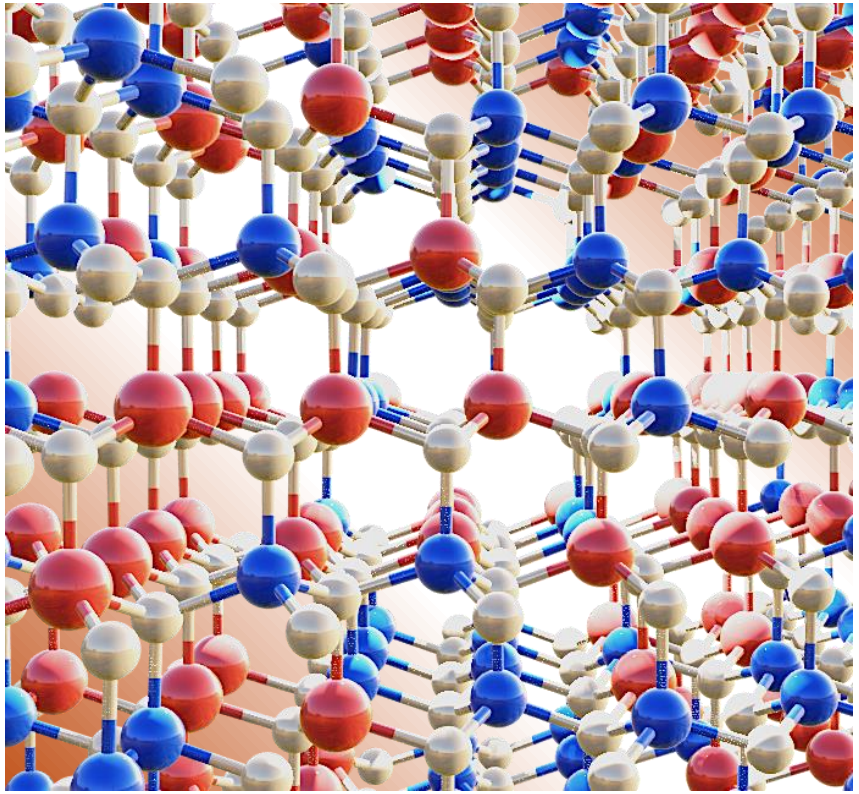
Summer School on the physics and Applications of Nitrides

Electrical polarization



Emmanouil (Manos) Kioupakis[1,2]

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

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

My expertise: predictive modeling of semiconductors

Material composition

Density functional theory

- Structure
- Thermodynamics
- Alloys
- Defects and dopants
- Anharmonic effects

Many-body perturbation theory

- Band gap
- Band structure
- Effective masses

Density functional perturbation theory

- Phonons
- Electron-phonon coupling

Quantum processes

- Optical absorption
- Carrier mobility
- Thermal conductivity
- Recombination rates

Material properties

Modern predictive calculations explain the properties and enable the discovery of new semiconductors that can surpass the state of the art.

Invited Feature Paper-Review:
E. Kioupakis *et al., J. Mater. Res.* **36**, 4616 (2021)
✓ Both for theorists and for experimentalists

Overview

- Definition of polarization
- Polarization parameters of III nitrides
- Polarization in quantum wells: quantum-confined Stark effect
- Polarization discontinuity and 2D carrier gases at interfaces
- Ferroelectric nitrides

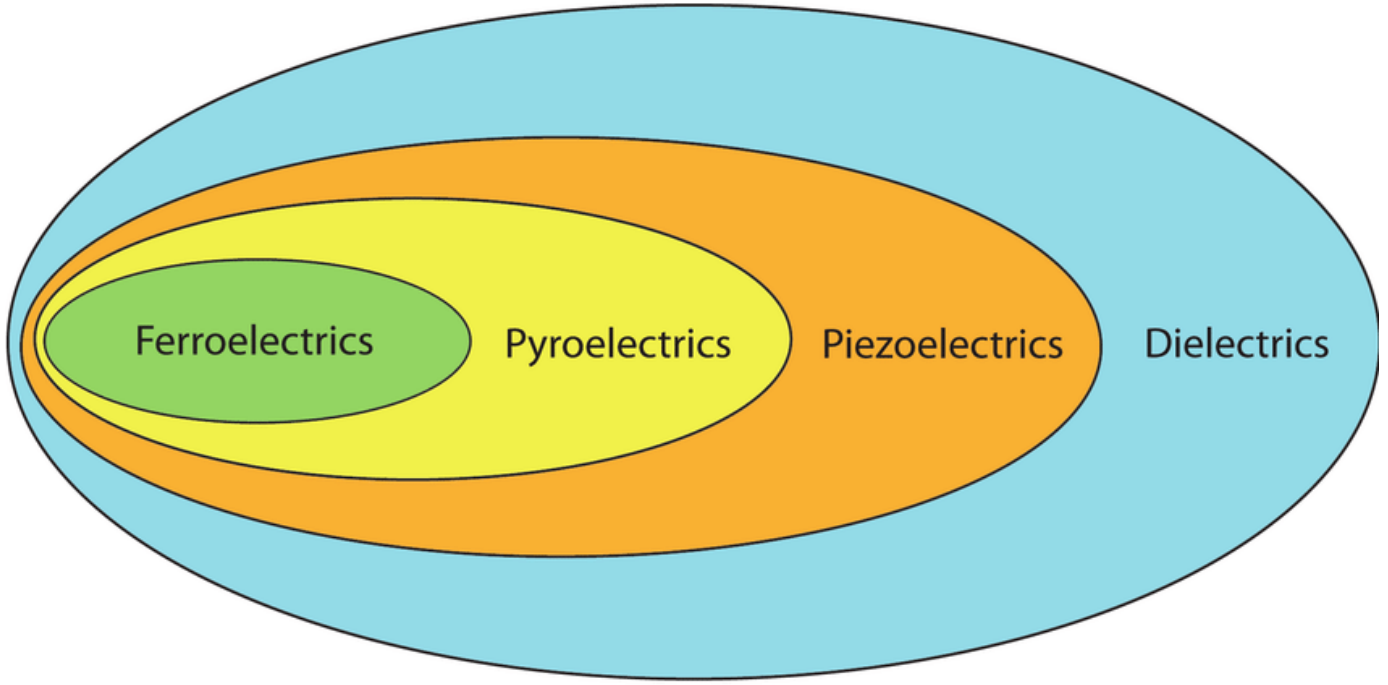
Response of materials to electric fields

Piezoelectric materials: develop polarization due to strain.

Pyroelectric materials: permanent electric polarization.

Ferroelectric materials: polarization can be switched by an electric field.

All made possible by lack of inversion symmetry.

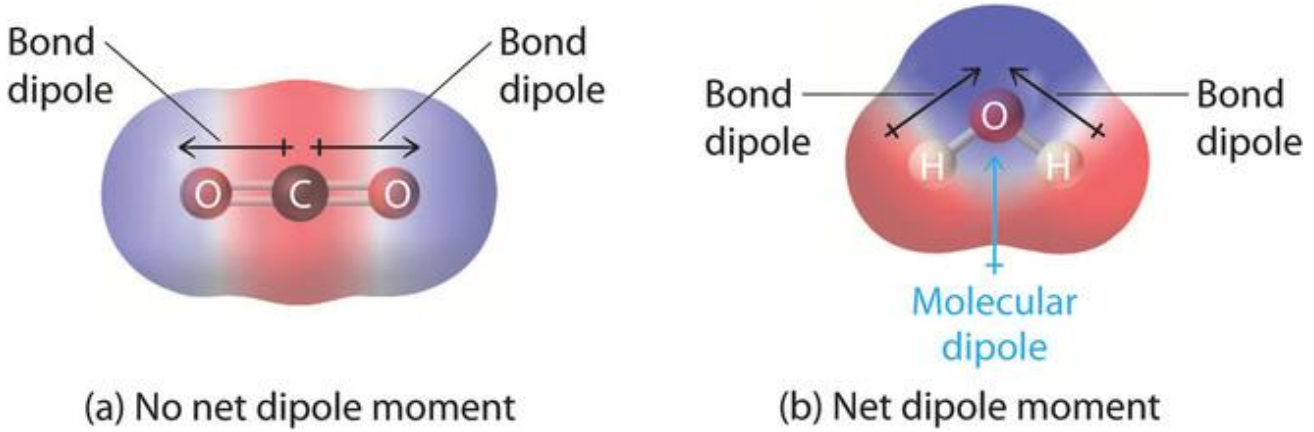


Khanbareh, PhD thesis, Delft University of Technology

Classical polarization for finite system

For isolated molecule, the electron dipole moment is the sum over occupied wave functions:

$$\mathbf{d} = -e\sum_j \langle \psi_j | \mathbf{r} | \psi_j \rangle$$



chem.libretexts.org

But: position operator is not well defined for an infinite periodic solid, polarization is not well defined if we use this formula.

Modern theory of polarization: Berry

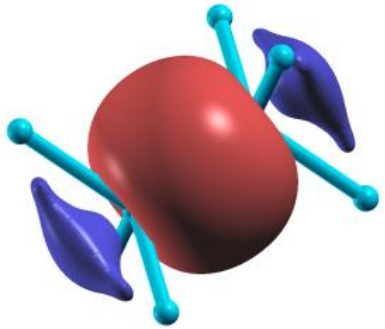
Based on the geometric **Berry** phase of the electron wave functions $u_{n\mathbf{k}}$ integrated over the Brillouin zone:

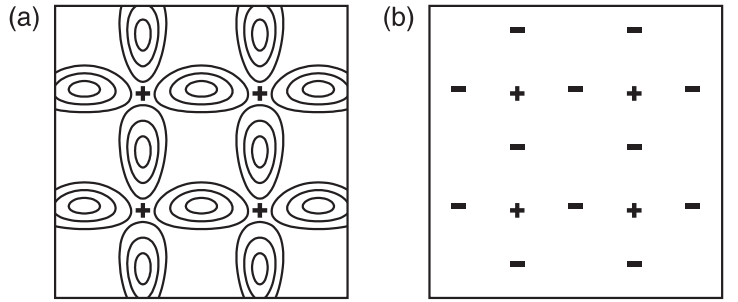
$$\mathbf{P}_{\mathrm{el}} = -\frac{e}{(2\pi)^3}\sum_n \int_{\mathrm{BZ}} d\mathbf{k}\langle \tilde{u}_{n\mathbf{k}}|i\nabla_{\mathbf{k}}|\tilde{u}_{n\mathbf{k}}\rangle$$

King-Smith and Vanderbilt, *Phys. Rev. B* **47**, 1651 (1993)

Equivalent: **sum of centers of Wannier functions**: from continuous electron distribution to sum of point charges.

Ions + electrons $\quad \mathbf{P} = \frac{e}{V}\left(\sum_\tau Z_\tau \mathbf{r}_\tau - \sum_n \mathbf{r}_n\right)$

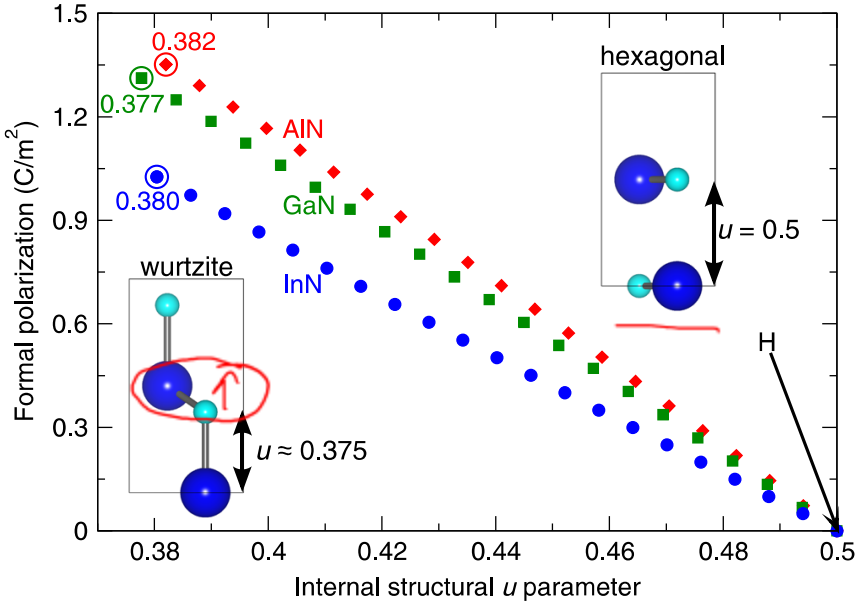




Each electron Wannier function $\quad \mathbf{r}_n = \langle \mathbf{0}n|\mathbf{r}|\mathbf{0}n\rangle = \frac{V}{(2\pi)^3}\int_{\mathrm{BZ}} d\mathbf{k}\langle \tilde{u}_{n\mathbf{k}}|i\nabla_{\mathbf{k}}|\tilde{u}_{n\mathbf{k}}\rangle$

Marzari et al, *Rev. Mod. Phys.* **84**, 1419 (1993)

Polarization parameters of III-nitrides



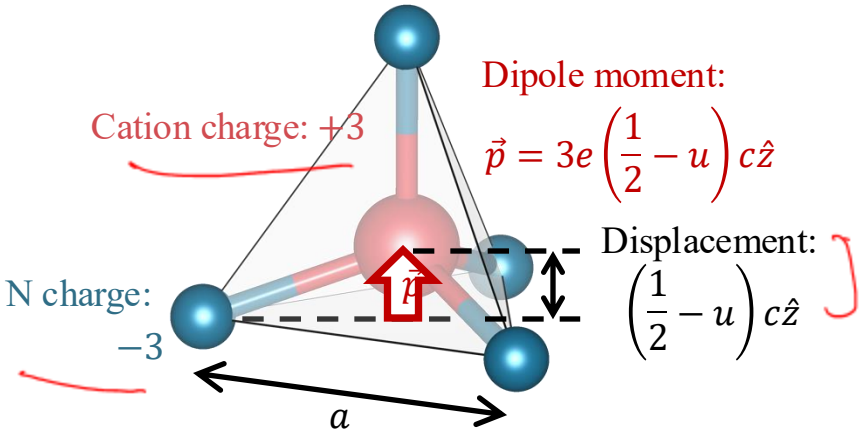


TABLE I. Effective spontaneous polarization constants in units of C/m^2 of WZ GaN, AlN, and InN calculated using either the hexagonal (H, space group $P6_3/mmc$) or ZB (space group $F\bar{4}3m$) reference structures.

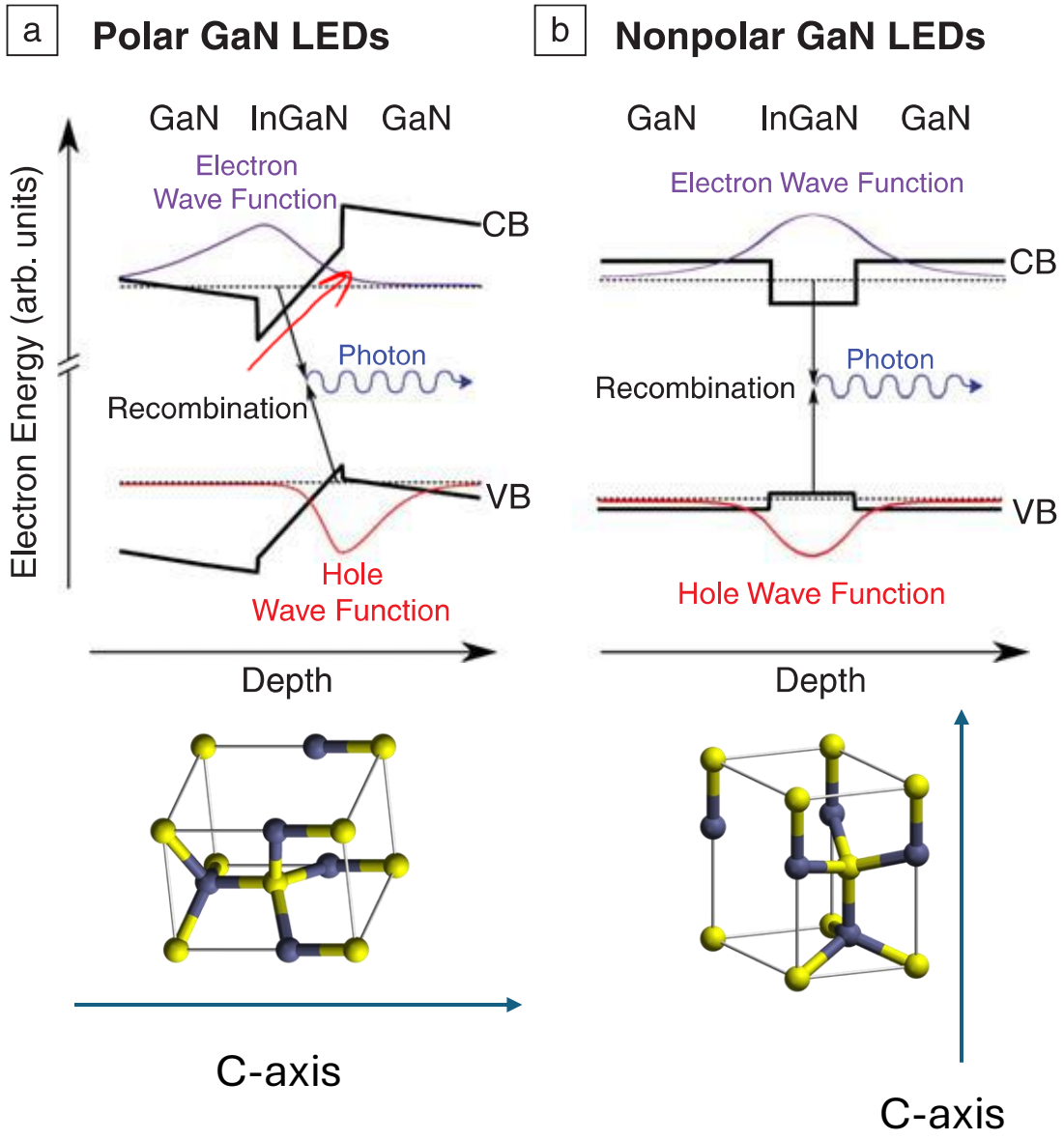
	$P_{\text{eff}}^{(\text{H ref})}$	$P_{\text{eff}}^{(\text{ZB ref})}$	$P_{\text{eff}}^{(\text{ZB ref})}$, previously reported
GaN	1.312	−0.035	−0.034
AlN	1.351	−0.090	−0.090
InN	1.026	−0.053	−0.042

TABLE II. Calculated piezoelectric polarization constants in units of C/m^2 compared with reported values from the literature.

		Proper	Improper	Previously reported[a]
GaN	e_{31}	−0.551	−1.863	−0.22 to −0.55
	e_{33}	1.020	1.020	0.43 to 1.12
AlN	e_{31}	−0.676	−2.027	−0.38 to −0.81
	e_{33}	1.569	1.569	1.29 to 1.94
InN	e_{31}	−0.604	−1.63	−0.23 to −0.59
	e_{33}	1.238	1.238	0.39 to 1.09

Dreyer, Janotti, Van de Walle, and Vanderbilt, *Phys. Rev. X* **6**, 021038 (2016)

Quantum confined Stark effect



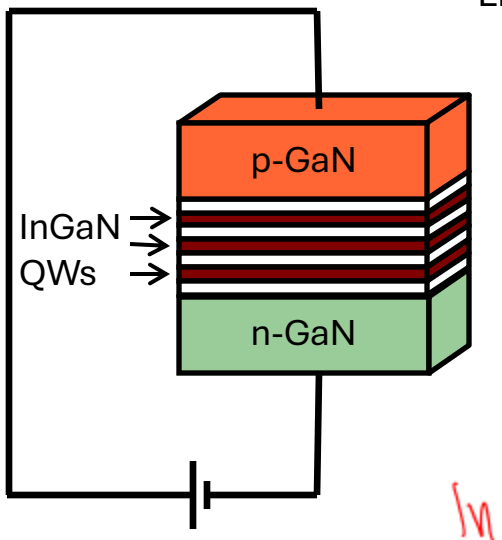
= spatial separation of electron and hole wave functions in polar nitride quantum wells due to polarization.

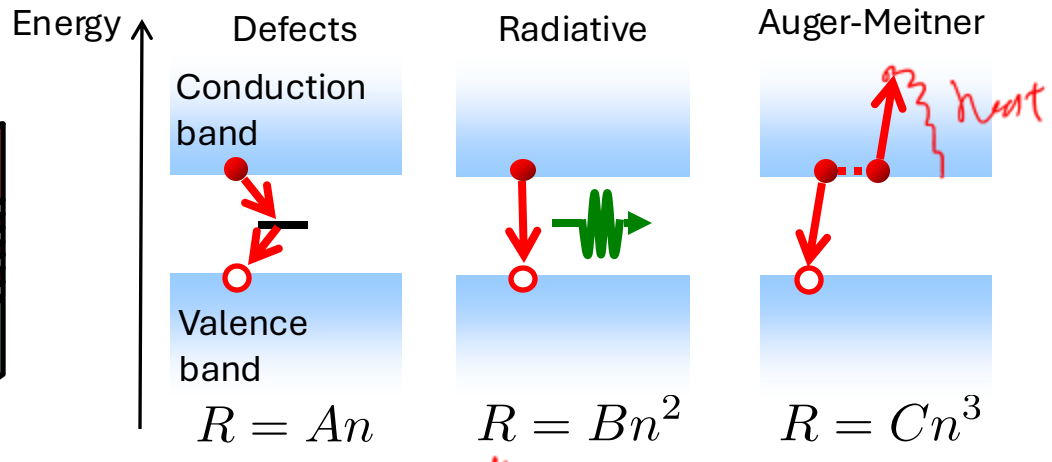
- Redshift of the emission compared to nonpolar
- Spatial separation of electrons and holes, reduced recombination rates

In polar quantum wells: optical balance between quantum-confinement-induced blueshift vs. spatial separation of electrons and holes occurs for a well width around 2.5-3 nm.

Speck and Chichibu, *MRS Bulletin* **34**, 304 (2009)

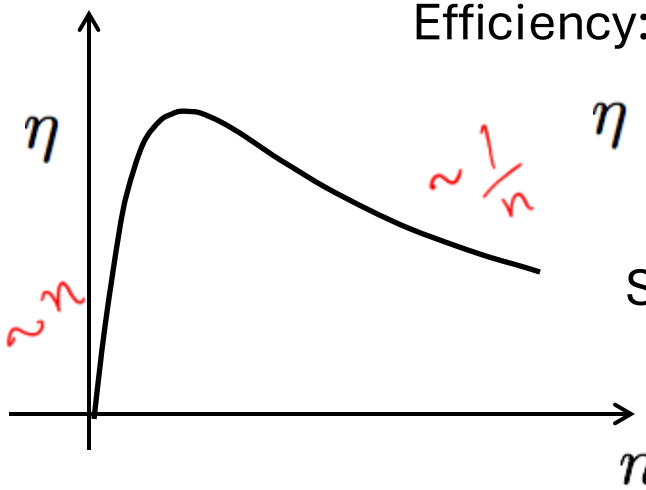
Carrier recombination in LEDs





Efficiency:

$$\eta = \frac{Bn^2}{An + Bn^2 + Cn^3}$$



Steady-state current J: (d = well width)

$$J = ed(An + Bn^2 + Cn^3).$$

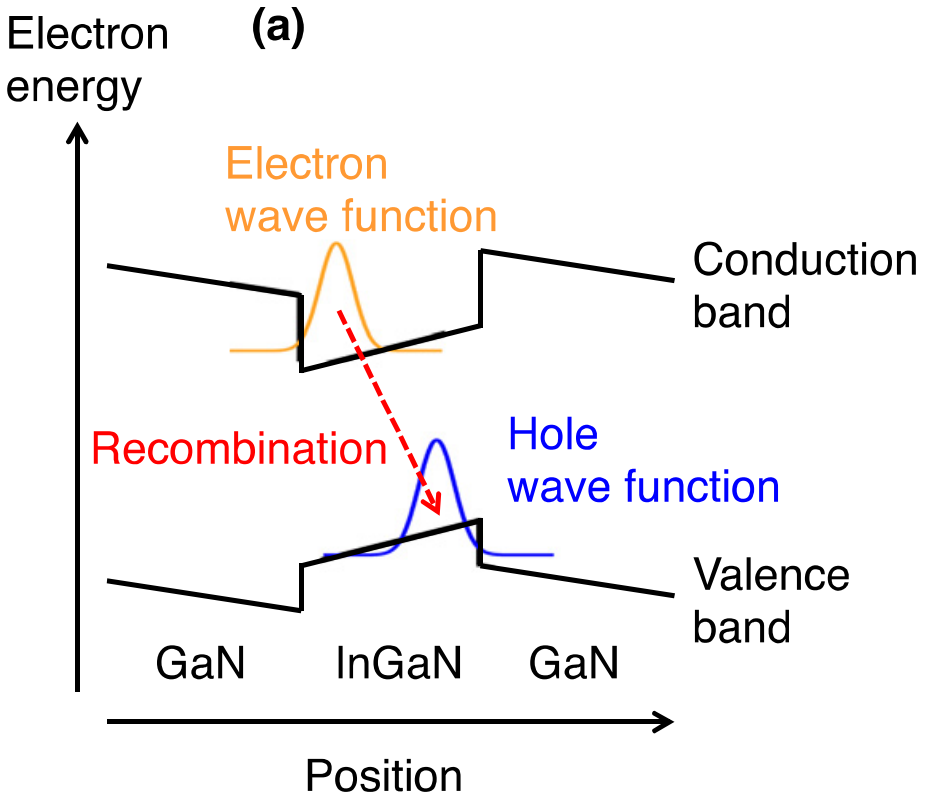
1. Defect-mediated **Shockley-Read-Hall recombination** through a mid-gap defect state. Rate increases linearly with free-carrier density. Important at high temperature and near surfaces, e.g., microLEDs

2. **Radiative** recombination rat: Needs 1 e + 1 h → quadratic with free-carrier density (assuming n=p)

3. **Auger-Meitner** recombination: 3 carriers scatter through Coulomb interaction. Needs 2e + 1h, or 2h + 1e: depends on the cube of the carrier density.

Overall efficiency: radiative/total recombination rate, shows a maximum.

Quantum confined Stark effect and radiative recombination

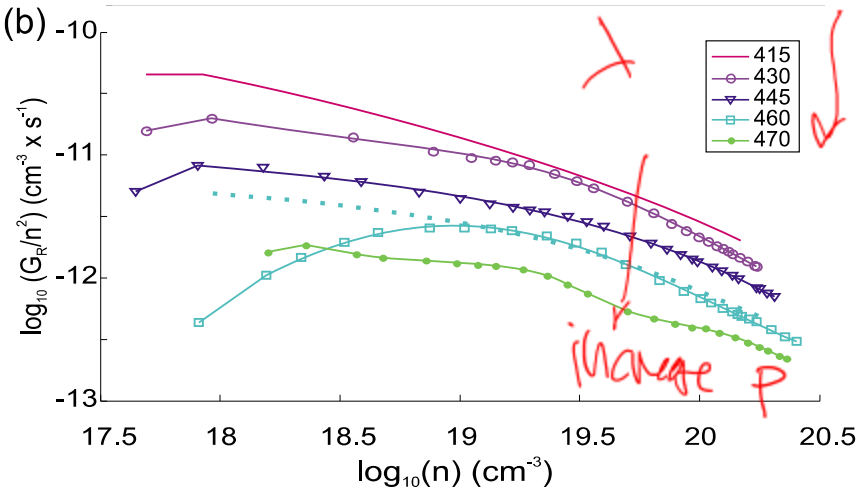


Radiative recombination rate

$$R = Bn^2$$

$$B_{\mathrm{QW}} = B_{\mathrm{Bulk}} \left| F_{cv} \right|^2$$

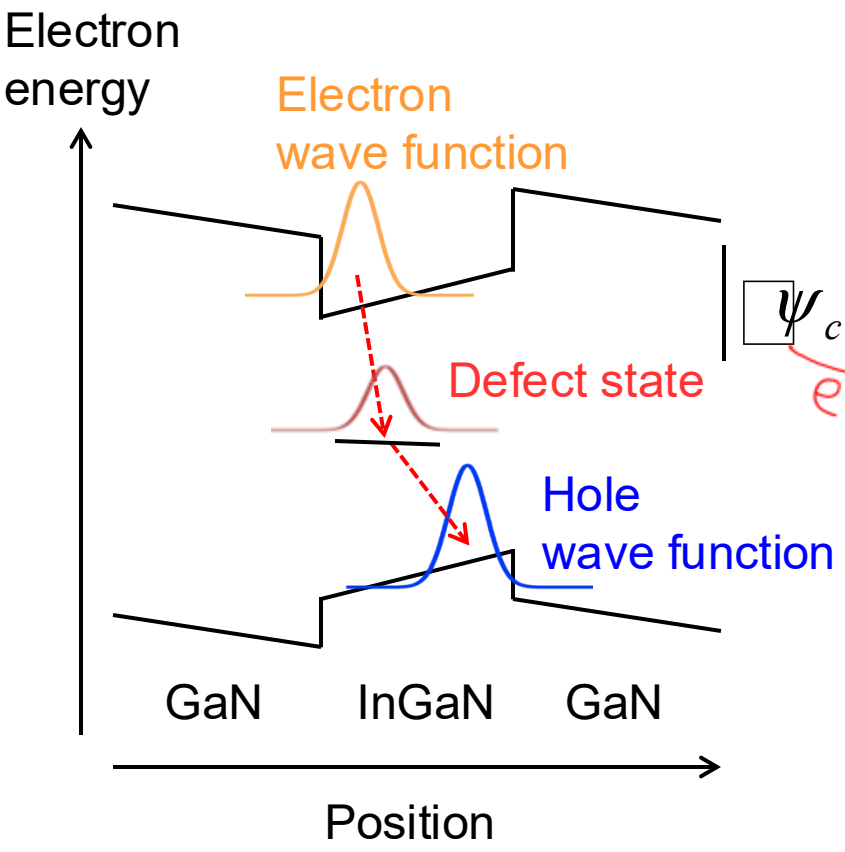
$$F_{cv} = \int \psi_c(z)\psi_v(z)dz,$$



Experimental data:
David and Grundmann, APL 2010

Radiative recombination rate is proportional to electron-hole overlap → polarization reduces radiative recombination rate.

Quantum confined Stark effect and Shockley-Read-Hall

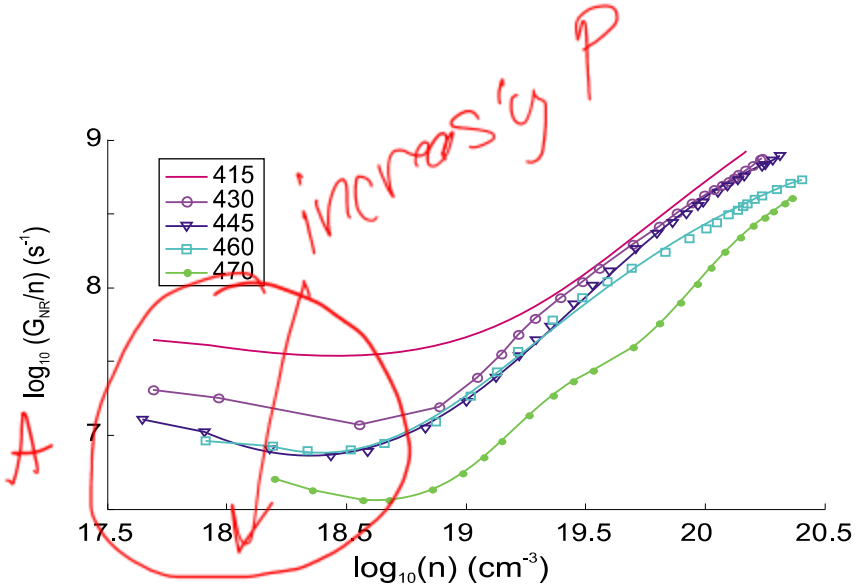


For a *fixed* defect:
Recombination rate proportional to:

$$\left| \int \psi_c(z)\psi_d(z)dz \int \psi_d(z)\psi_v(z)dz \right|^2$$

For a *random distribution* of defects:

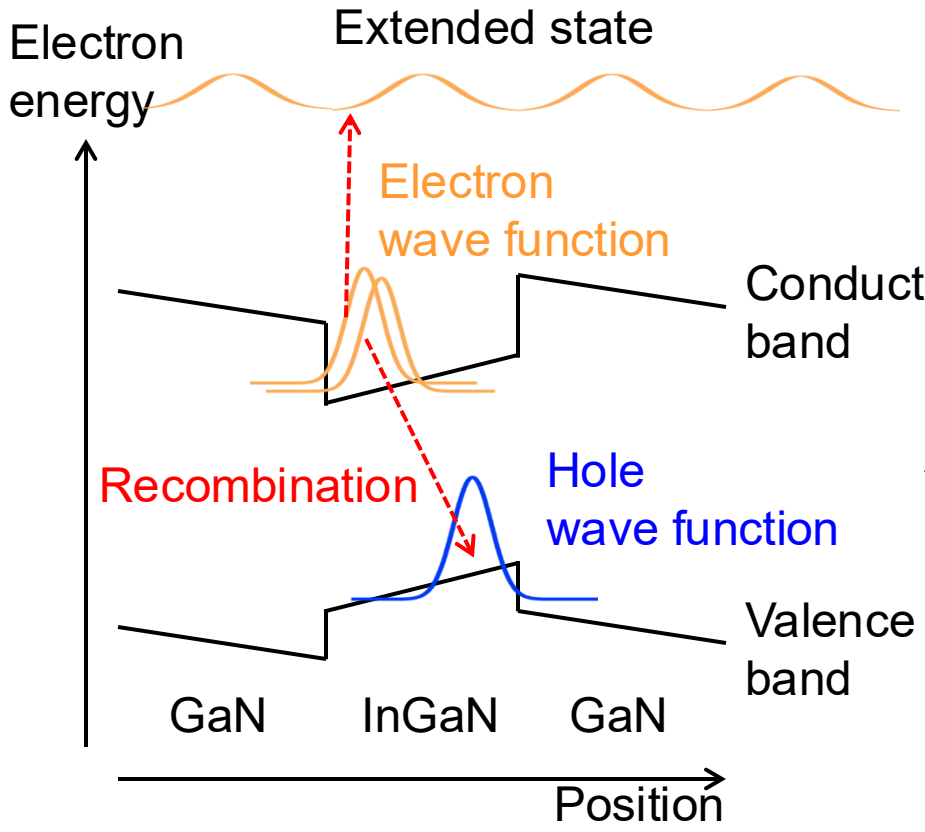
$$A_{QW} = A_{Bulk}\left|F_{cv}\right|^2$$



Experimental data:
David and Grundmann, APL 2010

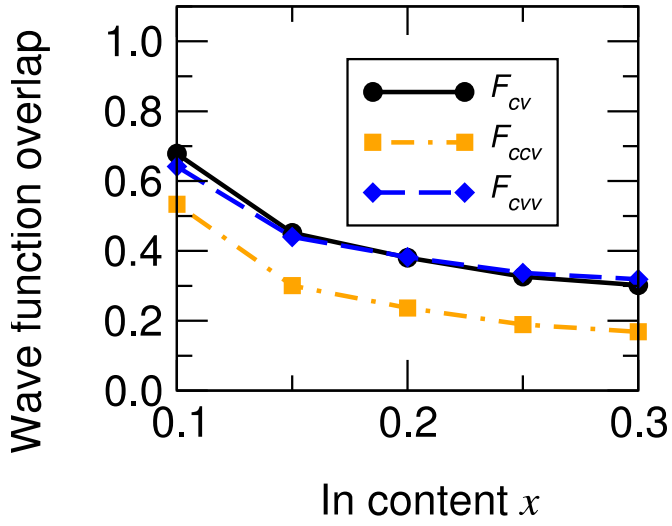
Shockley-Read-Hall recombination rate is also proportional to electron-hole overlap → polarization reduces non-radiative recombination rate as well.

Quantum confined Stark effect and Auger-Meitner recombination

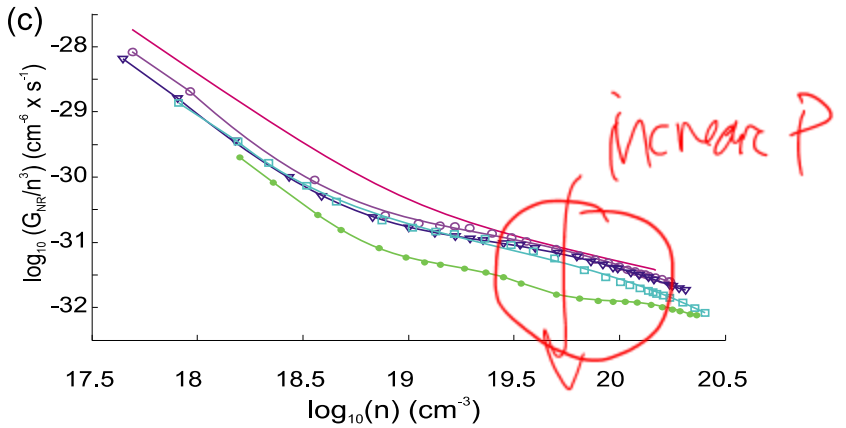


$$C_{QW} = C_{Bulk} \left| F_{ccv} \right|^2$$

$$F_{ccv} = \int \psi_c(z)\psi_c(z)\psi_v(z)dz,$$



Appl. Phys. Lett. 101, 231107 (2012)



Experimental data:
David and Grundmann, APL 2010

Auger-Meitner recombination rate is proportional to triple e-e-h or h-h-e overlap.

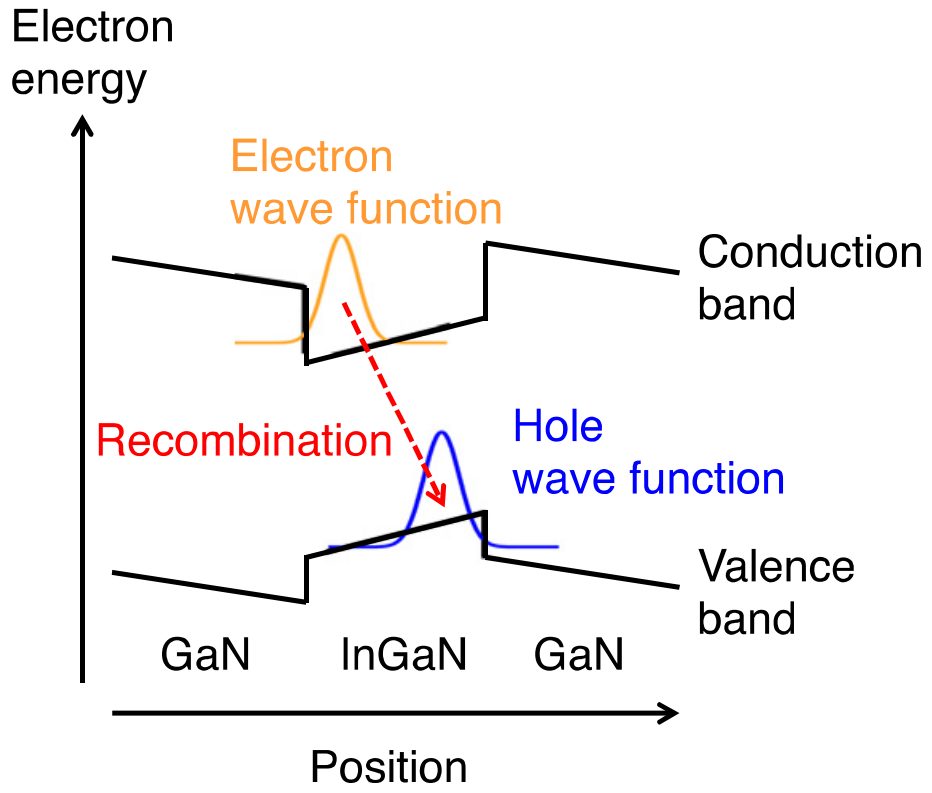
But: triple overlaps are very similar to e-h overlap. Reason: third carrier already overlaps with one of the recombining ones

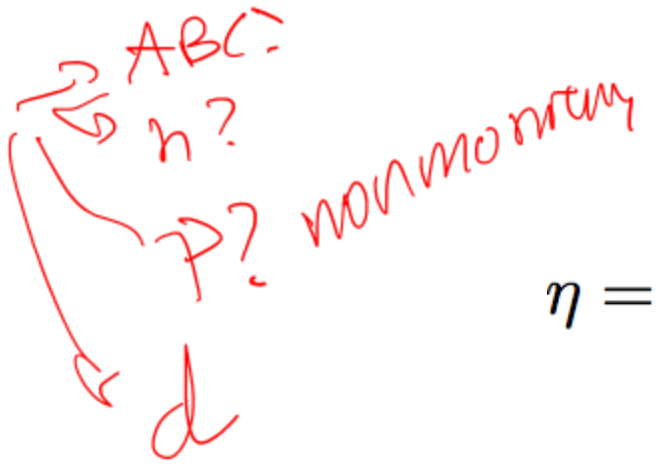
Combined effects of QCSE on efficiency:

Quantum confined Stark effect reduces all the recombination rates by a similar factor.

Question: is polarization good or bad for LED efficiency?

A) Good
B) Bad
C) No effect
D) It depends





$$\eta = \frac{Bn^2}{An + Bn^2 + Cn^3}$$

$$A_{\mathrm{QW}} = A_{\mathrm{Bulk}} \left| F_{cv} \right|^2$$

$$B_{\mathrm{QW}} = B_{\mathrm{Bulk}} \left| F_{cv} \right|^2$$

$$C_{\mathrm{QW}} = C_{\mathrm{Bulk}} \left| F_{cv} \right|^2 \; ?$$

Effect of polarization on efficiency

IQE versus *carrier* density is the same:

$$\eta = \frac{Bn^2}{An + Bn^2 + Cn^3}$$

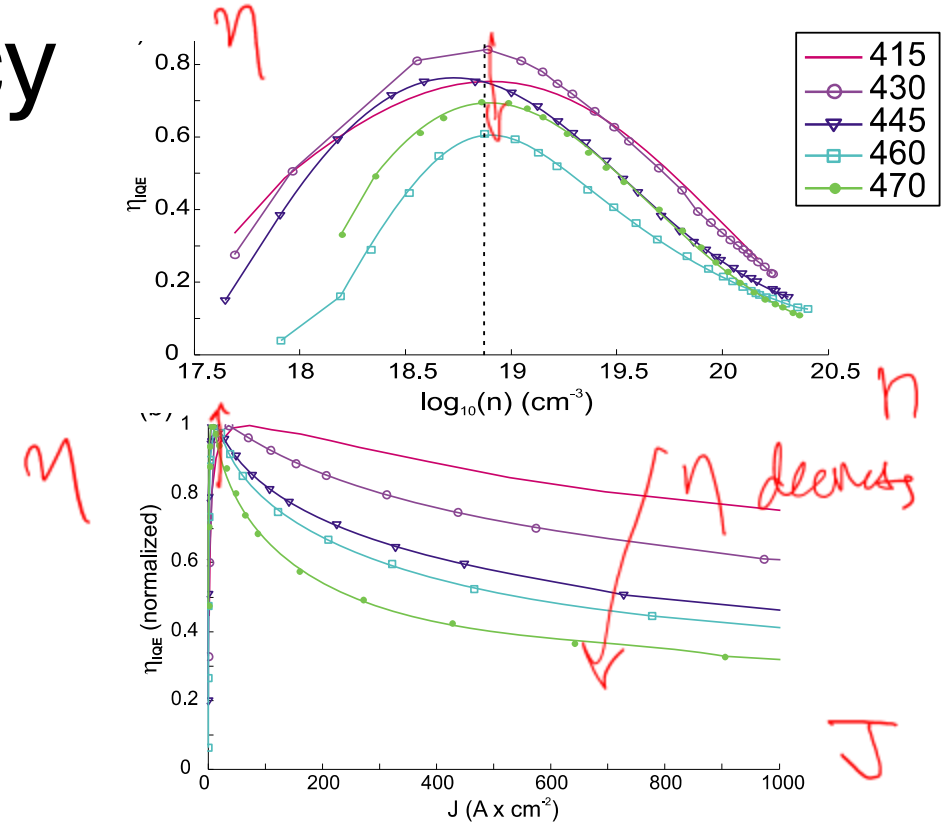
$$A_{\mathrm{QW}} = A_{\mathrm{Bulk}} \left| F_{cv} \right|^2$$

$$B_{\mathrm{QW}} = B_{\mathrm{Bulk}} \left| F_{cv} \right|^2$$

$$C_{\mathrm{QW}} = C_{\mathrm{Bulk}} \left| F_{cv} \right|^2$$

…but IQE versus *current* density is different:

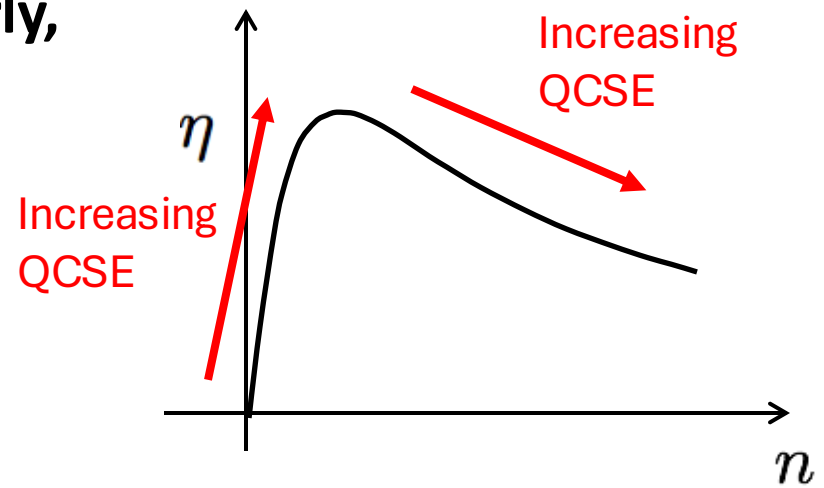
$$J = ed(An + Bn^2 + Cn^3).$$



Experimental data: David and Grundmann, APL 2010

Polarization fields slow down all recombination rates similarly, increase steady-state *n* for a given *j*.

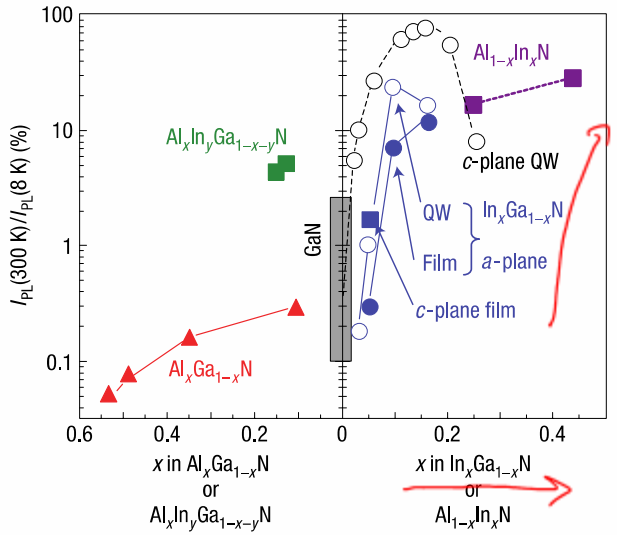
- At high *n*: polarization favors Auger (Cn^3) compared to radiative (Bn^2) → reduces efficiency for given *j*.
- At low *n*: polarization favors radiative (Bn^2) over Shockley-Read-Hall (An) → increases efficiency for given *j*.



Does localization lead to defect-insensitive emission?

Idea originally developed for dislocations; does it apply for point defects?

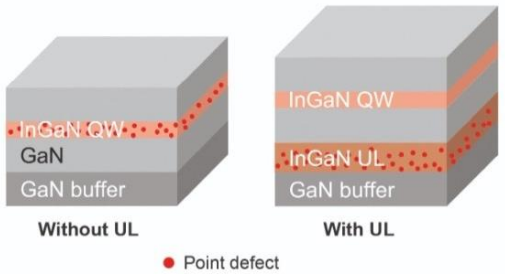
Chichibu et al. *Nature Mat*. **5**, 810 (2006)

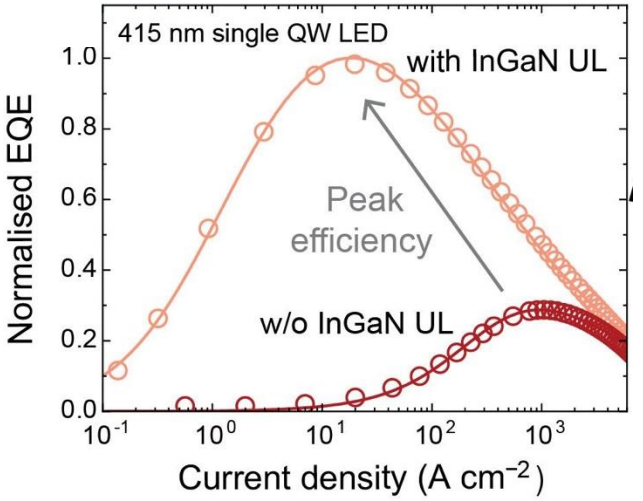


Later work on InGaN underlayers has shown that emission in InGaN is very sensitive to point defects.

Armstrong et al. J. Appl. Phys. 117, 134501 (2015)
Chen et al. Appl. Phys. Lett. 118, 111102 (2021)
Roccato et al. J. Phys. D: Appl. Phys. 54 505108 (2021)
Weatherly et al. Nano Lett. 21, 5217-5224 (2021)
Nicolas Grandjean plenary, ICSN-13

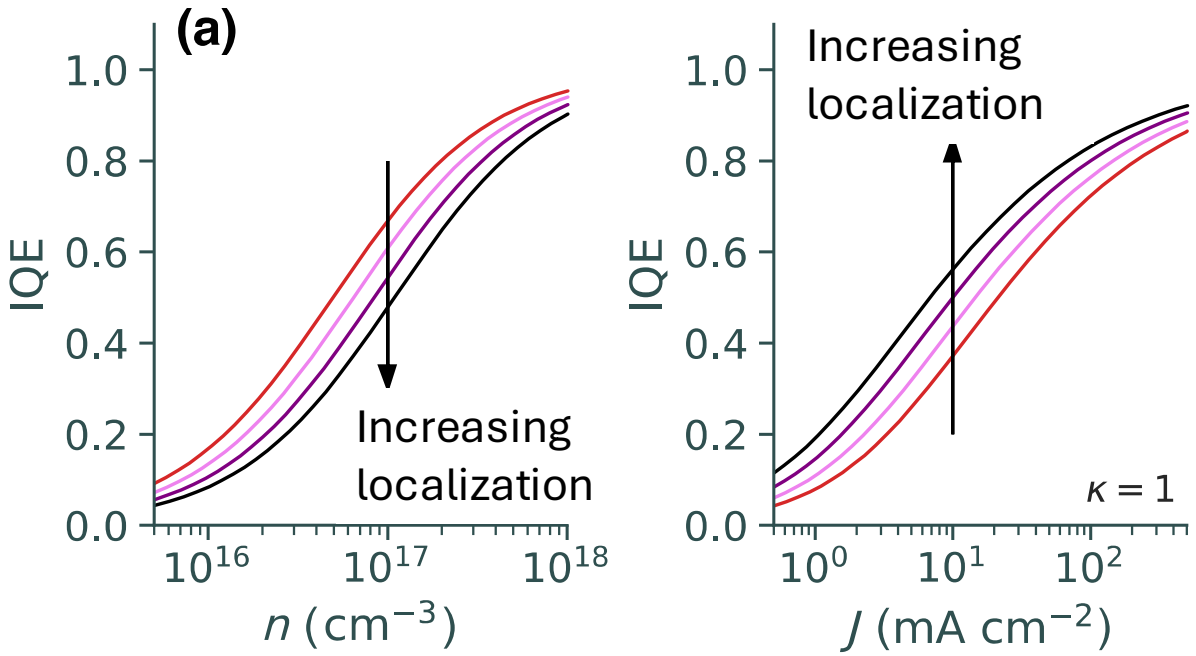
How does localization affect defect-mediated non-radiative recombination in InGaN?

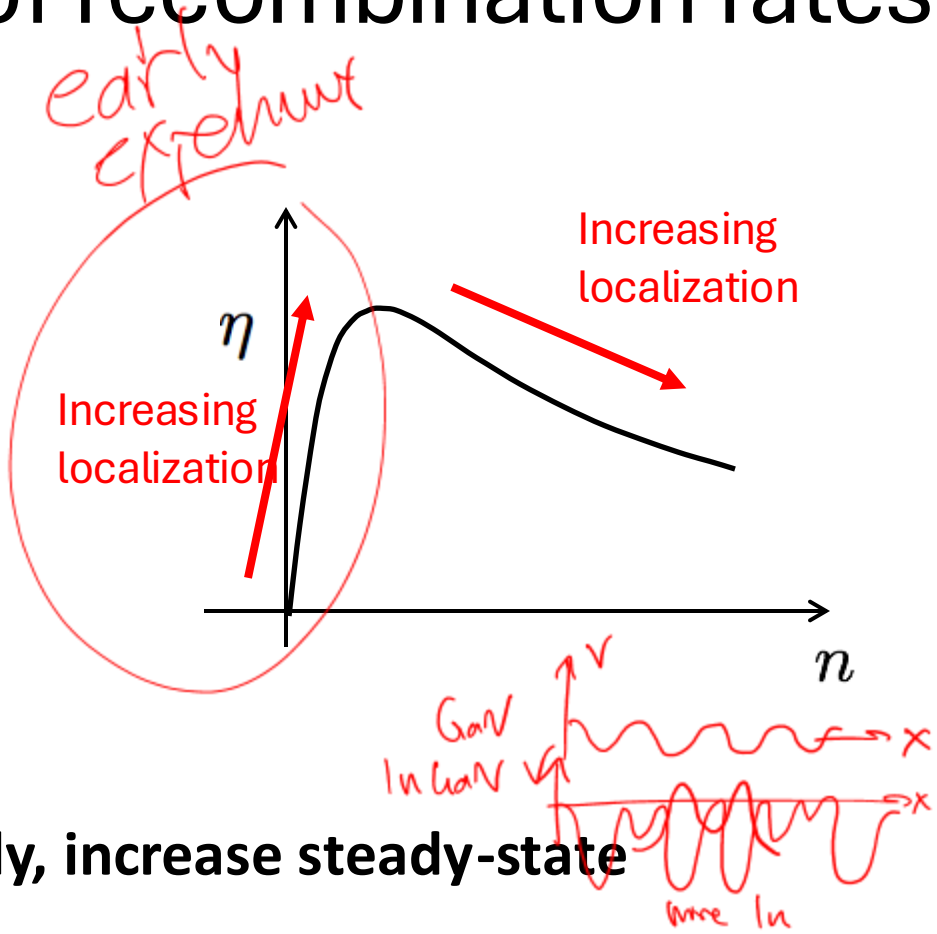




https://compoundsemiconductor.net/article/113729/Point_Defects_The_Ultimate_Blue_LED_Efficiency_Killers/feature

Localization: correlated reduction of recombination rates



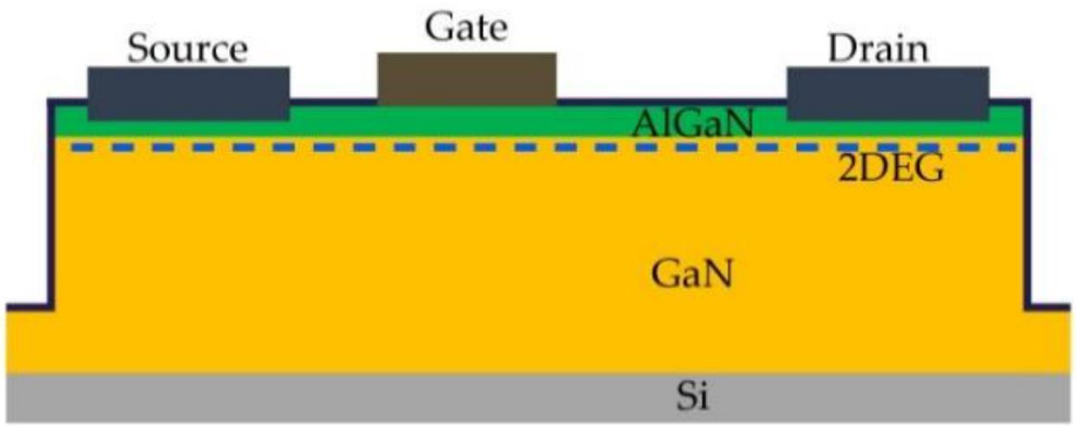


Localization slows down all recombination rates similarly, increase steady-state *n* for a given *j*.

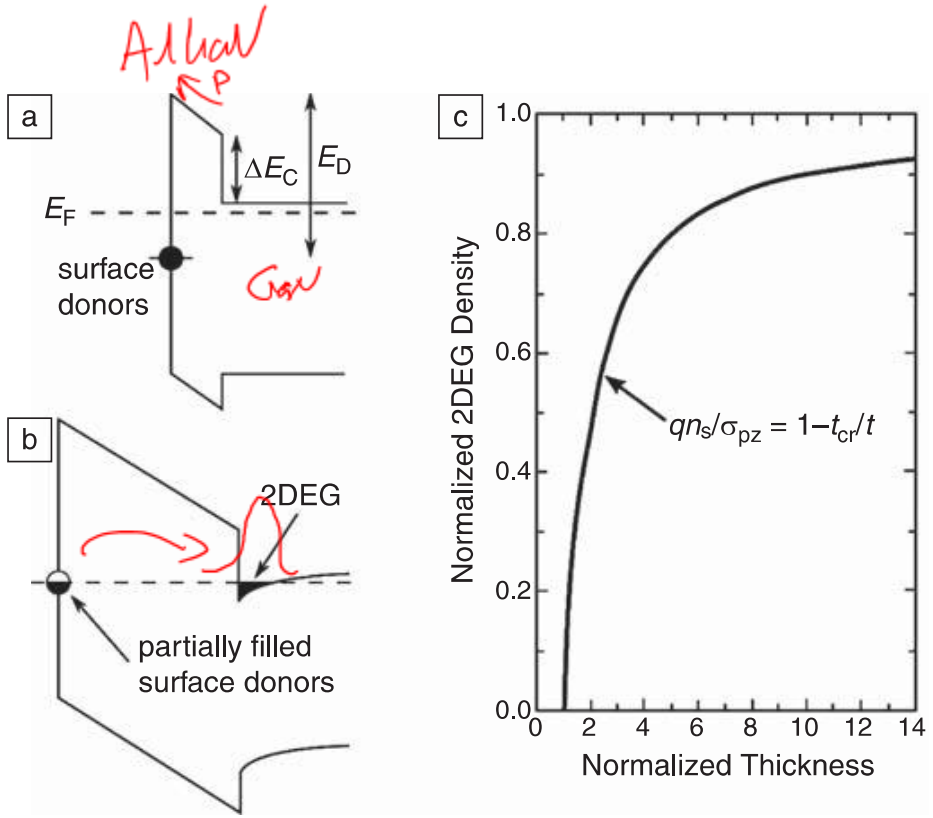
- At high *n*: polarization favors Auger (Cn^3) compared to radiative (Bn^2) → reduces efficiency for given *j*.
- At low *n*: polarization favors radiative (Bn^2) over Shockley-Read-Hall (An) (but *B/A* ratio decreases) → increases efficiency for given *j*.

Polarization discontinuity and 2D carrier gases

GaN High Electron Mobility Transistor (HEMT)



Electronics **2018**, *7*(12), 377

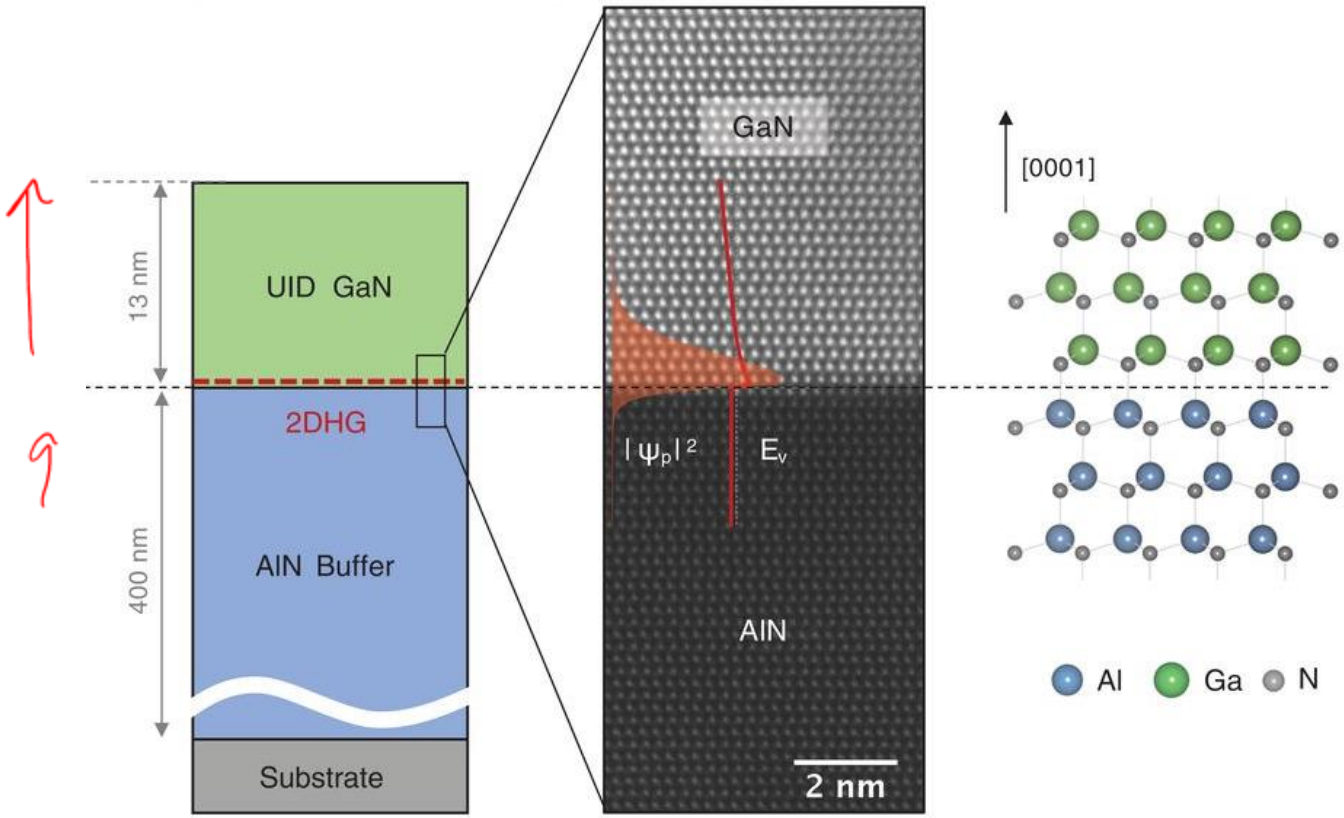


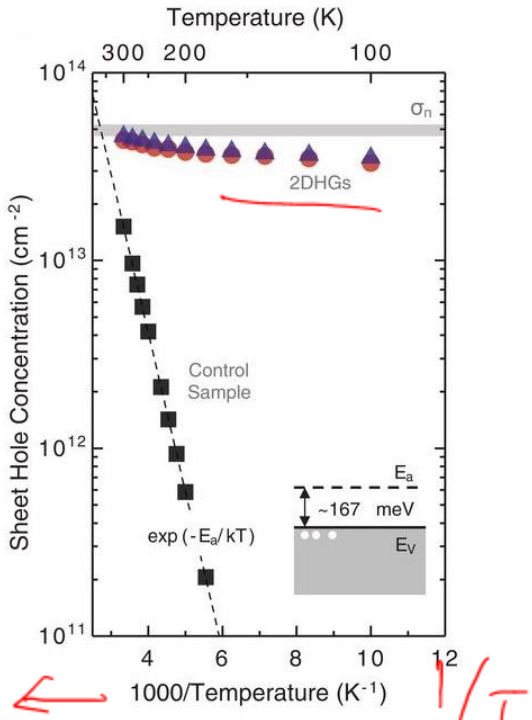
Bound surface charge density $\sigma = \Delta \boldsymbol{P} \cdot \hat{n}$
(here: positive charge)

→ Attracts negative charges from defects, forms two-dimensional electron gas

Speck and Chichibu, *MRS Bulletin* **34**, 304 (2009)

Two-dimensional hole gas





D. Jena and team, *Science* **365**, 1454 (2019)

The opposite stacking sequence creates an opposite polarization sign, forms a 2D hole gas.
Hole concentration is independent of temperature → not acceptors, evidence of 2DHG.

Ferroelectric nitrides

The electrical polarization of group-III nitrides can be reversed with the application of an electric field.

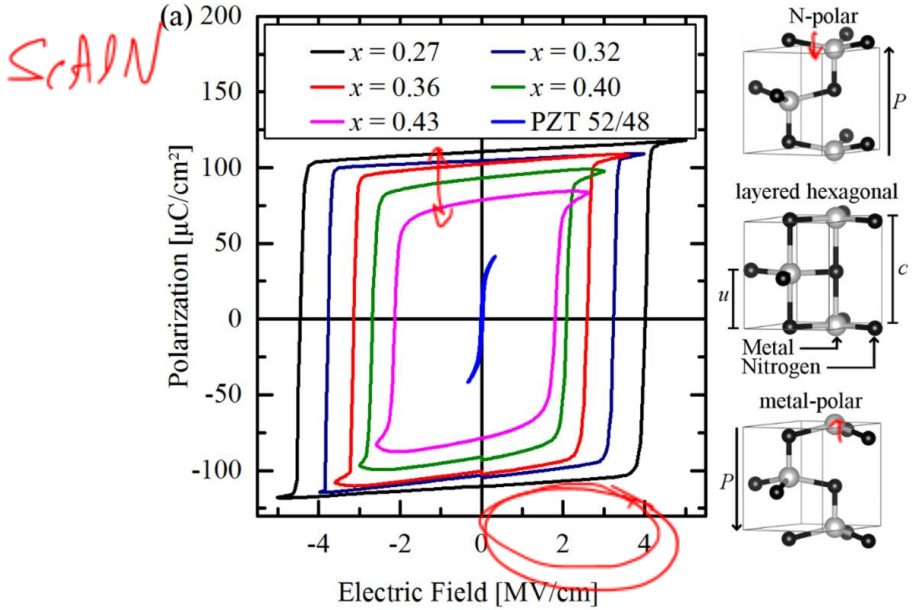
Observed in alloys of ScAlN, ScGaN, BAlN, but also MgZnO

AlN, GaN, InN: wurtzite (polar)
ScN, YN, LaN: rocksalt (nonpolar)

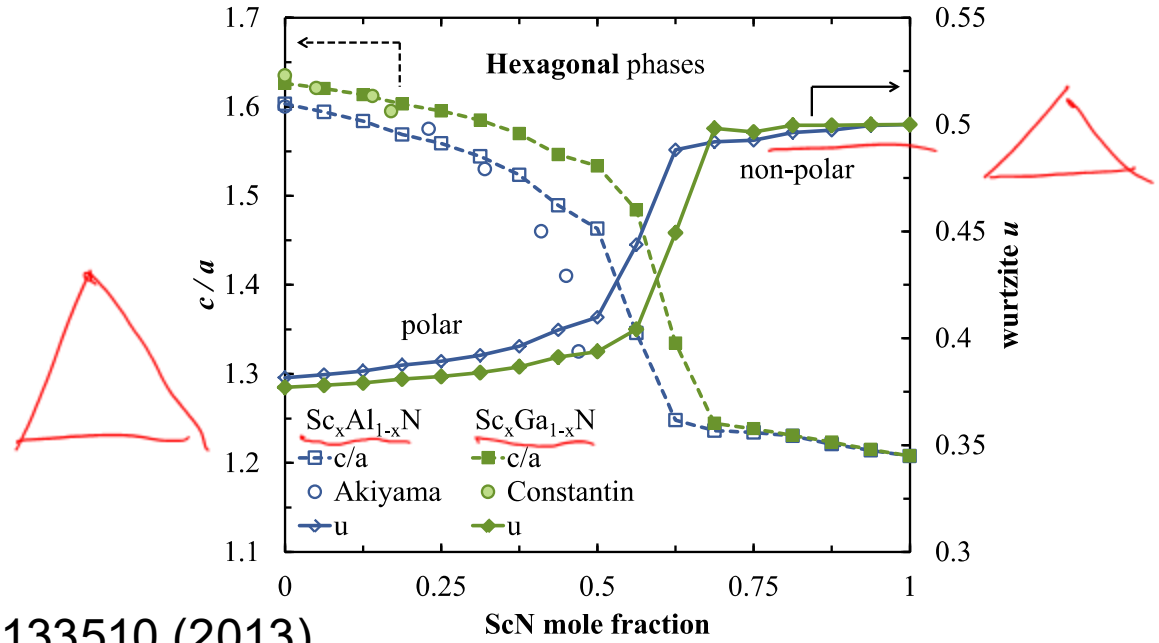
Non-polar element (e.g., Sc) weakens bonds in, e.g., AlN and distorts structure.

Much larger polarization than typical ferroelectrics, e.g., PZT, but also high coercive fields needed (~5 MV/cm, close to dielectric breakdown).

Promise: can nitrides retain their permanent dipole moment even at low dimensions?



J. Appl. Phys. 125, 114103 (2019)

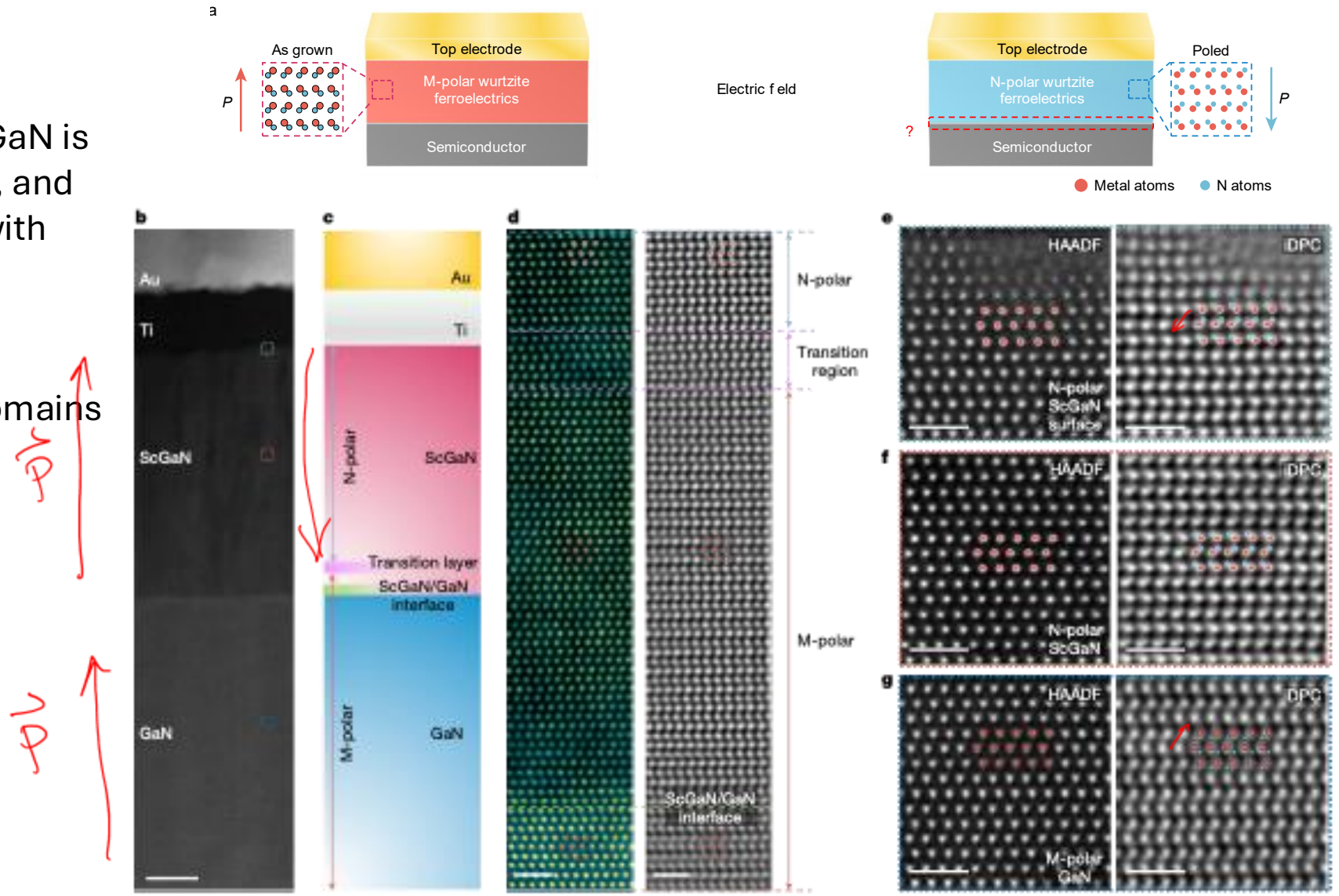


J. Appl. Phys. 114, 133510 (2013)

Domain walls in nitride ferroelectrics (I)

The polarization of a ScGaN film on GaN is reversed by applying an electric field, and the resulting structures are imaged with electron microscopy.

Resulting images can be analyzed to investigate domain walls between domains of opposite polarity.



Nature **641**, 76–82 (2025)

Domain walls in nitride ferroelectrics (II)

Two types of domain walls:

Vertical domain walls (planes parallel to c-axis). Common in III-nitride growth. All atoms at the interface are bonded, no dangling bonds. Low formation energy.

Horizontal domain walls (planes perpendicular to c-axis). Polarization inversion through a thin horizontal region of only a few atomic layers. Dangling bond at the interface give rise to midgap defect states and strong polarization discontinuity. Why are they stable?

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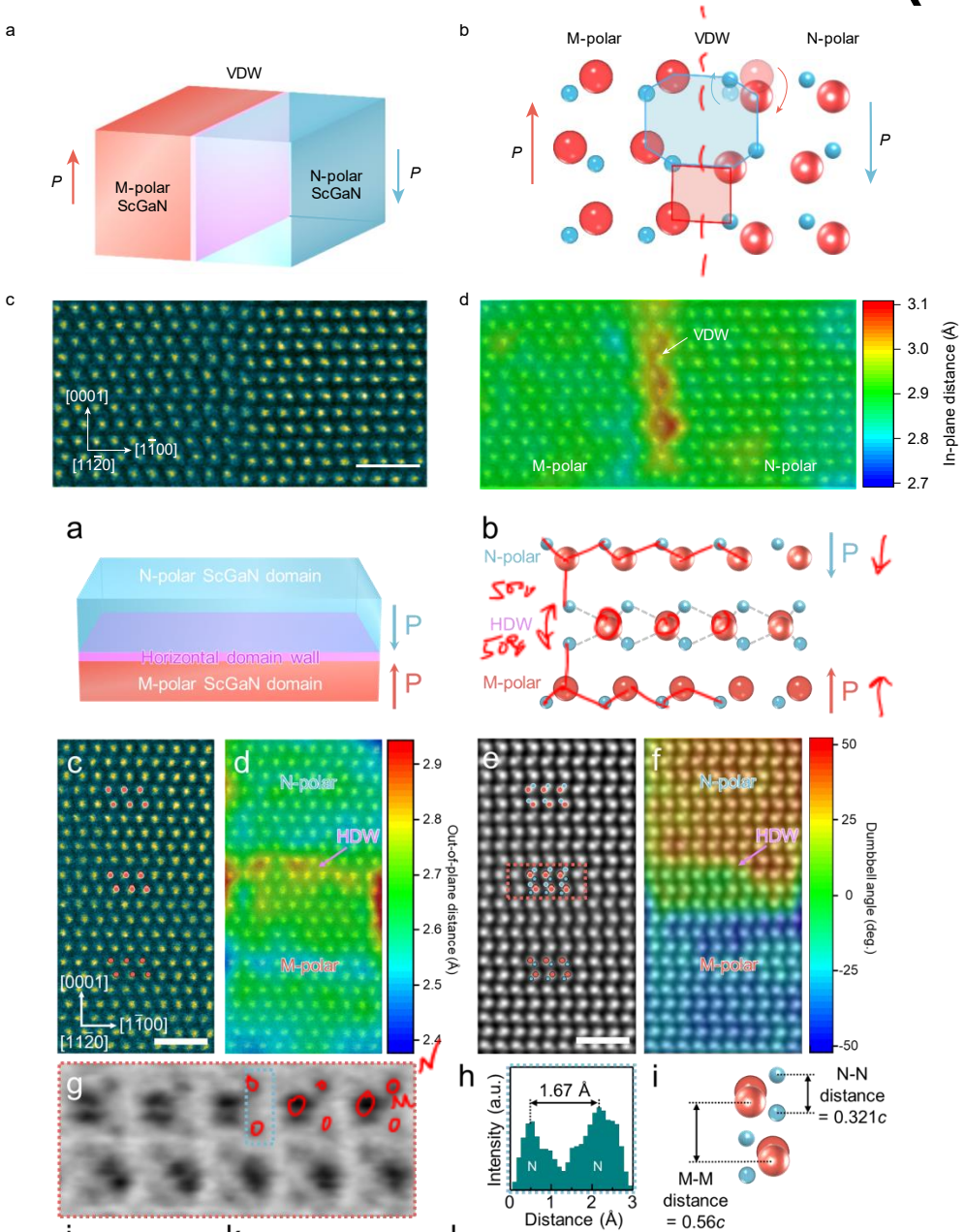
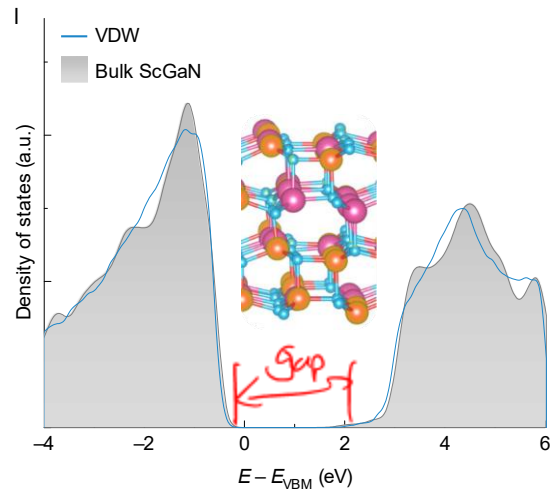
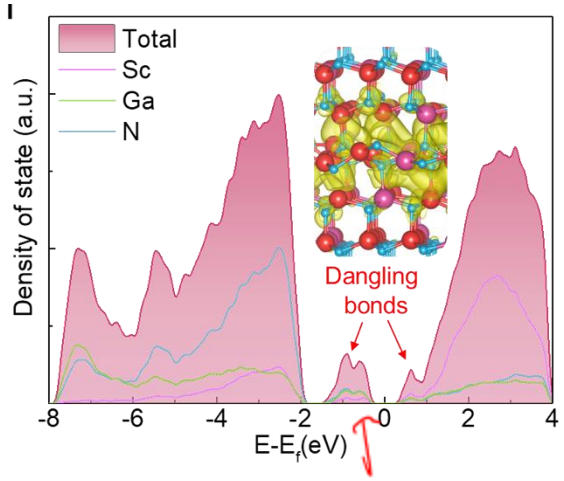






Domain walls in nitride ferroelectrics (III)

Universal cancellation of polarization discontinuity by dangling bonds.

Dipole moment per cation: $\mathbf{p} = 3e\left(\frac{1}{2} - u\right)c\hat{z}$

Polarization: $\mathbf{P} = 2\mathbf{p}/V_{\text{cell}} = 6e\left(\frac{1}{2} - u\right)\hat{z}/\left(a^2\frac{\sqrt{3}}{2}\right)$

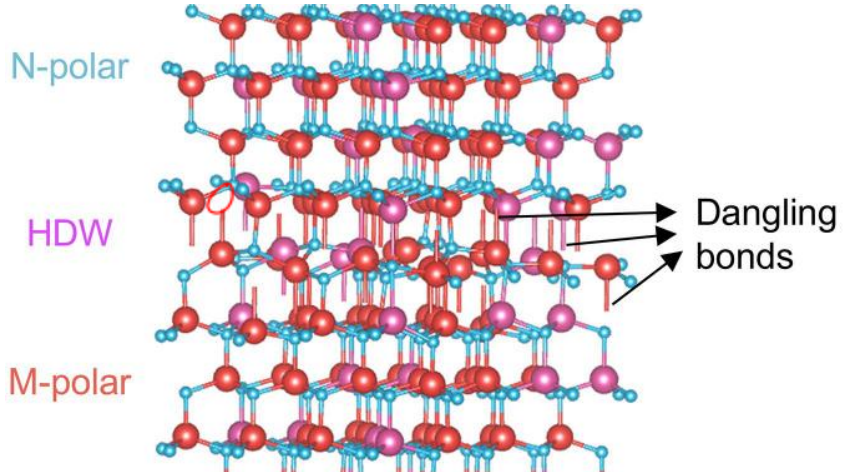
Surface bound charge: $\sigma_b = 2|\mathbf{P}| \approx \frac{\frac{3}{2}e}{\left(a^2\frac{\sqrt{3}}{2}\right)}$

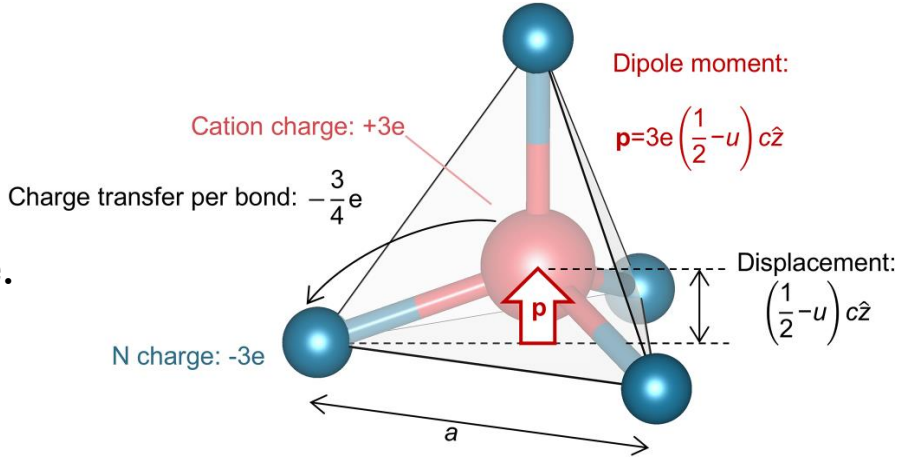
Dangling bond charge: $\sigma_e = -2\frac{3}{4}e/\left(a^2\frac{\sqrt{3}}{2}\right) \approx 1.6 \times 10^{15}\ \text{cm}^{-2}$!!

Record high, but not mobile.

→ Negative charge of dangling bonds cancels out the charge from polarization discontinuity.

→ A universal mechanism for all tetrahedral ferroelectrics that explains the unusual stability of antipolar domain walls.





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