An Introduction to Wurtzite Ferroelectrics

Slides from:

Simon Fichtner and Niklas Kyoushi

Funded by the European Union

OUTLINE

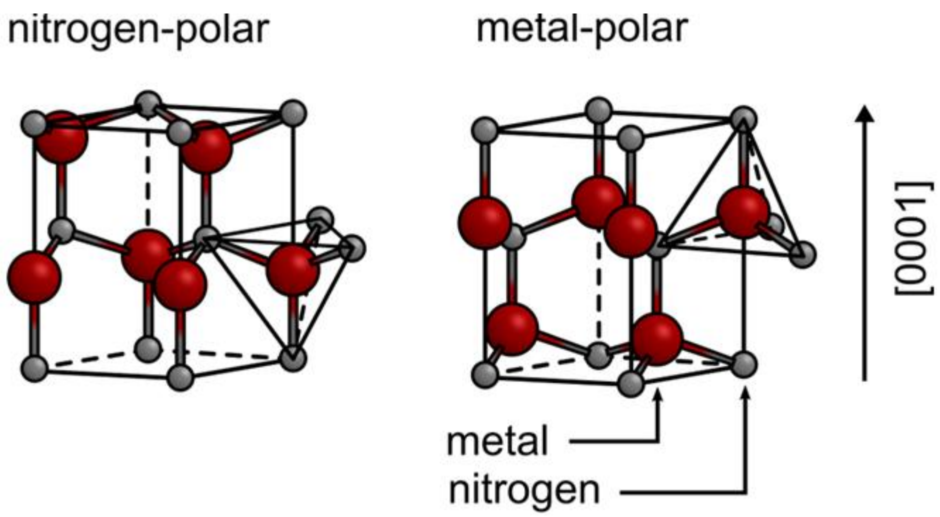
FIXIT

Funded by the European Union

WURTZITE COMPOUNDS

FIXIT

Wurtzite III-N semiconductors



„Wurtzite is the structure with the highest symmetry compatible with the existence of spontaneous polarization,…“

Bernadini, Fiorentini, Vanderbildt, PRB **56**, R10024 (1997)

III-N Semiconductors:
AlN, GaN, InN + their solid solutions

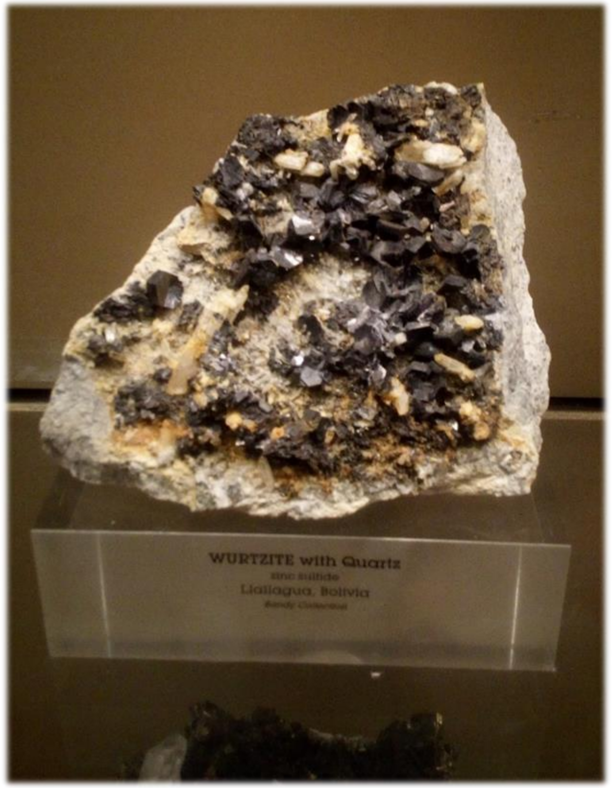
Oxides:
ZnO, BeO

Sulfites:
ZnS, CdS

Iodites:
AgI

Selenides:
CdSe

Wurtzite (Mineral): ZnS



Funded by the European Union

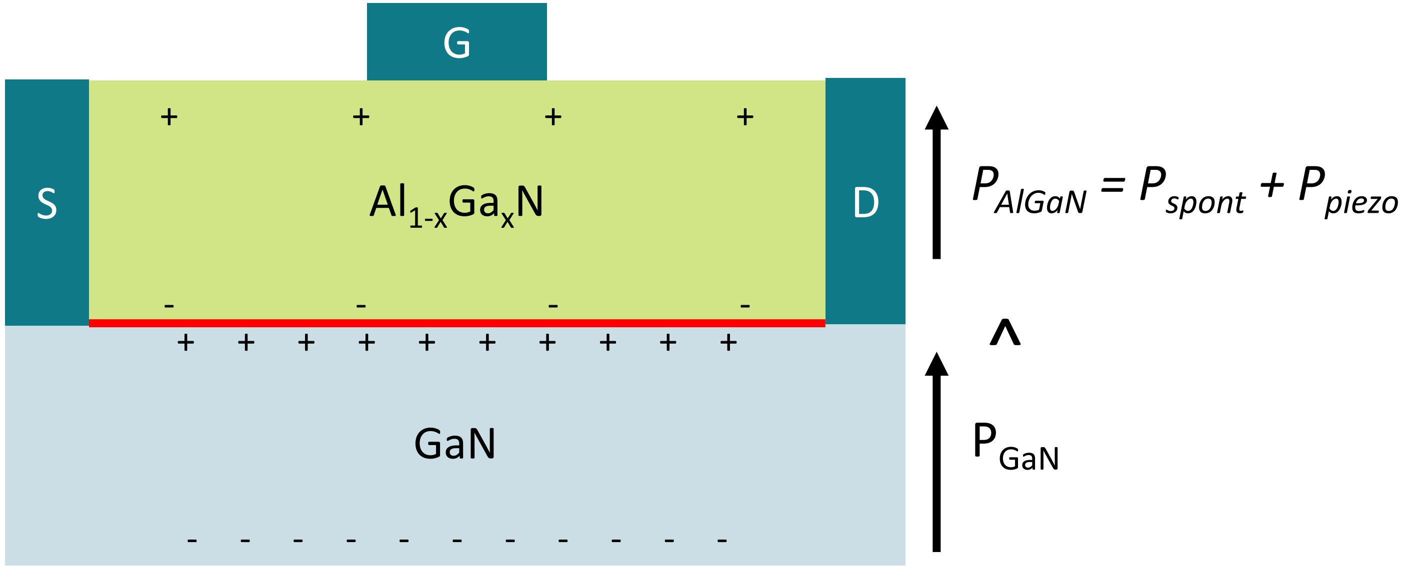
APPLICATION: GaN-HEMT

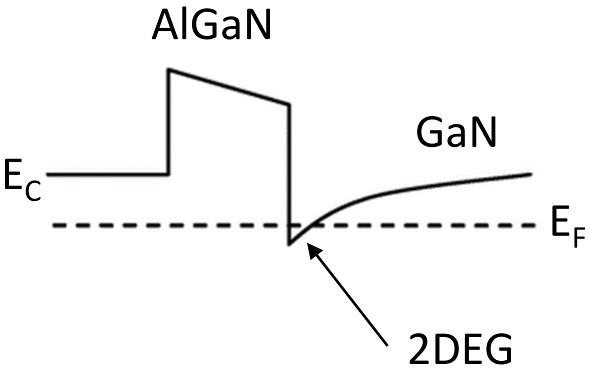
High electron mobility transistor (HEMT)

- WBG: High breakdown voltage (up to 600 V)
- High mobility
- Large carrier density

⇒ Well suited for RF and Power applications

Compensating charges:
2DEG (2D electron gas)





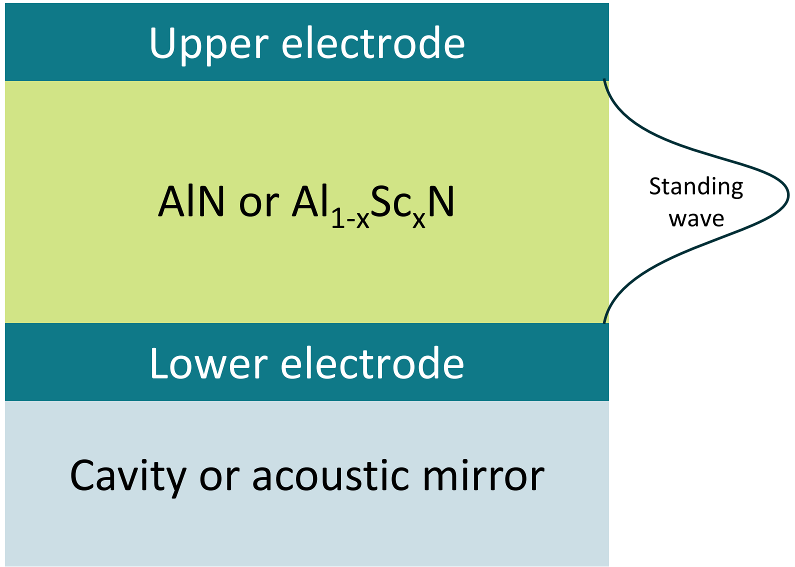
Funded by
the European Union

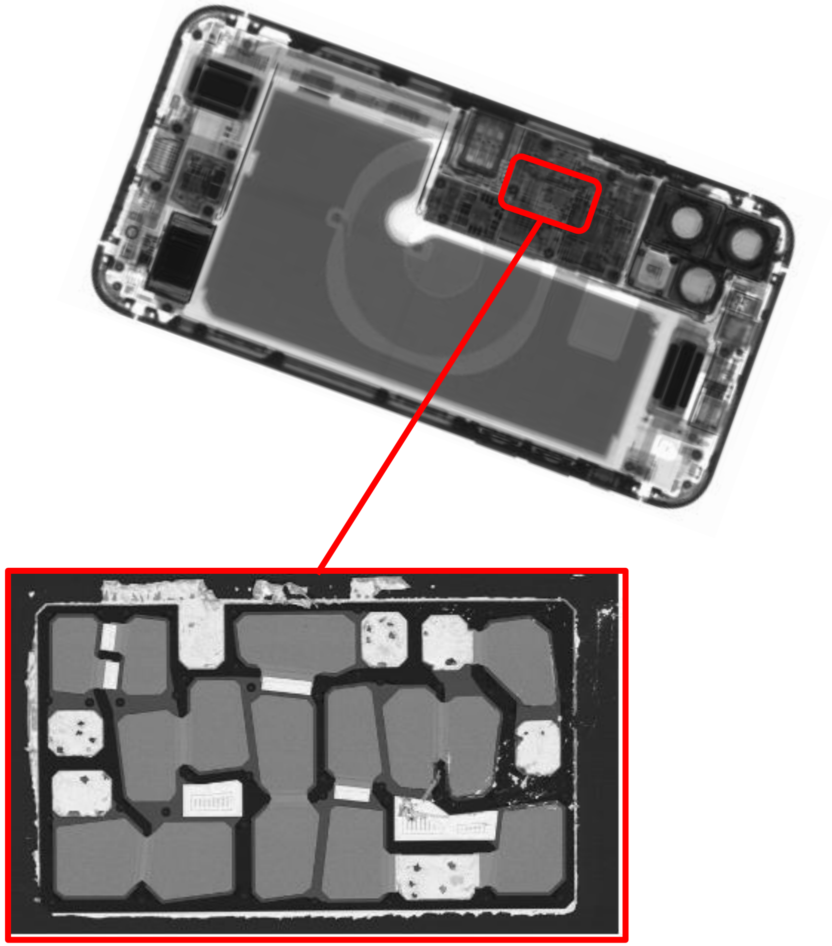
APPLICATION: RF-RESONATOR

FIXIT

Bulk acoustic wave (BAW) resonators: bandpass filters for mobile communication

- Uses piezoelectric effect
- High coupling coefficients/bandwidth
- High quality factors/low losses
- Low temperature drift





Coupling coefficient:

$$k^2 = \frac{d_{33,f}^2 c_{33}}{\epsilon_0 \epsilon_r}$$

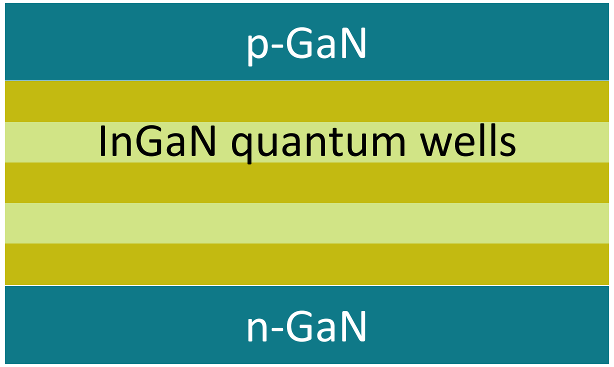
Funded by the European Union

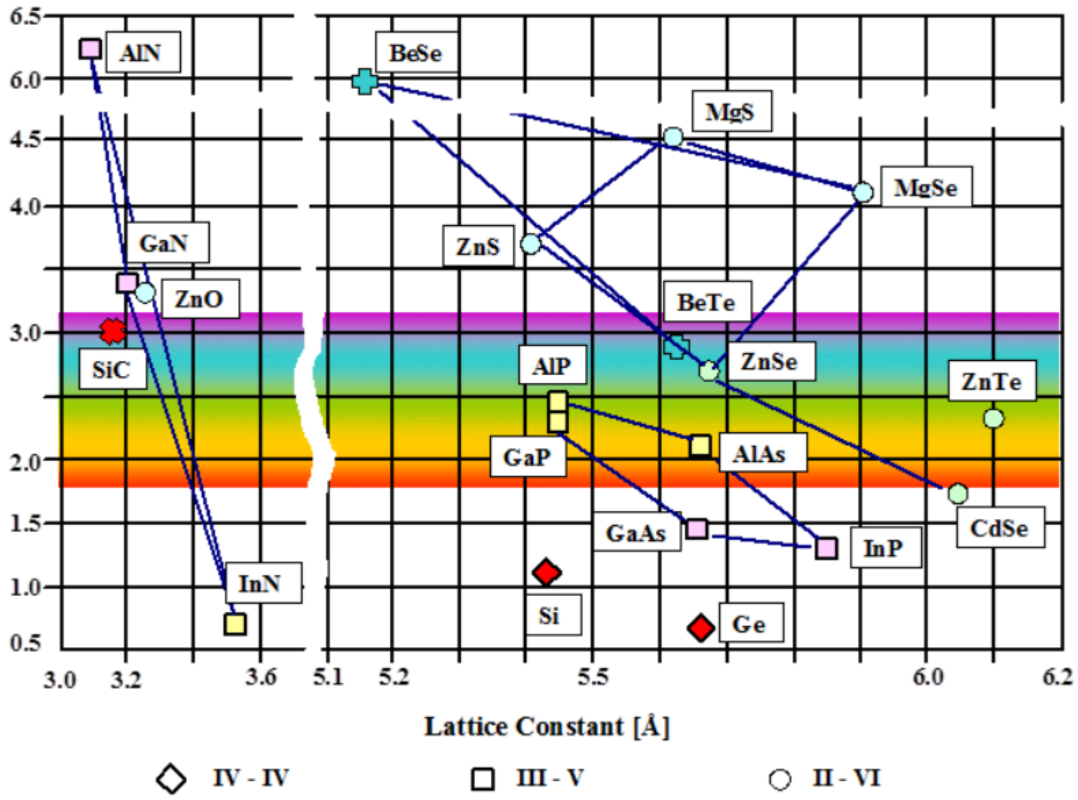
APPLICATION: LEDs

FIXIT

LEDs: $In_{1-x}Ga_xN/GaN$ (blue to green)

- Tunable bandgaps
- Blue emission with high efficiency
- …but (still) low efficiency for red
- No direct connection to polarization
- …but quantum confined Stark effect can shift emission wavelength due to polarization along c-axis





https://www.tf.uni-kiel.de/matwis/amat/semitech_en/kap_2/backbone/r2_3_1.html

Funded by the European Union

W-STRUCTURE: POLARIZATION

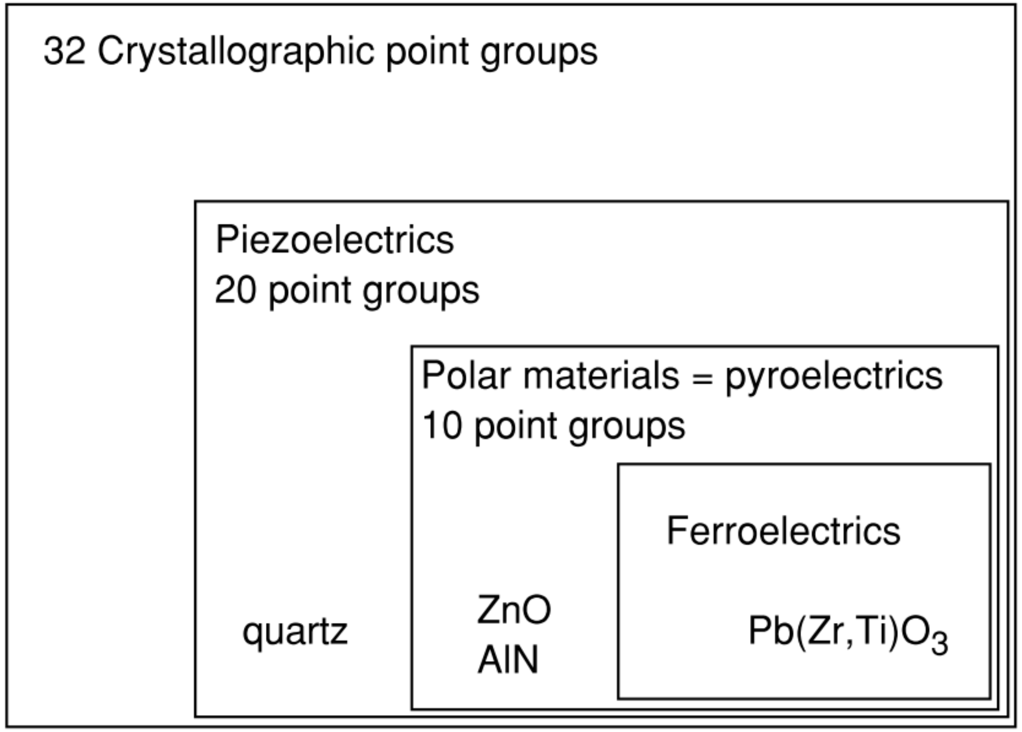
Magnetization: $$\vec{M} = \frac{d\vec{m}}{dV}$$

Polarization: $$\vec{P} = \frac{d\vec{p}}{dV}$$

Spontaneous polarization: $$\vec{P}_S \neq 0 \quad \text{for} \quad E = 0$$

Spontaneous polarization is innerhently tied to crystal lattices with low symmetry.

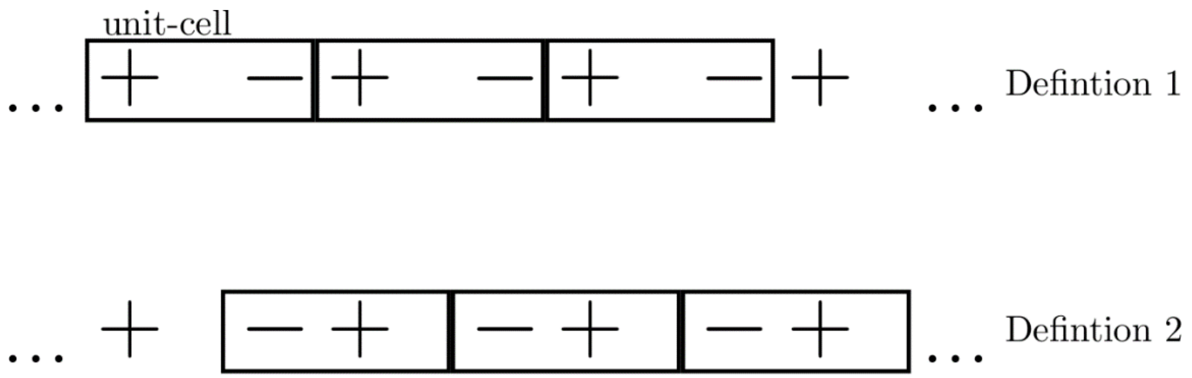
Spontaneous polariztion is the order parameter for ferroelectricity.



N. Setter (ed.), Electroceramic-based MEMS, Springer, 2004

Funded by
the European Union

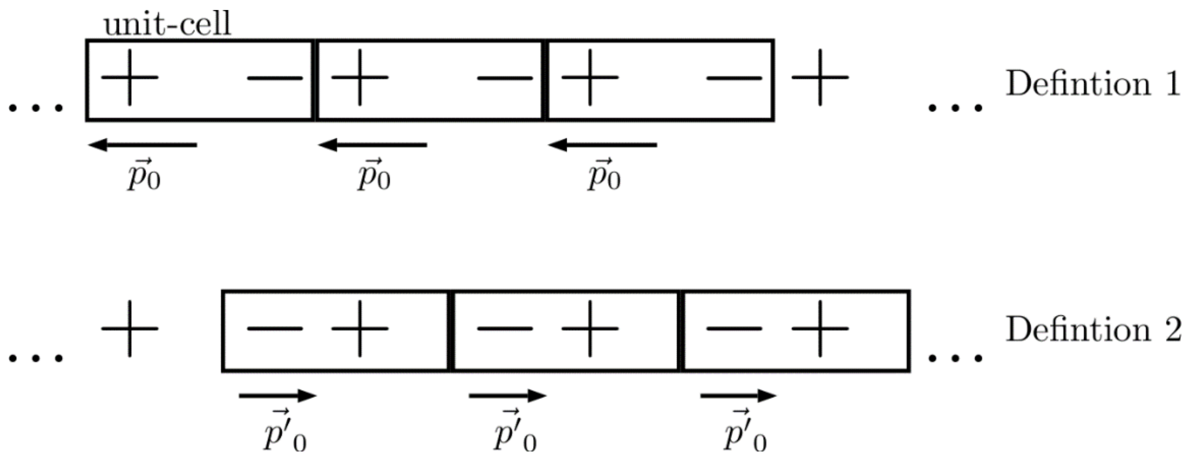
SPONTANEOUS POLARIZATION



Adapted from Spaldin, J. Solid State Chem. **195**, 2, (2012)

Funded by the European Union

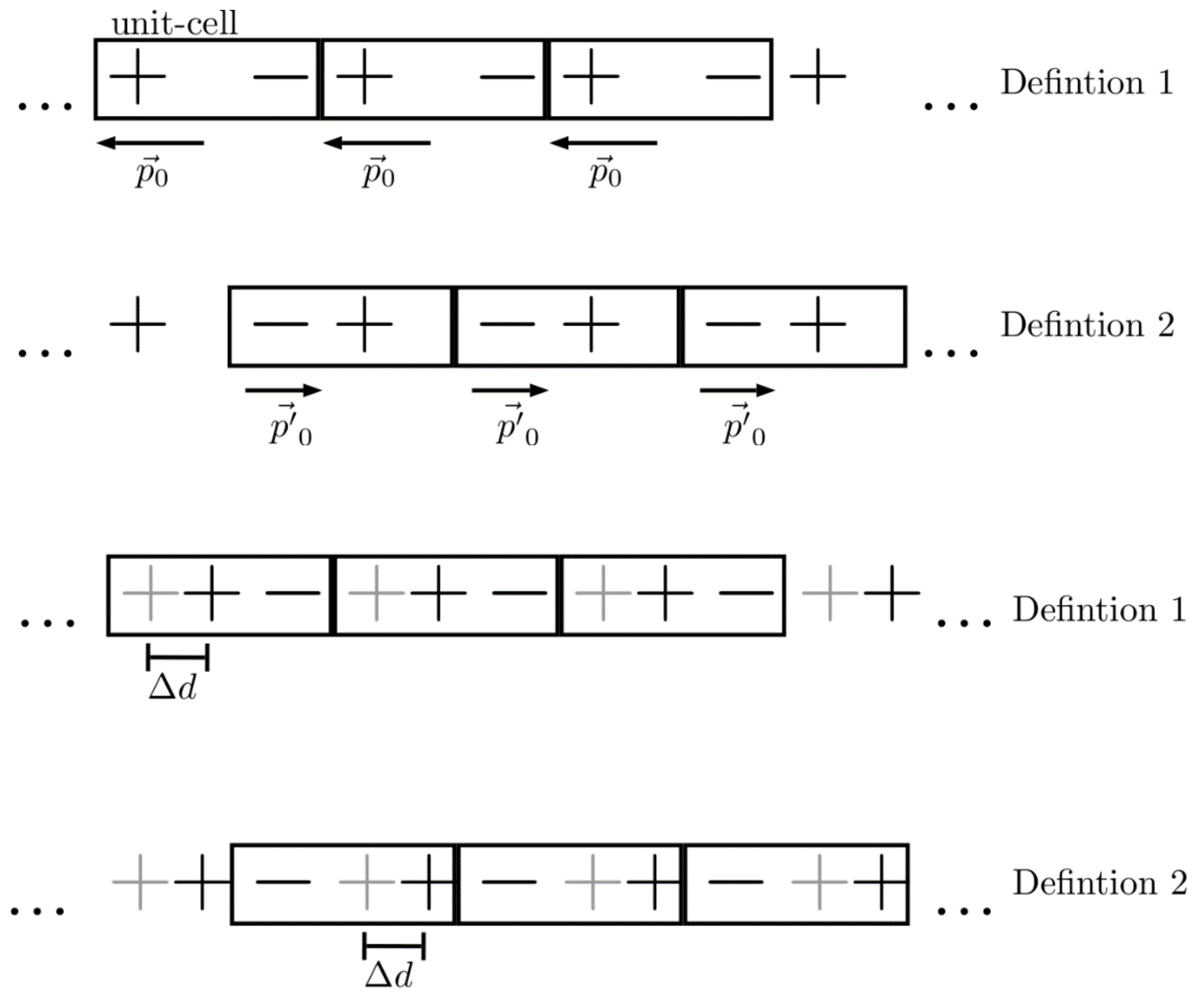
SPONTANEOUS POLARIZATION



Adapted from Spaldin, J. Solid State Chem. **195**, 2, (2012)

Funded by
the European Union

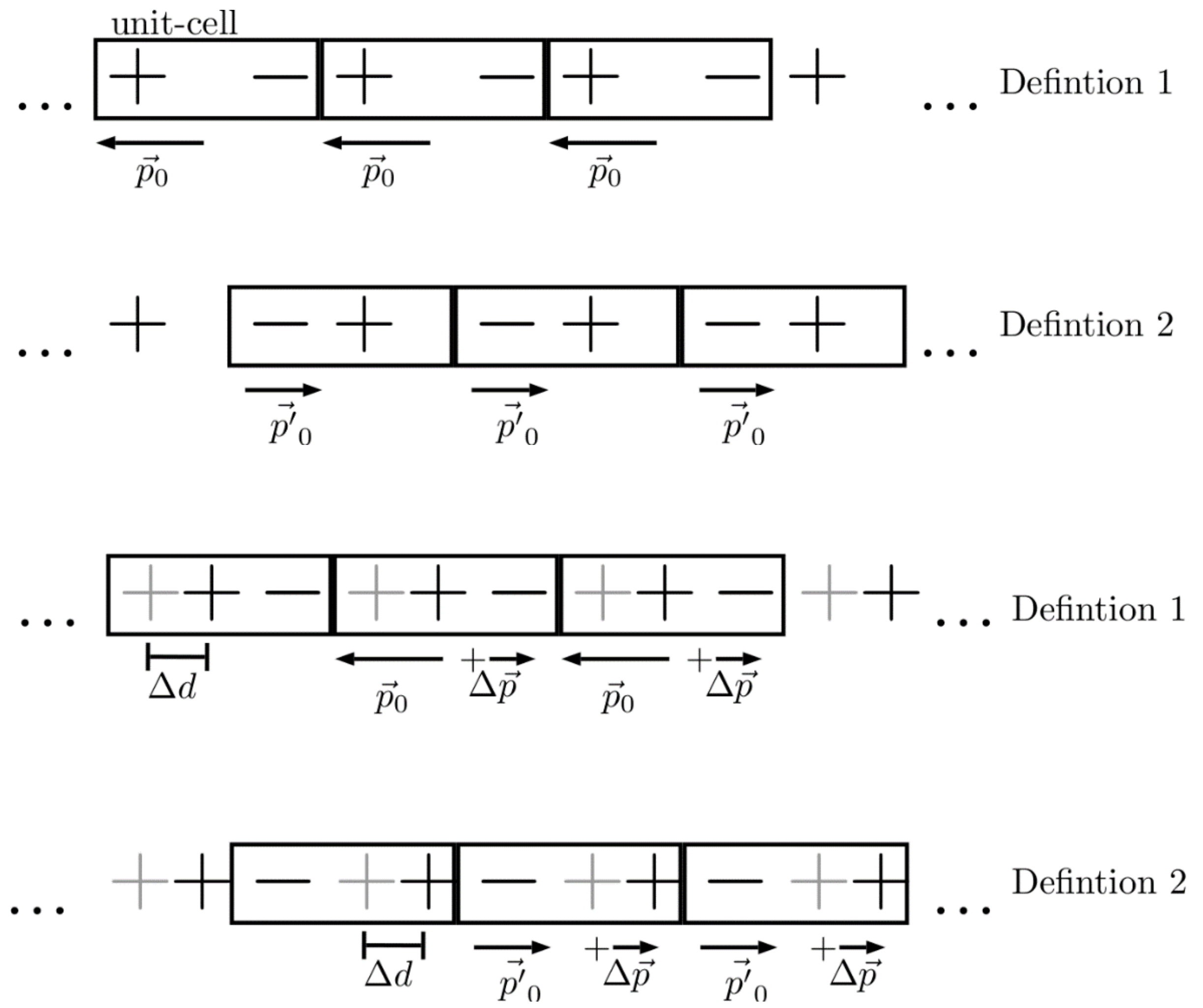
SPONTANEOUS POLARIZATION



Adapted from Spaldin, J. Solid State Chem. **195**, 2, (2012)

Funded by
the European Union

SPONTANEOUS POLARIZATION

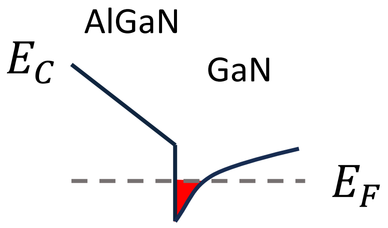


Only differences in $\vec{P}_S$ are well defined

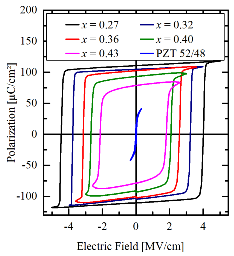
Adapted from Spaldin, J. Solid State Chem. **195**, 2, (2012)

Funded by the European Union

SPONTANEOUS POLARIZATION



Ambacher et al., JAP **85**, 3222 (1999)



$|\vec{P}_S| > 1$ C/m²

Fichtner *et al.*, JAP **125**, 114103 (2019)

Theoretical Prediction (ZB)

1997

	P^{eq} [C/m²]
AlN	–0.081
GaN	–0.029
InN	–0.032

Bernadini, Fiorentini, Vanderbild, PRB **56**, R10 024 (1997)

1997

Description of GaN-HEMT

Revised Predictions (LH)

2016

	$P_{\mathrm{eff}}^{(\mathrm{H\,ref})}$ [C/m²]
GaN	1.312
AlN	1.351
InN	1.026

Dreyer *et al.*, PRX **6**, 021038 (2016)

2019

Ferroelectric III-Ns: experimental determination of $\vec{P}_S$

Concensus & first applications?

2024

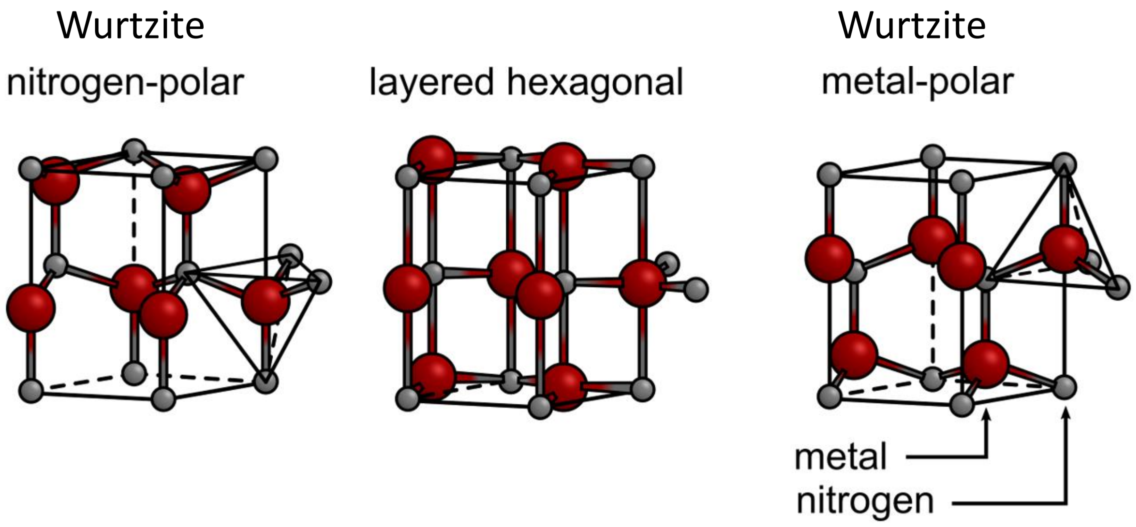
Yassine et al., JAP **135** 155702 (2024)
Fichtner et al., APL **125**, 040501 (2024)
Wang et al., APL **124**, 263502 (2024)

Funded by the European Union

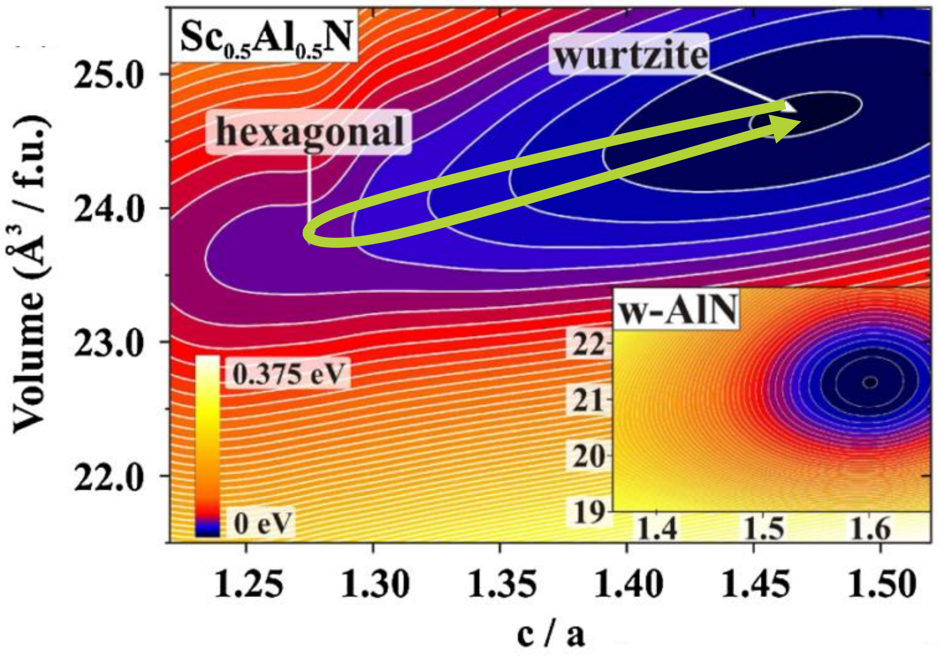
EMERGENCE OF FERROELECTRICITY

FIXIT

Unit cell level



Ternary compounds, e.g. $Al_{1-x}Sc_xN$



Tasnadi *et al*. PRL **104**, 137601 (2010)

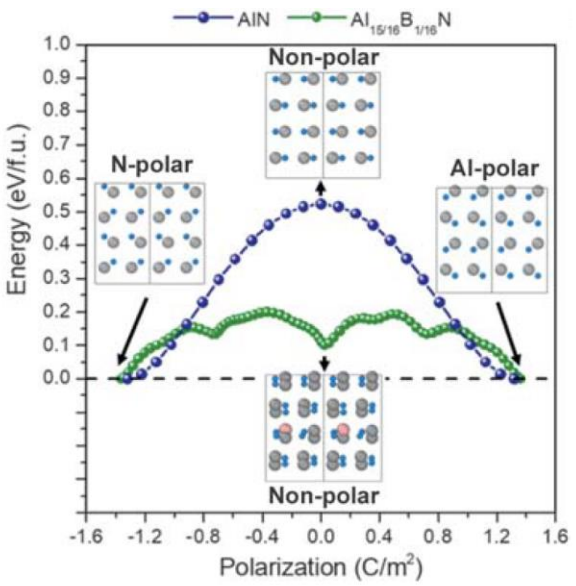
Funded by the European Union

EMERGENCE OF FERROELECTRICITY

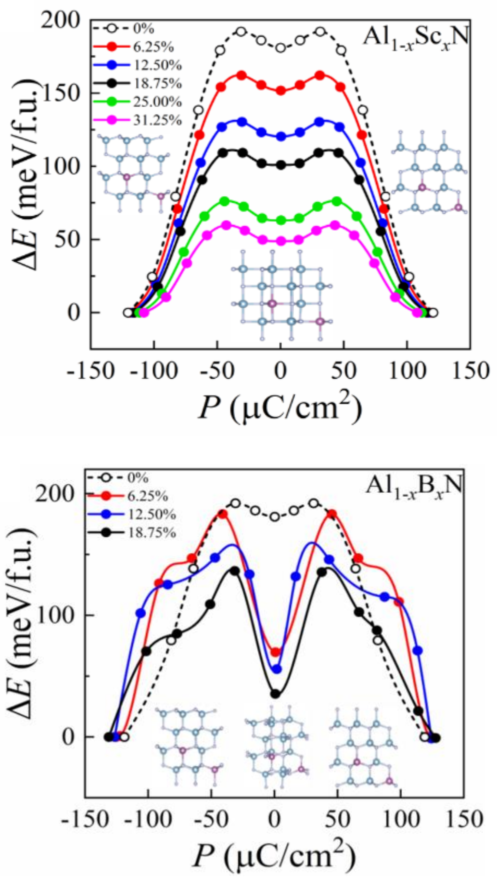
FIXIT

Supercell level

- Double well shape for AlN and $Al_{1-x}Sc_xN$ with x < 0.3
  - Intermediate state: Layered-hexagonal
- Metastable minimum for $Al_{1-x}B_xN$
  - Intermediate state: Supercell with antiparallel polarization ($P4_2$/mm)?
- Several switching pathways for w-type ferroelectrics?



S. Calderon et al., Science **380**, 1034 (2023)



Liu et al., APL **122**, 122901 (2023)

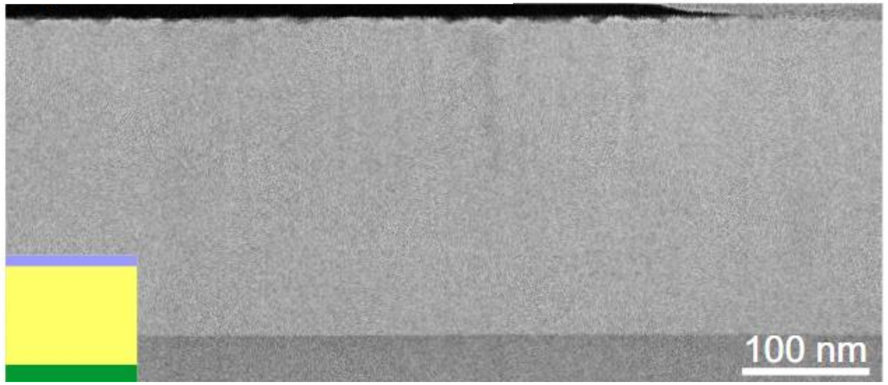
Funded by the European Union

EMERGENCE OF FERROELECTRICITY

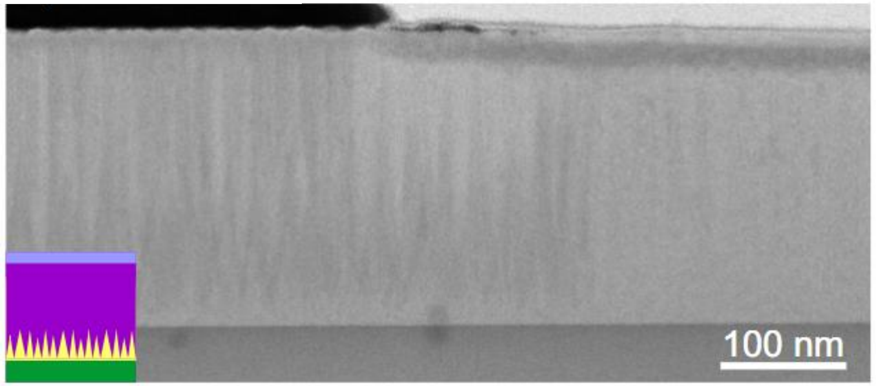
FIXIT

Real system:
$Al_{0.85}Sc_{0.15}N$

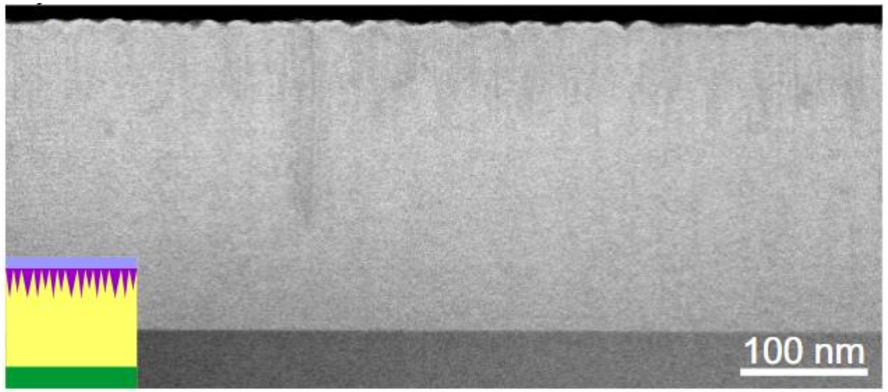
1: pristine film



3: saturation



2: nucleation



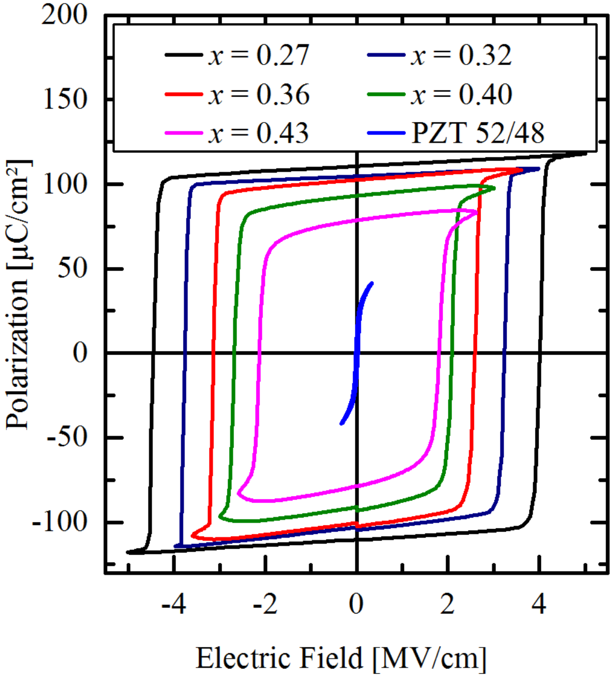
- Switching progresses from nucleation through the motion of narrow (1 nm) domain walls
- No non-wurtzite phase outside of domain walls

Funded by the European Union

A NEW CLASS OF FERROELECTRICS

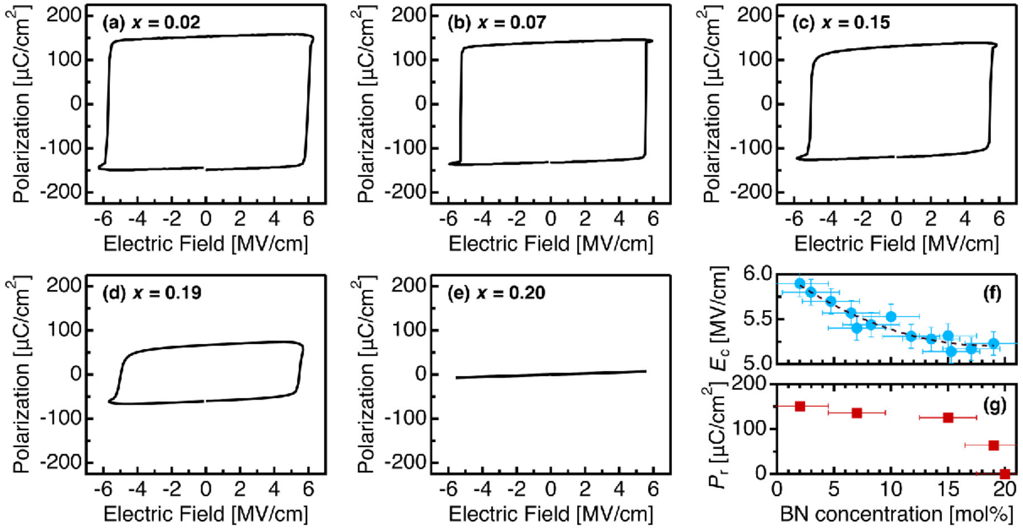
FIXIT

$Al_{1-x}Sc_xN$



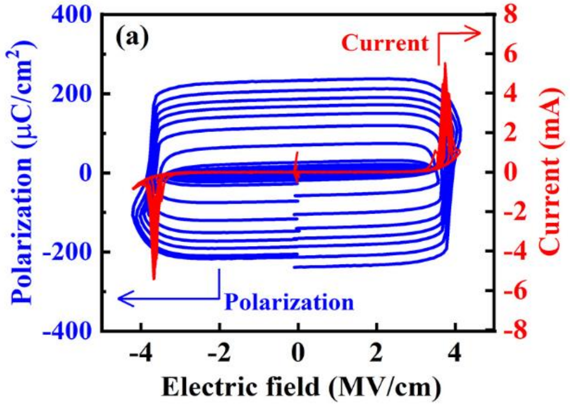
Fichtner *et* al. JAP **125**, 114103 (2019)

$Al_{1-x}B_xN$



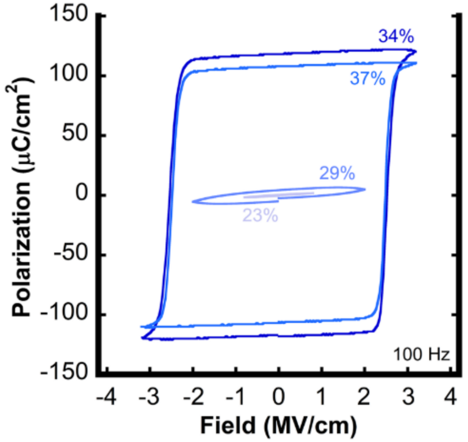
Hayden *et al.*, Phys. Rev. Materials **5**, 044412 (2021)

$Ga_{1-x}Sc_xN$



Uehara *et al.,* APL 119, 172901 (2021)

$Zn_{1-x}Mg_xO$



Ferri *et al.*, JAP 130, 044101 (2021)

+ $Al_{1-x}Y_xN$, $Al_{1-x}Hf_xN$, $Al_{1-x}Gd_xN$, AlN,…

Funded by the European Union

DEPOSITION METHODS

Physical Vapor Deposition (Sputtering)

Metal Organic Chemical Vapor Deposition (MOCVD)

Molecular Beam Epitaxy (MBE)

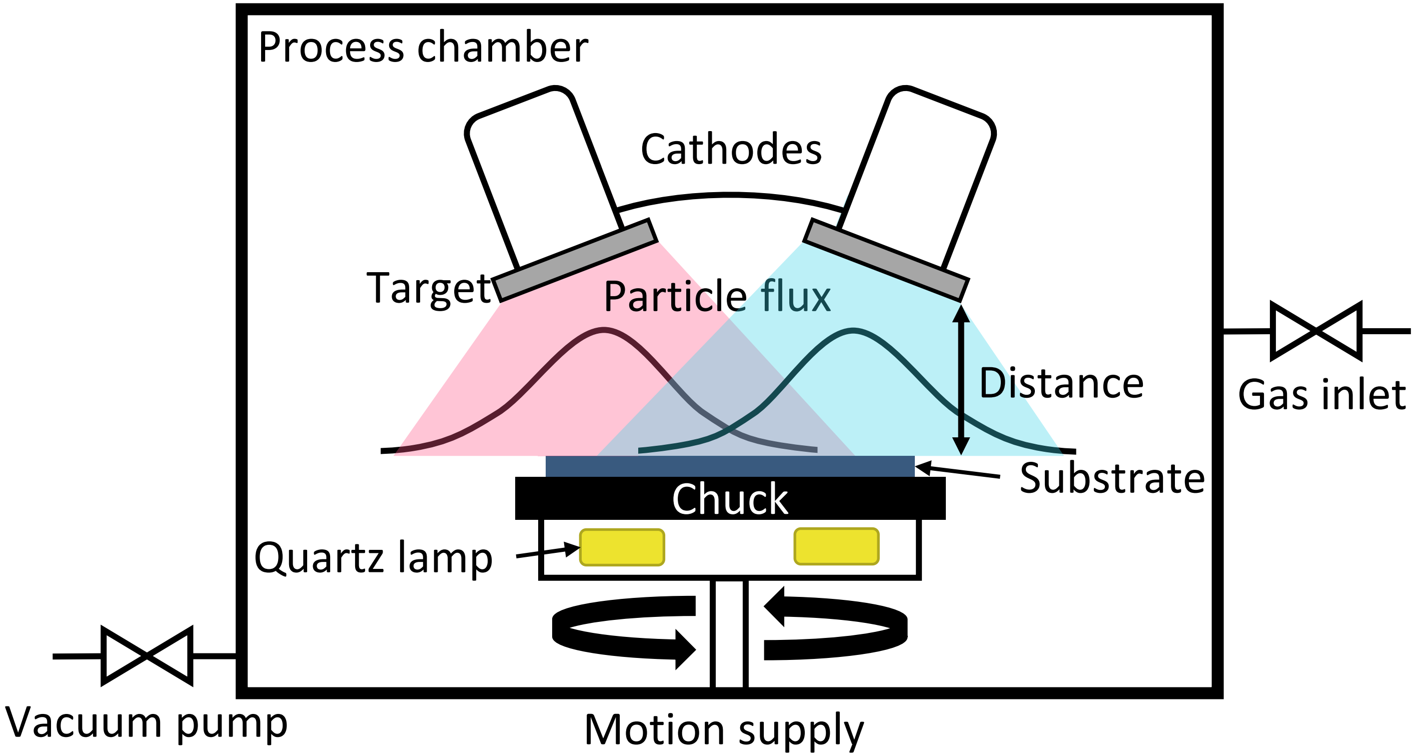
Funded by
the European Union

SPUTTERING

- Co-sputtering
- Reactive sputtering

<u>Important Process Parameter:</u>

- Target power:
  up to 1000 W
- Gas flow rate (Ar_2, N_2, etc.)
- Chuck temperature
  350 °C – 450 °C
- Target distance
- Rotational speed



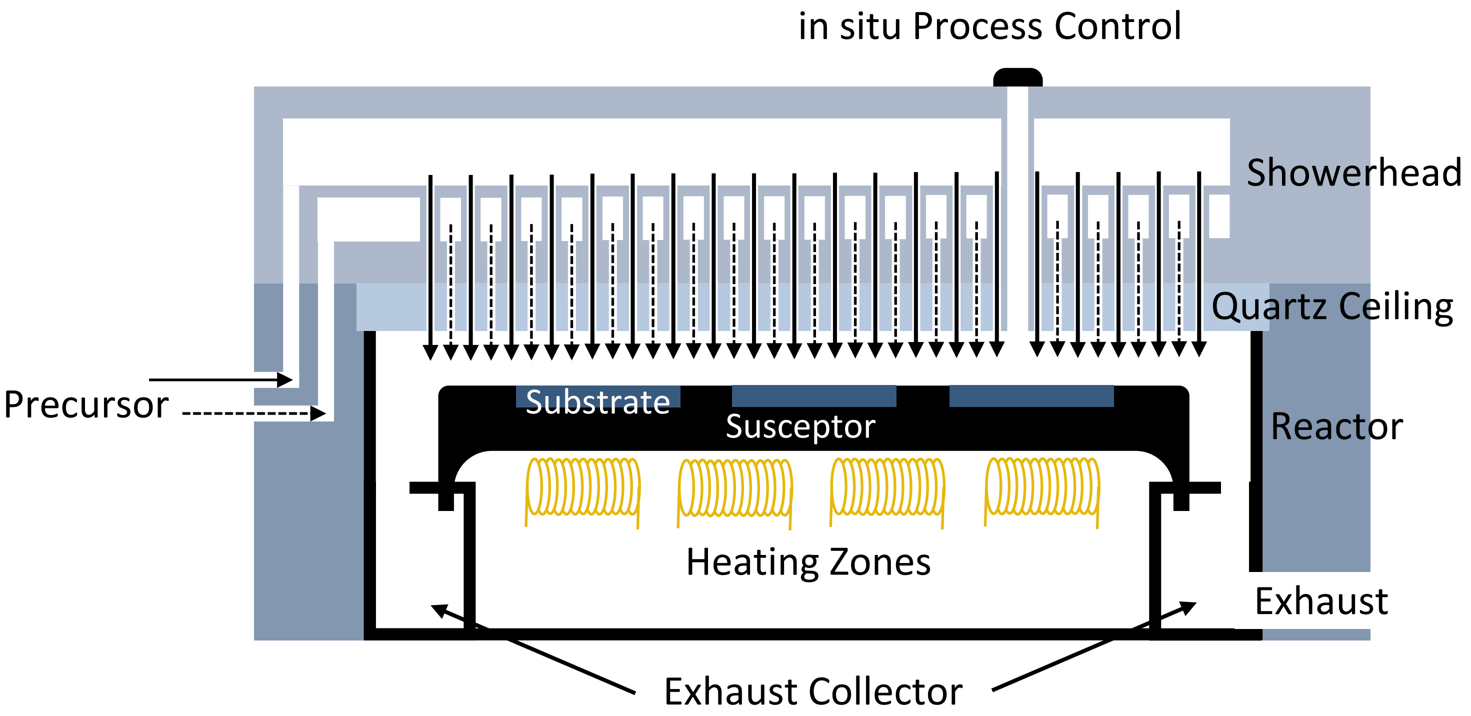
Funded by
the European Union

MOCVD

- In situ process control
- Fraunhofer IAF leading

Important Process Parameter:

- Precursor flow rate
- Precursor concentration
- Substrate temperature
- Rotational speed
- Pressure



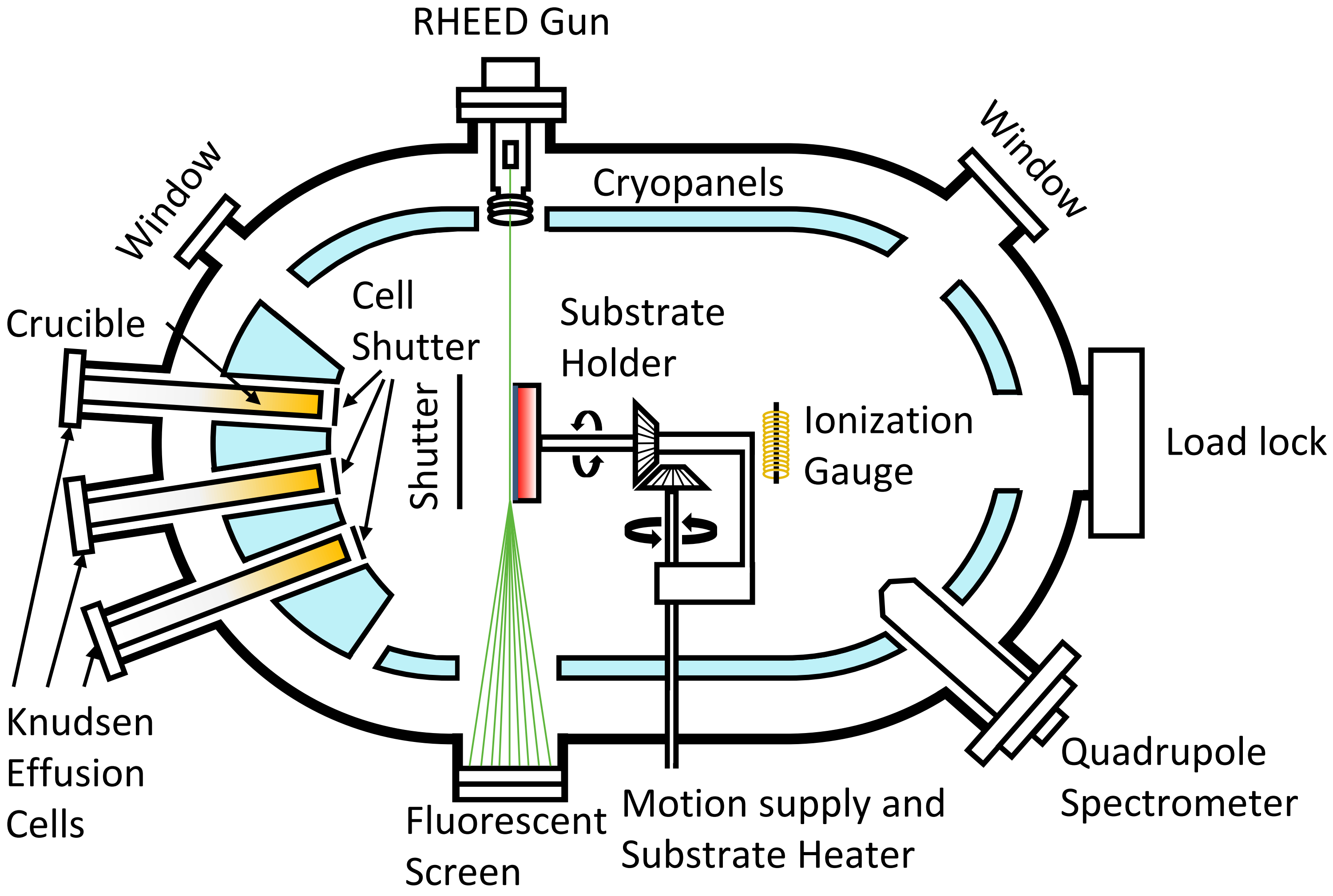
Funded by
the European Union

MBE

- Substrate temperatures
  20 °C - 1400 °C
- Ultrahigh vacuum
  10^{-10} mbar, $L > 0.2$ m
- In situ epitaxial growth control
- Molecular Monitoring

Evaporation rate:

$$R = 8.33 \times 10^{22} \frac{p \cdot A_e}{\sqrt{M \cdot T}} \left[\frac{molecules}{s}\right]$$



Funded by the European Union

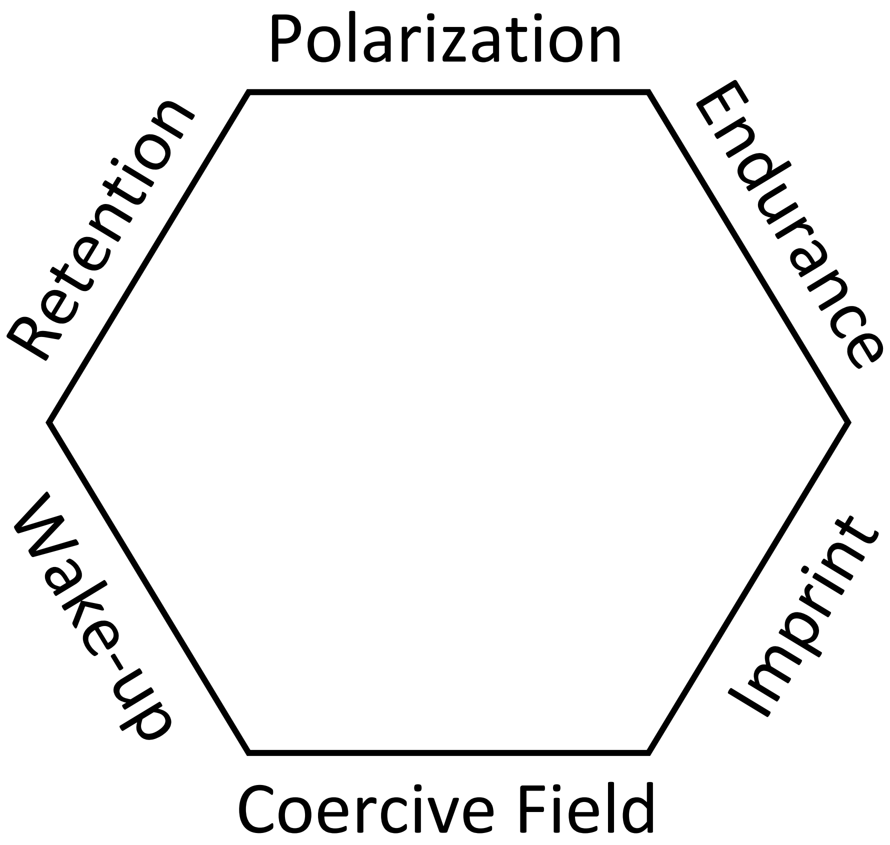
STATISTICS ON DEPOSITION TECHNOLOGY

FIXIT

	Sputtering	MOCVD	MBE
Process Temperature	20 °C - 500 °C	900°C – 1200°C	400 °C - 900 °C
Vacuum	10^{-7} mbar	40 mbar	10^{-10} mbar
Mechanism	Plasma induced momentum transfer	Chemical reaction	Evaporation
BEOL Compatibility	yes	no	no
Growth rate	fast	0.01-5 µm/h	slow
AlScN	Polycrystalline films, high Sc content	Epitaxial films, up to 30% Sc Content	Epitaxial films, high Sc content
Source	Zhang et al. Nano-Micro Lett. 16, 227 (2024)	Leone et al., J. Appl. Phys. 127,190401 (2020)	Zhang et al. Nano-Micro Lett. 16, 227 (2024)

Funded by the European Union

KEY FERROELECTRIC PROPERTIES



Funded by
the European Union

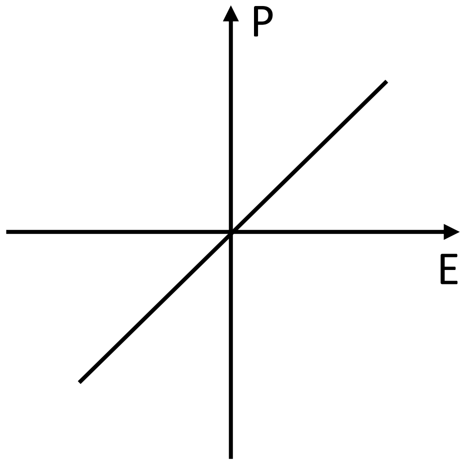
POLARIZATION AND COERCIVE FIELD

FIXIT

Polarization

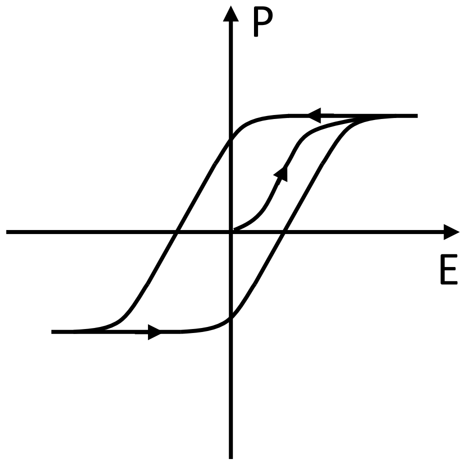
Classic dielectric:

- Induced polarization is proportional to electric field



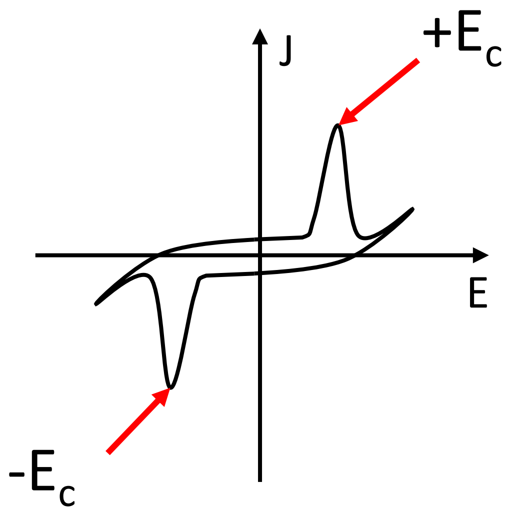
Ferroelectric material:

- Polarization is spontaneous and reversible
- Hysteresis loop
- Dependent on applied electric field and its history



Coercive field

- Maintaining a dielectric Polarization in an
- In reversing electric field
- Without depolarization



Funded by the European Union

RETENTION AND ENDURANCE

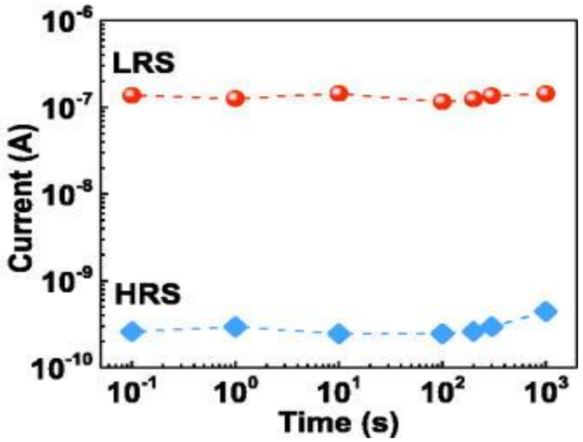
FIXIT

Retention

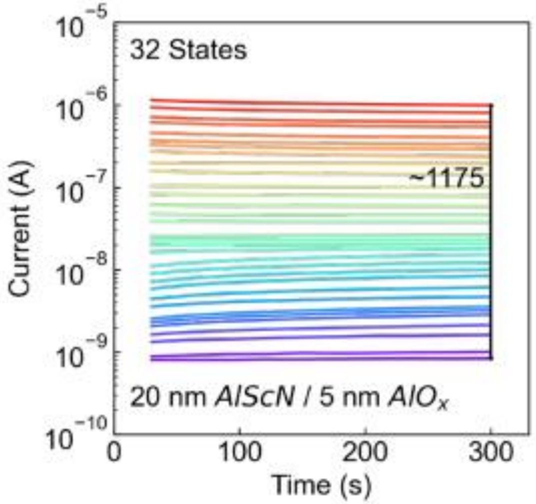
- The device can maintain its state over time
- Read pulses do not impact the state
- Multi state retention

Endurance

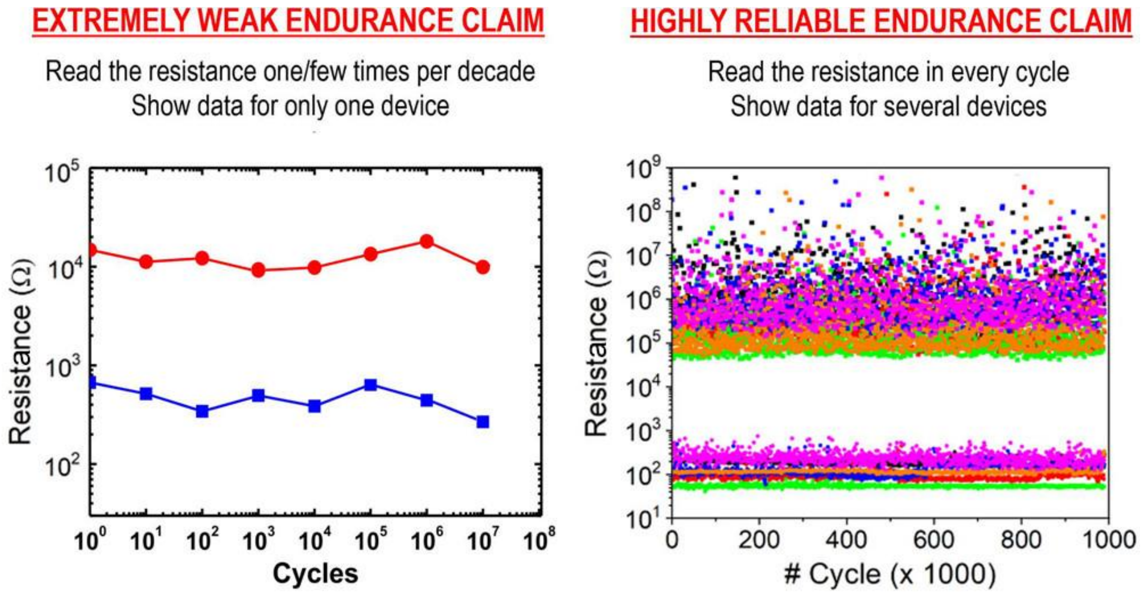
- The states of the device are addressable with write and erase pulses without fatigue



Liu et al., Appl. Phys. Lett. 118, 202901 (2021)



Kim et al., arXiv 118, 2403.12361 (2024)



Lanza et al., ACS Nano 15, 17214–17231 (2021)

Funded by the European Union

WAKE-UP

FIXIT

Definition:
Voltage cycles are increasing the remanent polarization (P_r) each cycle until saturation

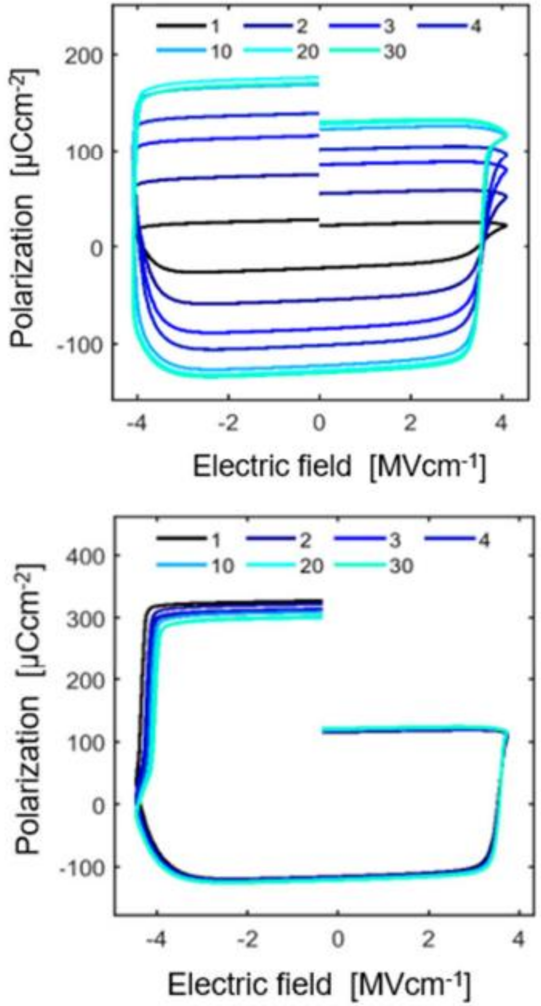
Alexe et al., Appl. Phys. Lett. 79, 242 (2001)

Cause:
Formation of permanent inversion domains

- Conditioning needed for idle operation mode

- Or for CAU $Al_{1-x}Sc_xN$ films:

→ a high enough voltage results in a saturated P_r and wake-up free film



M. Gremmel et al., ArXiv Preprint, 2310.17718 (2023)

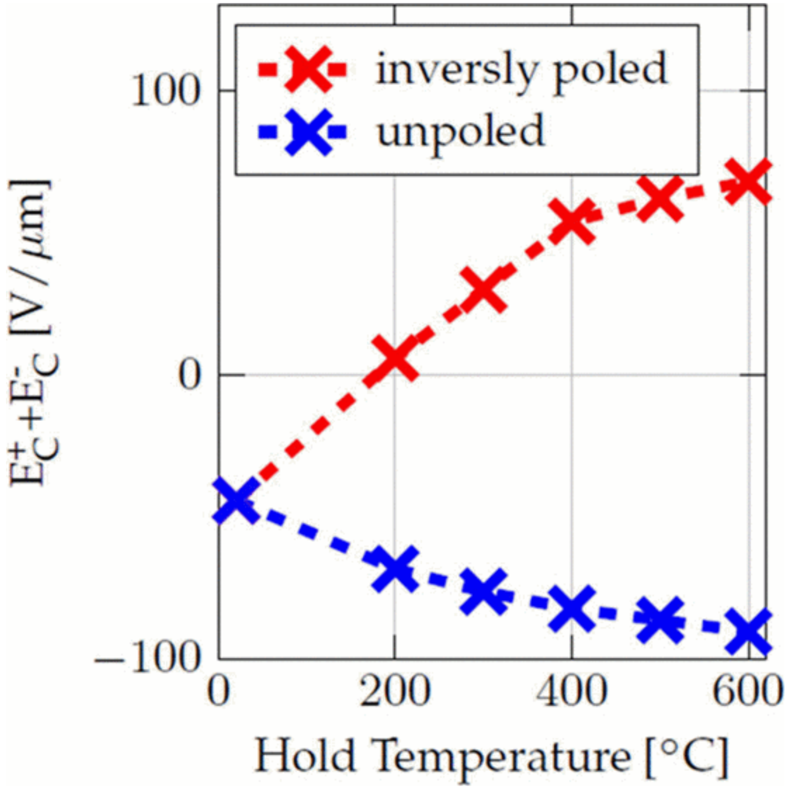
Funded by the European Union

ALSCN IMPRINT

FIXIT

Imprint is the miss alignment of charged defects

- hysteresis loop shifts + and - voltages
- As deposited imprint favors N-polar state → $-E_c$
- Reduced by cycling, temperature and majority polarization
- Defect species still unknown



Fichtner et al., IFCS-ISAF, 1-4 (2021)

Funded by the European Union

FERROELECTRIC DEPENDENCIES

- Structural Quality
- Thickness
- Epitaxial Strain
- Stress and Coercive Field
- Domains and Domain Walls
- Switching kinetics

Funded by
the European Union

DOMAINS AND DOMAIN WALLS

A ferroic domain is a spatially extended region with constant values of its order parameters (magnetization, polarization, or strain).

Interface separating two domains of different orientation state. Within the wall, the order parameter defining the domains progressively changes from the orientation state of one domain to the other. The width of domain walls can range from 1 to 100 nm, depending on the material and the ferroic order involved, as, for instance, ferroelectric domain walls are thinner than magnetic domain walls.

https://www.sciencedirect.com/topics/engineering/coercive-field

Funded by
the European Union

SWITCHING KINETCS

FIXIT

It has been shown that increasing the Sc alloying decreases the Ec of AlScN. Therefore, an increase of Sc% from 28% to 36% leads to lower operating voltages.

Fichtner, S.; Wolff, N.; Lofink, F.; Kienle, L.; Wagner, B. AlScN: A III-V semiconductor based ferroelectric. Journal of Applied Physics 2019, 125 (11). DOI: 10.1063/1.5084945.

Funded by the European Union

TO BE ADDED….

Funded by
the European Union

THANK YOU!

QUESTIONS?

Funded by
the European Union