

An efficient route to fabricate fatigue-free P(VDF-TrFE) capacitors with enhanced piezoelectric and ferroelectric properties and excellent thermal stability for sensing and memory applications

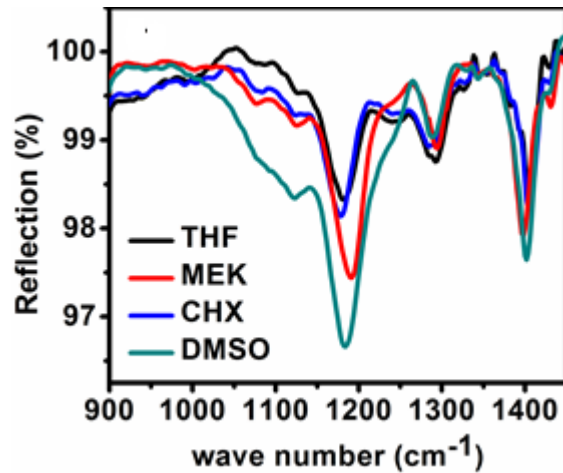
Deepa Singh^{a,b}, Deepak^{a,b} and Ashish Garg^{a,b}*

^{a,b}Department of Materials Science and Engineering

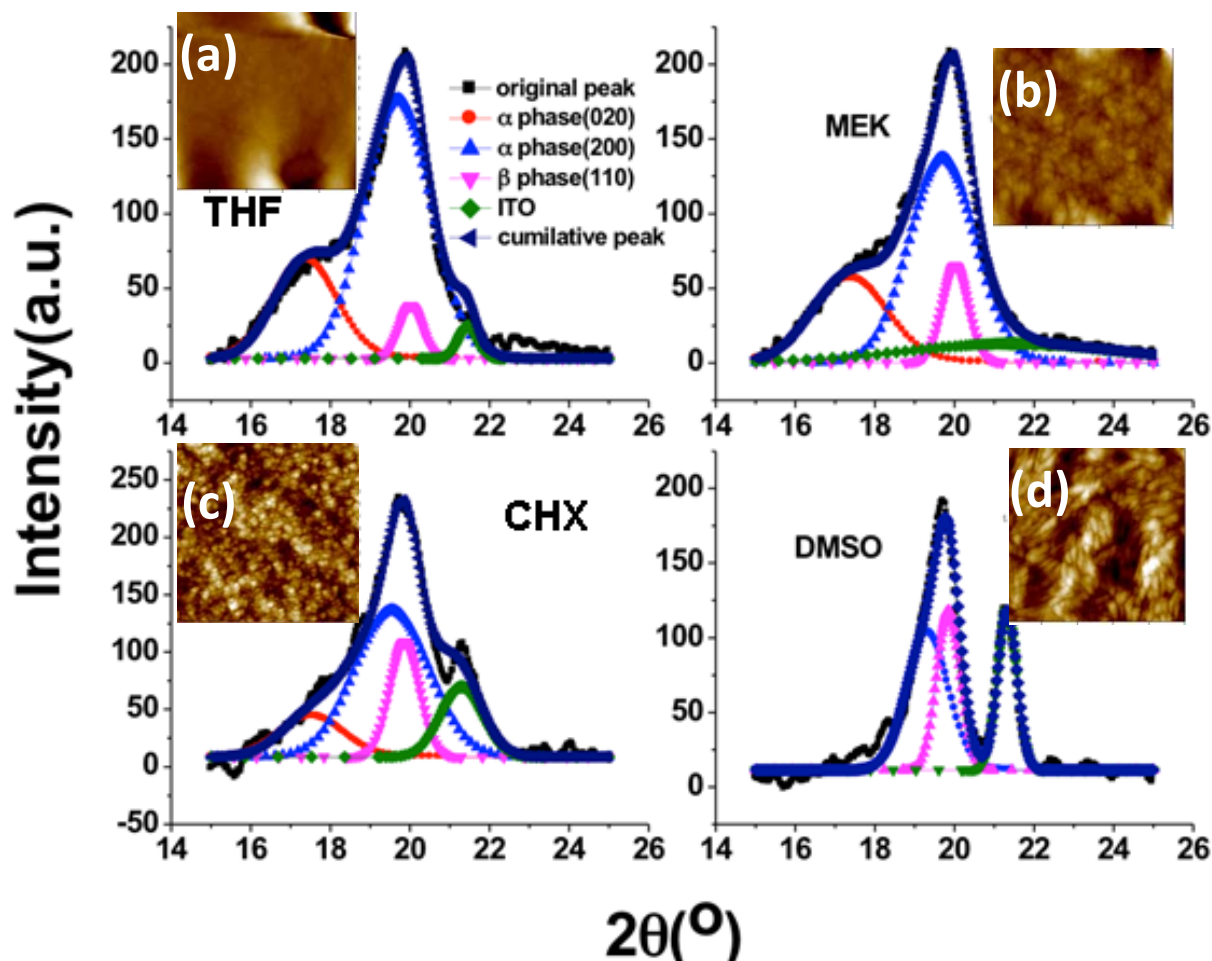
^{a,b}Samtel Center for Display Technologies

^{a,b}Indian Institute of Technology Kanpur, Kanpur 208016

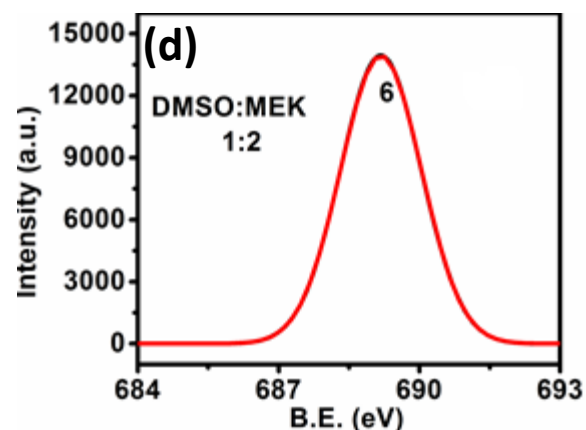
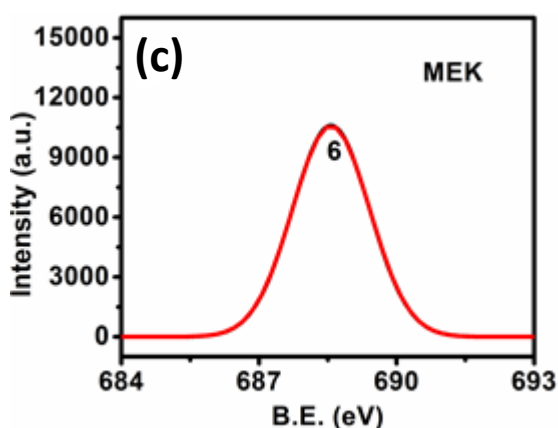
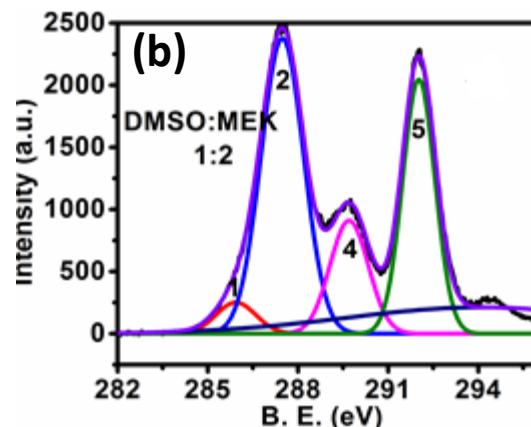
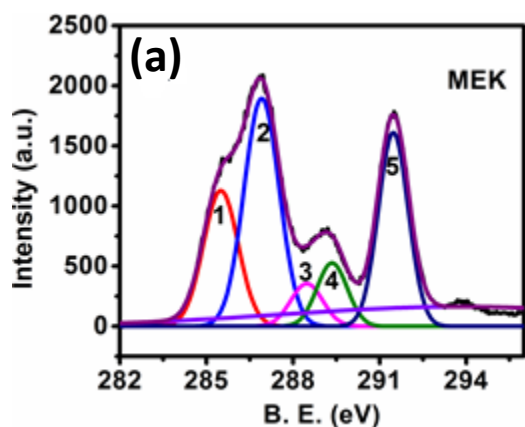
Email: deepas@iitk.ac.in



Supplementary figure S1: Fourier transform infrared (FTIR) spectroscopy of annealed P(VDF-TrFE) films on UV-ozone treated ITO substrate from various solvents. In orthorhombic β -PVDF, the molecular chains are aligned along the *c*-axis and CF_2 dipoles are parallel to polar *b*-axis. For the best performance of the ferroelectric metal-insulator-metal (MIM) capacitors, the polymer chains (*c*-axis) should lie in the substrate plane whilst the polar *b*-axis should be oriented in the direction as close as possible to the perpendicular to the substrate plane. The infrared absorbance should be zero when the electric field vector of the incident beam and the transition dipole moments of the materials are normal to each other. In the FTIR experiment, infrared beam is perpendicular to the sample surface plane i.e. the electric field of the infrared beam is nearly within the plane of the film. The absorption band at 1296 cm^{-1} of polar *b*-axis is lowest in DMSO derived films and largest in THF derived films while absorption band at 1400 cm^{-1} , corresponding to the wagging vibration of CH_2 with dipole transition moments parallel to the chain *c* axis and at 1187 cm^{-1} (dipole transition moments parallel to *a*-axis) is largest in DMSO derived films and lowest in THF derived films. This indicates that the polar *b*-axis of P(VDF-TrFE) crystals has better degree of inclination towards the sample normal with *c*-axis lying in the plane of sample surface in DMSO samples. This orientation of molecules in DMSO-derived films leads to the largest polarization values at lower coercive voltages, latter due to easier domain switching and larger grain size. MEK derived films also have similar *b/c* ratio but lesser *b/a* ratio as compared to CHX derived films. That is why both the films have comparable polarization values with MEK films having slightly lower E_c than CHX films. Further THF films, yield lowest polarization and largest E_c .



Supplementary figure S2 shows the XRD scans of as-deposited P(VDF-TrFE) films (without post annealing) between 2θ range of 15-25°. We note that there are two peaks corresponding to nonferroelectric α -phase: the most prominent peak (020) and a weaker peak (200). Both of these peaks are the strongest in THF films and the weakest in DMSO films. On the other hand, the (110) peak of ferroelectric β -phase becomes stronger as dipole moment of the solvent increases i.e. is the strongest in DMSO films. These results suggest that β -phase proportion is the highest for DMSO films whilst α -phase dominates in THF derived films and clearly prove that increased dipole moment of solvents favors extended chain formation and crystallization of β -phase of P(VDF-TrFE) in its thin films resulting in improved ferroelectric properties.



Supplementary figure S3: Deconvolution of C1s and F1s spectra of (a, c) MEK and (b, d) co-solvent (DMSO:MEK :: 1:2) derived films showing various contributions to the spectra. The C1s spectra of co-solvent derived films composed of peaks originated from the C-C/CH (peak 1), CH₂ (peak 2), CHF (peak 4) and CF₂ (peak 5) [1]. In MEK derived films, an extra peak of semi-ionic C-F (peak 3) bonds is also present. C1s spectra (b) also shows an increase in the intensities of CH₂, CF₂ and CHF and a fading away of C-C bond in co-solvent derived films suggesting higher F and H content in these films. Peak 6 denotes the CF₂ bond in F1s XPS spectra.

Reference:

[1]. D. Mandal, K. Müller, K. Henkel and D. Schmeißer, Applied Surface Science 261 (2012) 209.