High temperature XRD and XRR studies on atomic layer deposited Nb_2O_5 – SiO_2 nanolaminates

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NANOLAMINATES AND MULTILAYERS

- Enables tailoring the electrical, mechanical, or optical properties of the layers
  - Multilayers and mixtures of Nb_2O_5 – SiO_2 have been investigated *e.g.* as
    - – optical coatings
    - – memristors
    - – other memory devices

- Be sure to check the related presentation by Dr. Kaupo Kukli after the coffee break!

  16.00 - *Atomic layer deposition of metal oxide nanolaminates exhibiting nonlinear electrical and magnetic polarization with tunable resistivity*

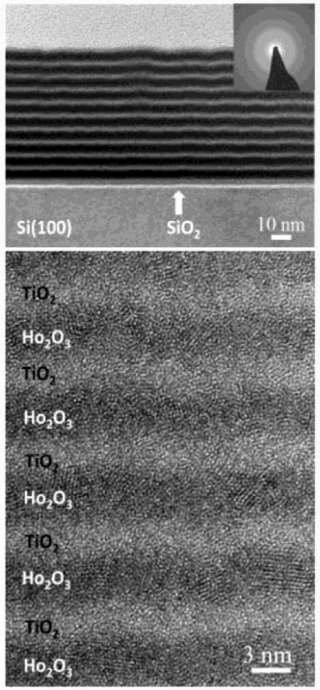
NANOLAMINATES AND MULTILAYERS

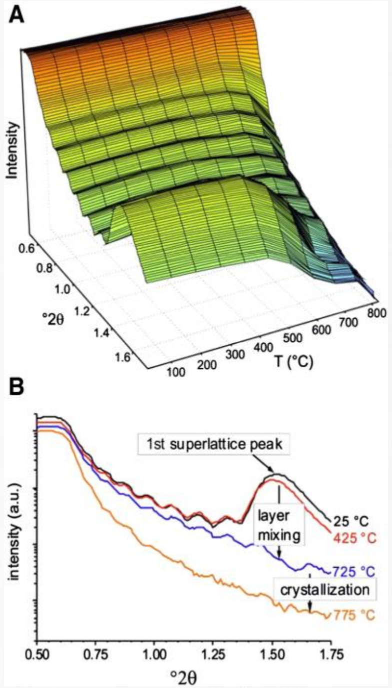
- Devices often require post deposition treatments such as annealing that might alter the properties

- Understanding what happens during the annealing is important

  → **one way is to perform *in situ* high temperature XRD and XRR measurements**

SOME BACKGROUND

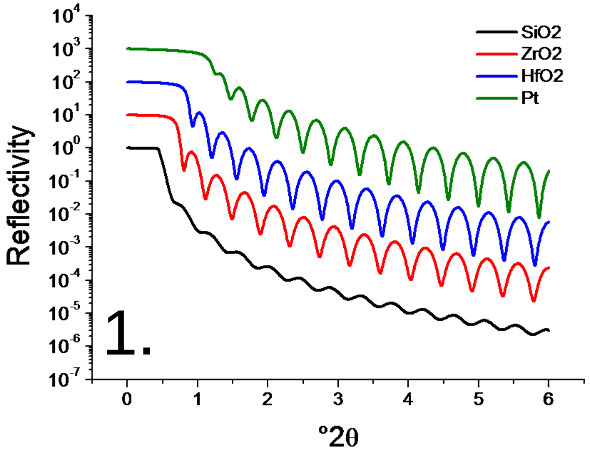


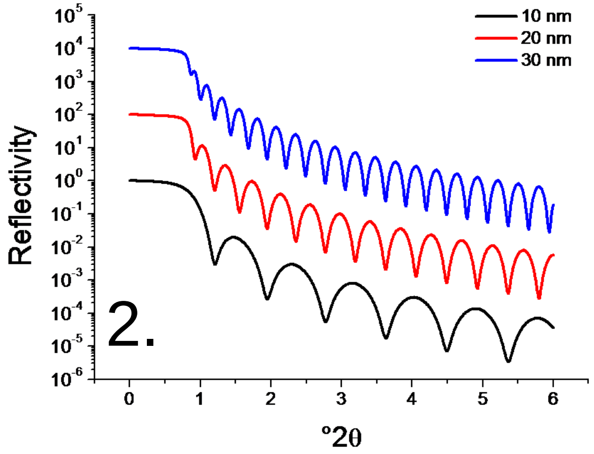


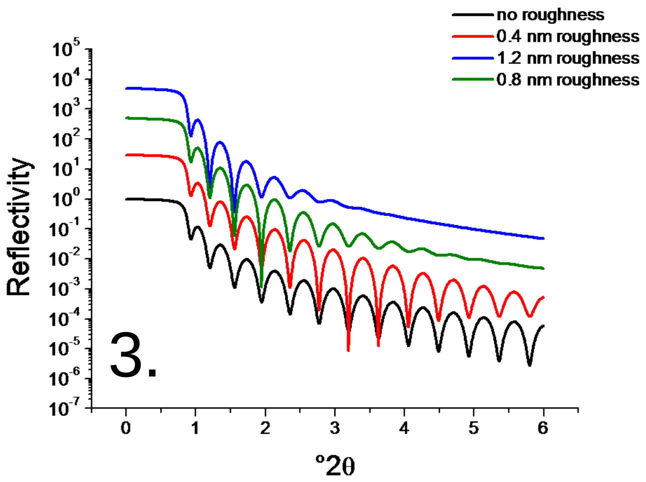
- Short HTXRD+HTXRR history of our lab
  - started with oxidation of Pt, Ir, Rh and Ru films in 2010
  - IrO_2 thin films annealed in O_2, N_2, forming gas or vacuum
    - submitted
  - first superlattice experiments with TiO_2/HoO_x laminate in 2014
    - Kukli *et al.*, *Thin Solid Films*, 565 (2014) 165
  - Al_2O_3–TiO_2 nanolaminates, comparison of stress behaviour and nanolaminate structural changes
    - Heikkilä *et al.*, to be submitted
  - solid state reactions between alkali metal carbonates and transition metal oxides
    - Atosuo *et al.*, to be submitted

X-RAY REFLECTIVITY, A QUICK OVERVIEW

- Just a reminder what information XRR gives us:
  1. electron density, proportional to the critical angle
  2. layer thickness, inversely proportional to the fringe separation
  3. layer/interface roughness(es), proportional to the slope and decrease of amplitude
- One of the biggest issues is the huge intensity drop during the measurement
  - especially with our furnace, since additional 20% intensity is lost to furnace windows

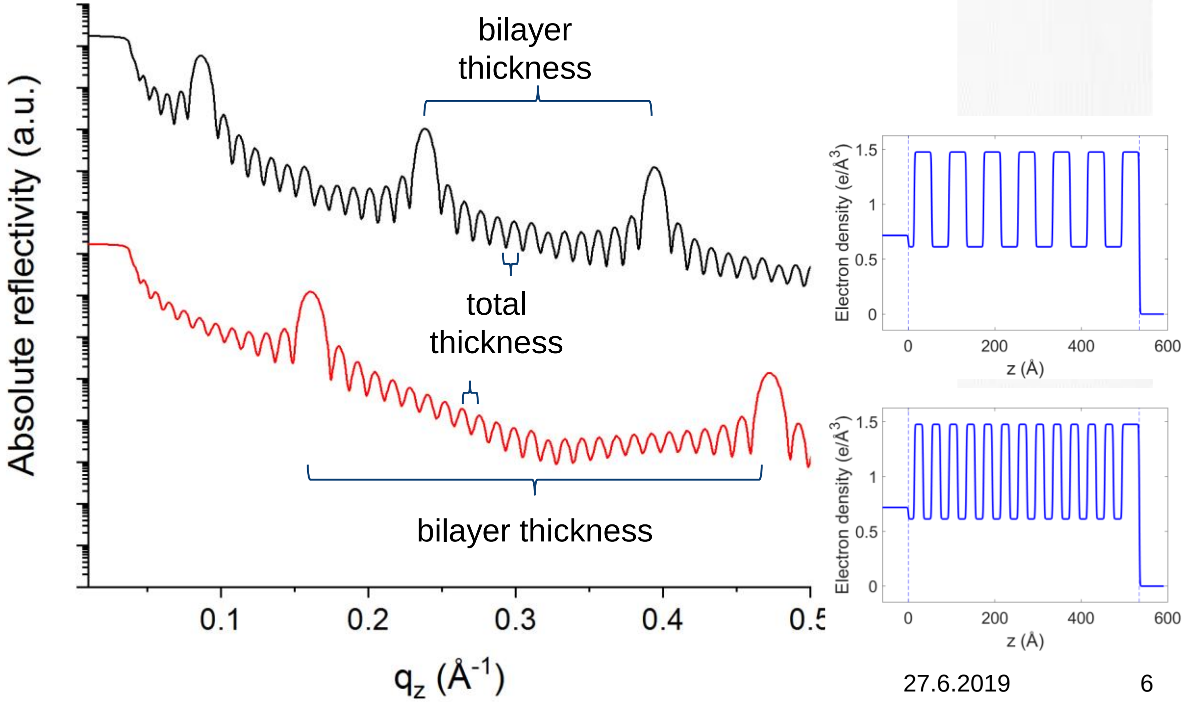






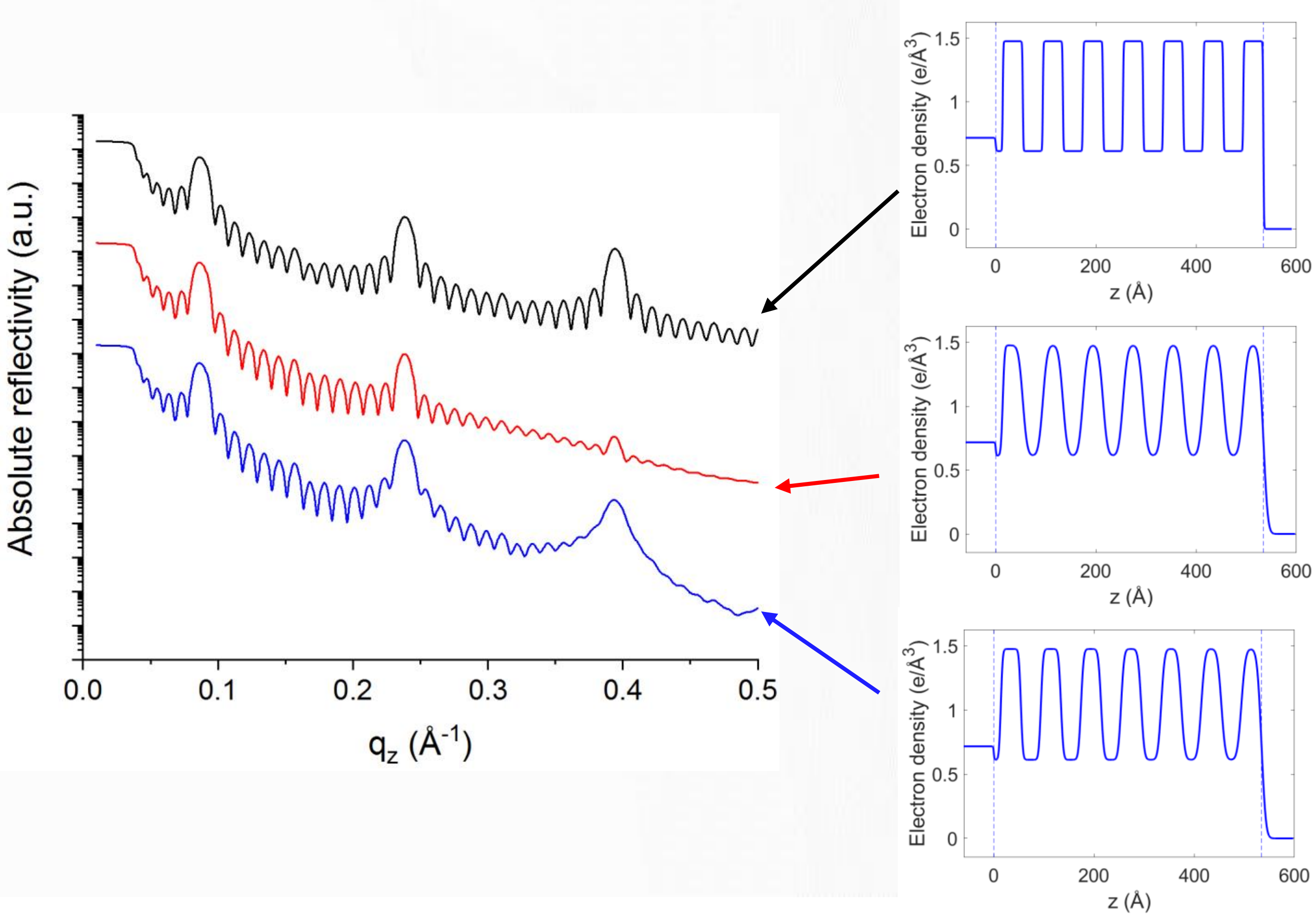
X-RAY REFLECTIVITY, A QUICK OVERVIEW

- Multilayers look a bit different
  - 6 x (40 Å Nb_2O_5 + 40 Å SiO_2) + 40 Å Nb_2O_5
- Larger intensity peaks are so called Bragg or superlattice (SL) peaks, and caused by the ordered bilayers
- Total thickness is given by the fringe separation of the highest frequency oscillation
  - with equal total thickness, halving the bilayer thickness changes the SL peak locations but keeps the small fringe separation the same



X-RAY REFLECTIVITY, A QUICK OVERVIEW

- Increased roughness decreases the intensity of the SL peaks, starting from higher angles
  - simulated here as 1 Å or 7 Å
  - high sensitivity to changes at the interface, possible to observe interlayer reactions during annealing
- Increasing the roughness gradually from 3 → 7 Å keeps the SL peak intensity higher but widens it



EXPERIMENTAL

- Deposition parameters [1]
  - flow-type hot-wall reactor (F120 by Microchemistry Ltd), deposition at 300 °C
  - precursors transmitted by N_2 flow to the substrates
    - – cations from open boats held inside the reactor
      - – Si from hexakis(ethylamino)disilane ($Si_2(NHEt)_6$, AHEAD) held at 65–67 °C
      - – Nb from $Nb(OC_2H_5)_5$ held at 90–93 °C
    - – oxidizer was ozone, generated from O_2 with concentration of ~100 g/m^3 at the generator
  - cycle times were 0.5 – 0.5 – 2.0 – 0.5 s
    for the Si/Nb precursor pulse – purge – ozone pulse – purge


Good old 90s tools, nothing quite like them

[1] Kukli *et al.*, submitted for publication

EXPERIMENTAL

- Deposition parameters
  - desired layer thicknesses were acquired by adjusting the number of repeated SiO_2 and Nb_2O_5 deposition cycles
  - in the study by Kukli *et al.* [1], films of various different structures were deposited, ranging from completely mixed to Nb_2O_5/SiO_2 doped and to SiO_2–Nb_2O_5 nanolaminates.
  - here we focused mainly on two nanolaminates with bilayers consisting of either thicker Nb_2O_5 or SiO_2, and the amount of cycles was:
    - 10 x [50 x Nb_2O_5 + 150 x SiO_2] + 50 x Nb_2O_5
    - 10 x [170 x Nb_2O_5 + 20 x SiO_2] + 170 x Nb_2O_5

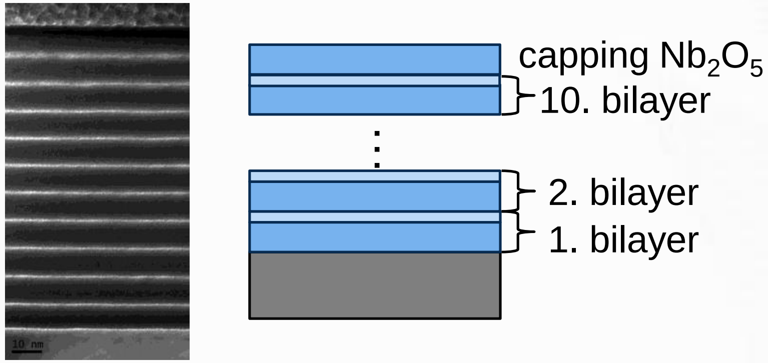
[1] Kukli *et al.*, submitted for publication

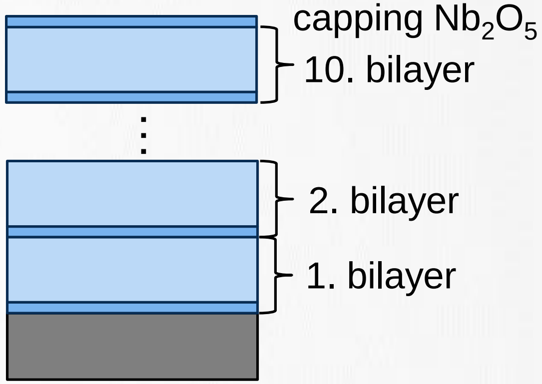
HTXRD AND HTXRR EQUIPMENT

- PANalytical X'Pert Pro MPD with Anton Paar HTK1200N furnace for HTXRD/HTXRR
    - all high temperature measurements in air
- HTXRD experiments using parallel beam with fixed 1° incident angle
    - usually from RT to 975 °C with 50 °C intervals, ~30 min for each measurement
- HTXRR is much more sensitive for accurate sample calibration
    - with our current system, omega offset and correct height are adjusted by user at each temperature with the exception of isothermal measurements
    - some minutes for aligning + ~11 min measurement at each T

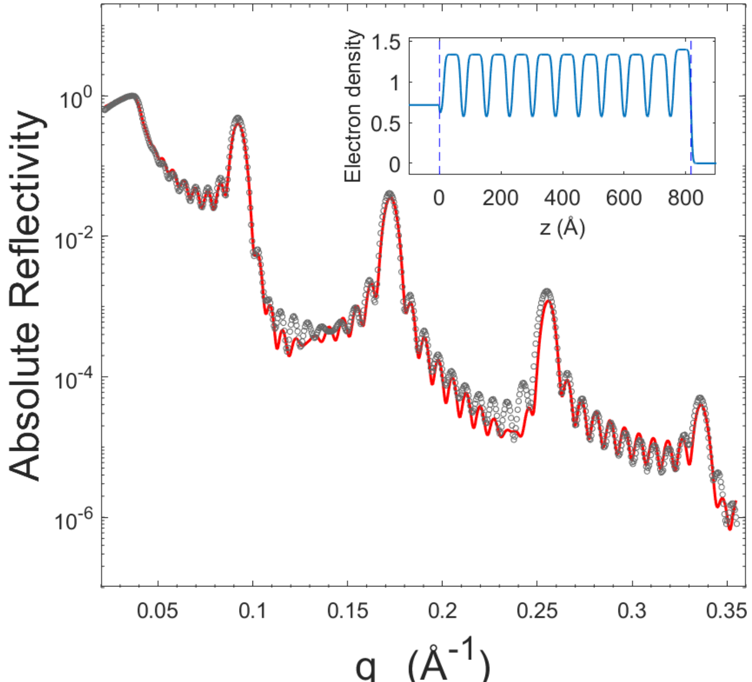
AS DEPOSITED SAMPLES

- According to XRD, the as deposited samples are amorphous
- Two XRR examples of laminates are shown on the right
- Fitting is adequate using equal bilayers, proving the quality of the laminate

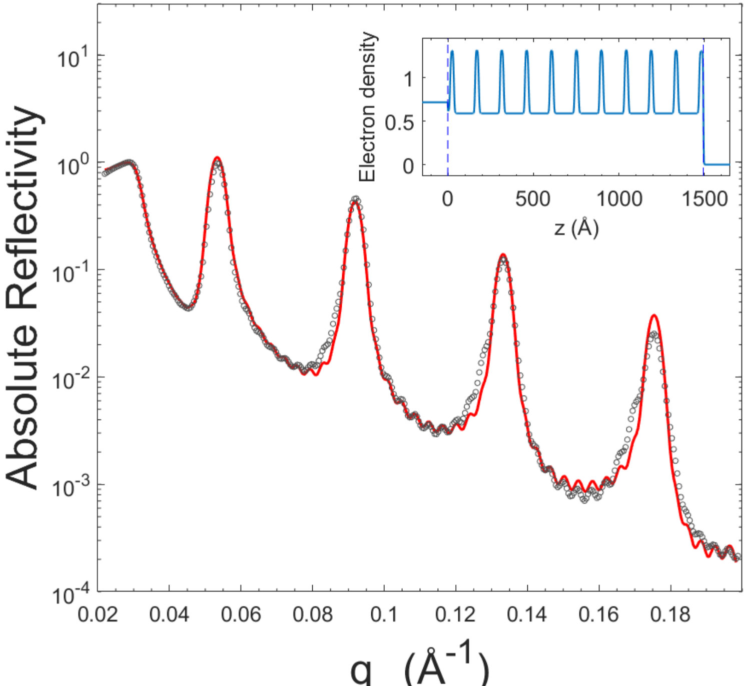




10 x (5.4 nm Nb_2O_5 + 2.0 nm SiO_2) + 5.6 nm Nb_2O_5

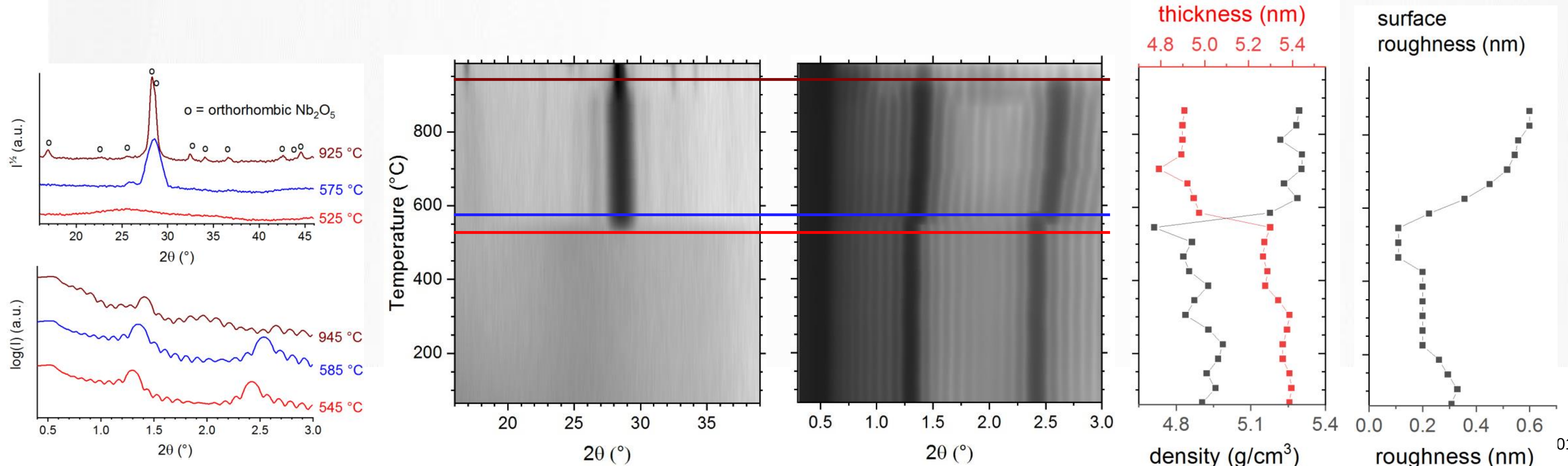


10 x (2.1 nm Nb_2O_5 + 12.4 nm SiO_2) + 2.4 nm Nb_2O_5



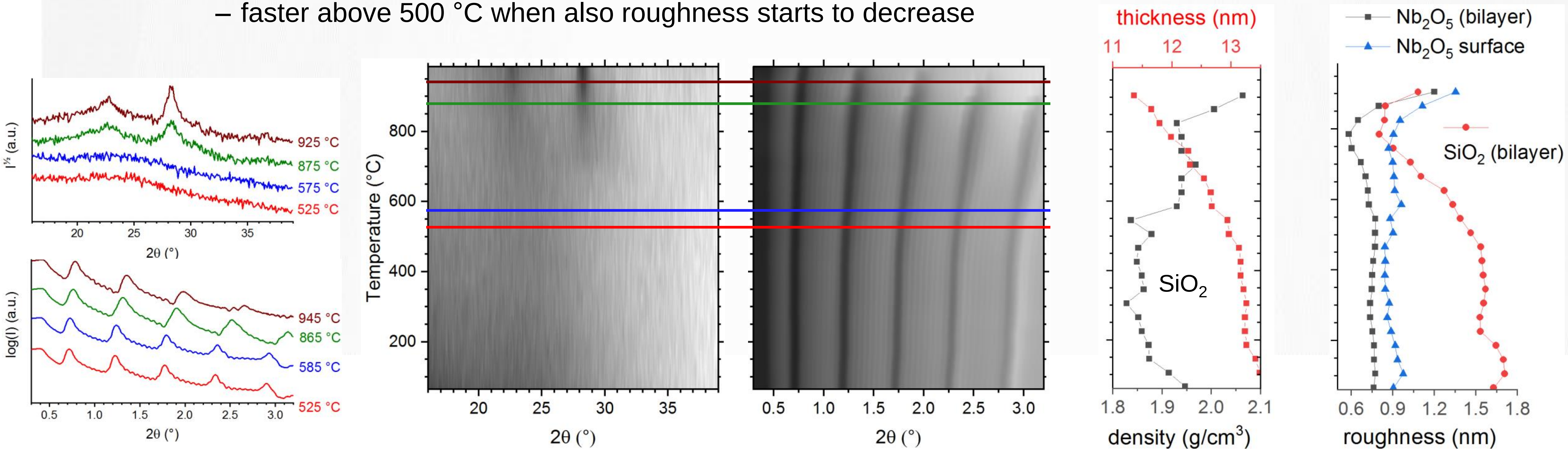
HTXRD and HTXRR results for
10 x (5.4 nm Nb_2O_5 + 2.0 nm SiO_2) + 5.6 nm Nb_2O_5

- Nanolaminate structure remains unchanged until the crystallization of the Nb_2O_5 layer
- Further changes take place at ~900 °C, when Nb_2O_5 crystals grow and film becomes much rougher as seen from the HTXRR
  - abrupt change in Nb_2O_5 thickness and density upon crystallization is seen in the fit results, surface roughness starts to increase as well



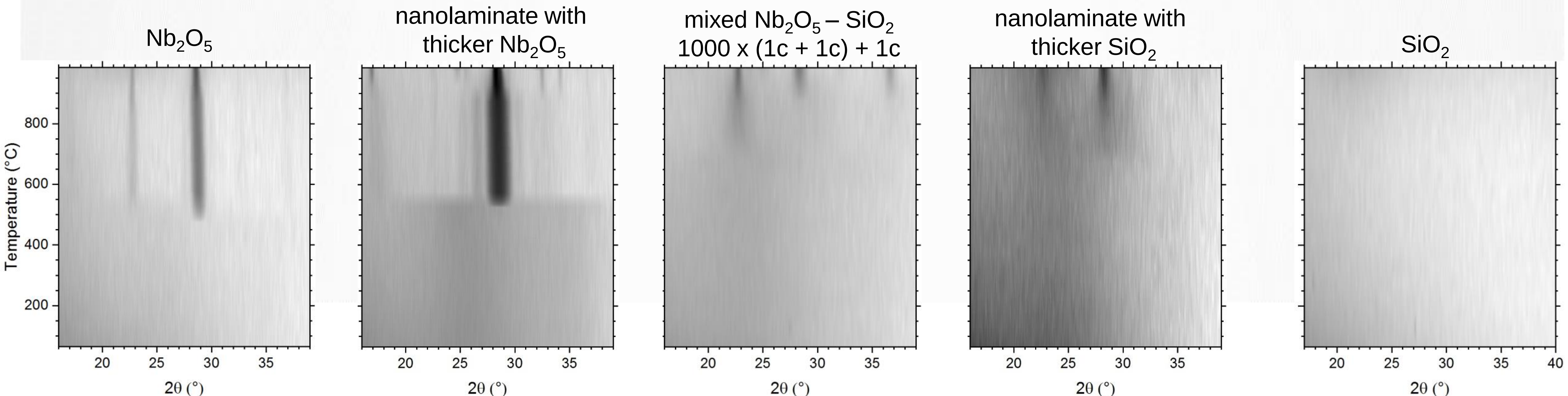
HTXRD and HTXRR results for
10 x (2.1 nm Nb_2O_5 + 12.4 nm SiO_2) + 2.4 nm Nb_2O_5

- Structure with thicker SiO_2 behaves very differently
  - Nb_2O_5 crystallizes above 875 °C, peak width suggests larger crystallites than the individual layer thickness → layers start to mix?
  - the laminate structure intact up to the crystallization, then fast roughness increase
    - – SiO_2 thickness starts to decrease immediately after the annealing begins
    - – faster above 500 °C when also roughness starts to decrease



COMPARING TO PURE AND MIXED LAYERS

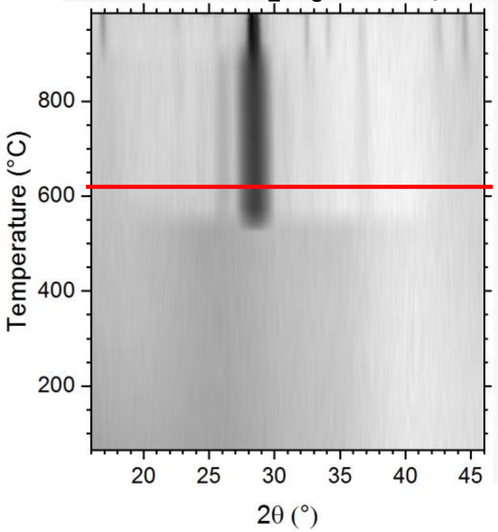
- Pure Nb_2O_5 starts to crystallize above 525 °C, just like the nanolaminate with thicker Nb_2O_5
  - also grain growth at 900 °C for both
- Pure SiO_2 doesn't seem to crystallize within this temperature range
- Mixed layer behaves like the nanolaminate with thicker SiO_2, so Nb_2O_5 crystallization is somehow inhibited at temperatures below ~700 °C

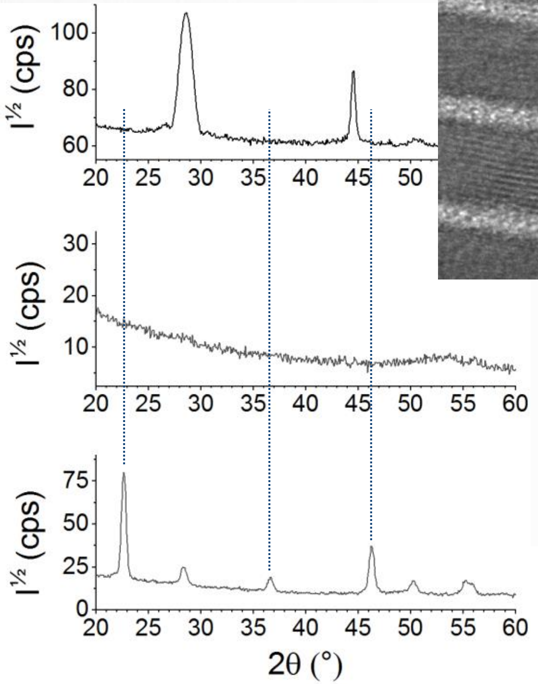


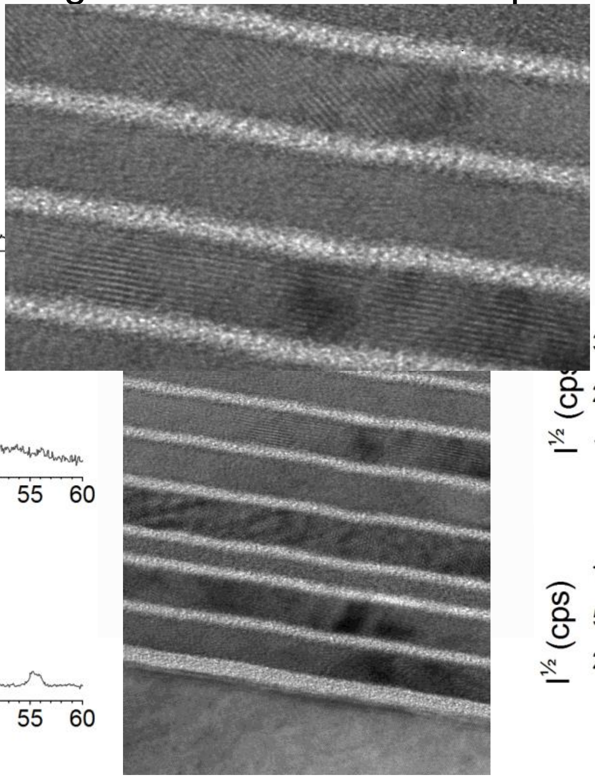
CRYSTALLIZATION IN MORE DETAIL

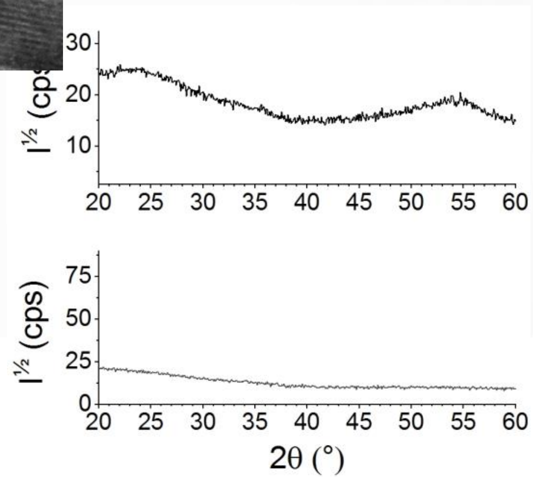
- Nanolaminates heated to 600 °C, held for 1 h and cooled back to RT
    - GIXRD: nothing observed for the sample 1, weak crystallinity for the sample 2 (probably just SiO_2)
    - in-plane XRD: strong crystallinity for the previous, almost nothing for the latter
    - out of plane XRD: confirms the strong orientation of the sample with thicker Nb_2O_5 in bilayer

SAMPLE 1
thicker Nb_2O_5 in bilayer

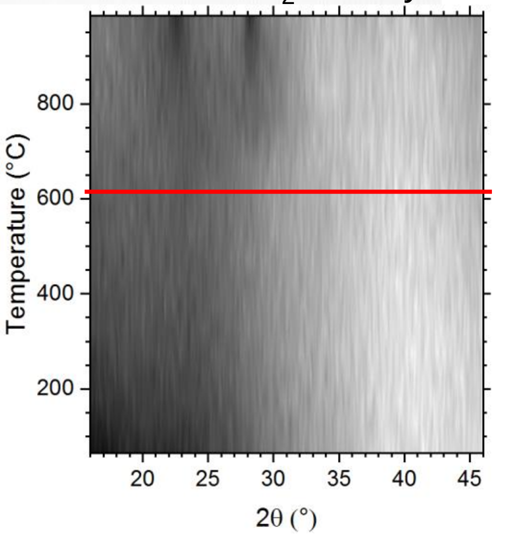








SAMPLE 2
thicker SiO_2 in bilayer



CONCLUSIONS

- More detailed analysis possible but requires
  - larger measurements ranges
    - for XRR: improved analysis on roughness, possibility to detect new layers forming during annealing
    - for XRD: improved microstructure/texture analysis
  - shorter measurement times
    - smaller temperature steps, more accurate phase change temperatures, reaction kinetics
    - or more measurements at each temperature (e.g. rocking curves for diffuse scattering studies, better background determination in XRR)
- In practice all those require synchrotron, but even laboratory equipment gives useful results!

CONCLUSIONS

- Combined HTXRD and HTXRR is an efficient tool for analysing the annealing of the nanolaminates
  - might help in interpreting electrical properties as changes in
    - phase composition affects the dielectric constant
    - layer thickness affects the capacitance as well
    - crystallization affects the amount of leakage current

$$C = \frac{k\varepsilon_0 A}{d}$$

  - tailoring of the final properties by selecting proper annealing conditions
  - possible to monitor solid state reactions and/or interdiffusion between the adjacent layers

ACKNOWLEDGEMENTS

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