Localized nano-mechanical and nano-chemical analysis by atomic tri-force microscopy of polyvinylidene fluoride (PVDF)

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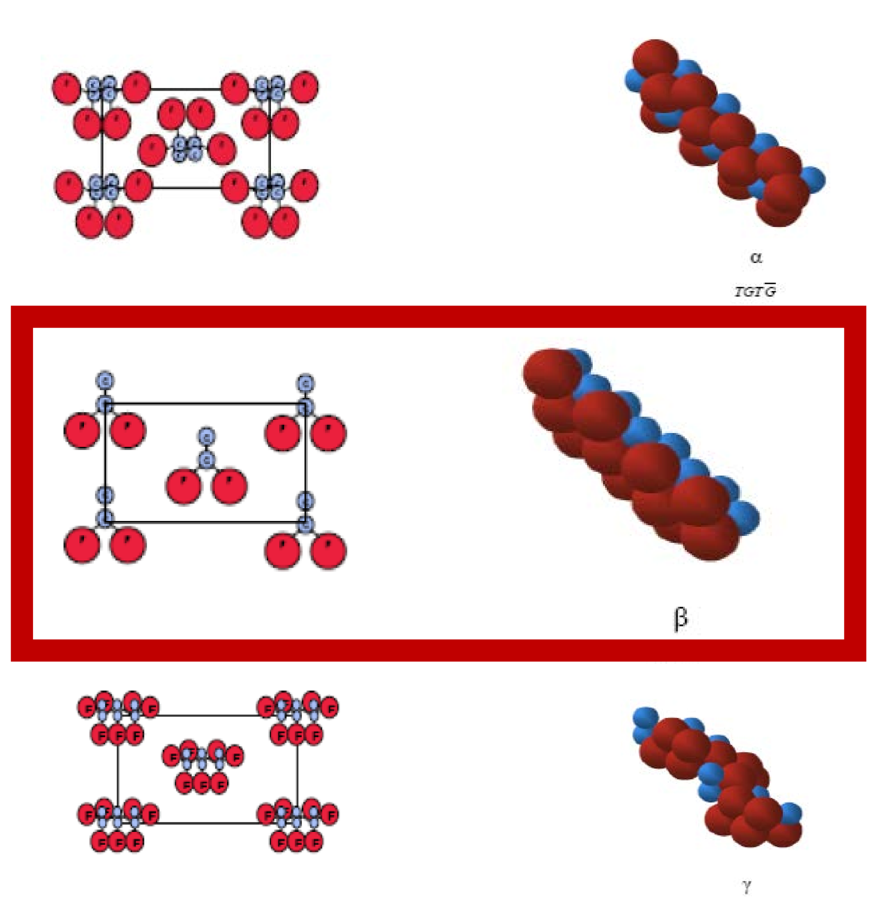
Introduction

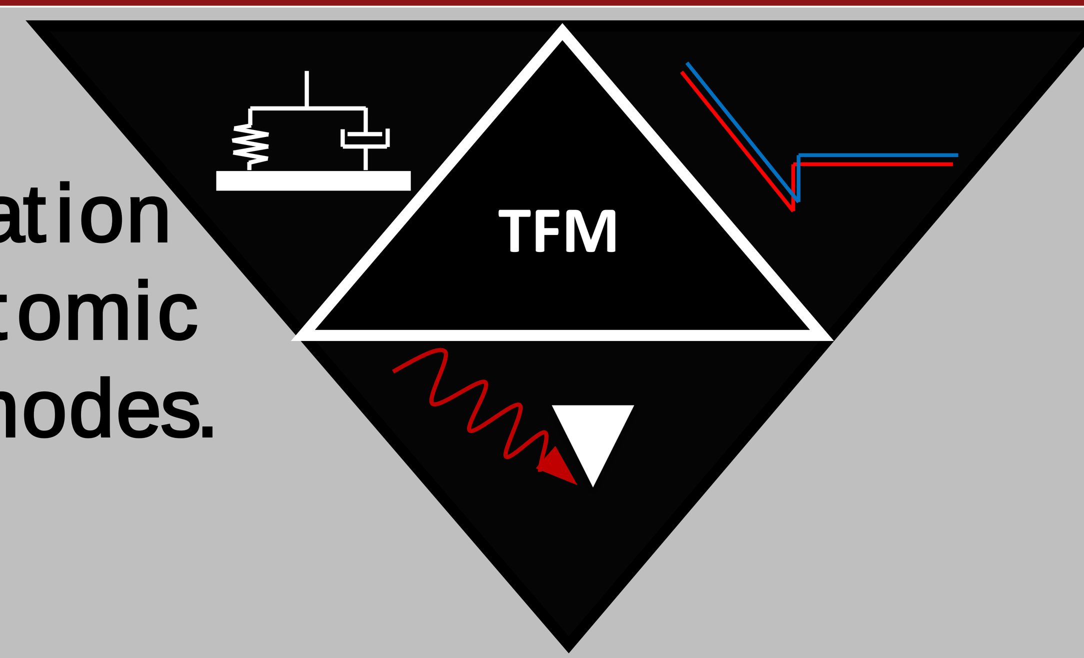
- **Poly (vinylidenefluoride) (PVDF)** and its copolymers are electroactive polymers that can crystallize in a quasi-hexagonal close-packed "β-phase.
- Piezoelectric properties of PVDF are linked with nanostructure.
- *Currently*, there is **limited** availability of **quantitative** methods for nanoscale molecular structure and mechanical analysis.
- **This study** utilized atomic tri-force microscopy to investigate PVDF in the β-phase and its copolymers on the nanometer length scales.



Methods

- Fabrication of PVDF-TrFe 70/30 copolymers (forms: mesa, nanowells, & films)
- CR-AFM measurements on samples
- Force mapping analysis
- NanoIR analysis

Atomic Tri-force Microscopy - Utilization of three different atomic force microscopy modes. Namely, CR-AFM, NanoIR, and FM



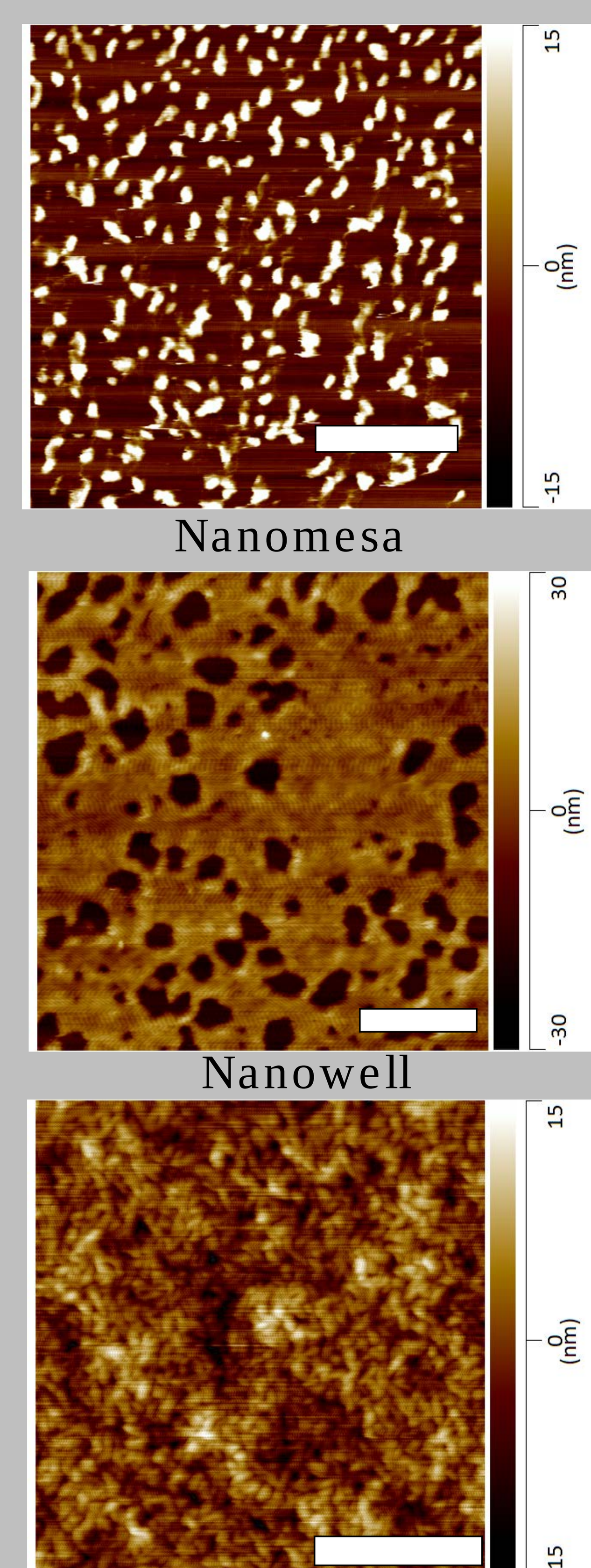
Contact resonance atomic force microscopy (CR-AFM): Viscoelastic property determination

NanoIR: Incorporates infrared spectroscopy coupled with an AFM tip to obtain chemical/molecular information on the nanoscale

Force Mode (FM): Quasi static force curves and elastic modulus mapping (traditional)

Method

- Create/control how PVDF forms on the nano length scales
  - Nanomesa
  - Nanowells
  - Films
- Utilize different AFM modes on PVDF nanostructures



CR-AFM

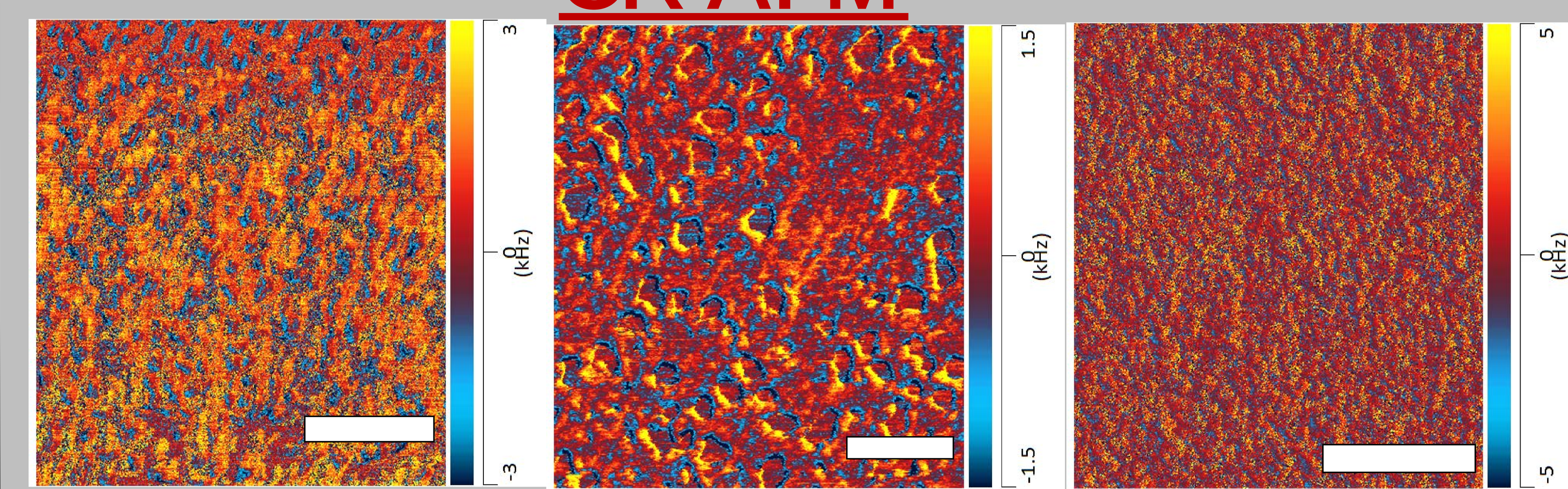


Figure 1: CR-AFM Scans of different nanostructures of PVDF. Frequency mapping images. All scale bars are 2 μm

NanoIR

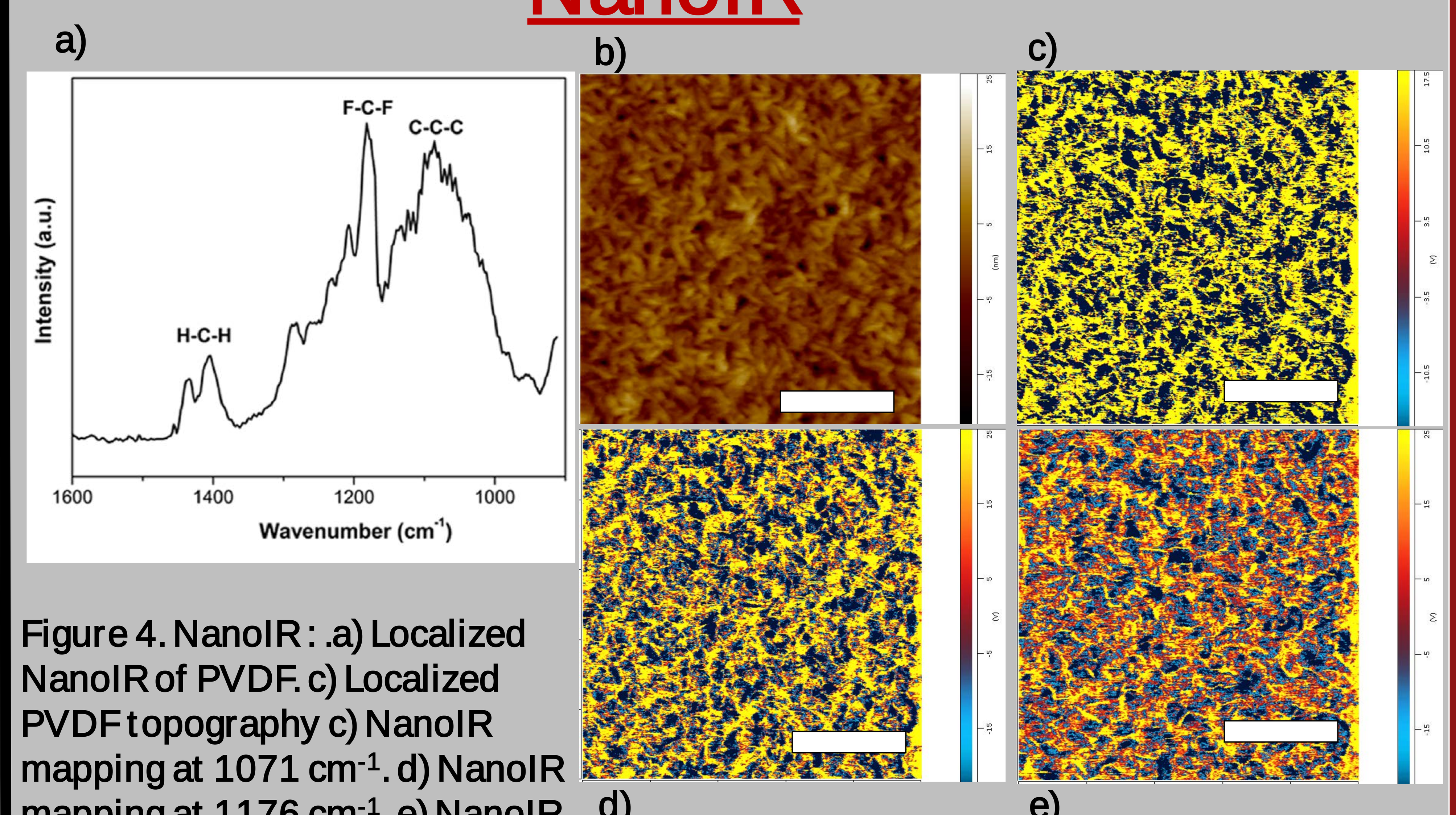


Figure 4. NanoIR : .a) Localized NanoIR of PVDF. c) Localized PVDF topography c) NanoIR mapping at 1071 cm^{-1}. d) NanoIR mapping at 1176 cm^{-1}. e) NanoIR mapping at 1397 cm^{-1}

FM

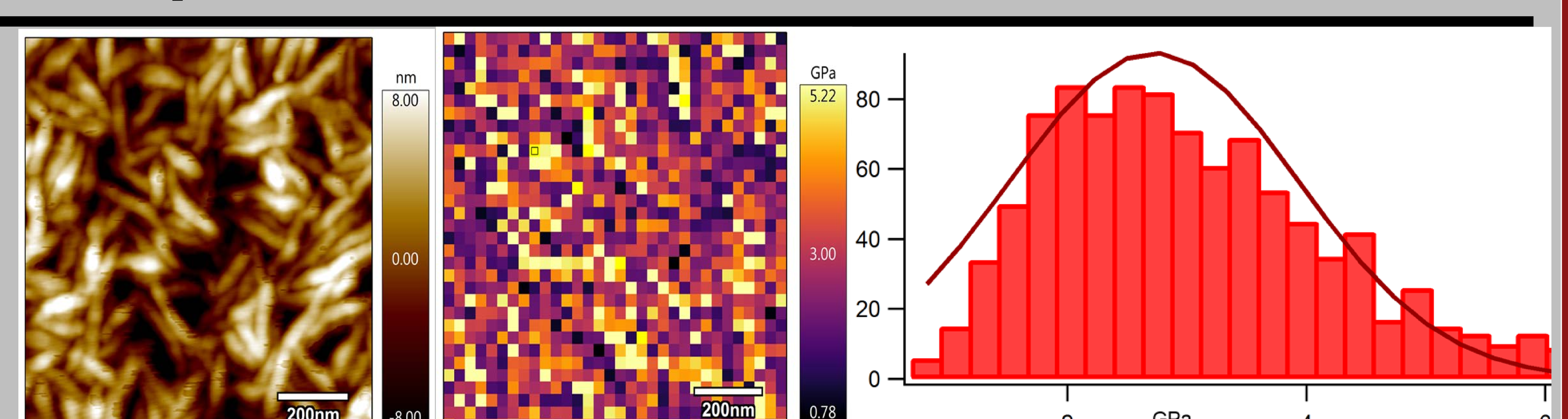


Figure 5 Force Mapping: a) AFM topography image of PVDF b) Corresponding force map; c) Histograms of elastic modulus from force map shows that the elastic modulus primarily ranges from 1.75-3.50 GPa.

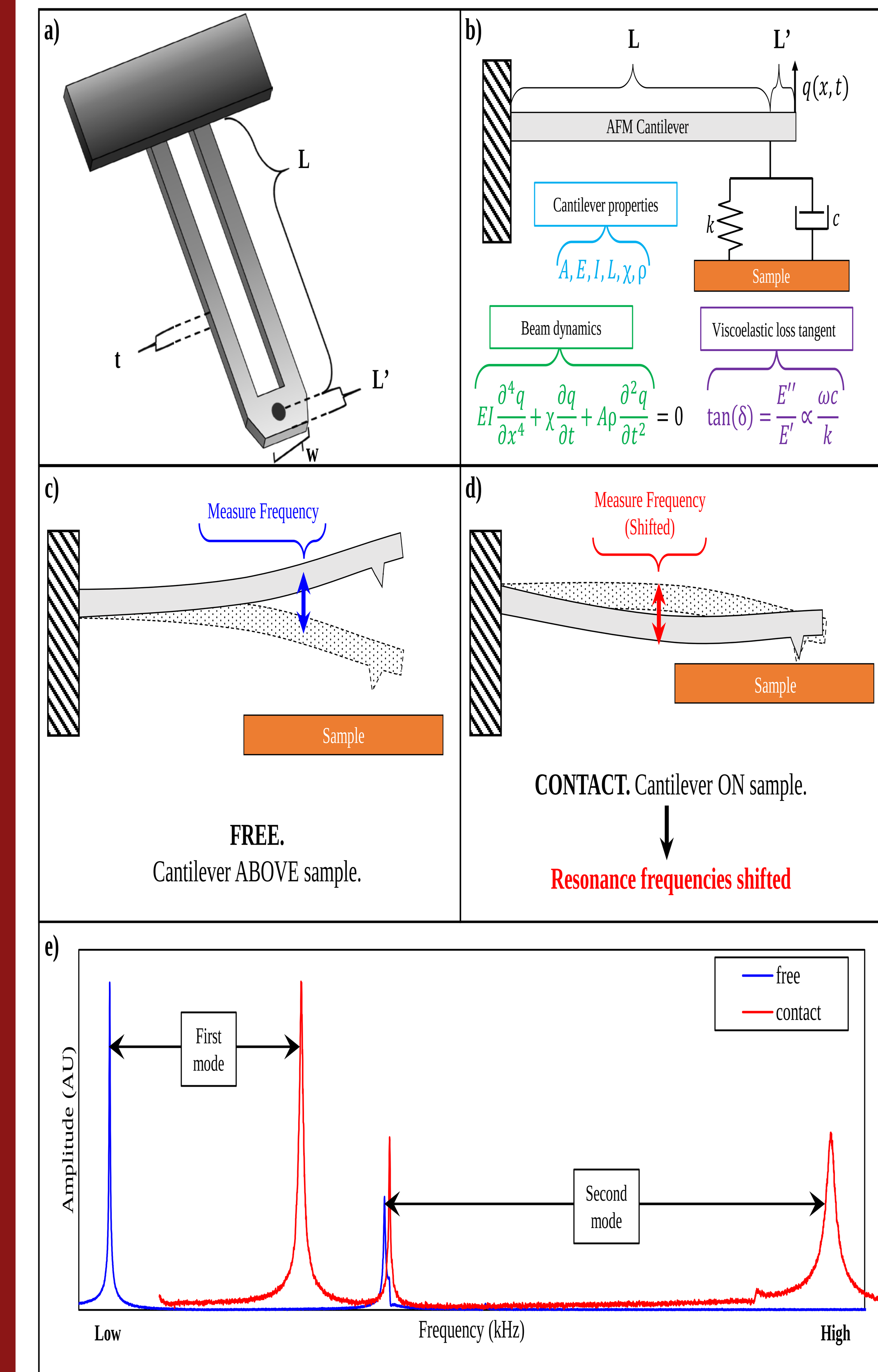


Figure 6. Illustration of basic CR-AFM theory. A) cantilever geometry. B) Cantilever dynamics. C) Free case. D) Contact case. E) Frequency shifts to higher frequencies implies higher stiffness. Fit spectra/map to obtain viscoelastic properties

Conclusions

Atomic tri-force microscopy can provides unparallel nanoscale information:

1. Morphology
2. Crystallinity
3. Molecular structure/Chemical
4. Elastic properties
5. Viscoelastic properties

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