

## Supplementary Information

### Degradation and Nano-Patterning of Ferroelectric P(VDF-TrFE) Thin Films with Electron Irradiation

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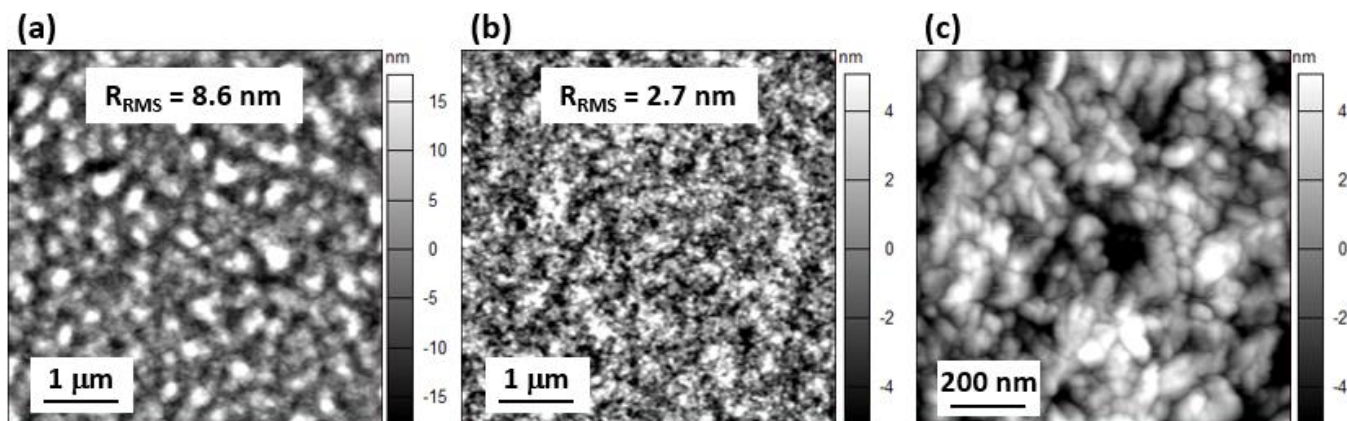
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#### S1 - Surface topography of P(VDF-TrFE) films

Fig. S1a and b are the AFM surface topography scan of P(VDF-TrFE) films prepared at different temperatures. By increasing the ambient temperature to 60 °C, the solubility of P(VDF-TrFE) in the solvent was improved, and the surface roughness  $R_{\text{RMS}}$  was reduced from 8.6 nm to 2.7 nm. Fig. S1c is a higher-magnification image of the sample in Fig. S1b, showing the crystalline grains of P(VDF-TrFE).<sup>1</sup>

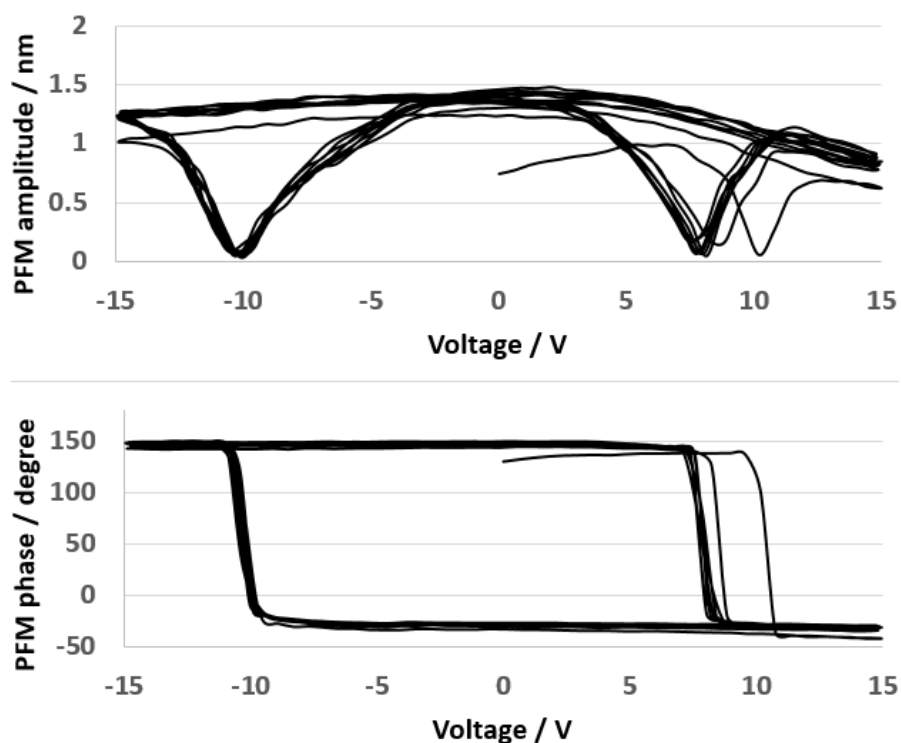


**Fig. S1.** Surface topography of P(VDF-TrFE) films prepared by spin-coating at different temperatures. (a) Room temperature spin coating. (b) and (c) 60 °C spin-coating.

#### S2 - Ferroelectric hysteresis of P(VDF-TrFE) films

The ferroelectric hysteresis of P(VDF-TrFE) was measured by AFM. Briefly, a voltage pulse was applied on the probe for poling the film, and a PFM measurement was performed immediately after the pulse. The pulse height was changed in the range between -15 V and +15 V in a triangular waveform at small steps

for several cycles. For PFM, drive amplitude was kept at 2.5 V and drive frequency was set at the resonance for signal enhancement. The result is in Fig. S2.

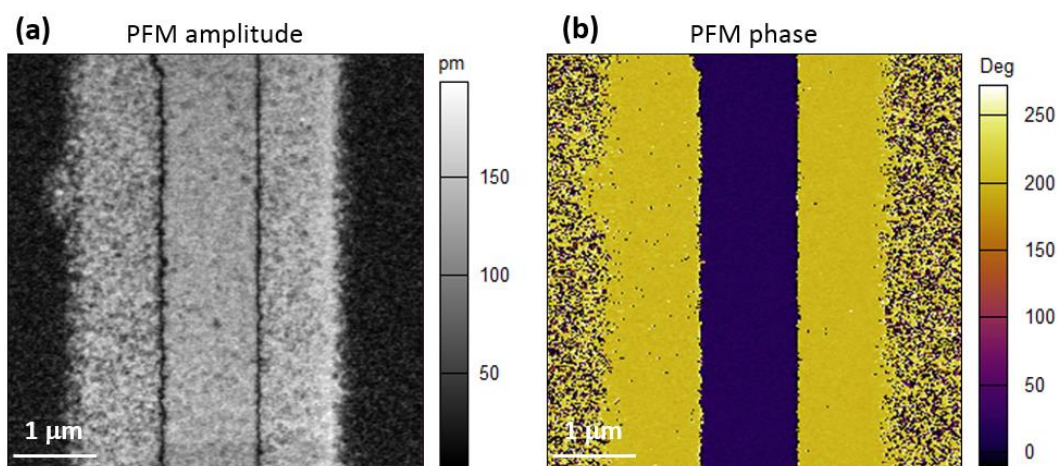


**Fig. S2.** Hysteresis data of P(VDF-TrFE). (a) PFM amplitude with varying poling voltage. (b) PFM phase with varying poling voltage.

The hysteresis loops show that the voltage for domain switching is about +8 V and -10 V. Based on the nominal thickness of those films, the coercive field is estimated to be about 100 MV/m. In comparison, values of coercive field have usually been reported to be 40-60 MV/m in the literature. The higher coercive field in our nanofilm may be due to the small size of crystalline grains (Fig. S1c). Kimura and Ohigashi<sup>2</sup> studied the polarization behavior of P(VDF-TrFE) films with different thickness, and found that the coercive field of films less than 100 nm thick was higher than that of thick films. The value was 40 MV/m for an 850 nm film and about 115 MV/m for an 80 nm film. Kimura and Ohigashi explained that the crystallites in thin films are much smaller than those in thick films, and smaller crystallites have a higher density of crystalline defects. Defects impede the domain growth during the poling process, and therefore increase the coercive field.

### S3 - Effect of Au etchant

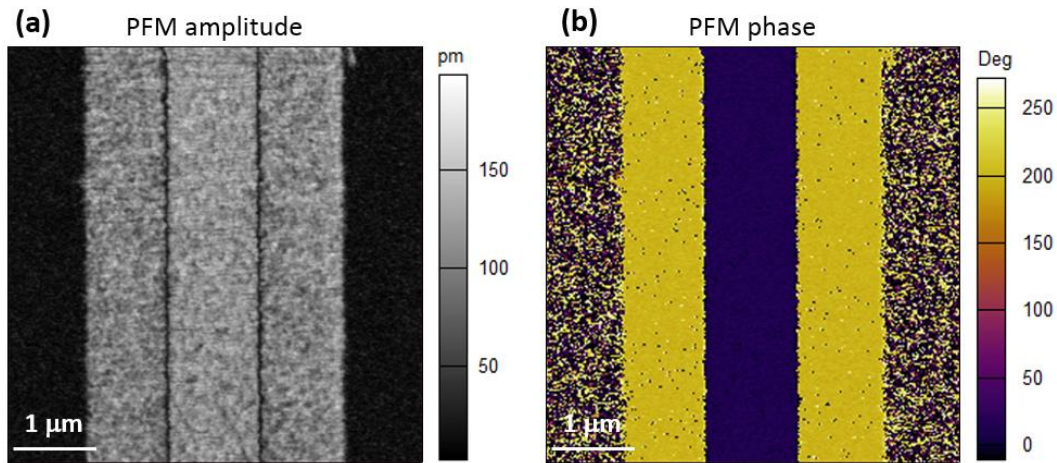
After Au deposition, the film was soaked in a wet etchant containing potassium iodide and iodine (GE-6, Transene Company) for 1 min to remove the Au layer, and then rinsed in deionized water and dried. In order to ensure that the etchant is compatible with P(VDF-TrFE), we put a film without Au coating in the solution for the same period of time. After cleaning, the film was tested by PFM. Result in Fig. S3 shows that the film had strong PFM signals, similar to an as-prepared film.



**Fig. S3.** PFM (a) amplitude and (b) phase images of a P(VDF-TrFE) film after contact with a wet Au etchant for 1 min. The film had no Au coating on it before it was immersed in the solution.

#### **S4 - Effect of thermal evaporation of Au**

To confirm that the loss of ferroelectricity in Fig. 1e and 1f was due to the e-beam instead of heat or Au atom flux in the evaporator, we used a thermal evaporator to deposit 60 nm Au on a P(VDF-TrFE) film. The Au layer was removed subsequently by the same etchant, and the film was poled through the same procedure and scanned by PFM. As shown in Fig. S4 below, the poled area has a strong PFM amplitude and a phase difference of about  $180^\circ$  between the two regions with opposite poling directions. Therefore, the thermal evaporation process did not affect the ferroelectric property of the film much, which implies that the heat or the Au atoms were not the cause of damage.

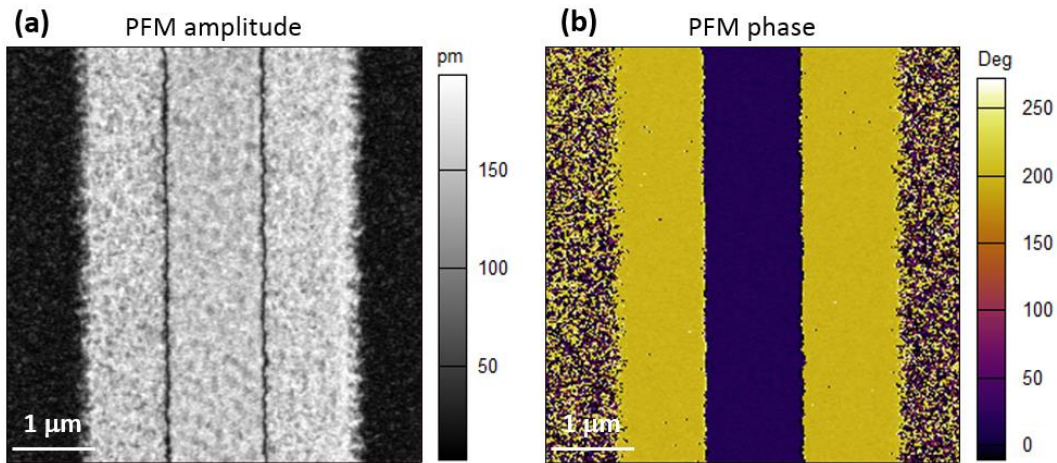


**Fig. S4.** PFM (a) amplitude and (b) phase images of a P(VDF-TrFE) film after Au deposition in a thermal evaporator.

### S5 - Effect of x-ray irradiation

P(VDF-TrFE) in the e-beam evaporator was exposed to both 8 keV BSE and 2.1 keV characteristic x-ray of Au. The possible effect from x-ray was studied by using an x-ray diffractometer (XRD) as an x-ray source. The x-ray is from Cu  $K_{\alpha}$  emission line and has an energy of 8 keV, which is more energetic than the x-ray in the evaporator. The photon flux density was determined to be  $3.3 \times 10^{13} \text{ sec}^{-1} \cdot \text{m}^{-2}$  on the plane normal to the beam, giving a power density of  $42 \text{ mJ} \cdot \text{m}^{-2}$ . A P(VDF-TrFE) film was placed in the XRD with an x-ray incidence angle of  $30^{\circ}$ . After 40 min of exposure, the film still had good ferroelectric property, Fig. S5.

However, radiation damage depends on the dose. Bhattacharya *et al.*<sup>3</sup> showed that the power density of x-ray was comparable to that of BSE in their e-beam evaporator, in the order of several  $\text{mJ} \cdot \text{cm}^{-2}$  and several tens of  $\text{mJ} \cdot \text{cm}^{-2}$ , which is significantly higher than the x-ray power density in our XRD system. On the other hand, x-ray intensity in different e-beam evaporation systems can vary a lot due to different acceleration voltage, beam current, chamber geometry, and target metal; in addition, the Au layer deposited on the P(VDF-TrFE) film could have absorbed some x-ray. Therefore, the actual x-ray dose received by the film in the evaporator is unknown, and the role of x-ray in the loss of ferroelectric property is not clear yet.

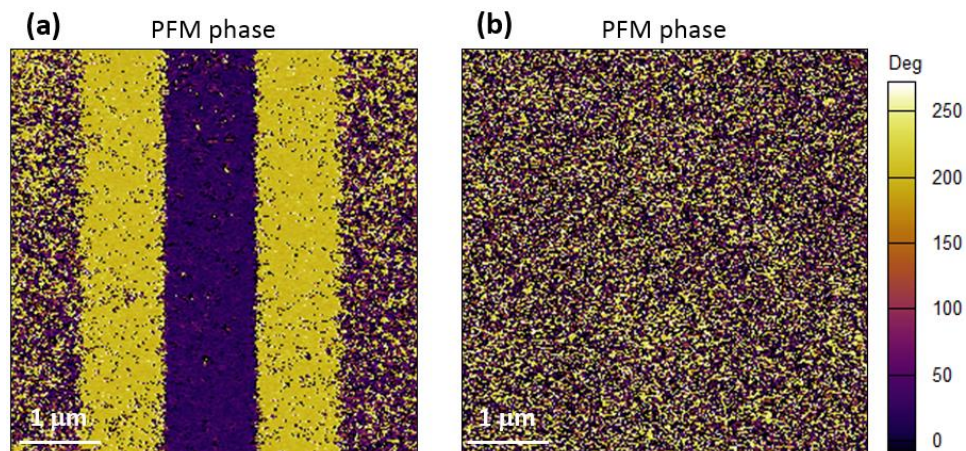


**Fig. S5.** PFM (a) amplitude and (b) phase images of a P(VDF-TrFE) film after being irradiated with 8 keV x-ray in an XRD system.

### S6 - Change of PFM phase over time

From the unpoled region of Fig. 2b and the whole area of Fig. 2d, we noticed that the 8 kV SEM scan had a side effect on the P(VDF-TrFE) film that the PFM phase became mainly around  $0^\circ$ .

PFM images in Fig. 2 were obtained within one hour after the SEM treatment. The same samples were tested by the same PFM procedure 7 days later. Fig. S6a below is the PFM phase map of the sample with 1 min SEM scan, and Fig. S6b is from the sample with 5 min SEM scan. The unpoled region in Fig. S6a and the whole area of Fig. S6b had a random mixture of different phases, similar to Fig. 1f. Therefore, the dominating phase around  $0^\circ$  in Fig. 2 might have been due to the electrostatic effect from trapped charges on the surface of the film, and such an effect disappeared after the charges had dissipated.



**Fig. S6.** PFM phase images of P(VDF-TrFE) films with (a) 1 min SEM treatment and (b) 5 min SEM treatment. Images were obtained 7 days after the SEM treatment.

## References

1. W. Li, Y. Zhu, D. Hua, P. Wang, X. Chen and J. Shen, *Appl. Surf. Sci.*, 2008, **254**, 7321-7325.
2. K. Kimura and H. Ohigashi, *Japanese journal of applied physics*, 1986, **25**, 383-387.
3. P. K. Bhattacharya, A. Reisman and M. C. Chen, *J. Electron. Mater.*, 1988, **17**, 273-283.