Ferroelastic twin angles at the surface of $CaTiO_3$ (001) observed by Photoemission Electron Microscopy

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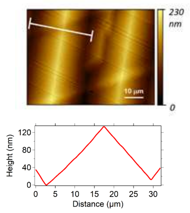
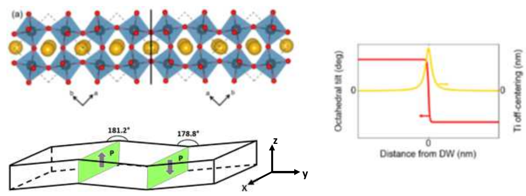
Abstract

We have used photoemission electron microscopy imaging at threshold to quantify the physical topography of the $CaTiO_3$ (001) surface with its characteristic valley/ridge factory roof-like structure. By off-centering the aperture in the diffraction plane from the optical axis, image contrast is enhanced by collecting high angular photoelectrons in a quasi dark field mode. Higher off-centering improves dramatically the domain contrast but also introduces artefacts resulting in higher apparent threshold values. Moderate off-centering is therefore to be preferred in order to estimate the respective contributions of physical and electrical topography to the observed contrast. Using a simple geometrical approach relating the take-off angle to angles inside the electron optics allows quantification of the tilt angle of a domain from measurement of the photoemission threshold.

Surface twins



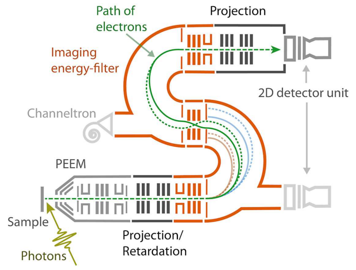
AFM image of $CaTiO_3$ (001) surface and profile along the solid white line



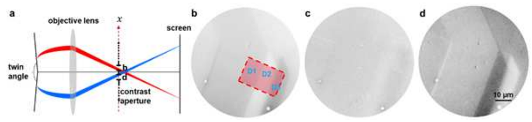
Twinning in $CaTiO_3$ showing emergence of domain wall polarity and factory roof topography

Experiment

- ScientaOmicron NanoESCA II
- $CaTiO_3$ (001) (SurfaceNet GmbH)
- 5 mins ozone before insertion
- Anneal 30 minutes 650°C in vacuum
- $T_{measure}$ = 300 °C
- hν = 21.2 eV (He I)
- Field of View 39 µm
- Δx = 50 nm
- ΔE = 0.1 eV
- CA ϕ150 µm

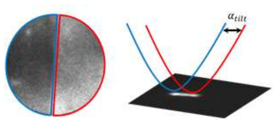


Angular sensitivity of CA

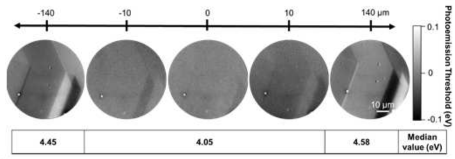


a. schematic of the contrast aperture angular selection. PEEM images at E-Ef = 4.3 eV with contrast aperture (CA) off-centered right **b.**, centered **c.** and off-centered left **d.** The red box is the analyzed surface tilt angle area with three domains labelled D1, D2 and D3.

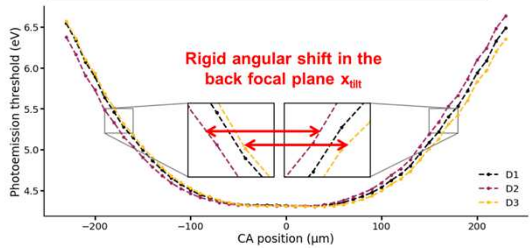
Real and reciprocal space image of $CaTiO_3$ domains with a twin angle α_{tilt}. Tilt induces an angular shift in the threshold of the free electron parabolae in ARPES



Threshold shift

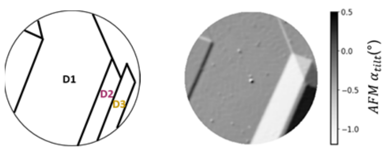


Pixel by pixel threshold map for five different CA positions x



Domain averaged photoemission threshold for x = −230 to 230 µm
Rigid CA shift x_{tilt} of threshold curve for domains with different surface tilt α_{tilt}.
Apparent threshold energy varies with $\cos^2\theta$, where θ is the take-off angle.

Twin angles AFM



Topography analysis of the twin angles by Atomic Force Microscopy (AFM). The resulting pixel-by-pixel height is used to calculate the surface tilt map shown above

AFM → angles for D2 and D3
Fit the mean threshold curves D2 and D3 to extract an x_{tilt}
Calculate x-α conversion

$$\alpha_{tilt} = \frac{\alpha_{D2} - \alpha_{D3}}{x_{tilt_{D2}} - x_{tilt_{D3}}} x_{tilt} \Leftrightarrow \alpha_{tilt} = 0.133\, x_{tilt}$$

Off centering – tilt angle

From phase conservation $\sqrt{E_0} r_0 \sin\alpha_0 = \sqrt{E_i} r_i \sin\alpha_i$

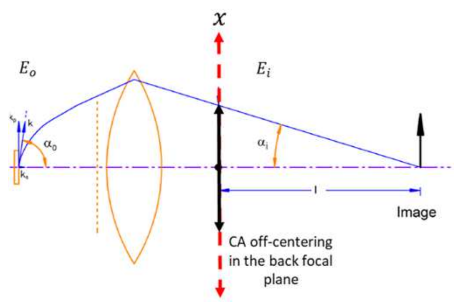
Assume $M = \frac{r_i}{r_0}, \alpha_0 = 90°$

For small angles $\sin\alpha_i \approx \frac{x + r_{ap}}{l}$

Twin angle → add x_{tilt} to x (CA position)

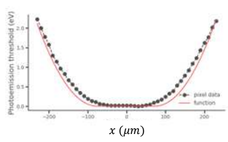
$$E_{Thr} = E_i M^2 \left(\frac{x + r_{ap} + x_{tilt}}{l}\right)^2$$

E_{Thr} the threshold energy
E_i the PEEM column energy (2000 eV)
M the magnification at the 1st intermediate image (35)
l the distance between the bfp and the first intermediate image
x the contrast aperture off centering wrt the optical axis



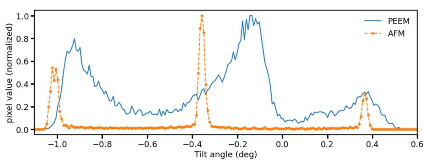
domains	α (AFM)	x_{tilt} (PEEM)	α-x conversion
D2-D3	$\alpha_{D4} = -1{,}006°$ $\alpha_{D5} = +0{,}368°$	$x_{tilt_{D4}} = -8{,}392\ \mu m$ $x_{tilt_{D5}} = +1{,}962\ \mu m$	0.133

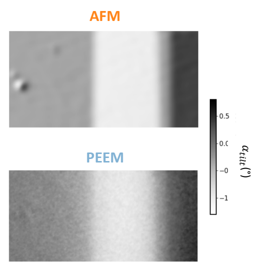
Pixel by pixel angle maps



$$E_{Thr} = E_i M^2 \left(\frac{x + r_{ap} + x_{tilt}}{l}\right)^2$$

Fit to the threshold curves at each pixel to extract x_{tilt} and hence an angle α_{tilt}





AFM and PEEM surface tilt maps are qualitatively similar
D1 AFM/PEEM difference due to the PEEM lens alignments adjustments

Conclusions

- PEEM imaging at photoemission threshold to quantify surface twin angles of $CaTiO_3$ (001)
- Off-centering the contrast aperture from the optical axis enhances image contrast due to physical topography in a near dark field mode
- Relating the take-off angle to the angles inside the PEEM allows to quantify the tilt angle of a domain surface from measurement of the photoemission threshold
- To be consolidated with a wider range of twin angles

Nataf et al. *Phys. Rev. Mater.* **1**, 074410, (2017)
Zhao et al. *Phys. Rev. Mater.* **3**, 043601 (2019)

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