# Study of lead-free ferroelectric composite coatings by impedance spectroscopy

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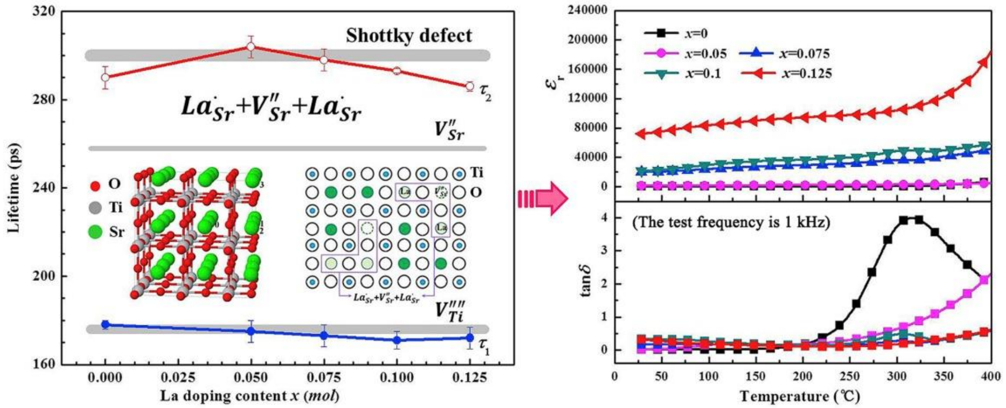
# Aims of the study

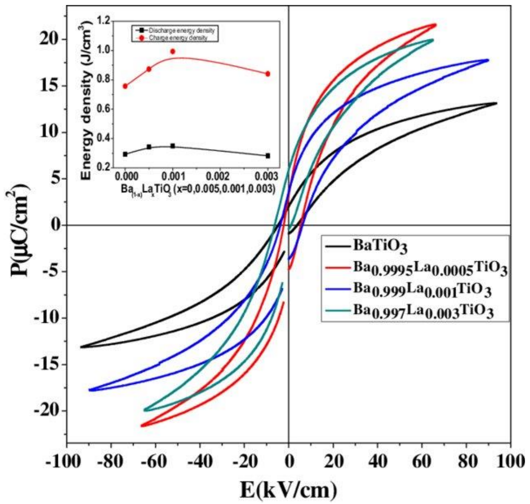
- Preparation and electrical characterization of lead-free ferroelectric oxide $BaSrTiO_3$ in composition with piezoelectric polymer PVDF – TrFE for sensing applications.

- Determination of dielectric permittivity and losses as a function of the temperature and frequency for ferroelectric films with variety of compositions.

- Application of impedance spectroscopy for ferroelectric sensors on silicon (due to the COVID-19 situation this part of the study is not yet completed and only partial results are shown).

# State-of-the-art

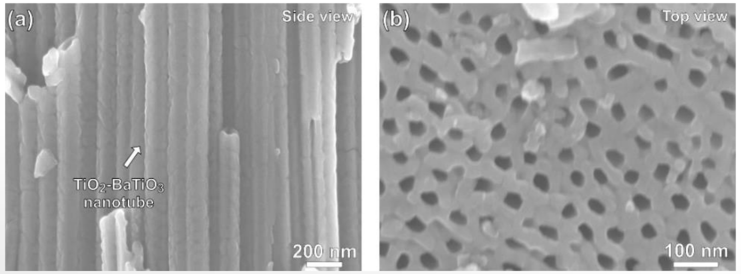



$SrTiO_3$ dielectric parameters variation and $BaTiO_3$ polarization ability variation with the La doping concentration

Quin et al., Acta Materialia, 164, 2019, 76-89.

Recent studies have revealed that the ferroelectric properties can be controlled by the deposition conditions. To establish a relation between the microstructure and the ferroelectric response, a scanning electron microscopy (SEM) has been applied in combination with polarization P-E hysteresis curves. However, information about some fundamental processes, such as dipoles motion, cannot be directly accessed from the SEM and P-E measurements.



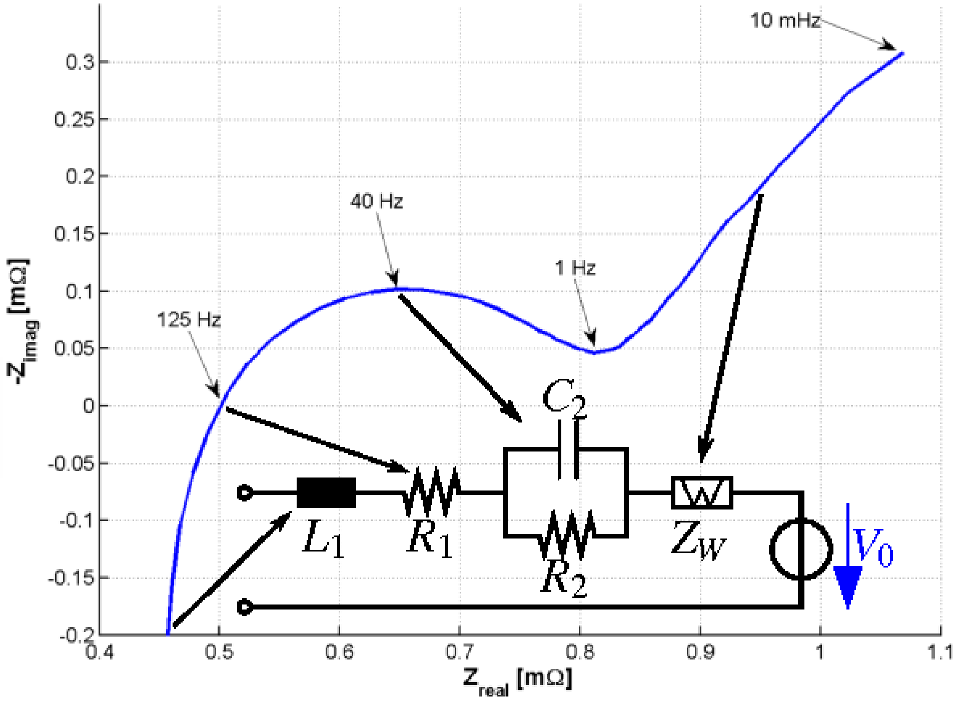

Soderznik et al., Proceedings 2019, 15, 9.

SEM images of a vertically aligned and uniformly shaped $TiO_2$-$BaTiO_3$ nanotubes

# State-of-the-art

Therefore, more sophisticated technique is necessary, such as impedance spectroscopy (IS). It relies on bias signal supplied to the sample, which can vary in magnitude and frequency. Parameters like the full impedance and admittance, contact resistance, interface capacitance, dielectric permittivity and loss tangent can be extracted from the impedance measurements.

R. Koch et al. 16th European Conference on Power Electronics and Applications (2014): 1-10.



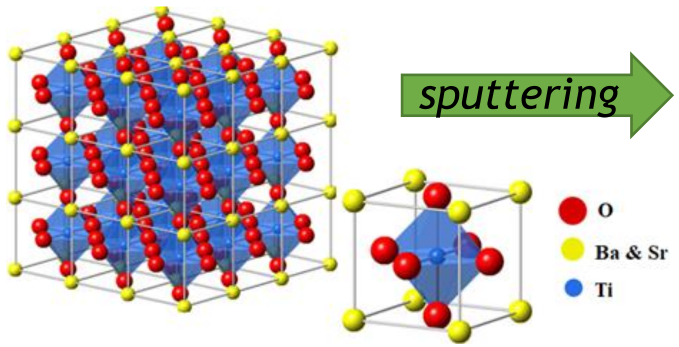

Impedance measurement with equivalent circuit parameters

# Methods

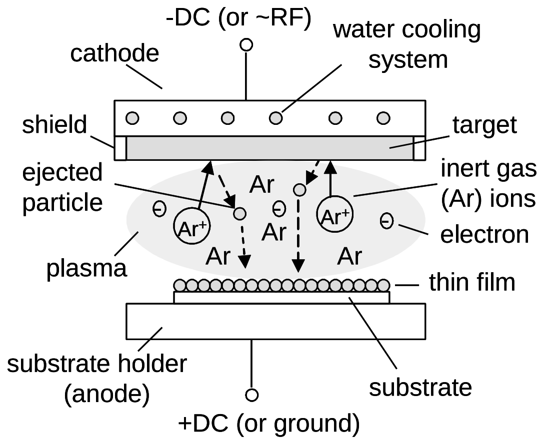
$BaSrTiO_3$ was RF sputtered on silver coated silicon wafers at sputtering pressure of $2.5.10^{-2}$ Torr and sputtering voltage of 0.75 kV, defining plasma power of 43 W/inch. The bottom and top electrodes were made of thermally evaporated silver films. The ferroelectric ink PVDF-TrFE was spin coated at 1000 rpm from Solvene 300 solution and then annealed at 120ºC in oxygen atmosphere for 15 min. Atomic force microscopy was conducted by AFM MFP-3D, Asylum Research, Oxford Instruments. Dielectric parameters were studied in the frequency range 100 Hz-100 kHz by IS Hioki IM3590. The temperature measurements in the range 5 ºC-130 ºC were realized by a home-made Peltier based heating-cooling system.

Ferroelectric ceramic $BaSrTiO_3$

- high piezoelectric coefficient of 33.4 pC/N,
- preferable for strong piezoelectric response provoked even by weak dynamic load.

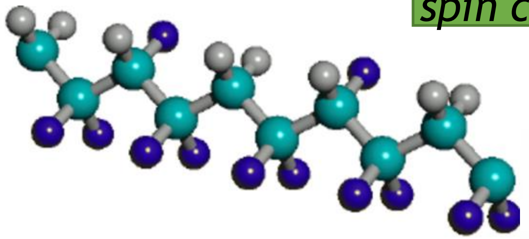



*sputtering*

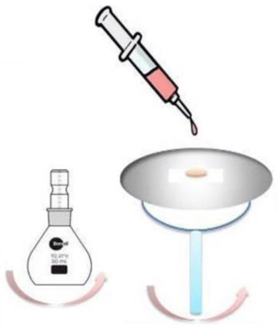



Ferroelectric polymer P(VDF-TrFE)

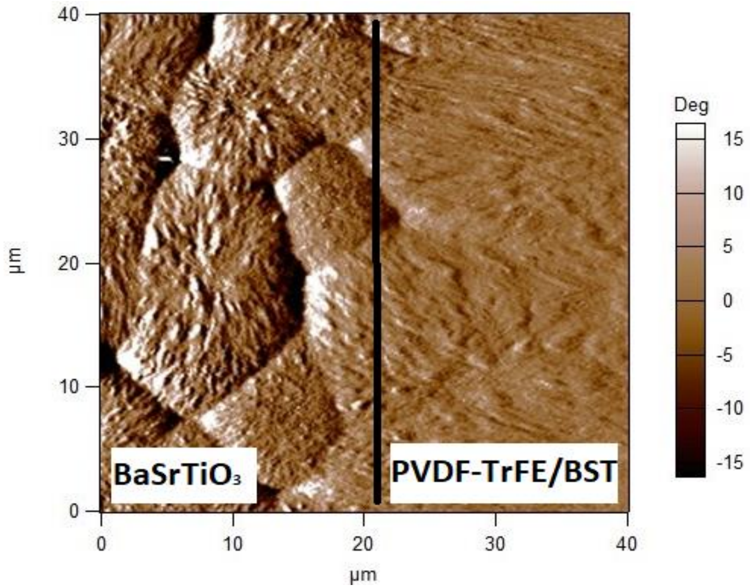
- low Young modulus of 0.61 GPa,
- favourable for durability at bending and twisting substrates.

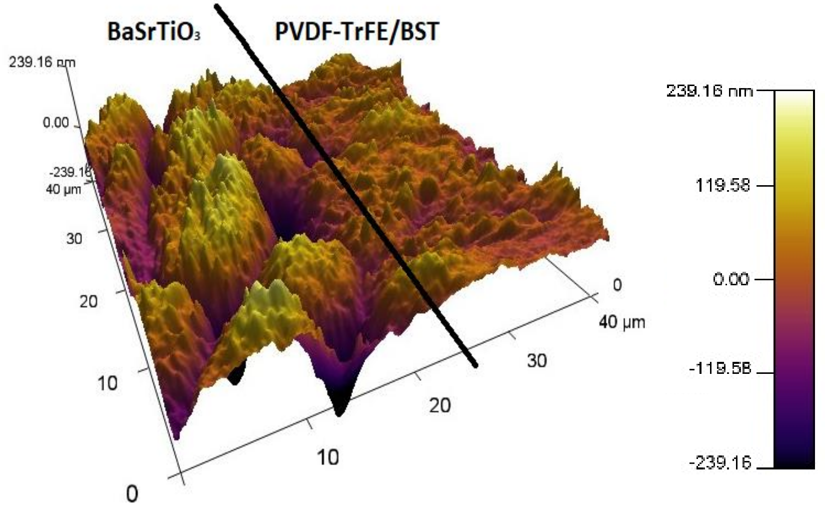


*spin coating*



# Results

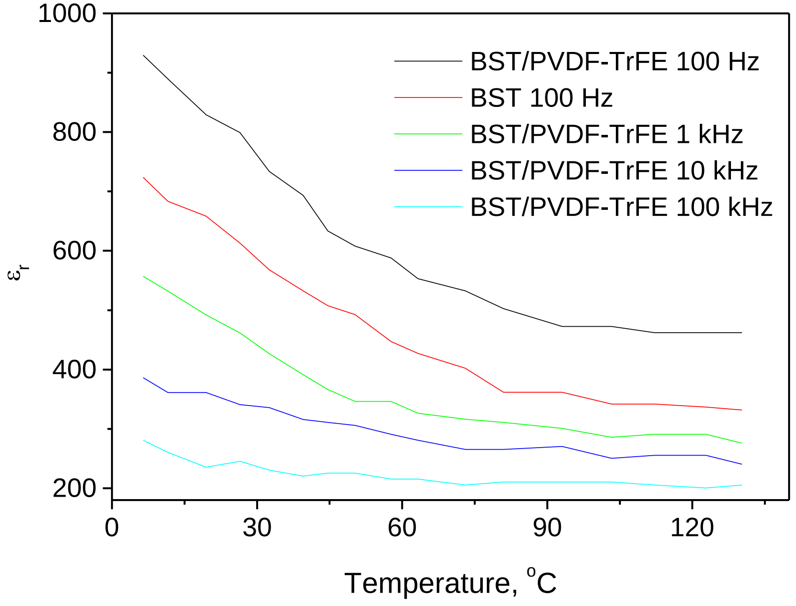


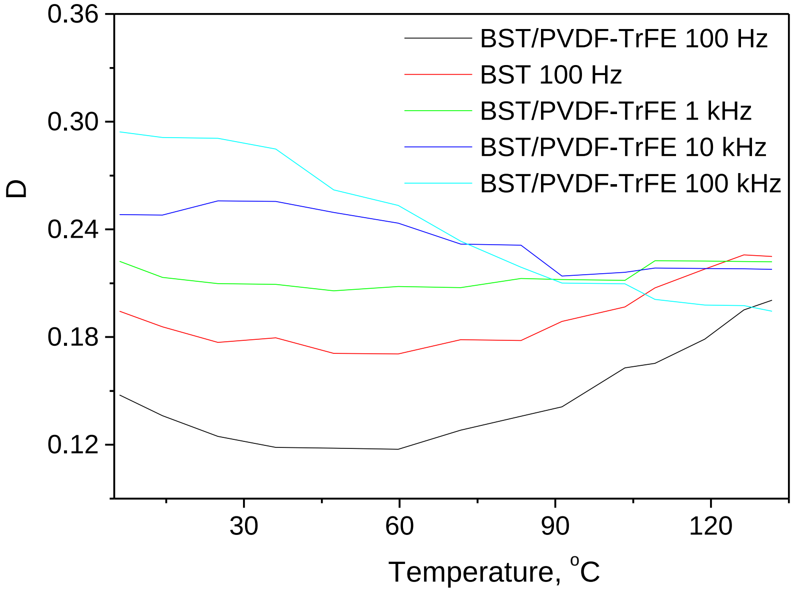




2D and 3D AFM images comparing the surface topography of BST film and PVDF-TrFE coated BST film.

The tilted 3D image shows that there is a great variation in the BST film height at the interface area between the large crystallites (the height difference between the largest hill and hole was approximately 211 nm related to a total thickness of 480 nm). The spin-coating of the polymeric solution caused gaps filling and smoothening of the BST film, as can be clearly seen from both images. Finer microstructure with an average roughness of less than 100 nm was observed for the smoother surface. It is expected that the improved film's flatness will result in a decrease of the losses and contact resistance due to the increased contact area at the interfaces electrode/functional film.

# Results

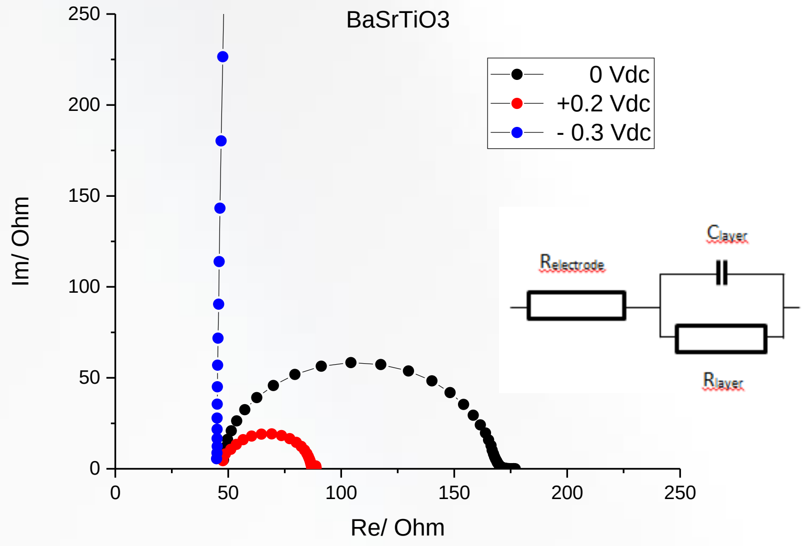


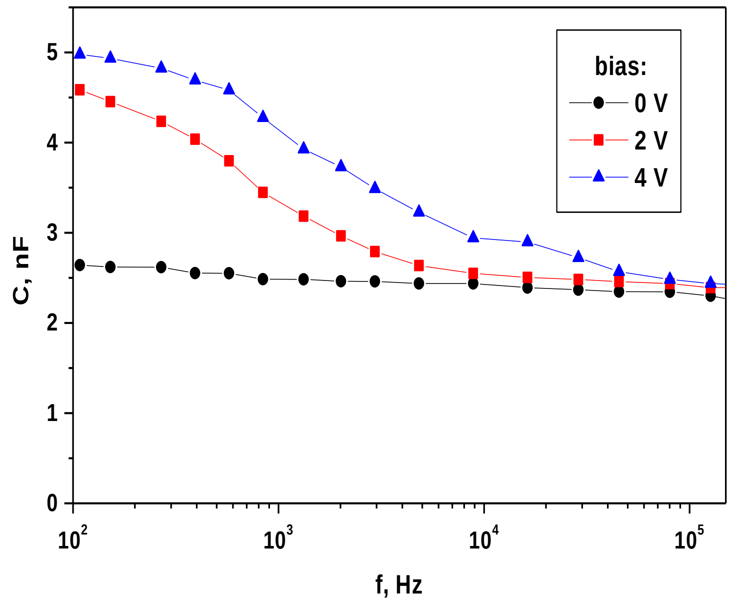

Variation of the dielectric permittivity and losses with the temperature, frequency and composition of the functional film.

It was found that the dielectric permittivity is greater for the composite PVDF-TrFE/BST that can be ascribed to interfacial polarization at the ceramic/polymer interface due to the difference of their conductivity and piezoelectric coefficients. It was also found that $\varepsilon_r$ slightly decreased with the temperature for all set frequencies. Dielectric losses were found to be smaller for the PVDF-TrFE/BST, slightly dependent on the temperature and more strongly dependent on the frequency. The results are in good agreement with the reported for ferroelectric composites.

# Results




Electrochemical impedance spectroscopy curves and corresponding electrical equivalent circuit of BST based sample - the contact resistance was estimated was estimated to be 47.73 Ohm.




Capacitance of the device BST sample at different frequencies.

To be done for the BST/PVDF-TrFE sample for comparison.

# Conclusion

- AFM images show smooth surface after insertion of PVDF-TrFE coating onto the BST surface. Uniformly distributed peaks form the average roughness of the film.
- The structure with composite film show high value of $\varepsilon_r$ and low loss factor, with poor temperature dependence, which is favorable for sensing applications relying on capacitor, or piezoelectric principle.
- Pristine $BaSrTiO_3$ can be modeled with single RC group.
- Future work will be related to full impedance measurements at different frequencies, analysis of the real and imaginary part behavior and relation with the polarization processes in the ferroelectric film.

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