Chemical Solution Deposition of $BiFeO_3$ Films with Layer-by-Layer Control of the Coverage and Composition

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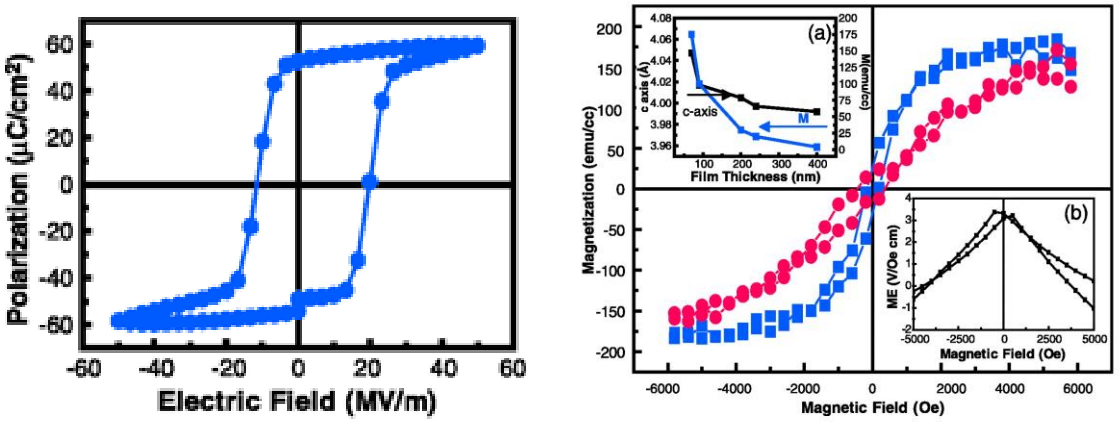
Motivation

- BiFeO_3 (BFO) is one of the most interesting multiferroic thin-film materials
  - ✓ Model multiferroic material with uniquely high Curie (~825°C) and Neel transition (~360°C) temperatures – simultaneous ferroelectric polarization and magnetic ordering at room temperature
  - ✓ Enormously high ferroelectric polarization in thin film form ($P_r \sim 55\ \mu C/cm^2$)



J. Wang, et al. Science 299, 1719 (2003).

- Chemical solution deposition (CSD) is of great interest because it is more suitable commercially, cheaper and makes it possible to cover large-scale wafers

- The use of the sol-gel route CSD allows multilayer films to be obtained by controlled layer deposition

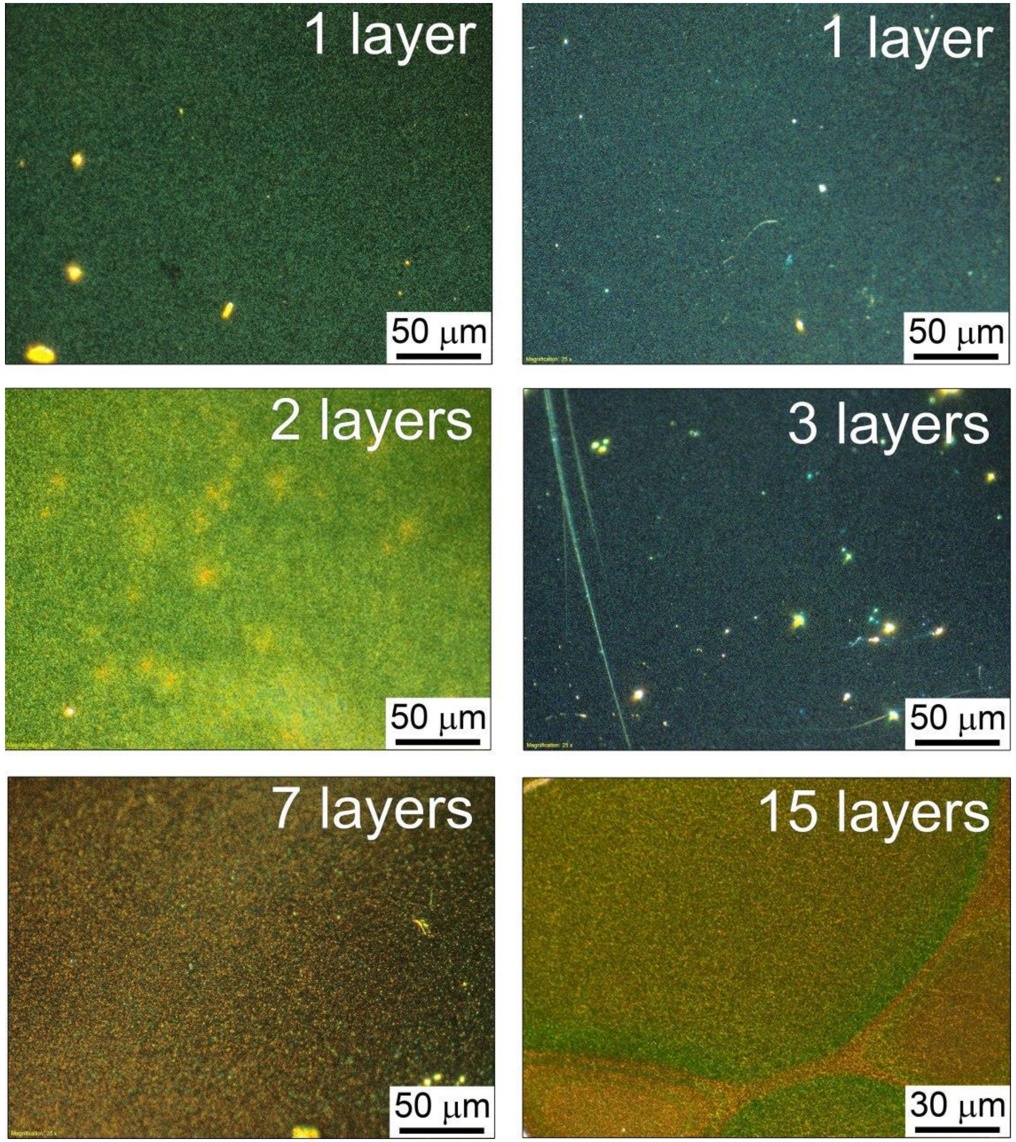
- The layer-by-layer deposition is used to avoid agglomeration of the particles in the solution and to achieve a thick enough film

Sample fabrication

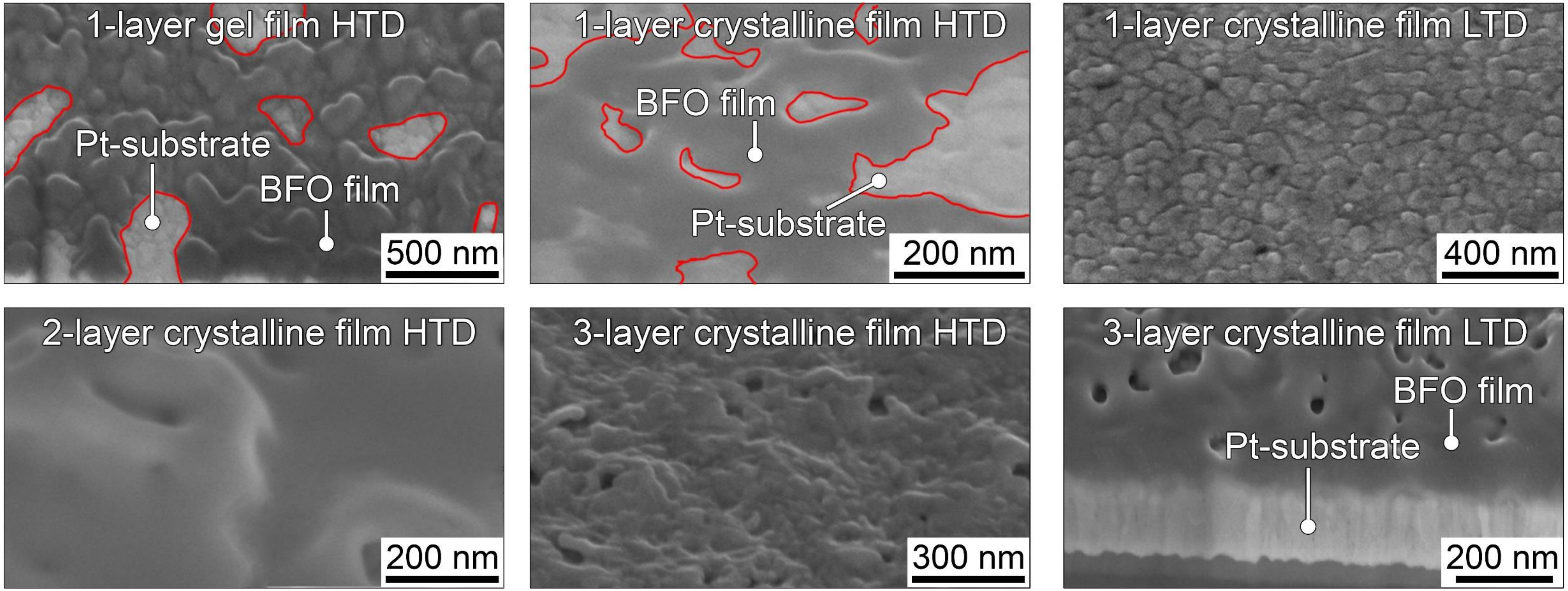
- Fabrication of $BiFeO_3$ thin films was done using a CSD method via sol-gel route
- The films were prepared on $Pt/TiO_2/SiO_2/Si(100)$ substrates
- Drying step:
  1. 125 °C, 40 min - "low-temperature-dried", LTD
  2. 300 °C, 5 min - "high-temperature-dried", HTD
- Pyrolysis and crystallization step:

✓ 300 ℃, 60 min, and 600 ℃, 40 min in air atmosphere

✓ Slowly cooling down at 5 °C/min rate

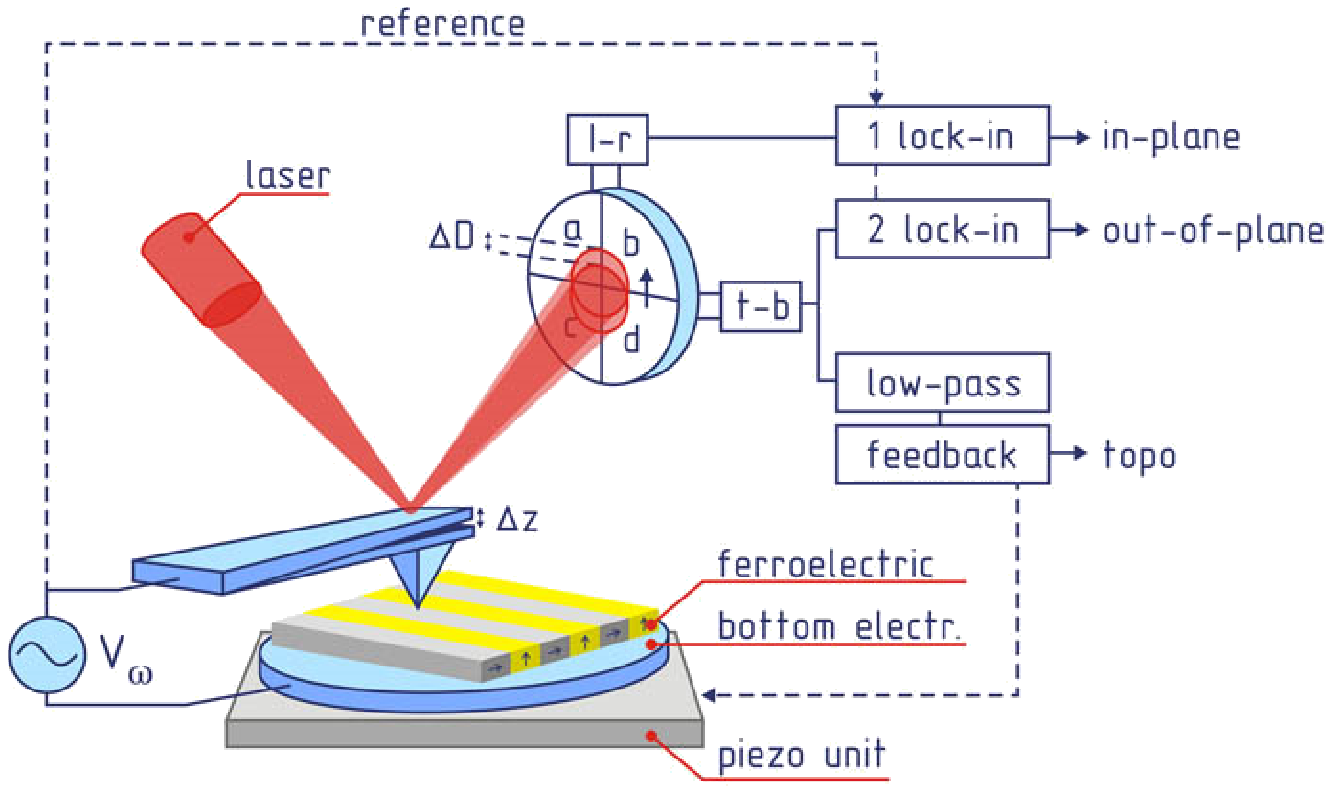


Scanning electron microscopy



- The average thickness of the layer – around 30–50 nm
- The coverage of the surface is an “island-like” with a fraction around 85% in 1-layer HTD film
- Two- and three-layer films were homogeneous without extra inclusions
- LTD-prepared films cover the substrate uniformly without any morphological features

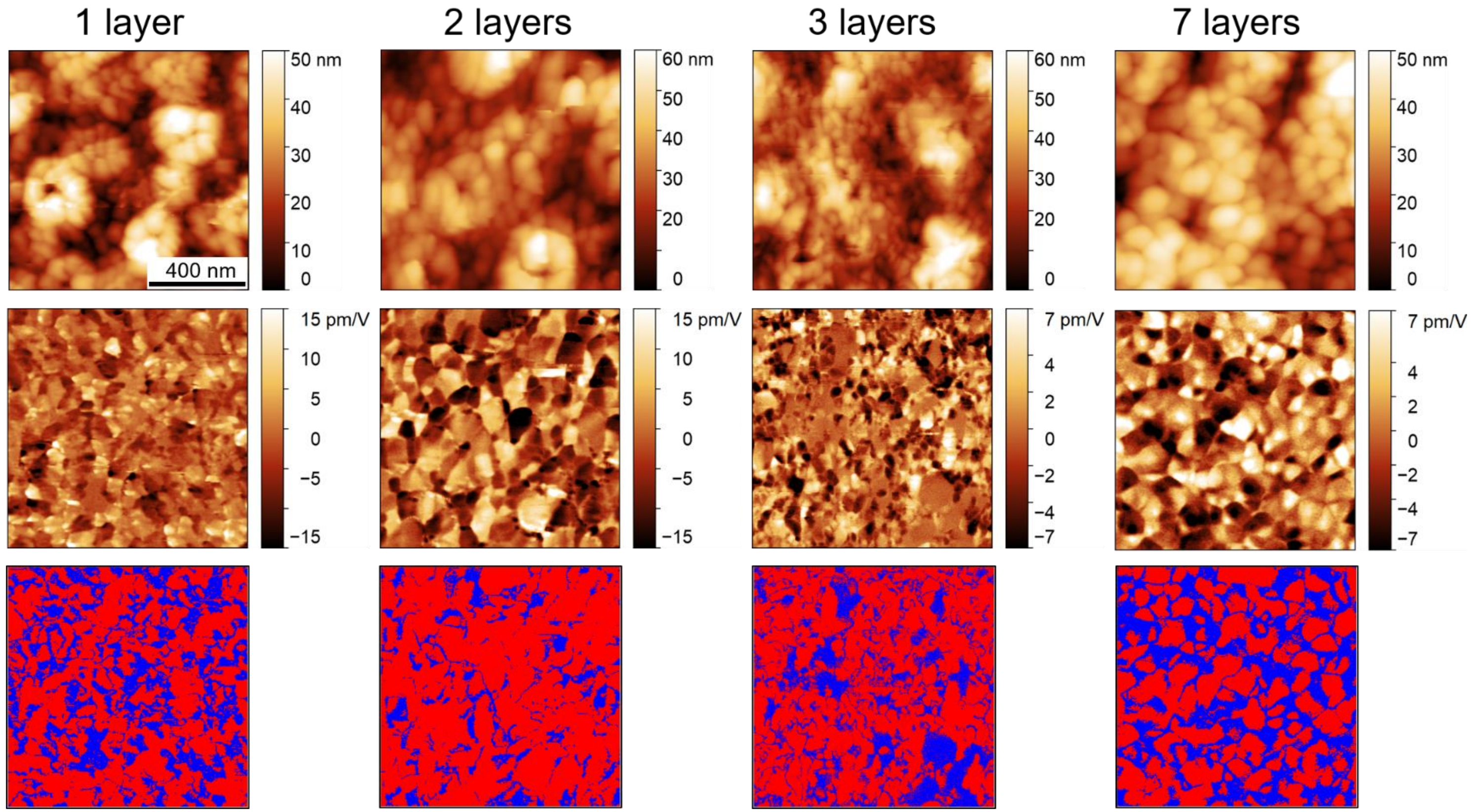
Atomic force microscopy



- ❑ Piezoresponse force microscopy (PFM)
  - ❑ Amplitude of AC voltage: 3 V
  - ❑ Frequency of AC Voltage: 20 kHz
- ❑ Conductive atomic force microscopy
  - ✓ DC voltage 5-10 V

- ❑ NTEGRA Aura (NT-MDT Spectral Instruments, Russia)
- ❑ HA-NC cantilevers (ScanSens, Germany)

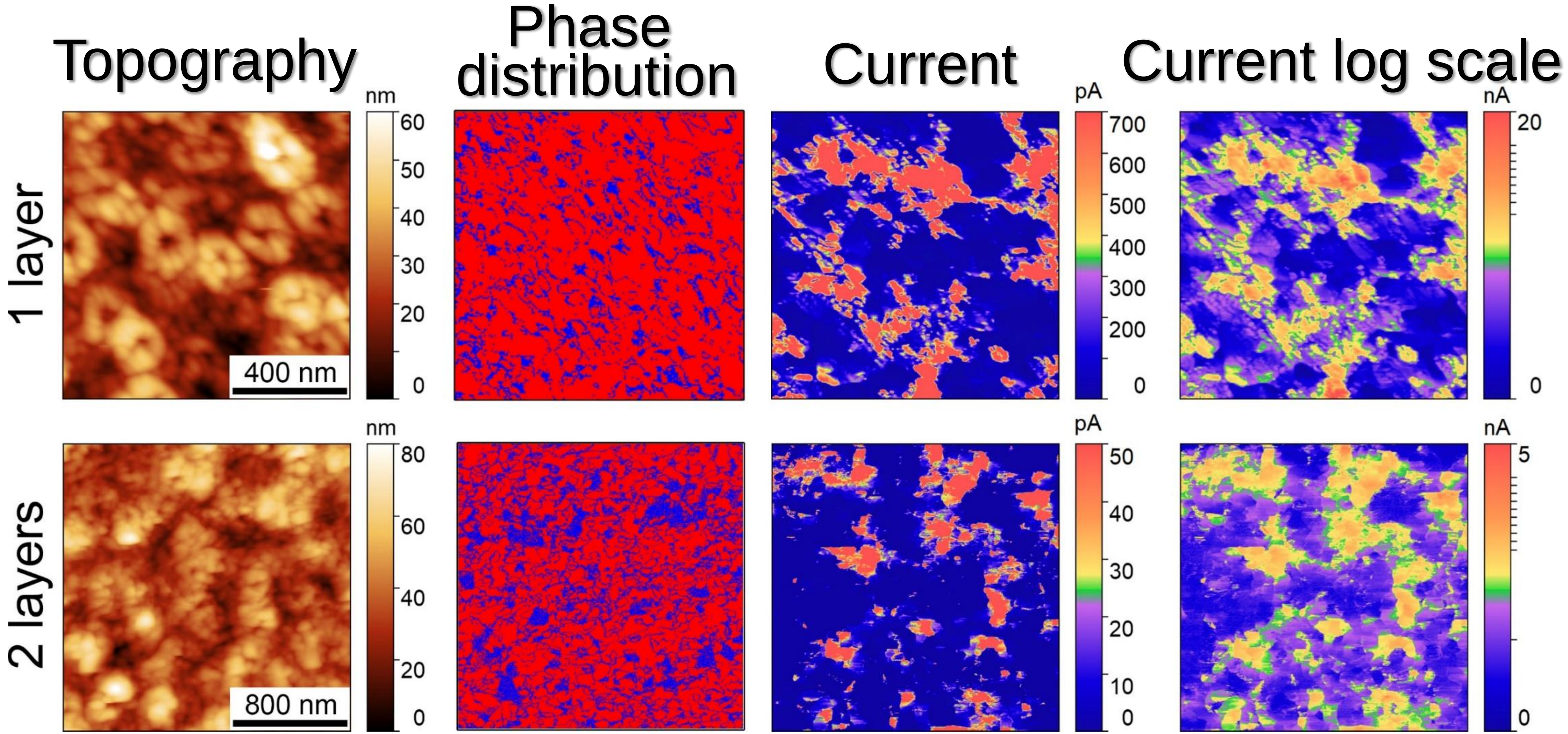
PFM measurements of HTD films



Thickness	1 layer	2 layers	3 layers	7 layers
Polar phase	75%	86%	67%	65%
Non-polar phase	25%	14%	33%	35%
Effective piezoelectric coefficient, pm/V	2.5 ± 1.0	3. 5± 1.5	1.2 ± 0.8	1.3 ± 0.3

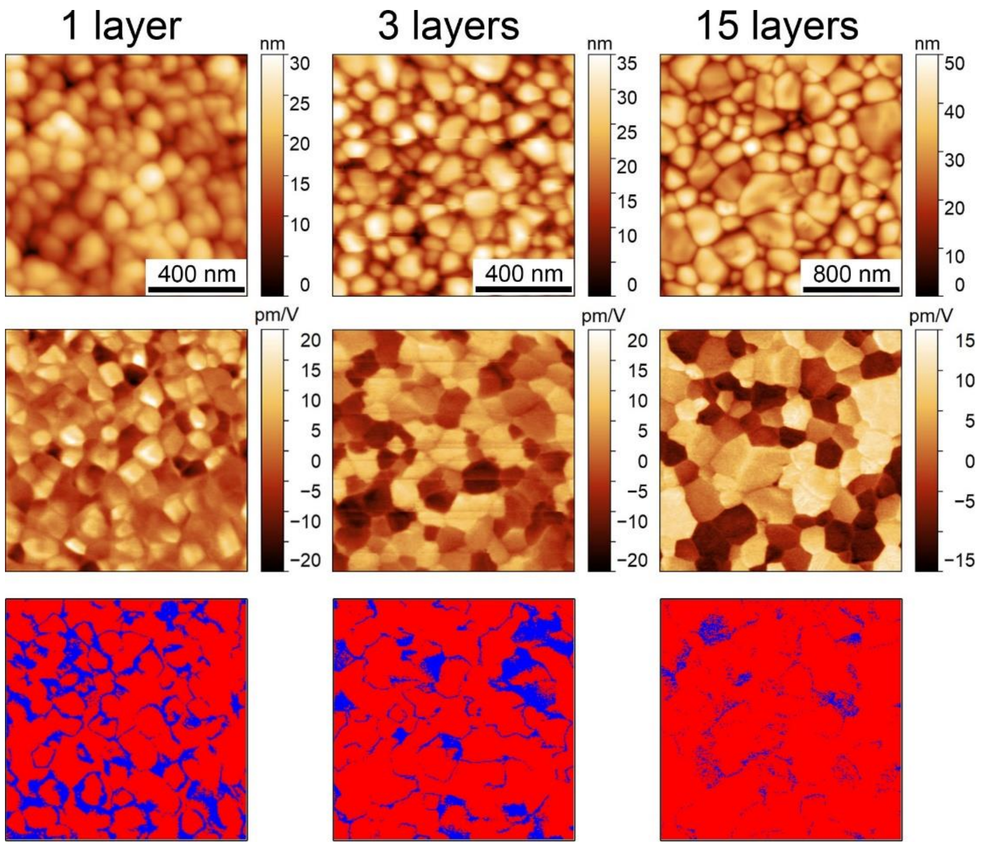
- Topography of the HTD BFO films revealed a porous microstructure with agglomerates of the grains
- In 3-layer films, distinct regions inside the grains without piezoresponse – secondary phases
- The increase of the secondary phase concentration and decrease of effective piezoelectric coefficient with the thickness of the film

Current measurements of HTD films



- The leakage was not spatially correlated with the position of the secondary phases
- The leakage current maxima are coincident with the positions of the pores in one-layer films
- The deposition of the additional layer does not completely prevent the leakage
- The pores formed as a result of HTD procedure contribute to the macroscopic leakage current

PFM measurements of LTD films



- The topography is smooth and independent on the number of deposited layers
- The grain size is larger in LTD films in comparison to HTD
- Fraction of the piezoelectrically-inactive phase is gradually reducing with increasing the thickness
- Effective piezoelectric coefficients are larger in LTD films

Thickness	1 layer	3 layers	15 layers
Polar phase	76%	87%	95%
Non-polar phase	24%	13%	5%
Effective piezoelectric coefficient	3.5 ± 0.8 pm/V	8.3 ± 1.6 pm/V	5.4 ± 1.6 pm/V

Conclusions

- We performed the deposition of $BiFeO_3$ thin films under different drying conditions that impact the effectiveness of the gelation step
- The layer-by-layer control of the morphology, local piezoelectric response, and phase leakage current distribution was done by means of piezoresponse force microscopy and conductive atomic force microscopy methods
- Long-time and low-temperature drying of the as-deposited solution in each layer of the film allows to achieve thick multi-layer films with 95 wt% of the main phase, larger grain size, and effective piezoelectric coefficient of about **5–8 pm/V**
- High temperature drying was demonstrated to be responsible for the deterioration of the initial layer coverage of the film and hampered chemical reactions leading to the formation of the small grain agglomerates with the large mix of the piezoelectrically inactive phases.
- Accumulated morphological changes during the deposition of the subsequent layers are responsible for the porosity and corresponding enhancement of the leakage current across the pores in the film bulk.

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