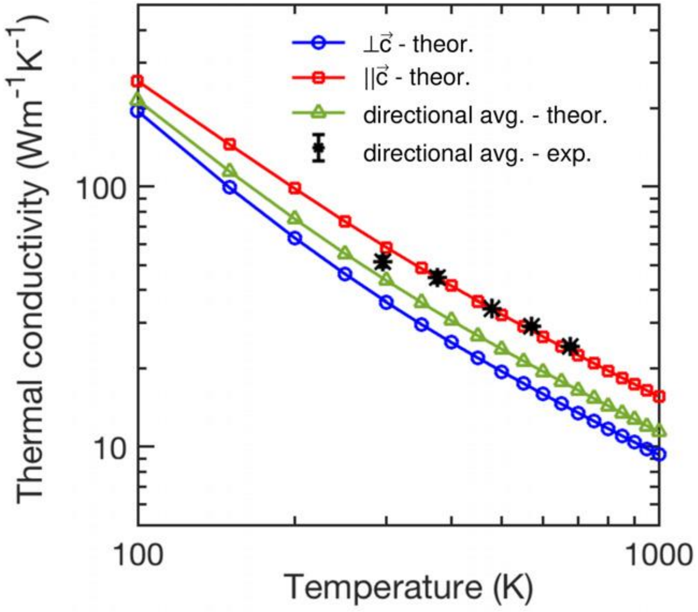
Phonon-limited carrier mobilities of rutile GeO_2 at 300 K:
$\mu_{elec,\perp c}$ = 253 cm^2 V^{-1} s^{-1}, $\mu_{elec,\parallel c}$ = 484 cm^2 V^{-1} s^{-1}
$\mu_{hole,\perp c}$ = 26 cm^2 V^{-1} s^{-1}, $\mu_{hole,\parallel c}$ = 27 cm^2 V^{-1} s^{-1}

→ Efficient electron and hole conduction

Bushick, Mengle, Chae, and Kioupakis, *Appl. Phys. Lett.* **117**, 182104 (2020)

Thermal conductivity of GeO_2

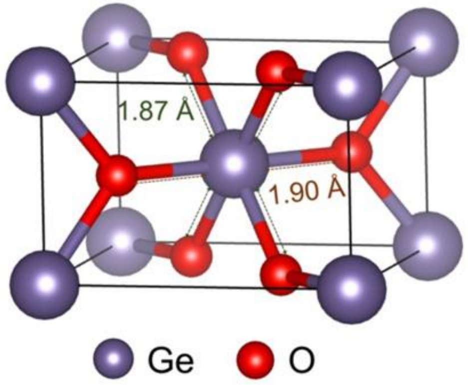




- Synthesis of polycrystalline bulk GeO_2 by hot pressing quartz GeO_2 powder.
- Calculated and experimental thermal conductivity (~50 W/m K) higher than Ga_2O_3

Chae, Mengle, Lu, Olvera, Sanders, Lee, Poudeu, Heron, and Kioupakis,
Applied Physics Letters **117**, 102106 (2020).

Record Modified Baliga Figure of Merit for r-GeO_2



Baliga Figure of Merit:

$$BFOM = \frac{1}{4}\epsilon_0 \mu E_C^3$$

Modified *BFOM* to account for donor ionization:

$$MBFOM = BFOM \times \exp(-\frac{E_a}{k_B T})$$

Material	Gap (eV)	Dielectric constant	Mobility (cm^2/Vs)	Breakdown field (MV/cm)	BFOM relative to Si	Donor ionization (meV)	Modified BFOM relative to Si	Thermal conductivity (W/mK)
Si	1.1	11.9	1240	0.3	1	40	1	130
4H-SiC	3.3	9.7	980	2.5	373	50	254	370
GaN	3.4	10.4	1000	3.3	938	40	938	253
β-Ga_2O_3	**4.5**	**10**	**200**	**6.3**	**1,255**	**40**	**1,255**	**11**
AlN	6.2	9.1	426	15.4	35,537	250	11	286
Cubic BN	6.4	7.1	200	17.5	19,102	150	278	1600
Diamond	5.4	5.7	1060	13	33,318	570	5×10^{-5}	2290
Rutile GeO_2	**4.6**	**14.5**	**480**	**6.7**	**5,254**	**40**	**5,254**	**62**

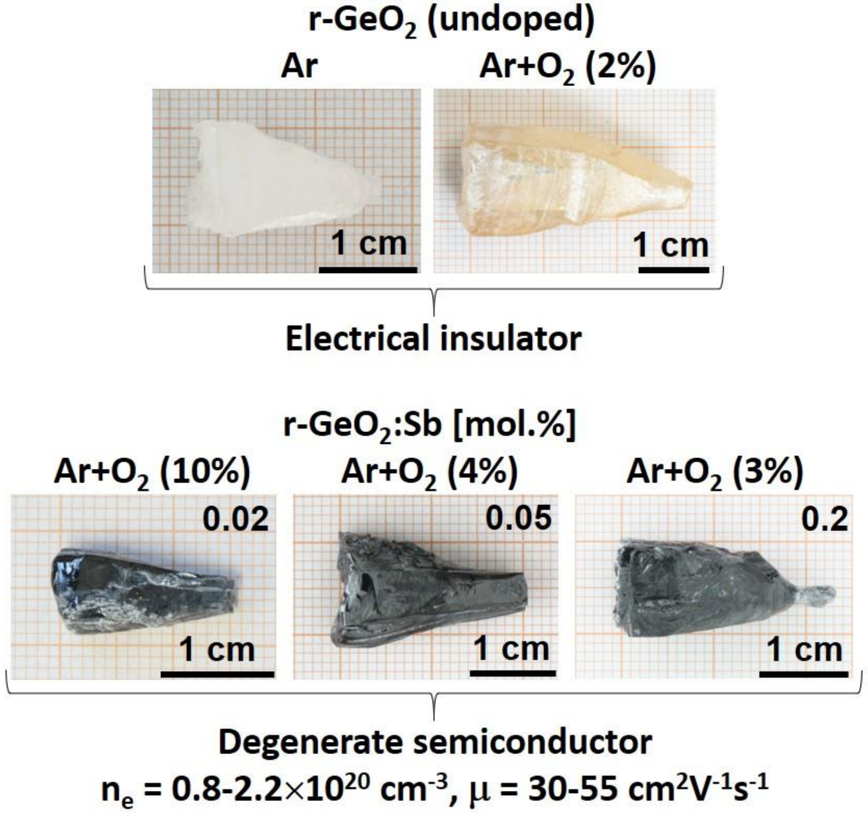
Semiconductor Science and Technology **35**, 125018 (2020)

Rutile GeO_2 predicted to have the **highest Modified BFOM among *all* semiconductors at room T**. Plus, higher thermal conductivity than β-Ga_2O_3, and possibility of p-type doping.

Breaking news: demonstration of doping of GeO_2

Data kindly shared by
Dr. Zbigniew Galazka at IKZ, Berlin

Rutile GeO_2 is an ultrawide-band-gap semiconductor, dopable by Sb and F, with properties that are in agreement with theoretical predictions.



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Leibniz-Institut für Kristallzüchtung, Berlin, Germany

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