X-ray Absorption studies of atomic environments in semiconductor nanostructures

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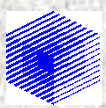

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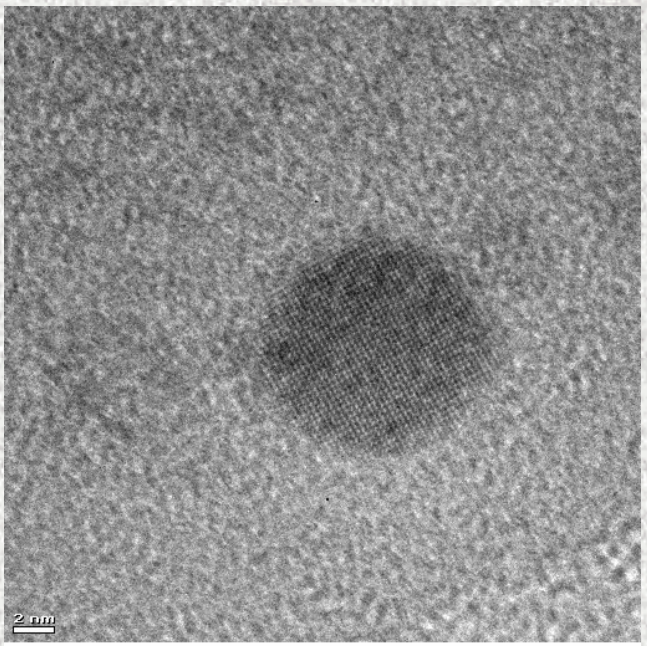
- Introduction
  - Why XAS for nanostructures
  - How XAS for nanostructures
- Interdiffusion in quantum dots and islands
- Relation between local and long-range elasticity in an “ideal” alloy: (InGa)As
- Growth of nitride epilayers: a local view

Atomic structure in nanostructures

- As a result of reduced dimensions:
  - atomic intermixing
    - in the “core”
    - at the interfaces
  - variations in bond lengths



XAS to study nanostructures

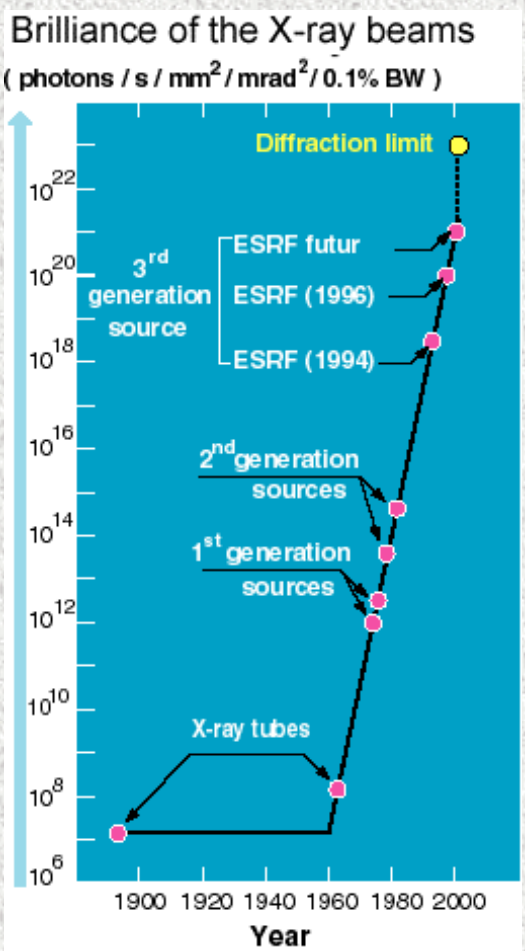
- XAS is a local, short range, effect
  - same formalism applies to molecule, cluster or crystalline solid
  - insenstive to variations of morphology
  - sensitive to low thicknesses, high dilutions
- Excellent probe of variations in local environment upon reduction of dimensions and/or dimensionality

Evolution of X-ray Absorption Spectroscopy

- X-ray Absorption Spectroscopy has greatly benefited from
  - third generation SR sources
    - high brilliance, extended energy range, stability, reliability
  - full theoretical understanding and reliable analysis programs

$$\sigma = \frac{\sigma_0}{3\,Sin^2\delta^0_{l=1}} \sum_m \mathrm{Im}\{T(1-TG)^{-1}\}^{0,0}_{1m,1m}$$

- XAS a reliable tool



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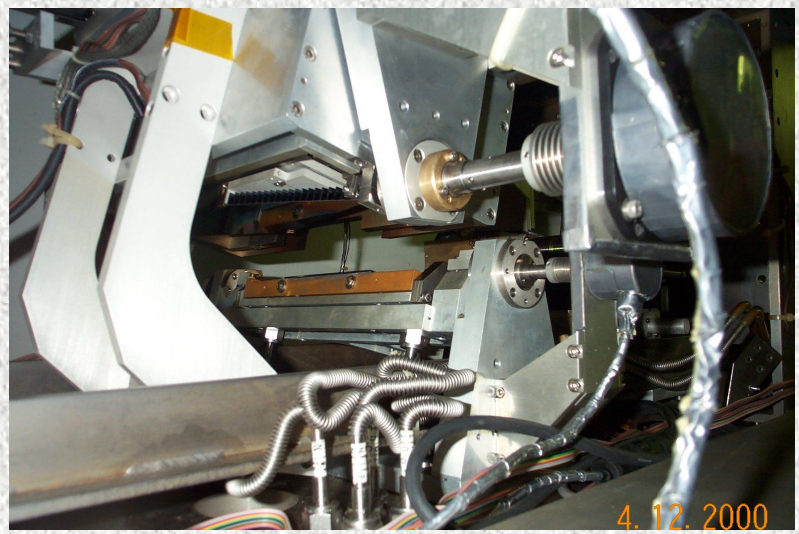
GILDA beamline at ESRF

- Dynamical sagittal focussing over wide energy range
- 13-element HP-Ge detector with digital electronics



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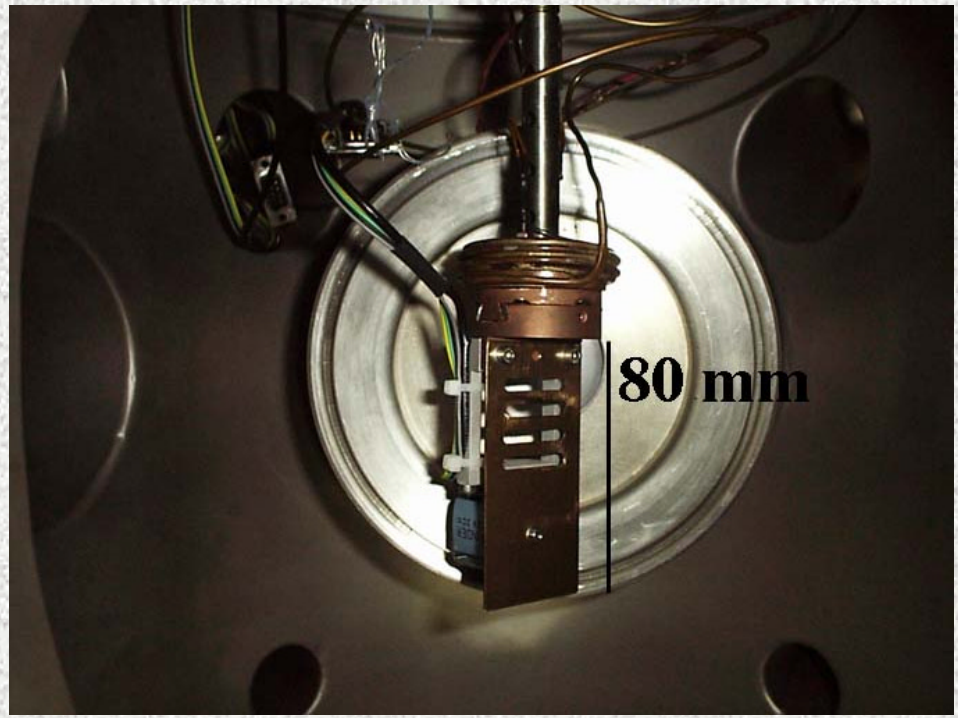
GILDA experimental chamber

- Transmission / fluorescence
- LNT - 150 °C
  - reduce thermal damping
- Rotatable holder
  - polarization studies
- Vibrating holder
  - “smooth” Bragg peak effects in single crystal epilayers



Atomic intermixing in Ge/Si and InAs/GaAs quantum dots

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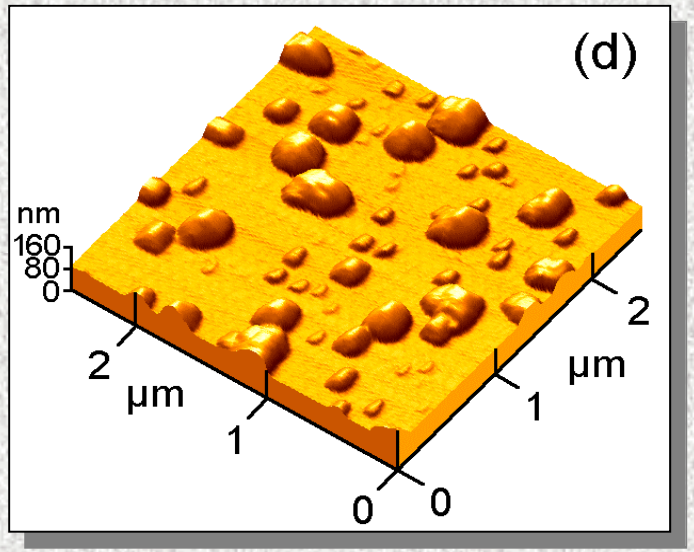
Quantum dots

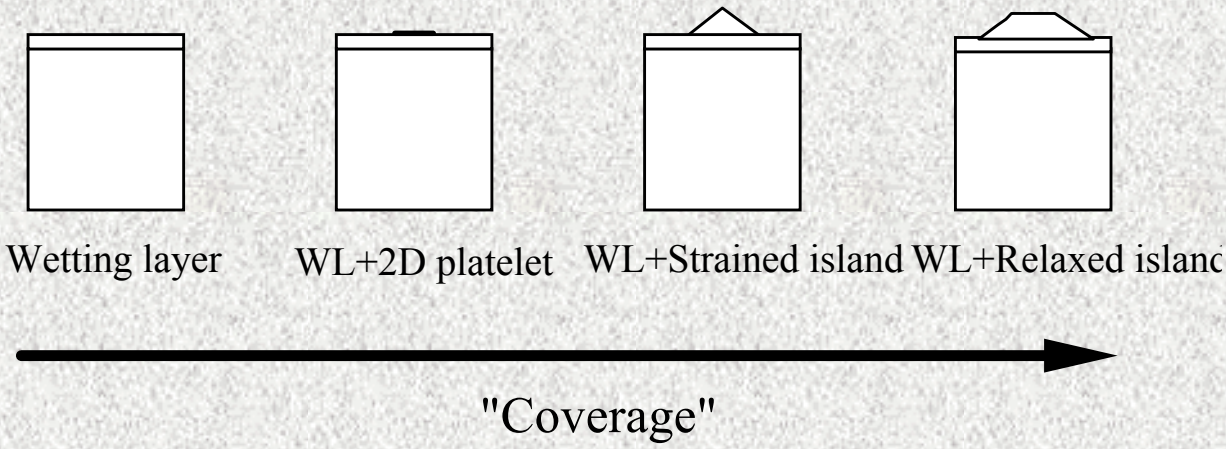
– F. Boscherini, G. Capellini, L. DiGaspare, F. Rosei, N. Motta, and S. Mobilio, Appl. Phys. Lett. 76, 682 (2000)

- Stranski-Krastanov growth leads to narrow size distribution of dots
- Need for understanding of local bonding



Energetics of island formation

- Competing energies:
  - strain
  - surface
  - dislocations
- Contributions from:
  - wetting layer
  - islands

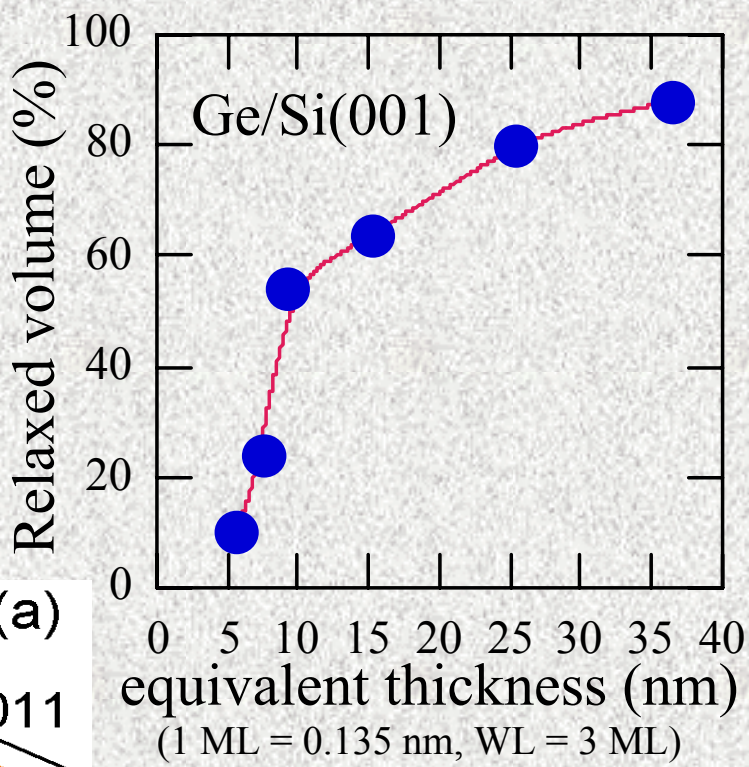


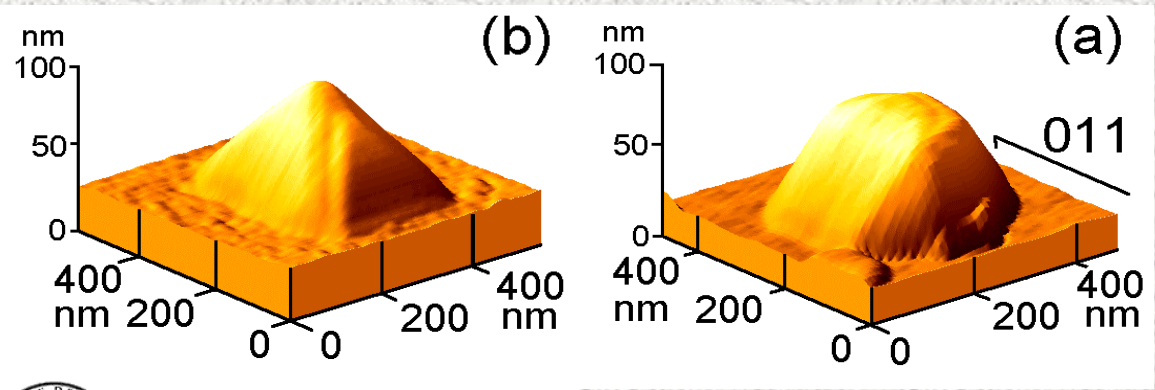
Preparation of Ge dots

- Ge/Si(001) by CVD at University of Roma Tre, 600 °C
  - *Ex-situ* AFM used to characterize degree of relaxation
- Ge/Si(111) by MBE at Tor Verg., 450 - 550 °C
  - *In-situ* STM/AFM

Ge/Si(001): AFM probes relaxation

- Analysis of aspect ratio provides measurement of relative amount of relaxed islands
- Ge/Si(001): Full range of relaxation examined





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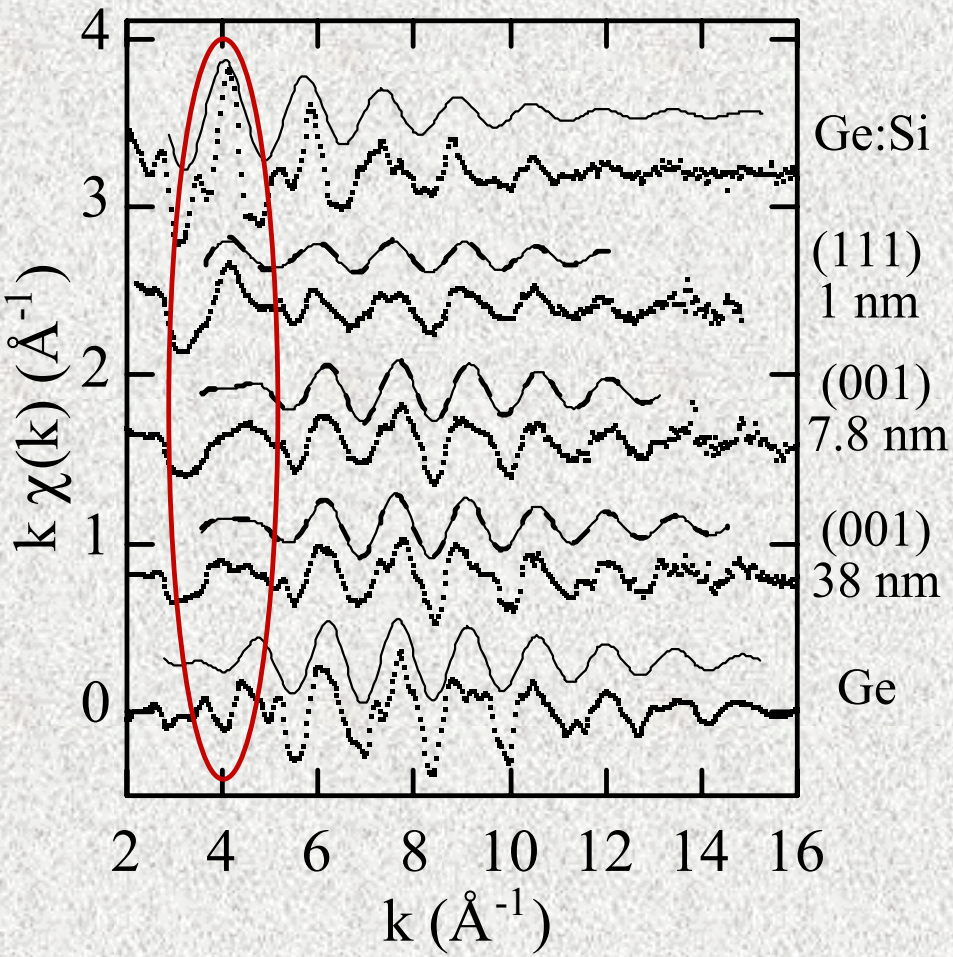
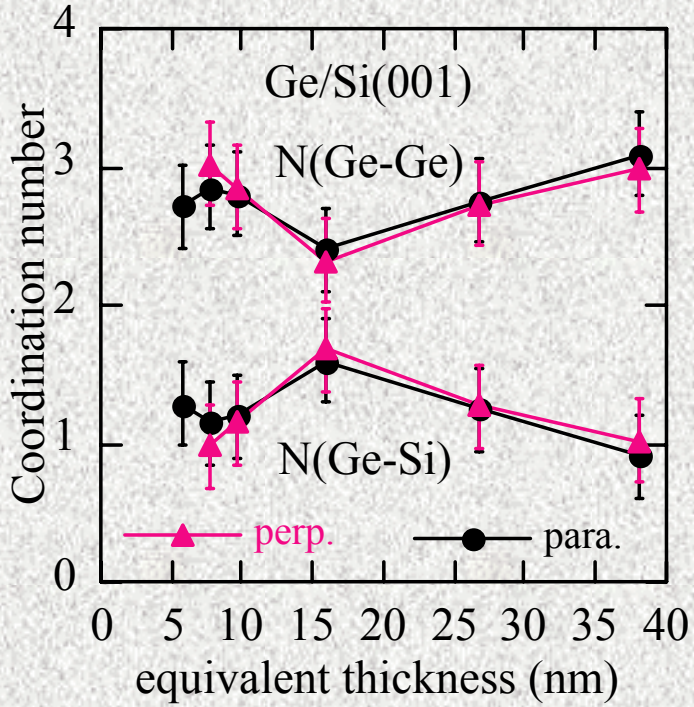
Ge/Si(001): Ge K-edge XAFS

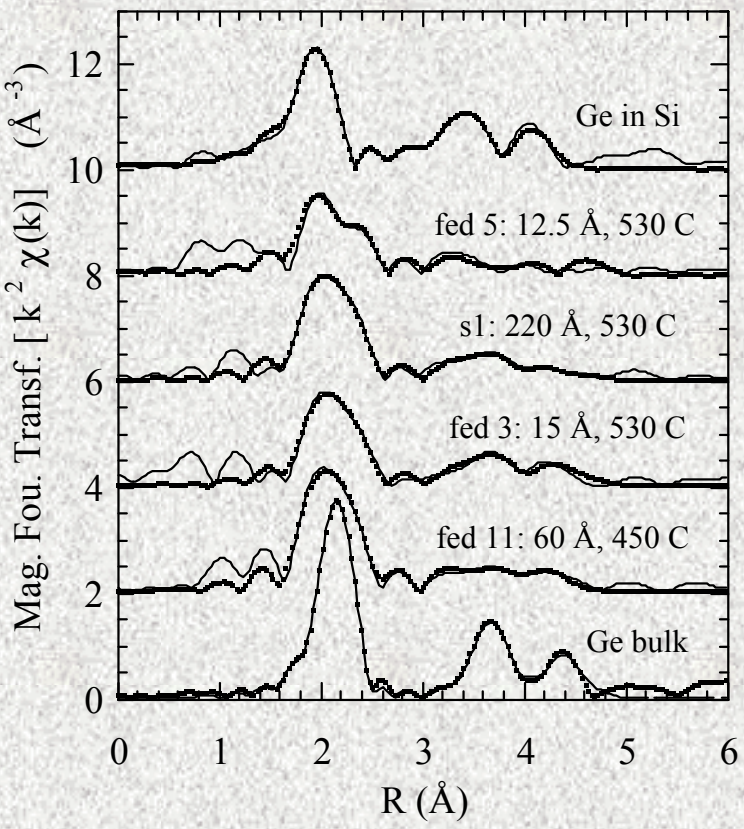


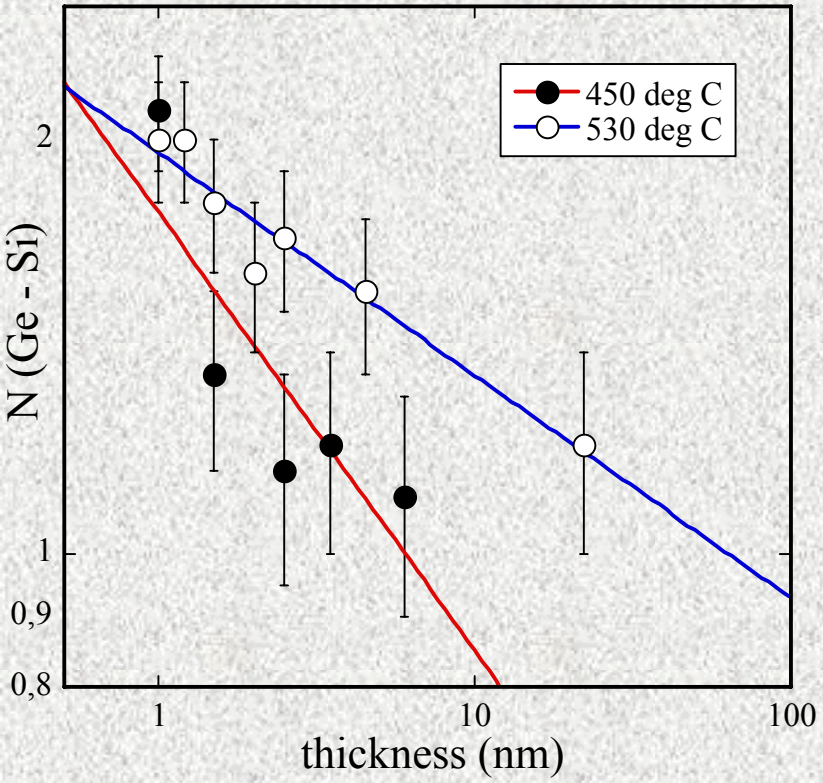
Ge/Si(001): XAFS results

- N(Ge-Si)=(1-1.5)±0.3
- Assuming random alloy average composition is $Ge_{0.70}Si_{0.30}$



Ge/Si(111): XAFS





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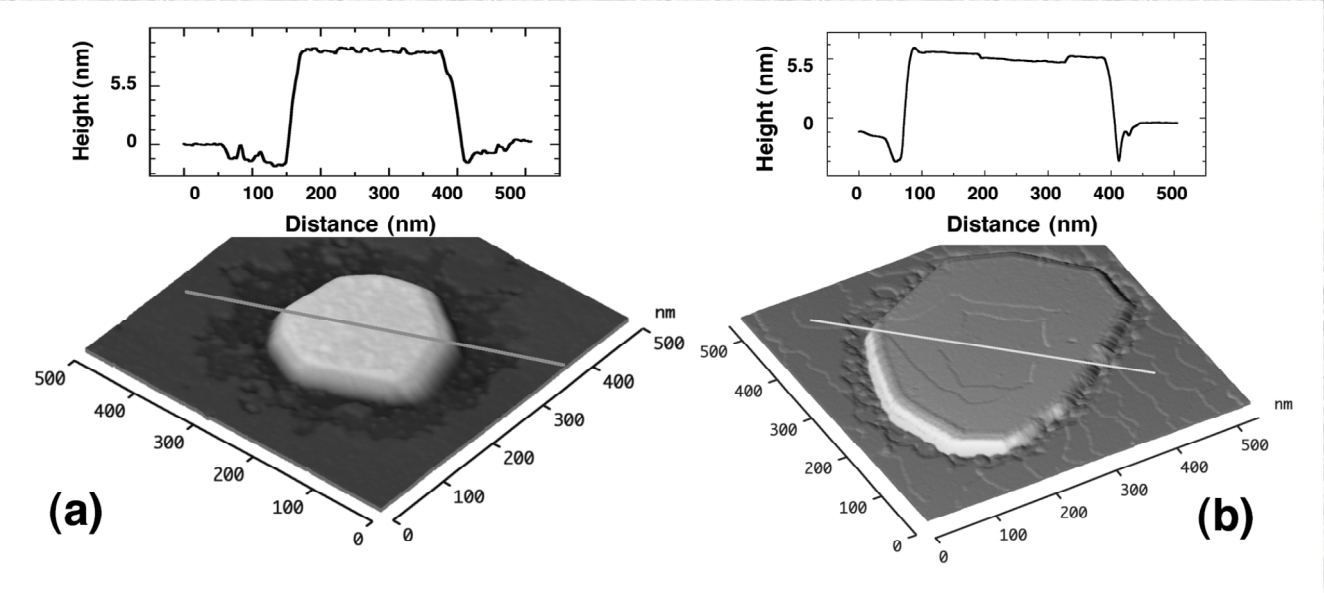
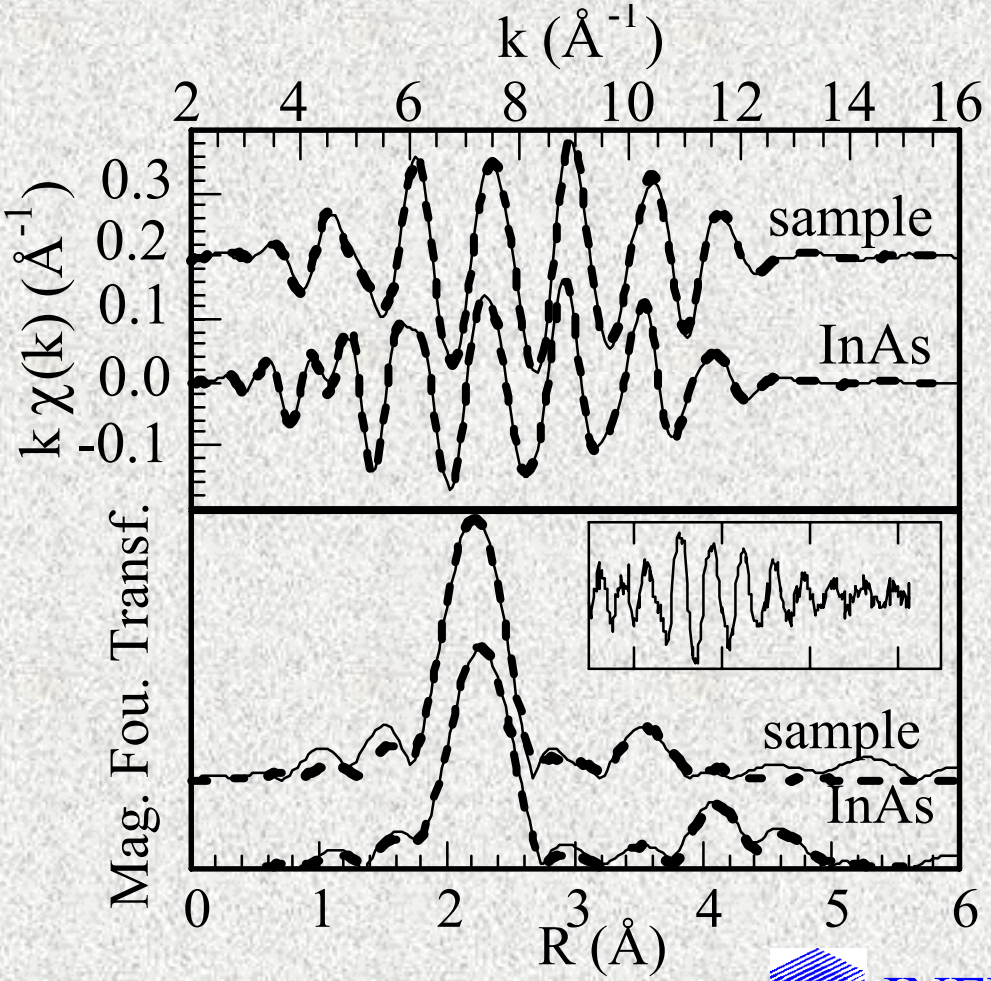
Ge/Si(111): STM

- A trench develops around the islands
  - Si from the substrate diffusing into the island



InAs/GaAs(001): In K-edge XAFS

- ALMBE, 10 × (3 ML InAs + 15 nm GaAs)
- Interdiffusion evident in 2nd shell signal
  - Contraction of bond length
- In concentration in dots: 0.25 - 0.45



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Intermixing and strain

- $E_s \propto \varepsilon^2$
- Alloying will decrease ε linearly with concentration x
  $a_{alloy} = x\, a_1 + (1- x)\, a_0$
- Intermixing must be considered in realistic models of Stranski-Krastanov growth

Local elasticity in strained epilayers

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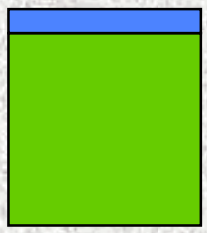
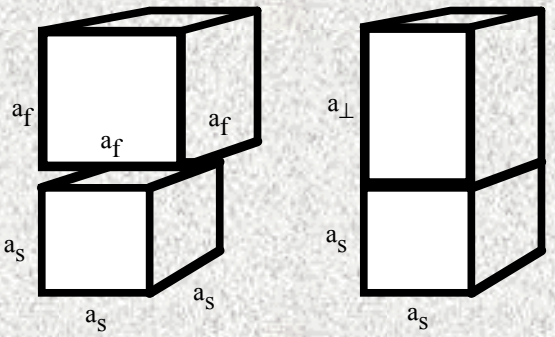
Local strain in 2D semiconductor epilayers

- Romanato *et. al.*, Phys. Rev. B **57**, 14619 (1998)
- Tormen *et. al.* , J. Appl. Physics **86**, 2533 (1999).
- Tormen *et. al.* , Phys. Rev. B **63**, 115326 (2001)

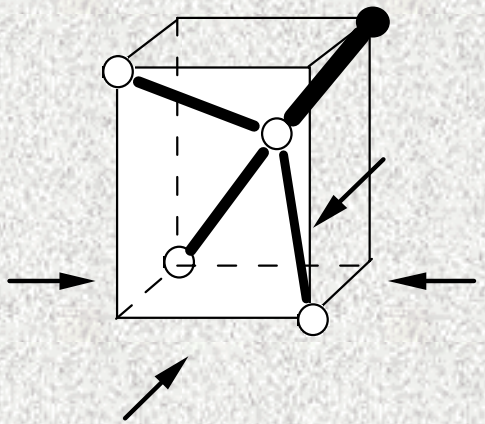
- What is the microscopic mechanism of accommodation of strain?
- What is the relation between long-range and short range description of the elasticity of solids?



Long vs. short -range elasticity



$\varepsilon_\perp = -[\,2\,c_{12}/c_{11}\,]\,\varepsilon_\parallel$



- Long range distortion, probed by diffraction:

$$-\varepsilon_\perp = -2\,\frac{C_{12}}{C_{11}}\,\varepsilon_\parallel$$

- Short range distortion, probed by XAFS:

$$V(\{R_{ij}\},\,\{\theta_{ijk}\}) = \frac{\alpha}{2}\sum_{ij}(R_{ij} - R_{ij}^0)^2 + \frac{\beta}{8}\,R_e^2\sum_{ijk}(\mathrm{Cos}\,\theta_{ijk} + \tfrac{1}{3})^2$$

Local distortions in unstrained alloys

$$V(\{R_{ij}\}, \{\theta_{ijk}\}) = \frac{\alpha}{2}\sum_{ij}(R_{ij} - R_{ij}^{0})^2 + \frac{\beta}{8} R_e^2 \sum_{ijk}(\mathrm{Cos}\,\theta_{ijk} + \tfrac{1}{3})^2$$

- Local distortions in unstrained alloys are well understood
- In semiconductors $\beta/\alpha = 0.1$ - 0.2
  - Bond lengths are “rigid”
- Fundamental behavior can be obtained with
  - no disorder in force constants
  - disorder in atomic radii

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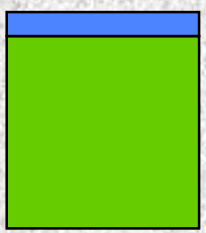
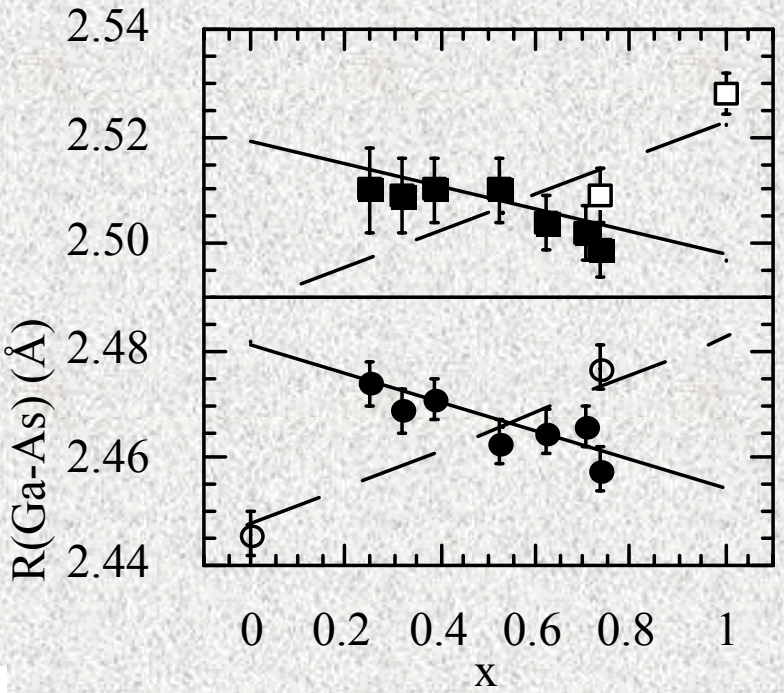
Samples used

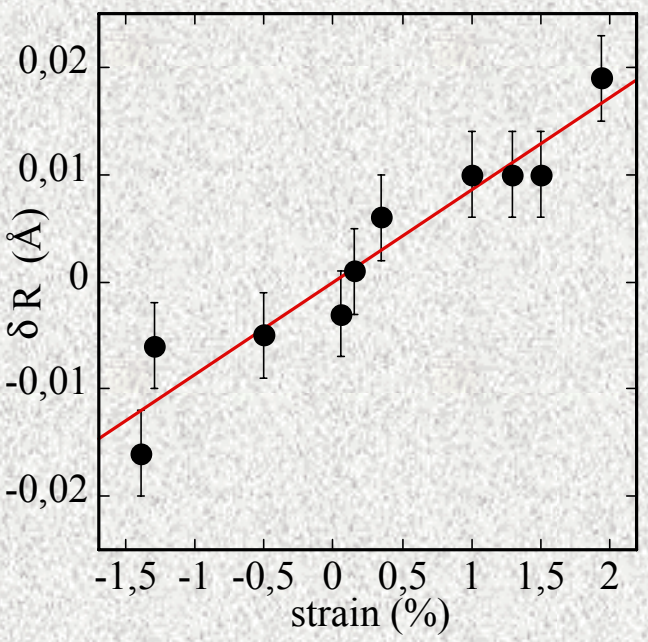
- High quality $In_xGa_{1-x}As/InP(001)$ layers were used to study this issue
- Samples deposited by MOCVD at ICTIMA-CNR
- Characterized by AFM, HRXRD, RBS, TEM
- Two series:
  - pseudomorphic as a function of strain, with $-1.42 < \varepsilon_{||} < 1.98$
  - fixed x=0.25, as a function of thickness, with $-1.42 < \varepsilon_{||} < 0$



Variation of bond lengths

- A linear variation of bond lengths with strain is clearly detected





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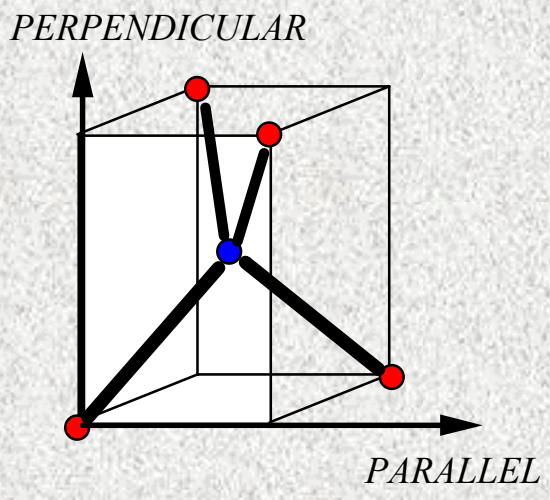
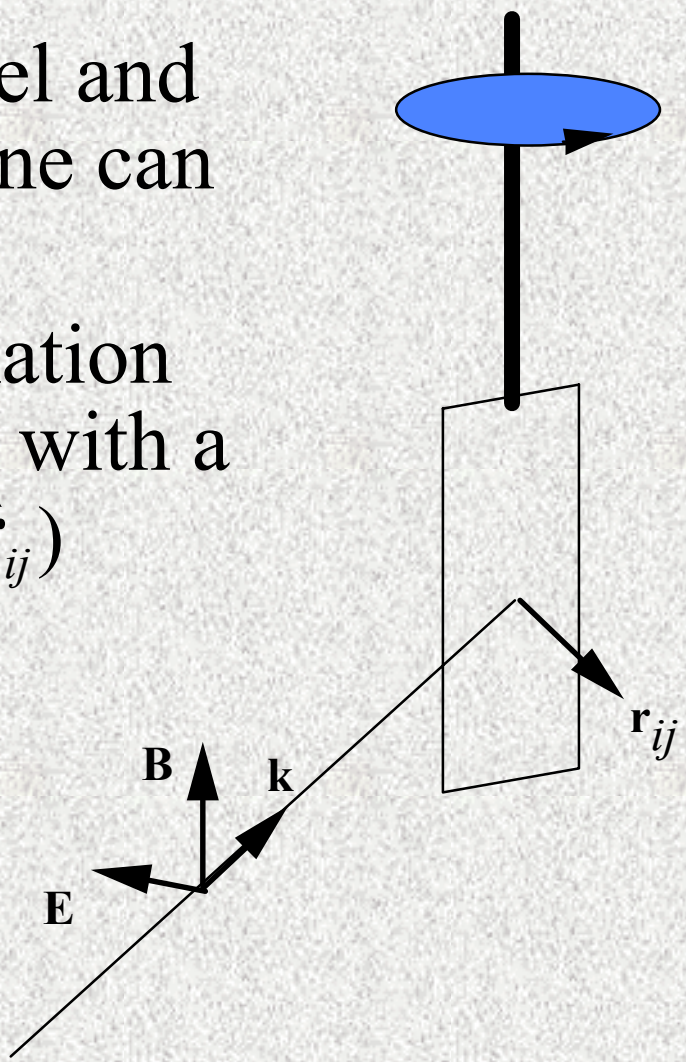
Polarization dependence

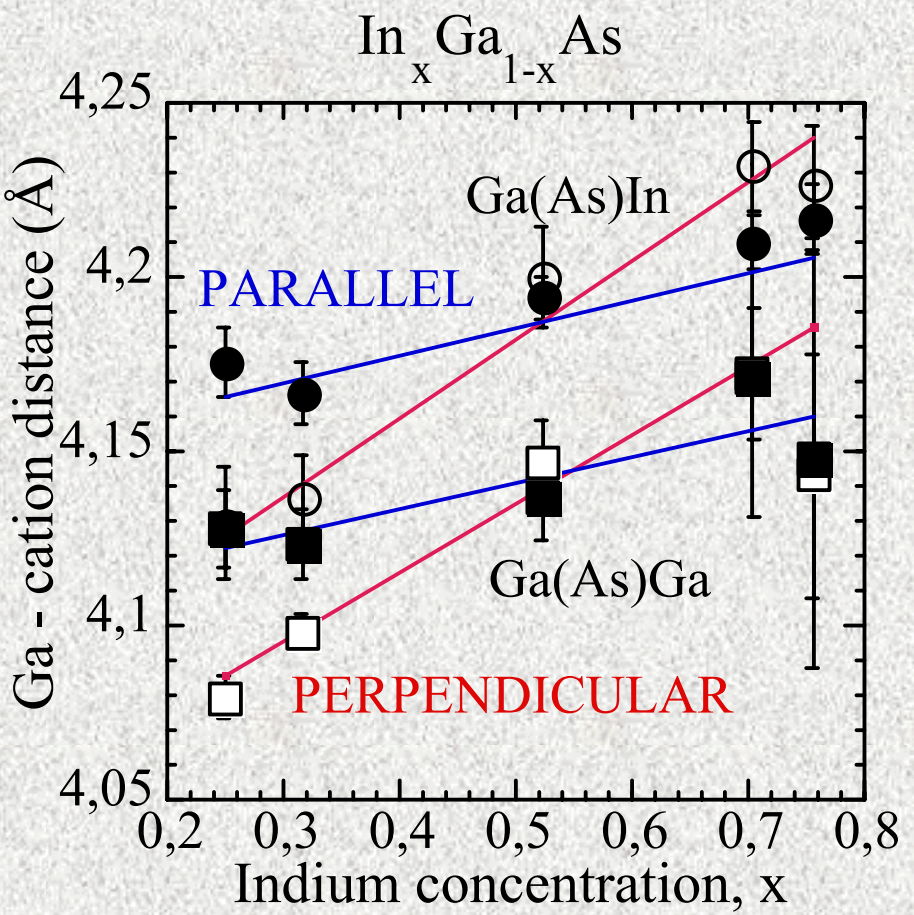
- Interatomic distances parallel and perpendicular to growth plane can be obtained
- In the plane wave approximation each correlation contributes with a weight equal to $3\ Cos^2(\hat{E} \bullet \hat{\mathbf{r}}_{ij})$





Variation of 2nd shell distances

- A strain - induced splitting $[\delta r_{PAR}(x) - \delta r_{PER}(x)]$ is detected
- The splitting is equal for all atomic distances



Local Effect of Strain

- The strain tensor is

$$\begin{pmatrix} \varepsilon_{\parallel} & 0 & 0 \\ 0 & \varepsilon_{\parallel} & 0 \\ 0 & 0 & \varepsilon_{\perp} \end{pmatrix} \quad \varepsilon_{\perp} = -\gamma\varepsilon_{\parallel} \quad \gamma = 2\frac{C_{12}}{C_{11}}$$

- Application of this tensor to 1st and 2nd shell interatomic distances yields

$$\delta r^{(1)}(x) = a(x)\frac{[2-\gamma(x)]}{4\sqrt{3}}\varepsilon_{\parallel}$$

$$\delta r^{(2)}_{OUT}(x) = a(x)\frac{[\gamma(x)-1]}{2\sqrt{2}}\varepsilon_{\parallel}$$

$$\delta r^{(2)}_{IN}(x) = a(x)\frac{\varepsilon_{\parallel}}{\sqrt{2}}$$

Local effect of strain

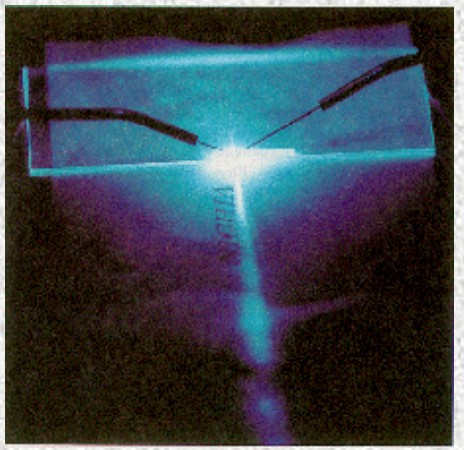
- The XAFS results can be reproduced by transfering the macroscopic strain tensor to the atomic scale, neglecting the type of bond
- The effect of strain is linearly summed to that of alloying
- CONCLUSION: Macroscopic elasticity theory is applicable to the local scale

Growth of GaN epilayers: a local view

Growth of GaN on SiC and AlN

– F. Boscherini, R. Lantier, A. Rizzi, F. D'Acapito, and S. Mobilio, Appl. Phys. Lett. **74**, 3309 (1999) and submitted to PRB (2001)

- Nitrides are of great interest for realization of blue-violet optoelectronic devices
- Understanding of basic physics and growth mechanisms still matter of active research
  - No substrate with similar lattice constant readily available



Issues addressed

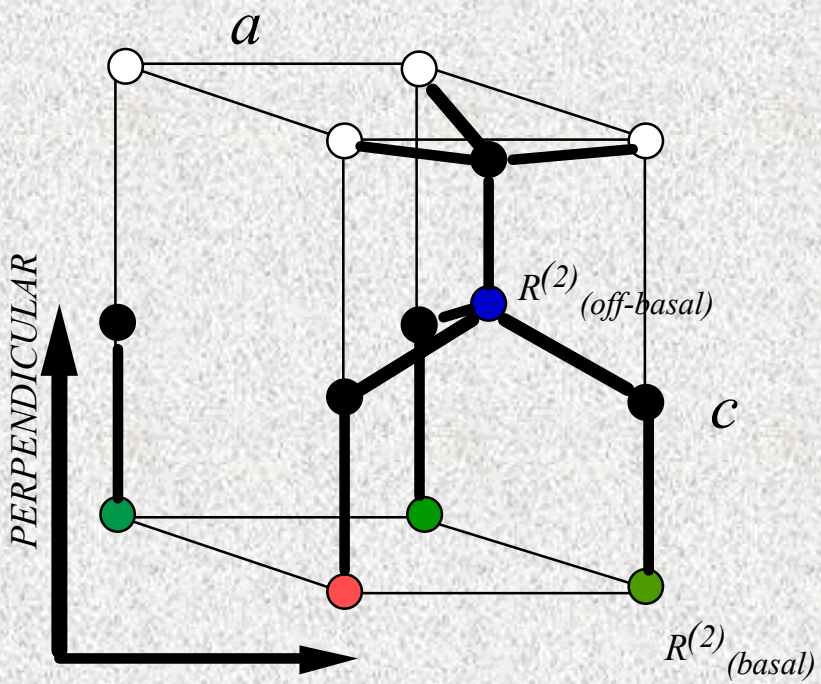
- Nitrides exhibit
  - spontaneous polarization
  - strain-dependent piezoelectric polarization
- GaN/SiC abrupt is expected to be charged and unstable
  - intermixing is expected (Ga/Si or C/N mixed planes)
- Relation between morphology and local strain
- Probe of elastic constants

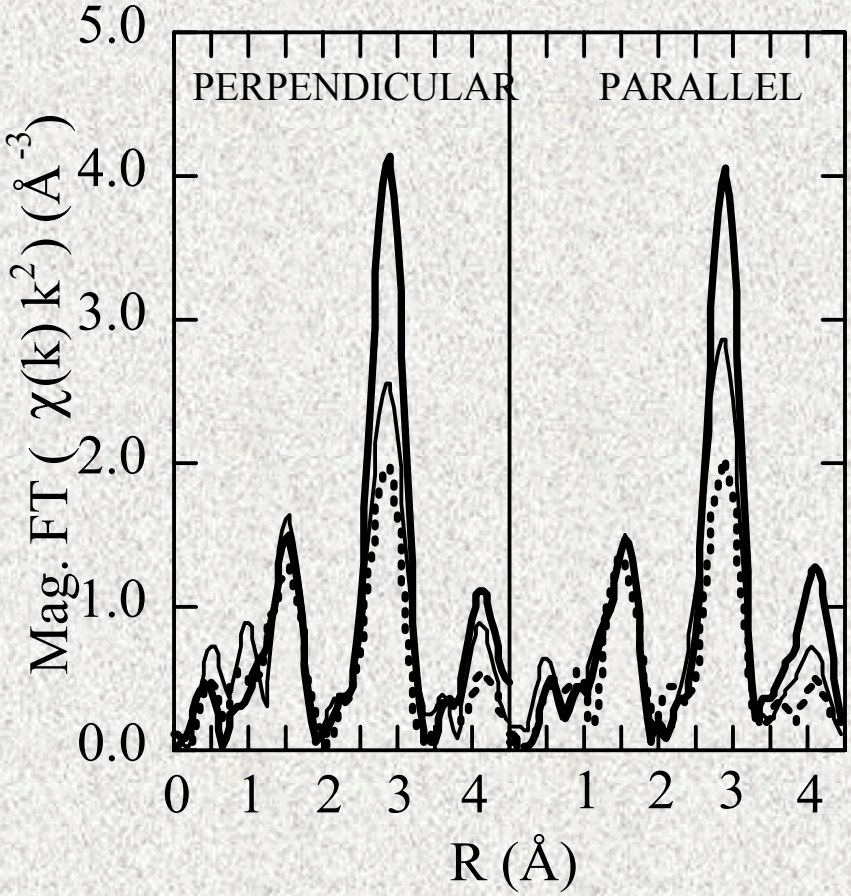
- Samples grown at ISI, Forschungszentrum Jülich by MBE with rf plasma source N_2
- XPS determination of band bending and band offsets

GaN/SiC: Ga XAFS

$$R^{(2)}_{basal} = a$$

$$R^{(2)}_{off-basal} = \sqrt{\tfrac{1}{3}a^2 + \tfrac{1}{4}c^2}$$





Thickness: 0.7 - 150 nm

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GaN/SiC

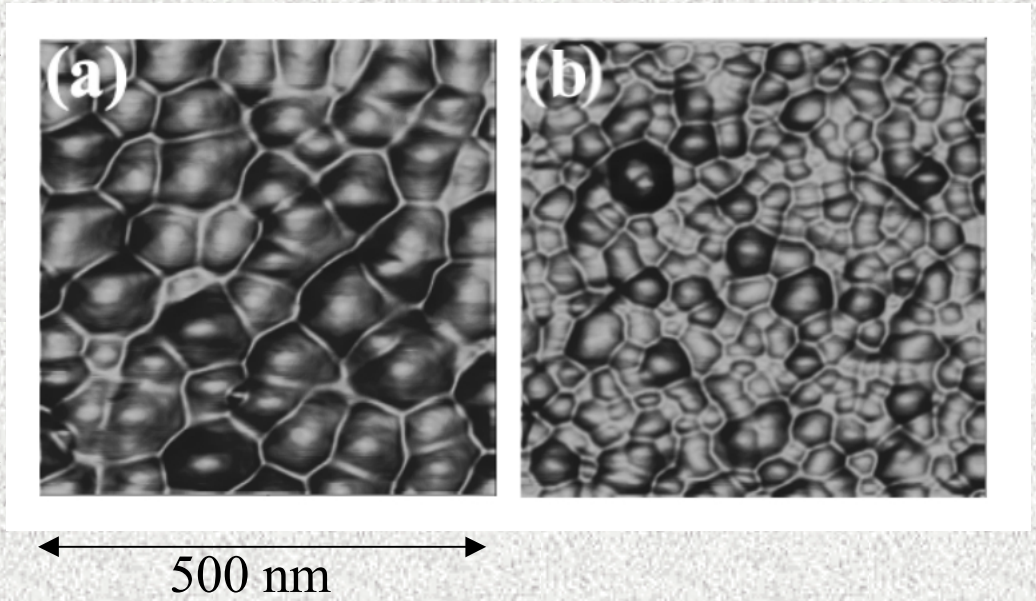
- No change in 2nd shell distances, no asymmetry between parallel and perpendicular directions
  - Relaxed growth (no piezoelectric polarization)
- No extensive intediffusion
  - High quality growth
- No Ga-Si mixed interface plane (C/N mixed plane cannot be excluded)

GaN/SiC: Impact

- These results provide basis for:
  - interpretation of XPS data
  - discussion and input to *ab-initio* electronic structure calculations
- Band-bending observed in XPS compatible with relaxed growth
- Valence band discontinuity of 0.8 ± 0.1 eV must be attributed to relaxed interface
- Note that all *ab-initio* calculations assume pseudomorphic growth

GaN/AlN: dependence of morphology on growth temperature

7 nm
620 ° C

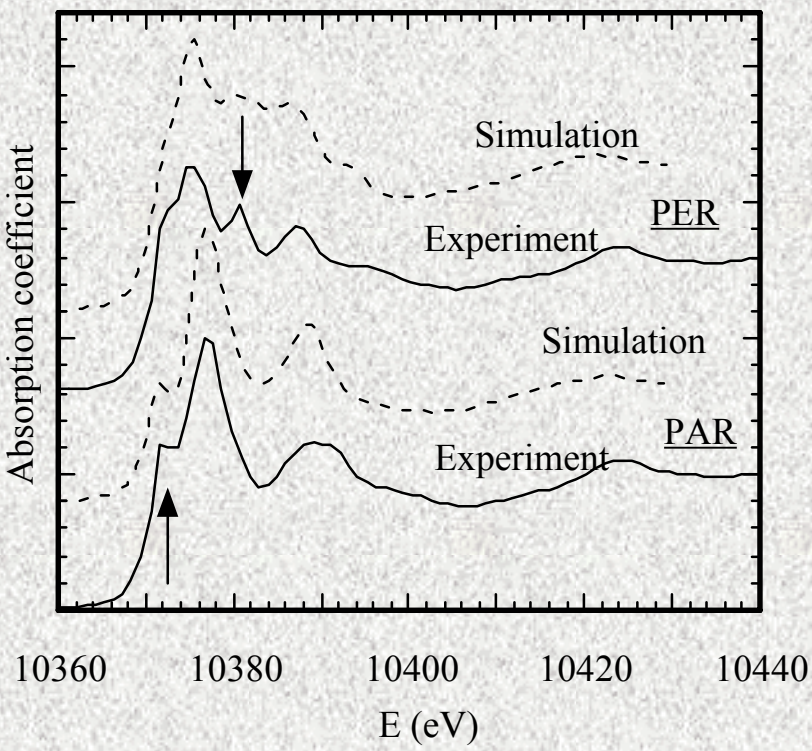


7 nm
790 °C

- "Smoother" epilayers for lower growth temperature

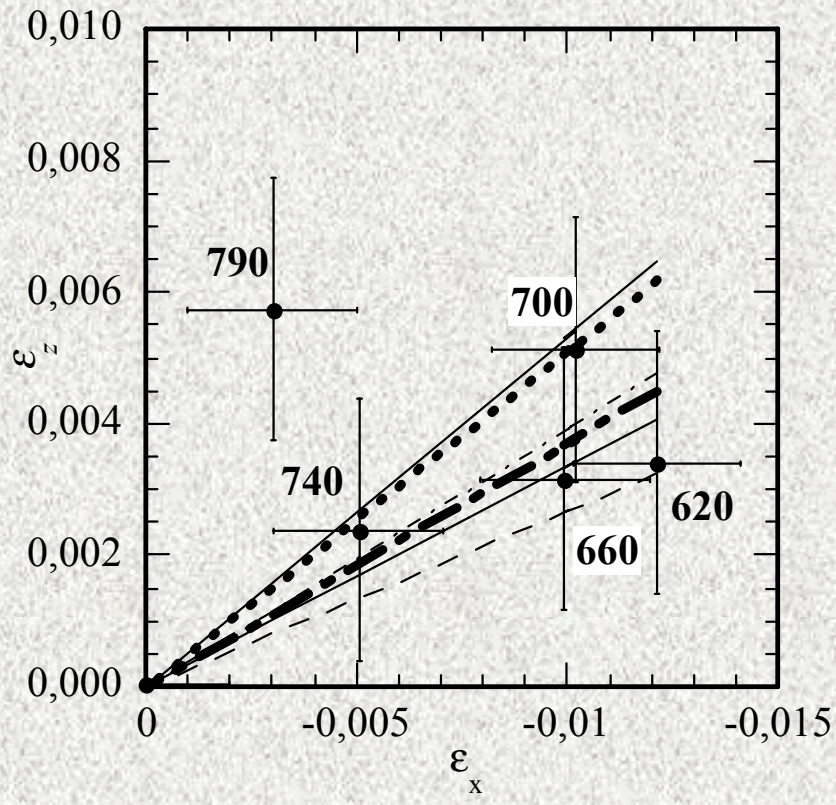
GaN/AlN: Polarization dependent Ga XANES

- Fingerprint of wurtzite structure
  - 6 nm layers are hexagonal
- Reproduced by full multiple scattering calculations



GaN/AlN: XAFS probes local elastic properties

- By measuring $R^{(2)}$ in two polarizations we obtain $\varepsilon_{||}$ and $\varepsilon_{\perp}$
- Strain increases for "smoother" epilayers but never reaches -0.024
- Values of $\frac{\varepsilon_{\perp}}{\varepsilon_{||}} = -2\frac{C_{13}}{C_{33}}$ in good agreement with spread of values in literature



Thanks

- Ge islands
  - G. Capellini, S. Mobilio, INFM +Univ. Rome 3
  - N. Motta, F. Rosei, INFM +Univ. Roma 2
- InAs dots
  - M. Capizzi, INFM + Univ. Rome 1
  - P. Frigeri and S. Franchi, MASPEC-CNR
- Local elasticity
  - D. De Salvador, F. Romanato, M. Tormen, A. Drigo, INFM + Univ. Padova
- GaN epilayers
  - A. Rizzi, Jülich and INFM + Univ. Modena
  - F. D'Acapito, INFM Grenoble
  - S. Mobilio, INFN and Univ. Rome 3

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