Investigation of microstructure of irradiated multilayer ZrN/Si_3N_4 thin coatings revealed by X-ray diffraction techniques

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Motivation of the research

Why nitride-based thin films?

Various applications as protective coatings

- microelectronics,
- optics,
- **nuclear applications**,
- …

Properties suitable for nuclear applications:

- high melting point
- high hardness
- stability under elevated temperatures
- wear and corrosion resistance
- good thermal conductivity
- good mechanical properties

Radiation tolerant coating materials

?

estimation of the effects of **radiation damage**

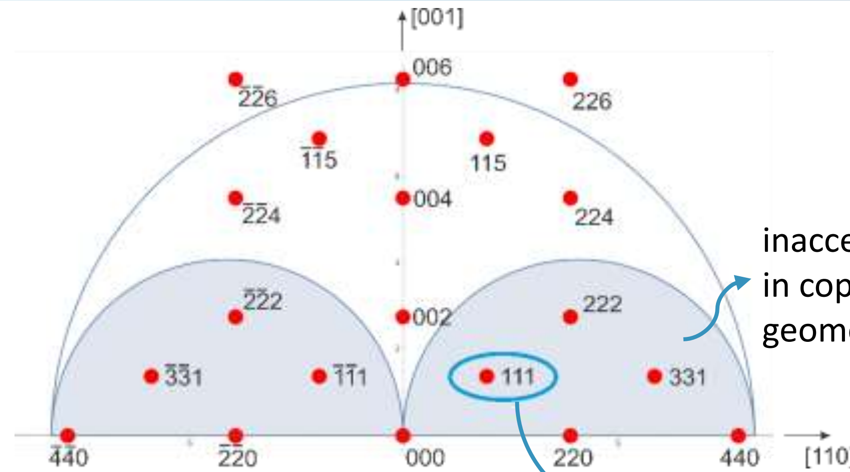
modification of microstructure under the irradiation process.

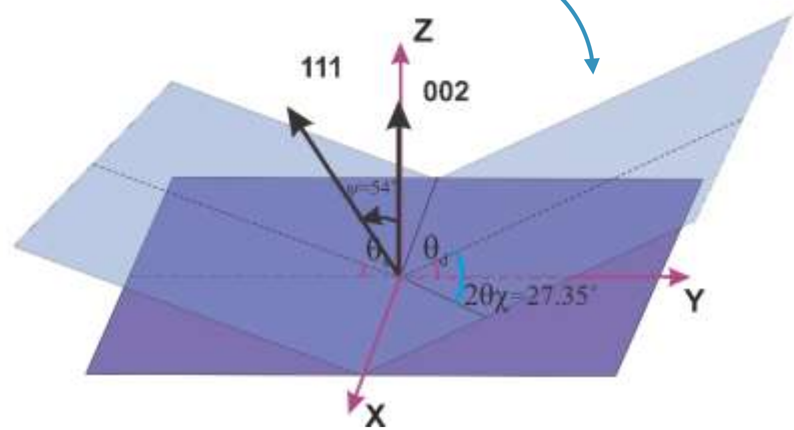
Why multilayers?

- Enhancement of the properties: the presence of interfaces and boundaries in the materials acts as an effective sink for the radiation induced point defects.
- Easy to control experimental growth and thickness of the sample.

Motivation of the research

Techniques to characterize thin films:
- Reciprocal space mapping (RSM),
- Pole figures
- Grazing incidence XRD (GIXRD)
- θ/2θ scanning (coplanar geometry)
- **Non-coplanar geometry**





Why non-coplanar measurement geometry?
- access to a larger number of Bragg reflections
- no tilt of the sample (important for high-temperature measurements)
- no rotation of the sample
- insufficient resolution: a set of two orthogonal Soller slits are used
- coplanar GIXRD does not permit to cover the whole range of ψ angles (because of 2θ limits)

Purposes of the research

Purposes of the research:

- evaluate microstructural parameters using theoretical analysis of XRD data, measured in non-coplanar geometry
- estimate if the microstructure undergoes changes under irradiation
- compare the results of XRD and HRTEM

Investigation techniques:

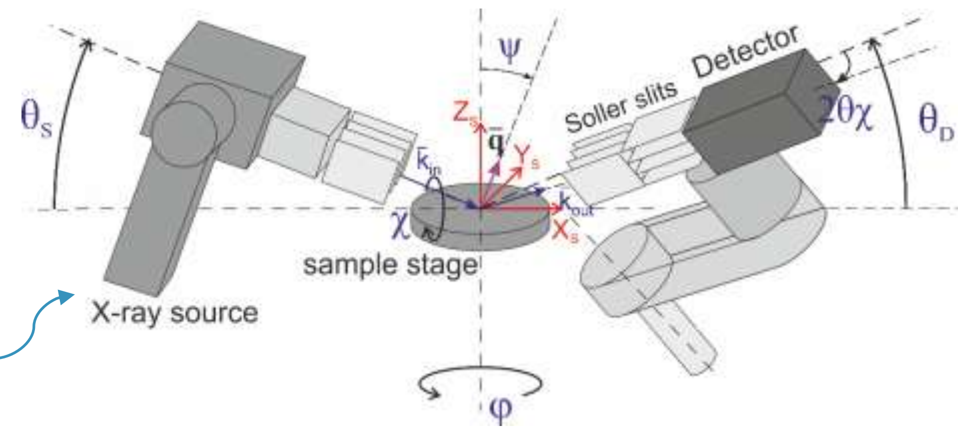
- X-ray diffraction (XRD)
- High-resolution transmission electron microscopy (HRTEM)
- Theoretical analysis

Experimental: general

Diffractometer setup:

- Cu Kα radiation (λ = 0.154056 nm)
- parallel beam geometry
- set of two orthogonal receiving Soller slits

Non-coplanar measurement configuration



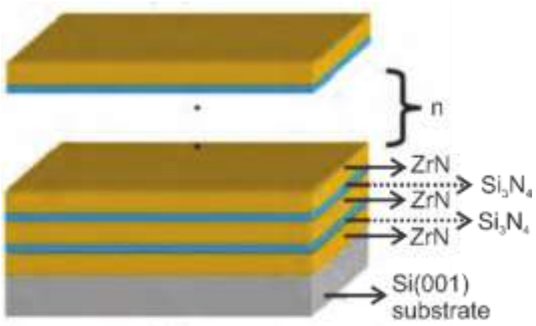
Samples:

- crystalline/amorphous multilayers ZrN/Si_3N_4
- single crystal Si (001) substrate
- total thickness of each multilayer: 300 nm

- **ML-1**: 5 nm/5 nm
- **ML-2**: 10 nm/5 nm
- **ML-3**: 5 nm/2 nm
- **ML-4**: 10 nm/0.4 nm

ML-1, ML-2, ML-3: unirr. + irr.

ML-4: unirr.



Irradiation conditions:

- 30 keV He+ ions
- integral dose: $5 \cdot 10^{16}\ cm^{-2}$

Experimental: workflow of the XRD measurement process

Pole figures: $I = I(\psi, \varphi)$

↓

Texture (preferred orientation)

↓

best conditions (ψ angles) for observing other reflections

↓

best conditions for scanning mode:
varying θ_S, θ_D ($\theta_S = \theta_D$),
fixed $2\theta\chi \neq 0$

↓

XRD measurements

Experimental: pole figures

Pole figures: $I = I(\psi, \varphi)$

↓

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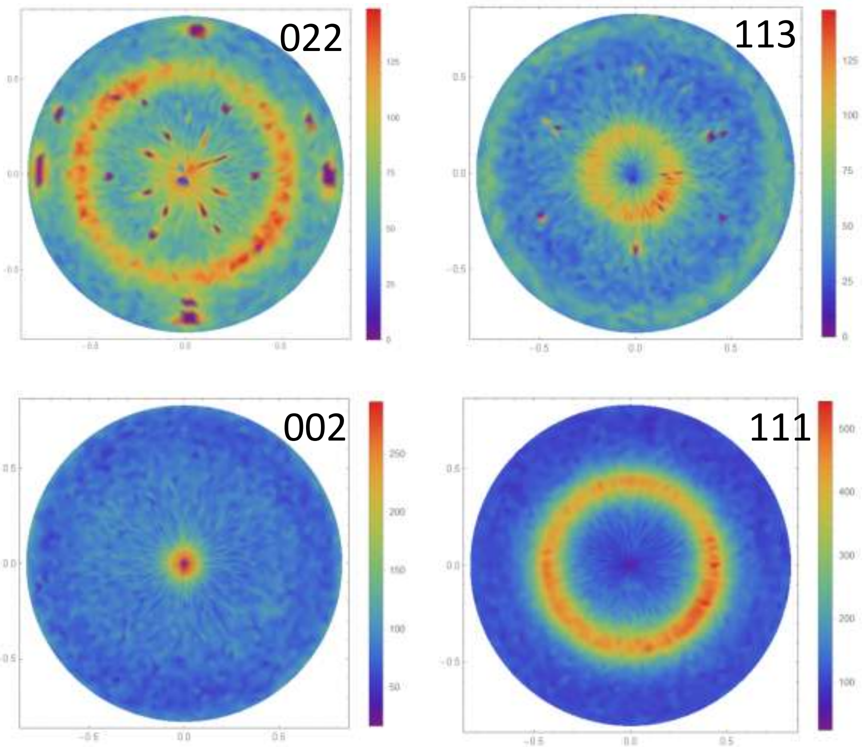
XRD measurements



Axial symmetry

[001] direction – orthogonal to the sample surface

Experimental: best conditions for measuring scans

Pole figures: $I = I(\psi, \varphi)$

Texture (preferred orientation)

best conditions (ψ angles) for observing other reflections

best conditions for scanning mode:
varying θ_S, θ_D ($\theta_S = \theta_D$),
fixed $2\theta\chi \neq 0$

XRD measurements

$$\cos\psi(\theta_S, 2\theta_\chi) = \frac{2\sin\theta_S\cos^2\theta_\chi}{\sqrt{2 - 2\cos(2\theta_S)\cos(2\theta_\chi)}}$$

$$\cos(2\theta) = \cos(\theta_S + \theta_D)\cos(2\theta_\chi)$$

Optimal instrumental angles for measuring scans

reflection	111	002	022	113	222	004
ψ, deg	54.00	0	45.00	24.00	54.00	0
$2\theta\chi$, deg	27.35	0	39.79	26.50	58.36	0
$2\theta s$, deg	20.00	39.00	45.00	62.00	53.00	84.00
2θ, deg	33.95	39.41	56.96	67.99	71.46	84.80

Experimental: XRD measurements

Pole figures: $I = I(\psi, \varphi)$

↓

Texture (preferred orientation)

↓

best conditions (ψ angles) for observing other reflections

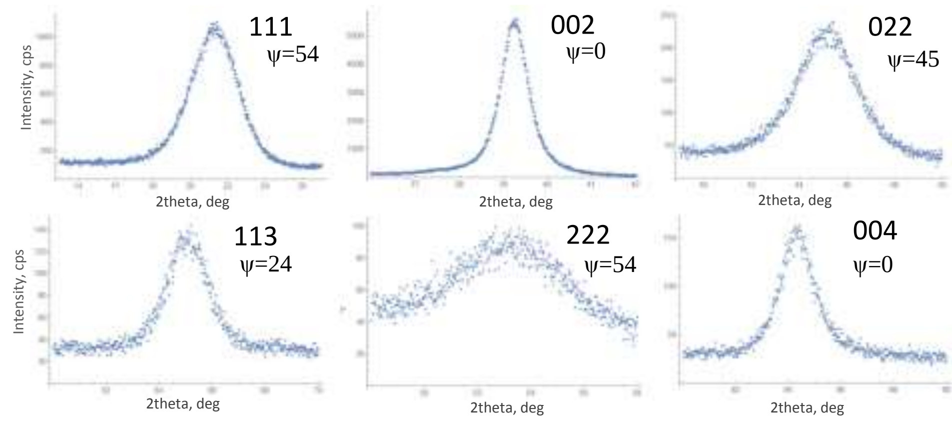
↓

best conditions for scanning mode:
varying θ_S, θ_D ($\theta_S = \theta_D$),
fixed $2\theta_\chi \neq 0$

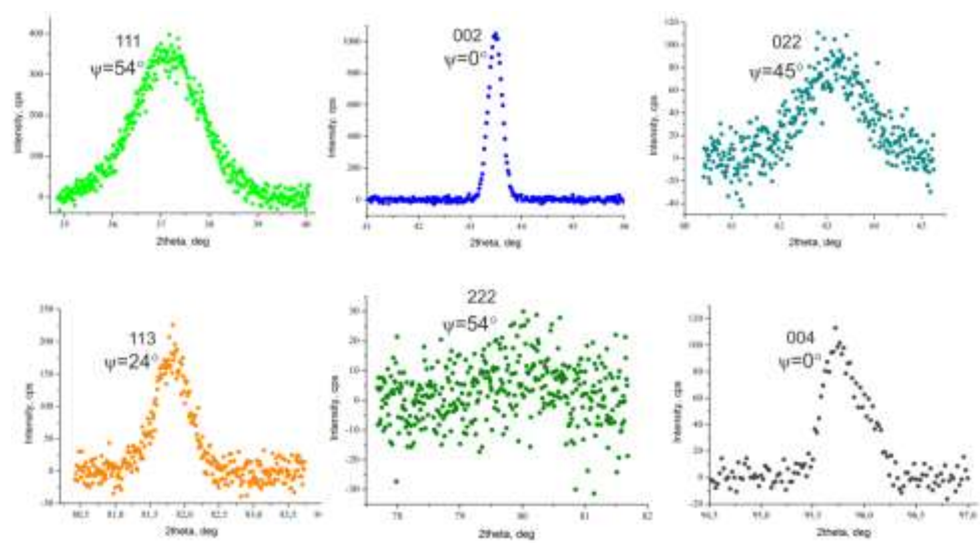
↓

XRD measurements

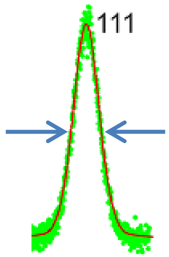
XRD profiles: polycrystalline ZrN layers



Instrumental function: LaB6 powder



Theoretical analysis



Profile shape and width → Microstructure analysis

Broadening of a diffraction profile = Broadening due to **grains size** + Broadening due to **instrumental effects**

Theoretical curve: $$I_{theor} = \sum_{hkl} I_{max}^{hkl} I_{size}^{hkl}(2\theta - 2\theta_0^{hkl}) * I_{instr}^{hkl}(2\theta - 2\theta_0^{hkl})$$

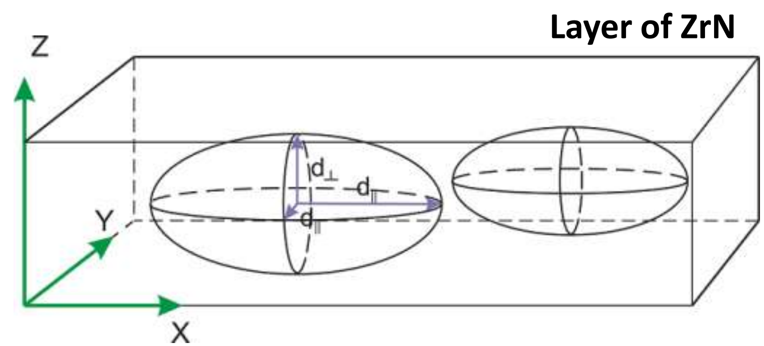
Faster performance → Calculations in Fourier space → $A(L) = A_{size}^{hkl}(L)\, A_{instr}^{hkl}(L)$

Grain sizes distribution: **Gauss distribution function**

$$f(x) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left[-\frac{(x - m_{hkl})^2}{2\sigma^2} \right]$$

Shape of grains?

- spherical (most simple and obvious) ✗ → ODS steels (structural material for nuclear applications)
- Proved by HRTEM
  - parallelepiped ✗
  - ellipsoidal ✓ → best consistence between measured and theoretical profiles



When applying an ellipsoidal grain shape model, the **size distribution** function becomes **anisotropic**, with the appearing dependence of the reflection intensity on the *hkl*.

$$m_{hkl} = \frac{m}{\sqrt{1 + \left(\frac{1}{e^2} - 1\right)\cos^2\psi}},$$

$$\cos\psi = \frac{l}{\sqrt{h^2 + k^2 + l^2}}, \qquad e = \frac{c}{a}$$

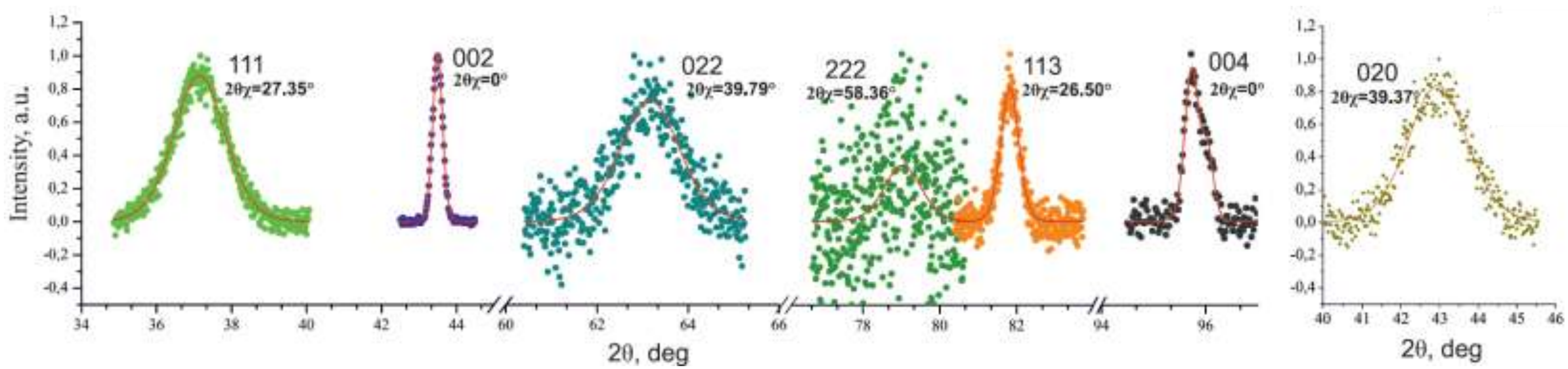
Theoretical analysis: size and instrumental broadening

Assuming ellipsoidal grains, the *hkl*-dependent **size broadening** is given by

$$A_{size}^{hkl}(L) = \frac{1}{6}\left(2m^3 + 6m\sigma^2 - 3\sigma^2|L|\right) + \frac{1}{6}\exp\left[-\frac{(m-|L|)^2}{2\sigma^2}\right]\sqrt{\frac{2}{\pi}}\sigma\left(-2m^2 - 4\sigma^2 + |L|(m+|L|)\right) -$$

$$-\frac{1}{6}\left\{2m^3 + 6m\sigma^2 - 3\sigma^2|L| - 3m^2|L| + |L|^3\right\}\mathrm{Erfc}\left[\frac{|\mathrm{L}| - \mathrm{m}}{\sqrt{2}\sigma}\right]$$

For accounting the **instrumental effects**, a set of LaB_6 profiles were measured and used as instrumental profiles I_{instr}^{hkl}



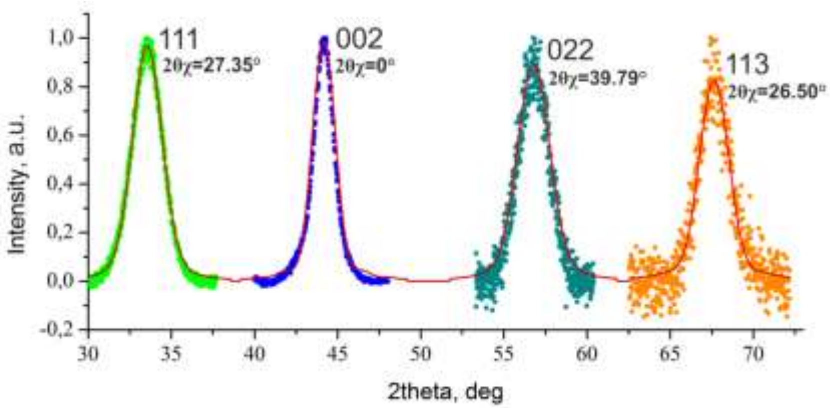
The instrumental function plays a crucial role in the non-coplanar measurements.

ψ angle **increases** → Instrumental broadening **increases** / Peak-to-background ratio **decreases** → Observation of 222 reflection for one (!) sample

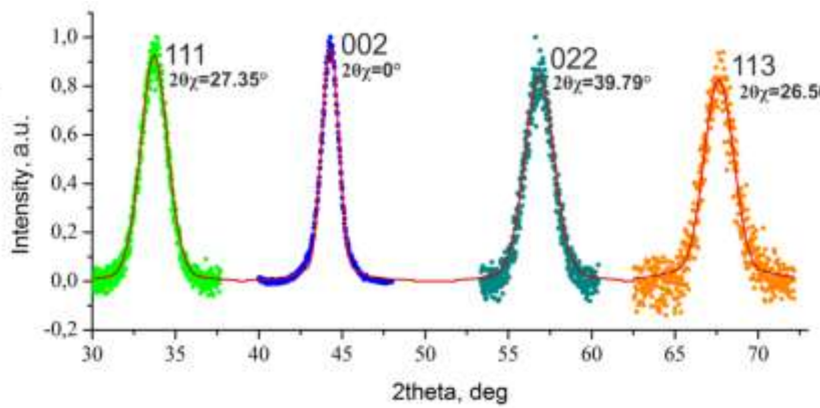
Theoretical analysis: results of fitting

The reflections, obtained under different ψ angles, are combined into a single scan for the simultaneous fitting with a theoretically simulated curve.

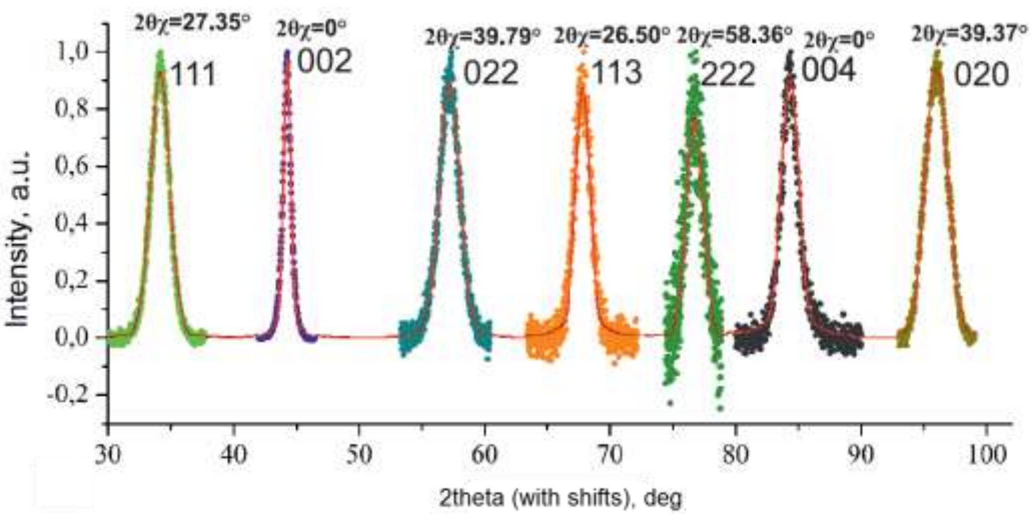
Four unirradiated and **three irradiated by the He+** ions samples were evaluated to estimate the modification of sample microstructure under the irradiation process.



Unirradiated ML-3 sample



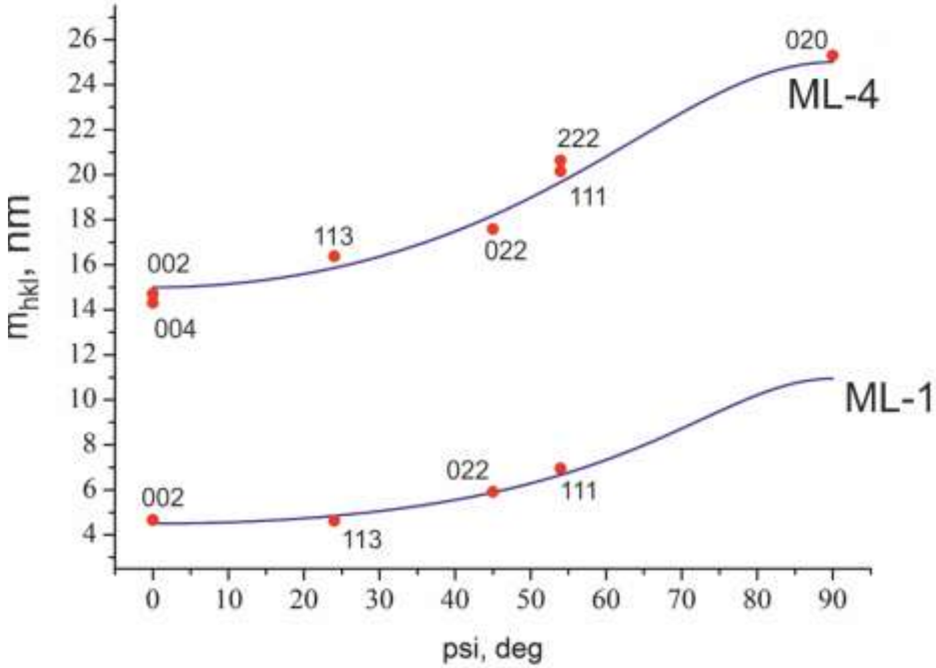
Irradiated ML-3 sample



Unirradiated ML-4 sample

Theoretical analysis: anisotropy due to shape

The measured **direction-dependent broadening** was in agreement with the assumed shape.



Theoretical curves
(assuming ellipsoidal grains)

$$m_{hkl} = \frac{m}{\sqrt{1 + \left(\frac{1}{\epsilon^2} - 1\right)\cos^2\psi}},$$

$$\cos\psi = \frac{l}{\sqrt{h^2 + k^2 + l^2}}, \qquad \epsilon = \frac{c}{a}$$

Experimental points
(from single profiles)

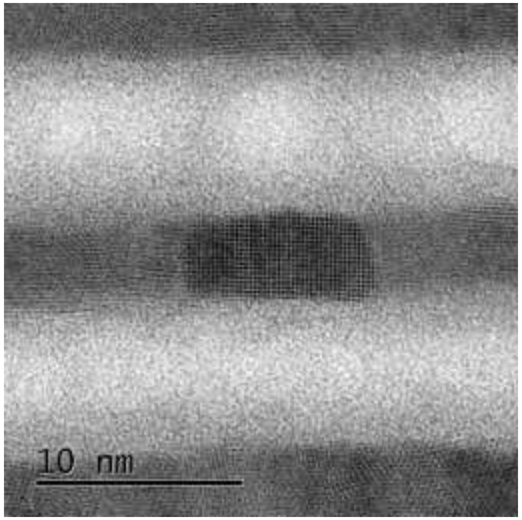
- The microstructural parameters obtained from the fitting of the whole scan and those obtained solely for 020 reflection ($\psi \approx 90$) are in a very good agreement, which confirms the correctness of the size estimation in the direction parallel to the sample surface.
- For the sample ML-4, the multiple reflections 002 and 004, 111 and 222 are observed, and *mhkl* for these reflections are close each to other, which confirms the absence of the line broadening caused by the defects.

Experimental: TEM measurements

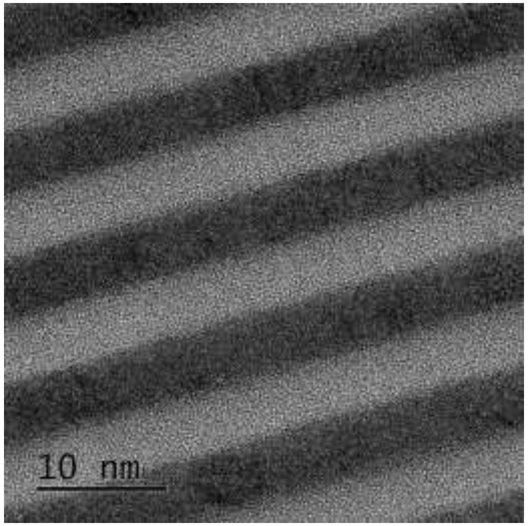
Preparation of the experiment:

- specimens were prepared using **FEI Helios Nanolab 650** focused ion beam
- initial milling – 30 keV Ga ions
- final thinning – 5 keV
- polishing - 2keV and 500 eV
- analysis - **JEOL JEM 2100** LaB_6 transmission electron microscope (200 kV)

Image of grains

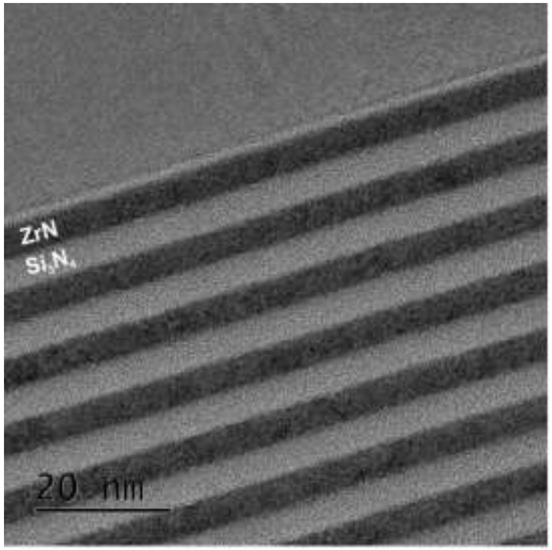


High-resolution TEM

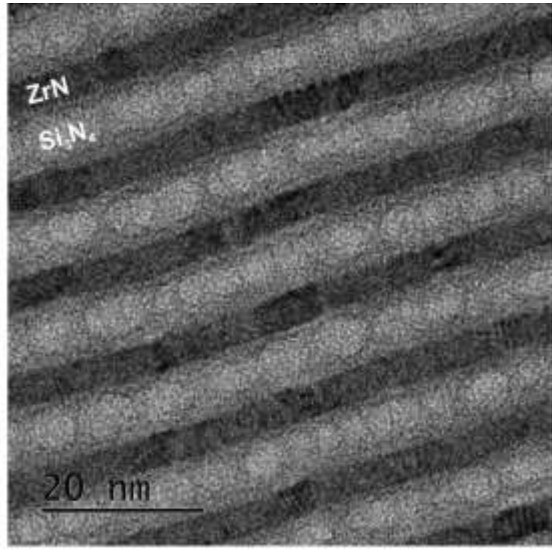


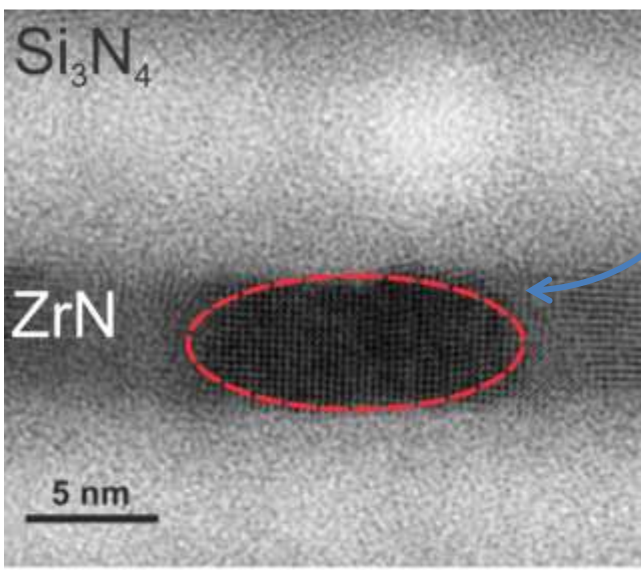
Microstructure of coatings: TEM analysis

Unirradiated ML-3



Irradiated by He+ ML-3





ellipsoidal grain

After the irradiation:

- the thickness of the ZrN is almost the same,
- the thickness of the amorphous layers undergoes a significant increase.

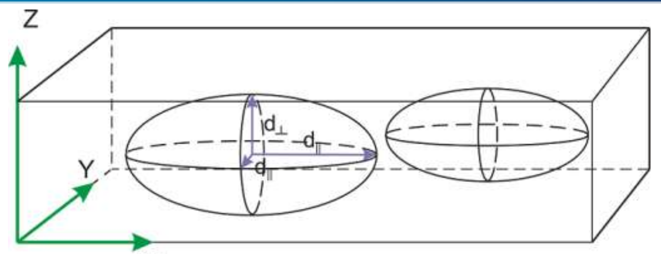
Possible explanation:
bubble formation during the irradiation

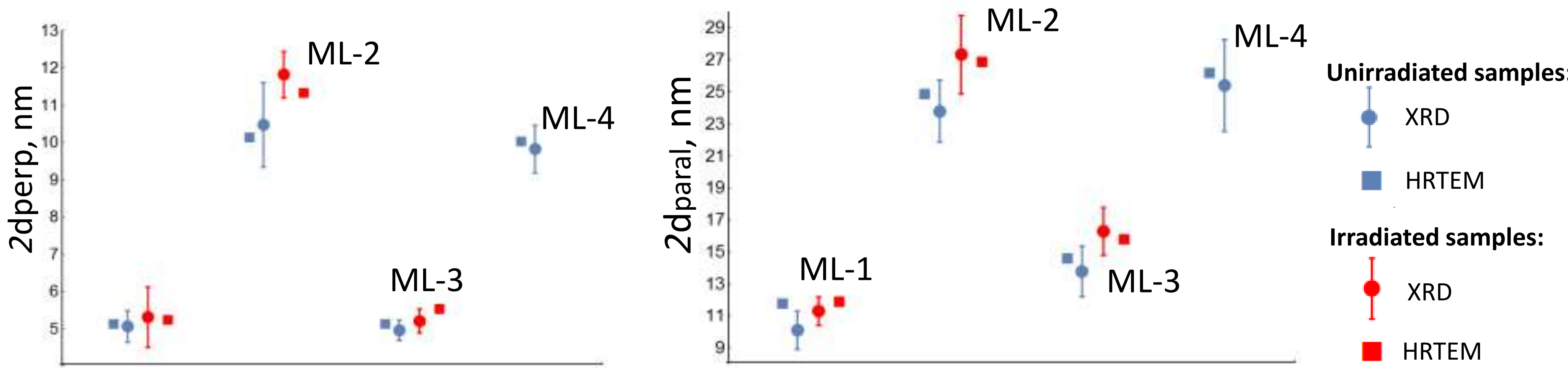
↓

deformation of the crystalline/amorphous interfaces due to the appearance of residual stresses

Microstructural parameters: XRD *vs* HRTEM

As a result of the fitting procedure, the **average grain size** in the **directions parallel** and **normal** to the sample surface have been evaluated.





- A good consistence between the XRD and HRTEM results for **unirradiated samples** confirms the validity of the used theoretical model.

- A good agreement between the results of XRD and HRTEM for **irradiated samples** means that after irradiation **no significant amount of defects appeared**.

- **Grains size** in the samples after irradiation **does not differ significantly** from that before the irradiation.

Conclusions

- The microstructural parameters of ZrN/Si_3N_4 multilayer thin coatings have been evaluated using X-ray diffraction technique in non-coplanar geometry.
- The non-coplanar X-ray diffraction geometry gives an access to a larger number of Bragg reflections comparing to the case of a coplanar configuration.
- The technique enables to perform a comprehensive and reliable analysis of the samples possessing the anisotropy of physical properties.
- Using the theoretical model for ellipsoidal grains, the sizes of grains in parallel and normal to the sample surface directions were calculated.
- The results obtained from XRD measurements are in a good agreement with those evaluated from HRTEM and STEM.
- Comparing the results of XRD analysis and HRTEM for unirradiated and irradiated samples, the microstructure of investigated samples is proved to do not undergo a significant change under the irradiation process.
- The proposed approach can also be extended to include other sources of diffraction line broadening which occurs in different materials.

Thank you for your attention!

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