Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

Surface charge dynamics on air-exposed ferroelectric $Pb(Zr,Ti)O_3(001)$ thin films

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The effect of electron irradiation on the surface

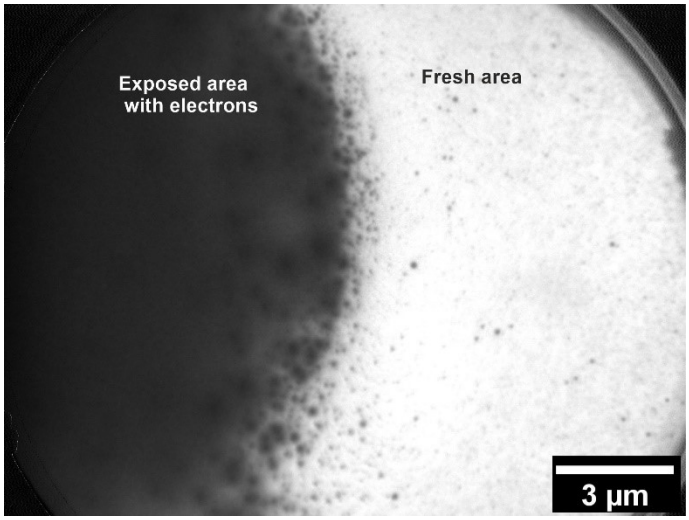

Figure SI1 – LEEM Image (E_0=21 eV) proving the charging effect of electron irradiation on exposed areas (dark contrast). Fresh area shows only small, localized domains.

Alignment of domains upon X-ray + electron exposure

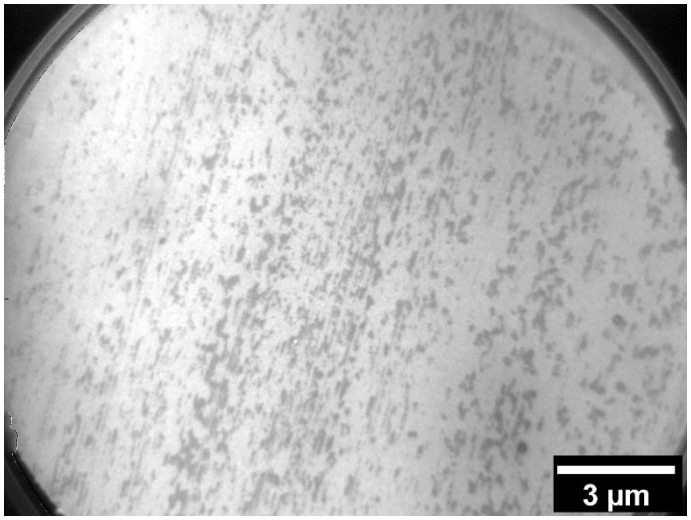

Figure SI2 – LEEM Image (E_0=21 eV) proving the alignment of radiation exposed contrast domains, in a 20 µm FOV.

Recovery of the LEEM contrast after 12 h in UHV

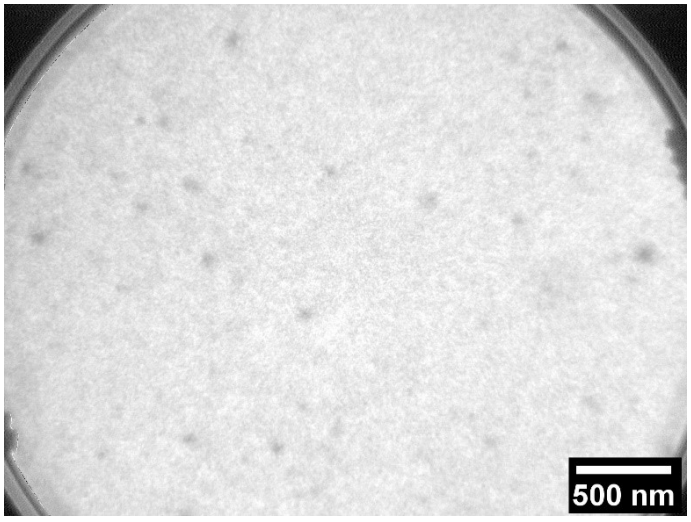

Figure SI3 – LEEM Image (E_0=20 eV) recorded on the same area as Fig. 1(c,f) in the main text, after the sample being kept in UHV for 12 h in the measurement position. The previous observed contrast is lost.

XPS results table

XPS line	BE (eV)
Pb 4f (SOS: 4.70 eV BR:1.30)	
Pb1 ($4f_{7/2}$)	138.87 (100%)
O KL_1L_{23} Auger	138.62 (KE = 494.8 eV)
Zr 3d (SOS: 2.31 eV BR:1.5)	
Zr1 ($5d_{5/2}$)	181.98 (90 %)
Zr2 ($5d_{5/2}$)	182.61 (10 %)
Ti 2p (SOS: 5.37 eV BR: 1.95)	
Ti1 ($2p_{3/2}$)	456.34 (63 %)
Ti2 ($2p_{3/2}$)	457.12 (37 %)
O 1s	
O1	529.43 (83 %)
O2	530.73 (10 %)
O3	531.48 (7 %)
C 1s	
C1	283.54 (14 %)
C2	284.58 (67 %)
C3	285.82 (15 %)
C4	286.88 (4 %)

Table 1 – Relevant information extracted from the fitting of XPS spectra recorded with hν=650 eV represented in the main text in Fig. 5. The uncertainty in the BE scale is in the order of ±0.15 eV.

Composition analysis determined by XPS

[Pb]:[Zr+Ti]	[Zr]:[Zr+Ti]	[O]:[Zr+Ti]
2.74	0.45	2.99

Table 2 – Results of the intensity analysis of core level spectra. The ratios are computed from integral intensities of photoemission spectra, normalized with respect to the integration time, instrument transmission function and photoelectron cross-section values. The ratios are fairly close to the composition of the target used in PLD, $PbZr_{0.2}Ti_{0.8}O_3$ except Pb which manifests an excess that was previously reported in the case of a 100 nm PZT[1]. The variance from the expected values

could arise from IMFP and termination effects are not taken into consideration, as well from photoelectron diffraction effects.

Survey spectrum

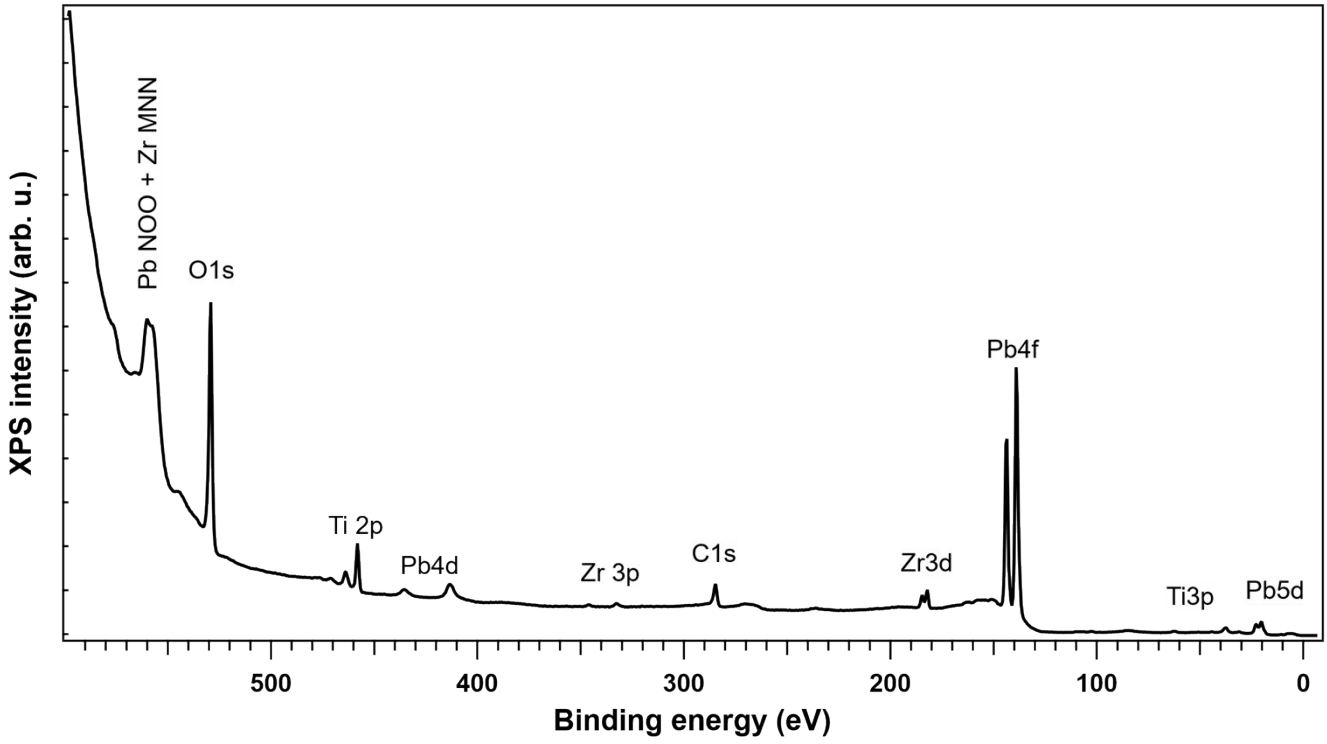

Figure SI4 – Photoemission survey spectrum recorded with photon energy hν=650 eV on 100 nm $Pb(Zr,Ti)O_3(001)$ sample in "as introduced" state.

XPS Fitting

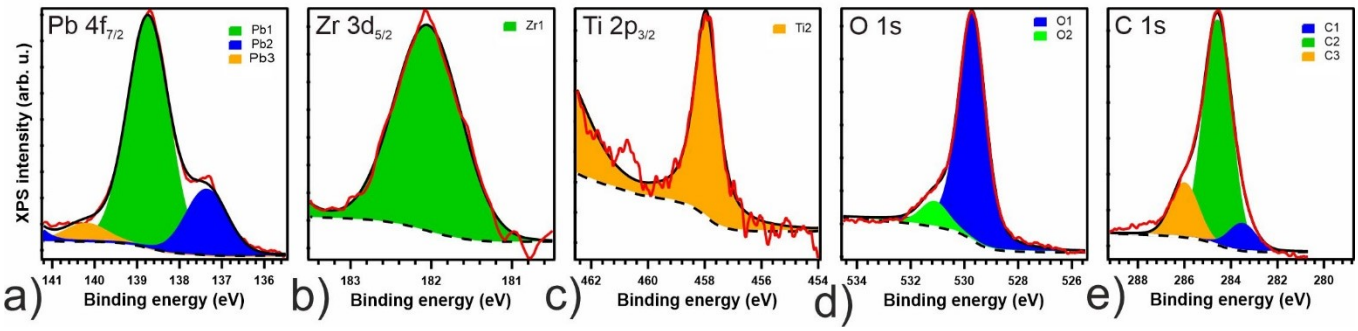

Figure SI5 – Detailed fitting of spectra extracted at t = 100 s moment for the time-resolved series representing in Fig. 6 in the main text on a fresh area representing (a) Pb 4f; (b) Zr 3d; (c) Ti 2p; (d) O 1s; (e) C 1s.

Time evolutions of amplitudes during X-ray irradiation

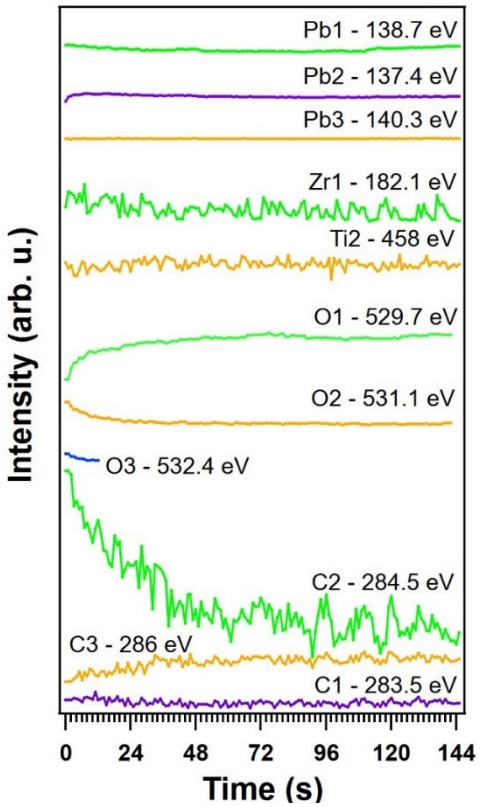

Figure SI6 – Amplitudes evolution as function of irradiation time of each component of the principal XPS profiles from Fig. 6 in the main text.

Time evolutions of binding energies during X-ray irradiation

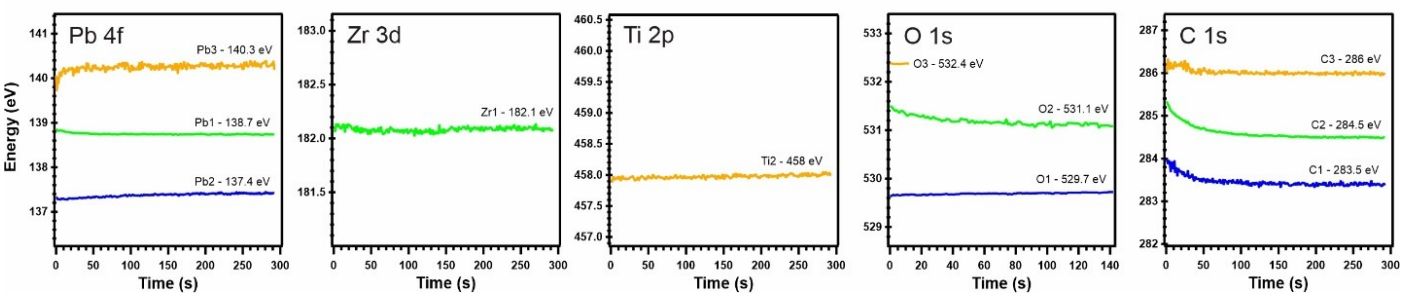

Figure SI7 – Binding energies evolution as function of irradiation time of each component of the principal XPS profiles from Fig. 6 in the main text.

Details about X-ray induced damage on Pb 4f core level

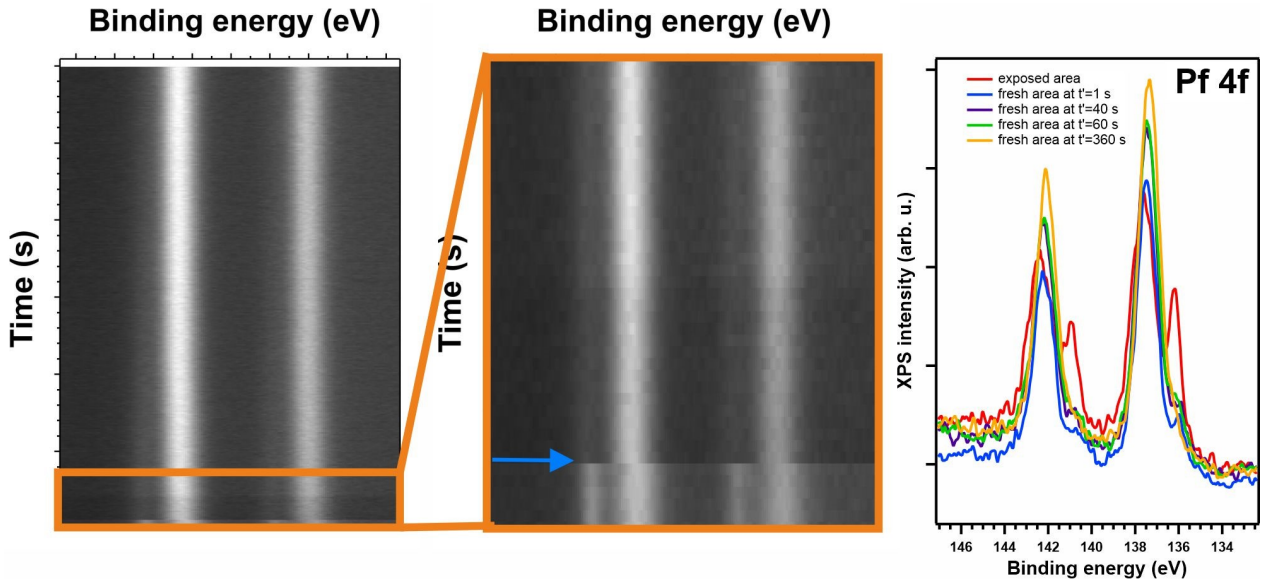

Figure SI8 – Time evolution of Pb 4f core level on a different area than the one discussed in the main text, measured with hν=215 eV.

This area was previously exposed both for measuring LEEM I-V (electrons up to 60 eV) and XPEEM survey (photons with hν=650 eV). The image proves that pre-exposed areas show a strong peak at lower binding energies. This peak is visible also on fresh areas, but gets faded in time. After 360 s, it cannot be distinguished anymore from the main peak.

Refrences

1. C. M. Teodorescu, L. Pintilie, N. G. Apostol, R. M. Costescu, G. A. Lungu, L. Hrib, L. Trupină, L. C. Tănase, I. C. Bucur and A. E. Bocîrnea, *Physical Review B*, 2017, **96**.