GaN grown on Mica: polarity, strain, and strain relaxation through the formation of telephone cord buckles

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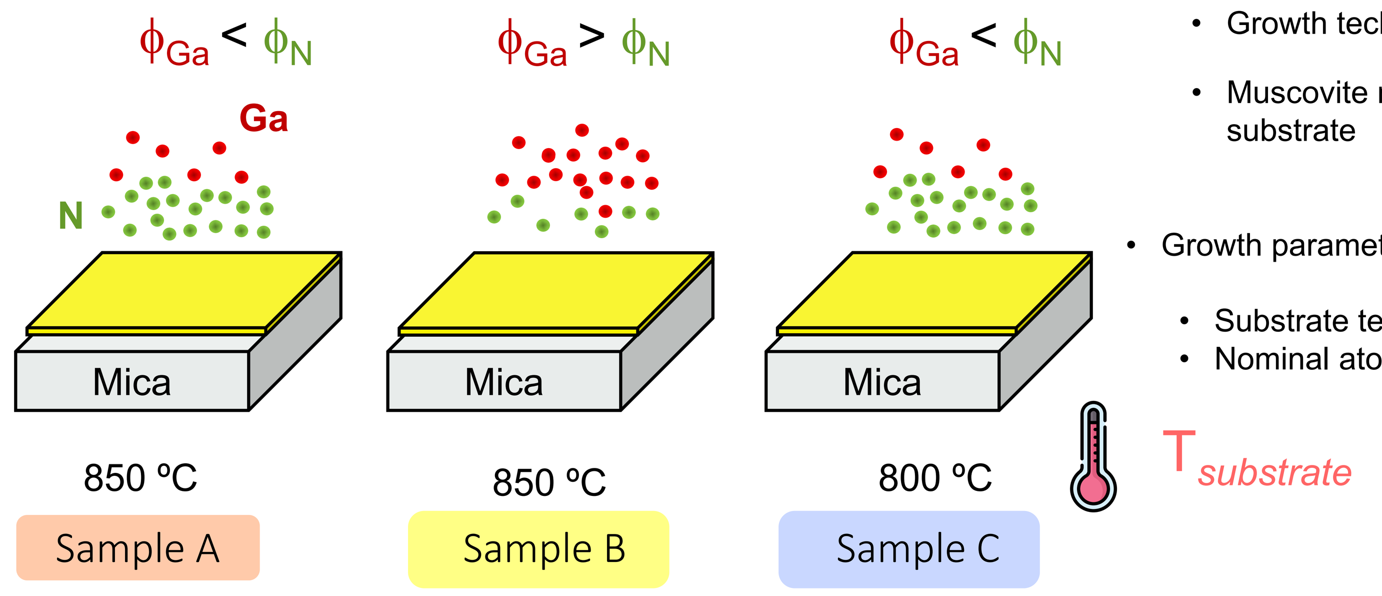
The plasma-assisted molecular beam epitaxial growth of GaN on muscovite mica was investigated by a combination of scanning electron microscopy, transmission electron microscopy, atomic force microscopy, cathodoluminescence, Raman spectroscopy and X-ray diffraction experiments. In spite of the lattice symmetry mismatch GaN was found to be in epitaxial relationship with mica, with the [11-20] GaN direction parallel to [010] direction of mica. Interestingly, almost pure zinc blende (cubic) GaN layers could be obtained, depending on growth conditions. This suggests the existence of a specific GaN nucleation mechanism on mica, opening a new way to the growth of the thermodynamically less stable zinc blende GaN phase. In addition, telephone cord buckles have been first reported in GaN. A strain relaxation process can be assigned to the formation of the buckles by Raman spectroscopy analysis. Finally, using its geometric parameters, two different modelling methods have been applied to obtain elastic information of the delaminated film.

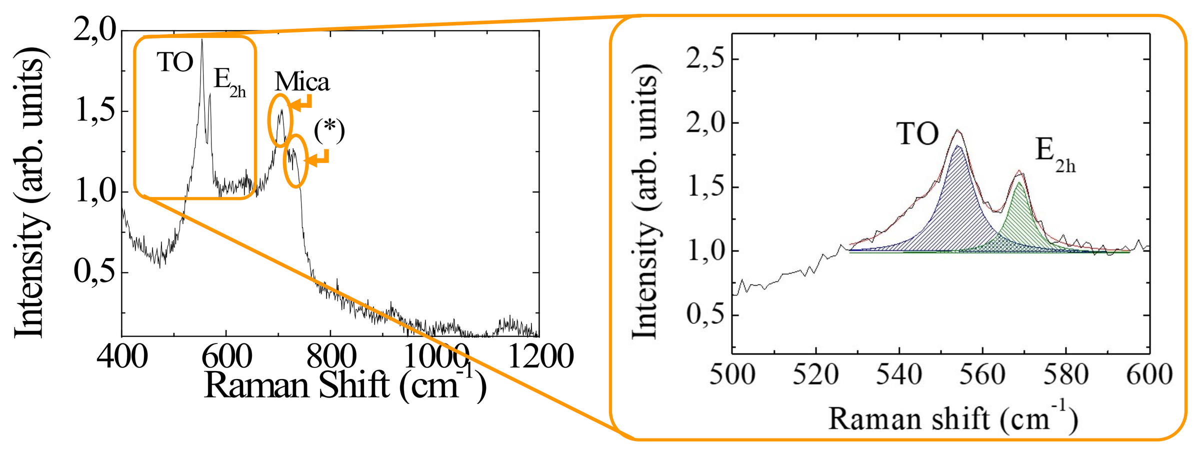
SAMPLES AND CHARACTERIZATION TECHNIQUES

GaN growth conditions



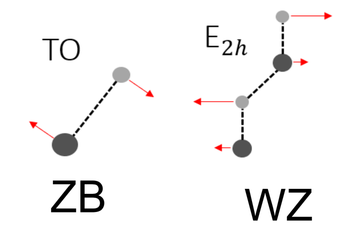
- Growth technique: PAMBE
- Muscovite mica is used as a substrate
- Growth parameters:
  - Substrate temperature $T_{substrate}$
  - Nominal atomic fluxes ϕ_{Ga}, ϕ_N

Raman spectroscopy



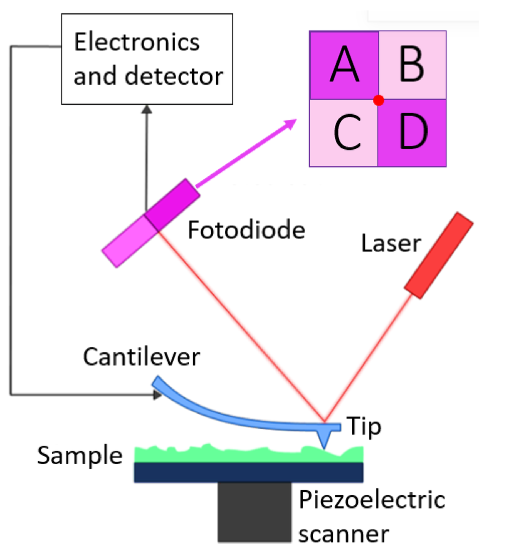
Reference frequencies:

$\omega^0_{E_{2h}}$ = 566.5 cm^{-1} | ω^0_{TO} = 552 cm^{-1}



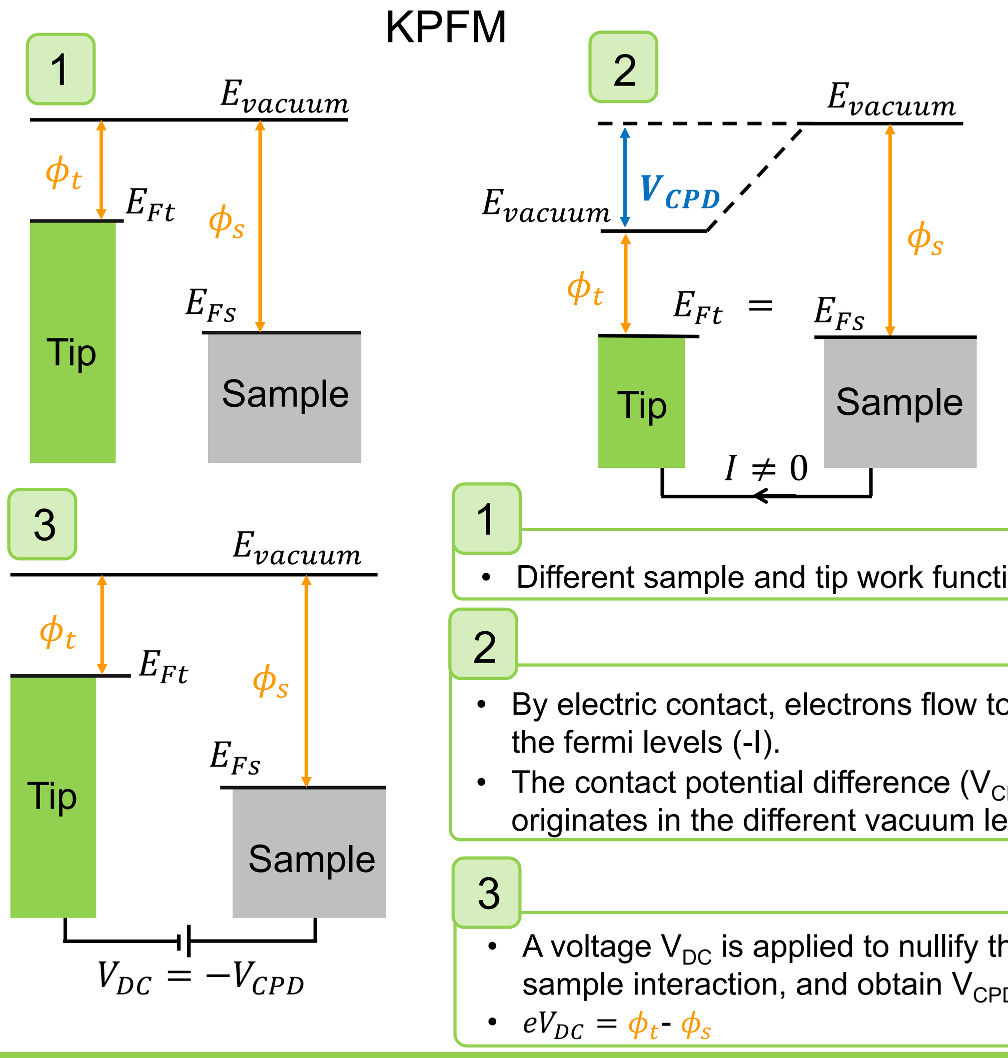
- Shift to high frequency: compressive strain
- Shift to low frequency: tensile strain
- TO mode: presence of ZB phase
- E_{2h} mode: presence of WZ phase

AFM



- The tip vibrates at its resonant frequency
- Tip-sample interaction changes the vibrational frequency and amplitude
- The variation of the amplitude allow us to obtain topographical information
- The variation in frequency allows to track the electrical interaction

KPFM



1
- Different sample and tip work functions

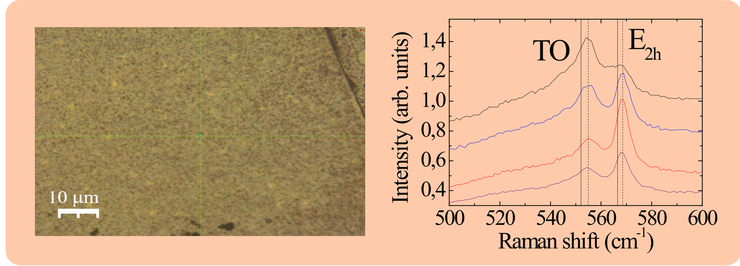
2
- By electric contact, electrons flow to match the fermi levels (-I).
- The contact potential difference (V_{CPD}) originates in the different vacuum levels

3
- A voltage V_{DC} is applied to nullify the tip-sample interaction, and obtain V_{CPD}
- $eV_{DC} = \phi_t - \phi_s$

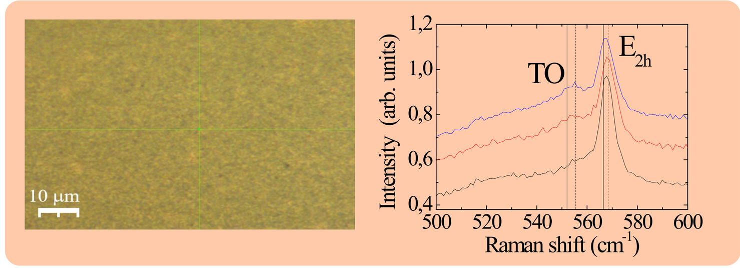
RAMAN AND KPFM CHARACTERIZATION

Crystallographic phase and quantification of strain

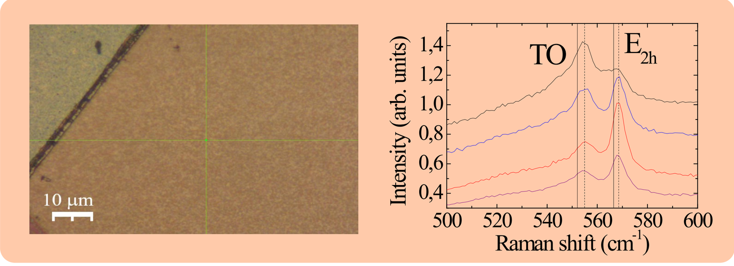
Sample A



- Predominance of WZ phase
- Relaxed GaN

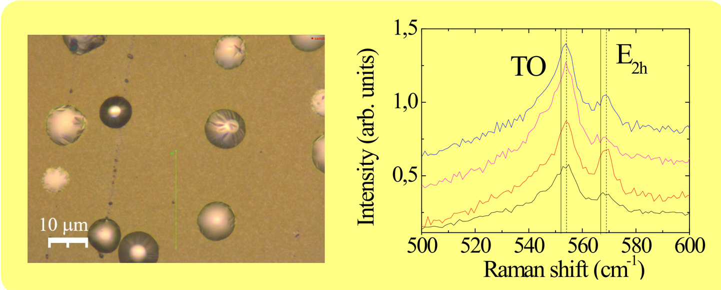


- Predominance of WZ phase
- Compressive strain ~ -0.15 %



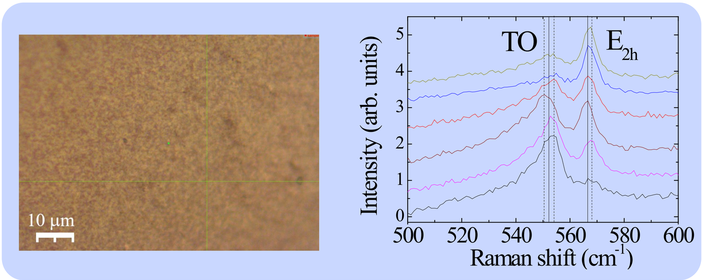
- Inhomogeneous WZ/ZB relative crystal phase depending on the region.
- Compressive strain ~-0.24%

Sample B



- Presence of droplets on the surface due to Ga-rich conditions
- Predominance of ZB phase
- Compressive strain ~ -0.20 %

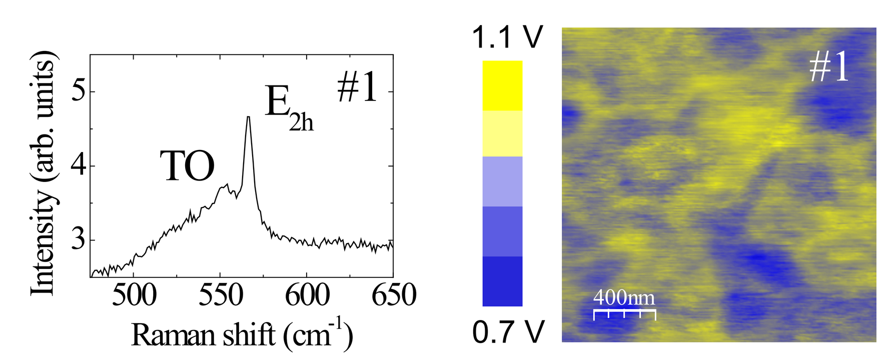
Sample C



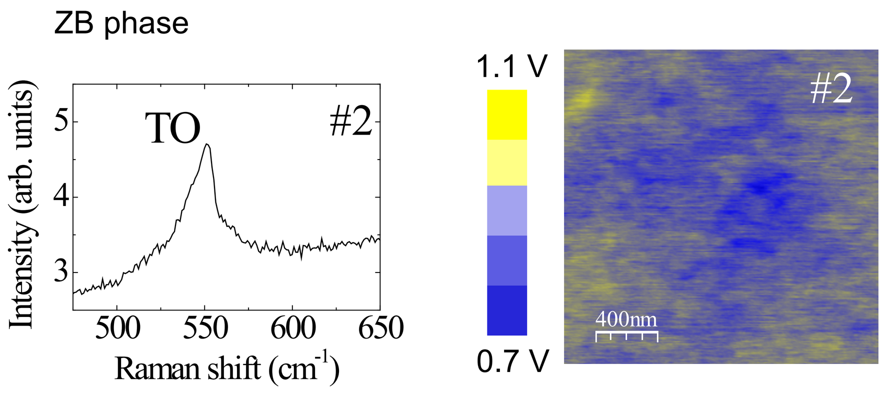
- Inhomogeneous WZ/ZB relative crystal phase depending on the region.
- Inhomogeneous strain: from compressive to tensile in the same region.

Polarity of wurtzite and zinc-blende GaN on Mica by KPFM

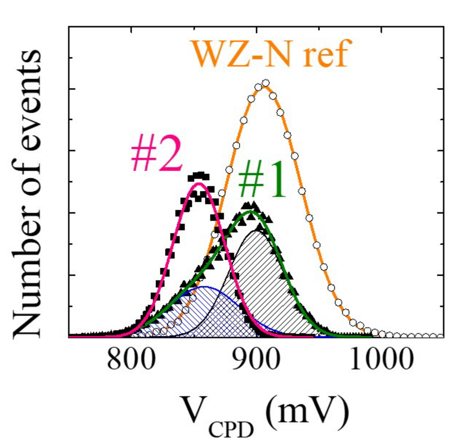
Sample A



- Mixite of GaN in WZ and ZB phase

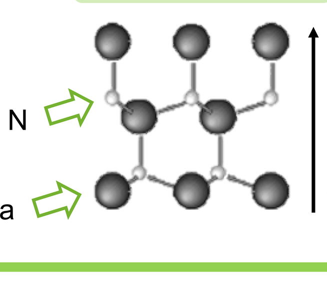


- Predominance of GaN in ZB phase



- V_{CPD} signal:
  - 850 mV ZB-N phase
  - 900 mV WZ-N phase

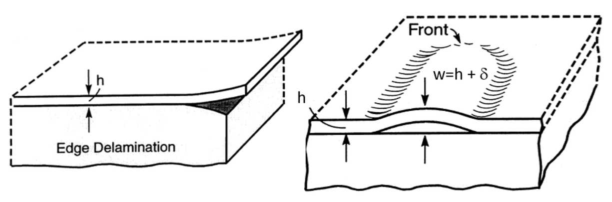
N-Polarity Ref.[1]



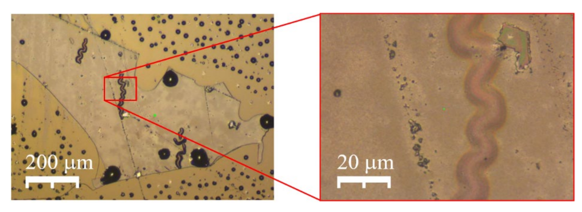
- N-Polarity is found in both ZB and WZ phases (corroborated by CBED patterns).

STUDY OF TELEPHONE CORD BUCKLES

Telephone cord buckles

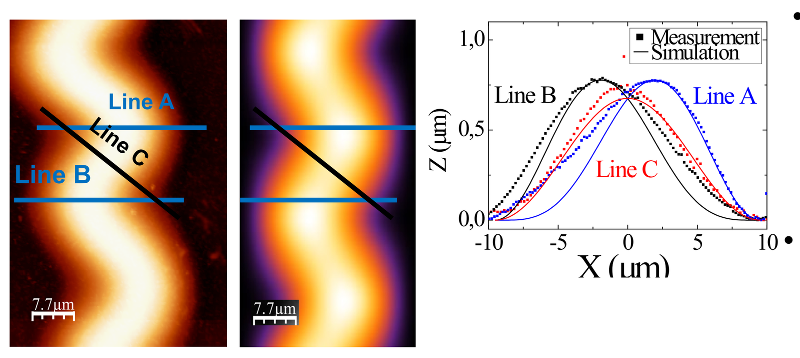


- Two possible delamination mechanisms associated to compression in thin films

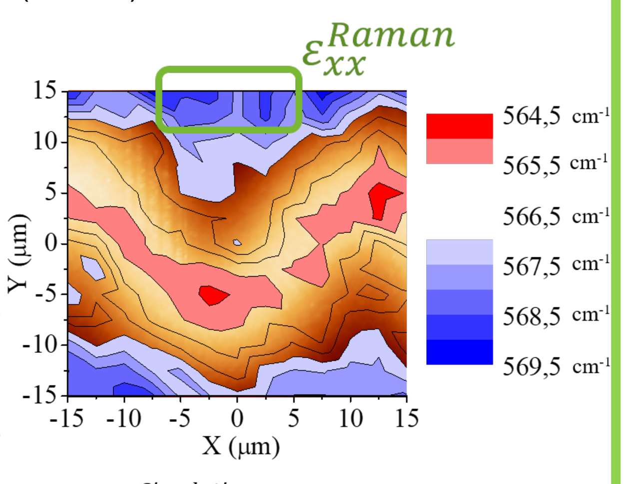


Sample B

- Telephone cord buckles (TCbs) are found for the first time in GaN thin films
- They are present in all samples (A, B, C)



- Right: Raman spectroscopy map showing the relaxation of strain by the formation of TCbs
- Raman spectroscopy allows us to compare the experimental and theoretical compressive strains (see table below).



$\varepsilon_{xx}^{Simulation}$ = -0.28 %

ε_{xx}^{Raman} = -0.24 %

- Two models are used to simulate the delamination behavior and obtain the elastic parameters:
  - Model based on Yong Ni et al. [2]
  - Elastic parameters obtained by applying the model of Moon et al. [3] using the *straight-sided* approximation

Sample	Γ(J/m^2)	$(\sigma_r/\sigma_b)^{1/2}$	$\varepsilon_{xx}^{Simulation}$(%)	ε_{xx}^{Raman}(%)
A	0.283	3.36	-0.28	-0.24
B	0.159	2.17	-0.31	–
	0.333	2.86	-0.38	-0.30
	0.170	2.05	-0.27	–
C	0.163	3.60	-0.27	-0.24
	0.396	3.78	-0.29	-0.20

- Γ is the work of adhesion, $(\sigma_r/\sigma_b)^{1/2}$ the square root of the ratio between the film residual strain and the critical strain promoting TCb delamination
- $(\sigma_r/\sigma_b)^{1/2} \in [2,8]$ implies TCbs are stable [4]
- $\Gamma_{mica\text{-}mica}$ = 0.2 J/m^2 – 0.6 J/m^2. Delamination takes place between mica planes.
- $\varepsilon_{xx}^{Simulation}$ is in accordance with Raman measurements (ε_{xx}^{Raman})

Conclusions

The growth of GaN layers with predominant ZB phase was achieved at high temperature and Ga-rich growth conditions. Both ZB and WZ GaN layers have N-polarity, determined by KPFM (and corroborated y CBED patterns). These features point towards a paradigm change when using mica as a substrate, suggesting a peculiar nucleation mechanism favoring the prevalence of the ZB phase. Moreover, the ZB/WZ phase ratio was found to increase for increasing growth temperature. The layers are under small compressive strain, although in some of the samples the strain state was strongly inhomogeneous, changing from slightly compressive to slightly tensile. In addition, telephone cord buckle (TCb) delaminations have been observed for the first time in GaN samples. Two models have been followed to simulate the 3D delamination and obtain the film elastic parameters. The results indicate that delamination takes place between mica layers, while GaN remains strongly bond to the mica substrate. Hence, growth is not of the van der Waals type, as initially presumed. Theoretical and experimental (Raman) strain values are in good agreement. Finally, Raman mapping analysis of the TCb delaminations gives direct evidence of film relaxation by the formation of these 3D structures. Further information can be found in Ref. [4]

References

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[2] Yong Ni *et al.*, Nature Communications, **8**, 14138, (2017).
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Acknowledgments

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