

Thin-film XSW investigation of polarization in ferroelectric PbTiO₃ films

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Introduction

Ferroelectricity in solids originates from the relative shifts of the anion and cation atomic sublattices [1] resulting in a net dipole moment (spontaneous polarization) along a certain crystallographic axis. Under an applied electric field, the direction of the polarization vector can be switched. This bi-stable property, in conjunction with thin-film heteroepitaxy, can provide the basis for nonvolatile random access memory (NVRAM) [2]. Electrical measurements can be used to study such structures on a macroscopic scale. In our study, we use the thin-film x-ray standing wave (XSW) method to probe the polarity of as-grown PbTiO₃ (PTO) ferroelectric thin films on an atomic scale.

Method

In a traditional XSW [3] experiment, a modulation in the fluorescence signal from an atomic species in the overlayer is monitored while scanning in angle through a strong dynamical Bragg diffraction peak of the substrate crystal. This modulation is due to the phase shift of the XSW, which in turn is created by the superposition of the incident and Bragg-reflected x-ray plane waves, see Figure 1(a). This technique has been used successfully for decades to pinpoint the lattice positions of adsorbate atoms on perfect

crystal substrates. In general, this traditional method is not applicable to thin-film overlayers since the period of the atomic layers in the film would not in general be equal to the period of the XSW probe generated by the substrate diffraction planes. For this case, we generate the XSW by a weak kinematical Bragg diffraction from the film itself as depicted in Figure 1(b) [4]. Since the thin-film reflection will be weak, the modulation in the fluorescence signal will also be weak. Therefore, a high-intensity x-ray source is required to observe this phenomena with the required counting statistics to extract atomic-scale structural information from the analysis of the data.

Results and Discussion

The first ferroelectric system examined by the thin-film XSW technique was PbTiO₃ [5]. PTO films of 100 Å, 200 Å, and 400 Å were grown on single crystal SrTiO₃(001) substrates by metal-organic chemical vapor deposition (MOCVD). The (001) XSW data for the 400 Å film is shown in Figure 2. Both the Pb L and Ti K fluorescence signals were monitored while scanning through the PTO (001) Bragg peak. The Pb signal was collected at an incident beam energy of 13.5 keV and the Ti signal at 8 keV. To collect Ti fluorescence from the PbTiO₃ film, but not from

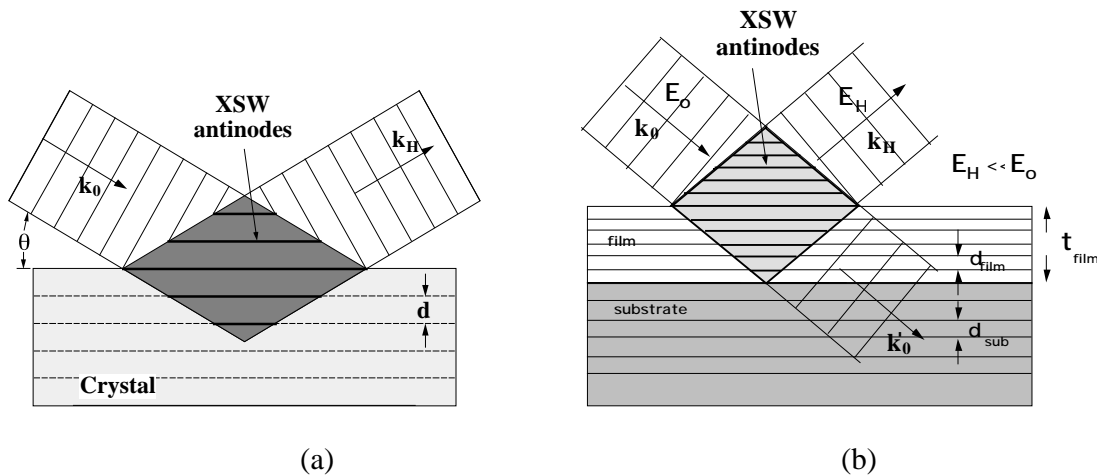


Figure 1: (a) The standard XSW method [3]: the standing wave field is generated by two-beam dynamical diffraction in a perfect crystal within an extinction length $L_{\text{ex}} \sim 1-10 \mu\text{m}$ (depending on the reflection order). The intensity of the reflected wave is nearly as strong as the incident wave and the visibility of interference fringes is $V \sim 1$. (b) Thin-film XSW method [4]: the standing wave field is generated inside the thin film with thickness $t_{\text{film}} \ll L_{\text{ex}}$, the intensity of the diffracted beam is $I_H/I_0 \sim 10^{-4}$ and the visibility of interference fringes is $V \sim 10^{-2}$.

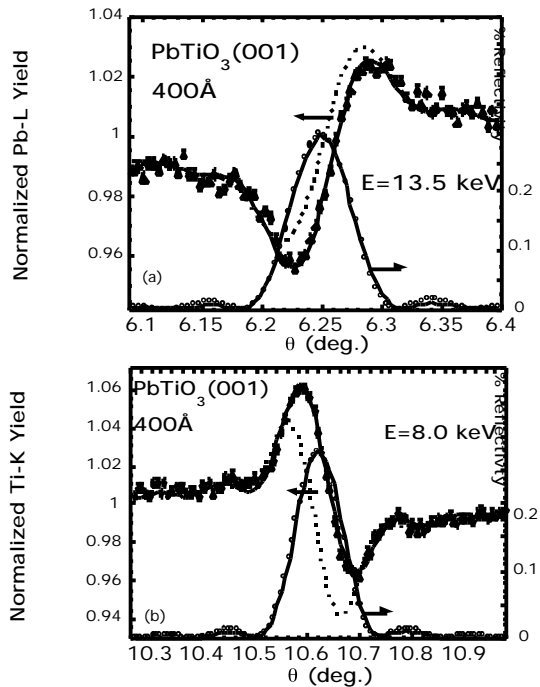


Figure 2: The experimental XSW data measured from a 400 Å thick PbTiO_3 film. (a) The angle dependence of the normalized Pb-L fluorescence yield and reflectivity at the PbTiO_3 (001) reflection at an incident energy of 13.5 keV; (b) the Ti-K fluorescence yield and reflectivity at the PbTiO_3 (001) reflection at 8 keV via the evanescent-wave technique. The best fits for the "up" and "down" polarities are shown as solid and dashed lines, respectively.

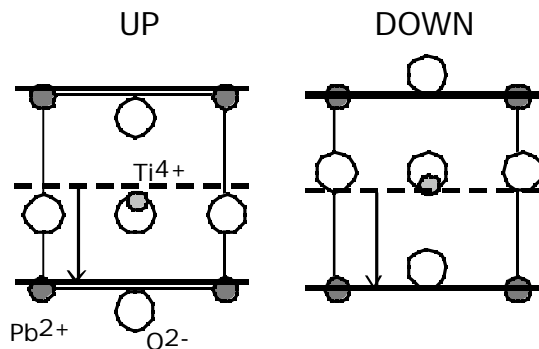


Figure 3: The a-axis projection of the PbTiO_3 tetragonal "up" and "down" perovskite unit cells. The solid lines represent the (001) diffraction planes and the dashed line represents the position of the XSW antinode on the low-angle side of the (001) Bragg reflection. The arrow marks the inward path that the XSW antinode follows as θ increases from the low- to the high-angle side of the (001) Bragg peak.

the SrTiO_3 substrate, fluorescence slits were employed to take advantage of the evanescent-wave technique.

Note that the Pb and Ti modulations are roughly counter-phase. This is due to the Pb and Ti atomic planes being separated by approximately one-half of a PTO (001) diffraction plane spacing. (See Figure 3.) On the low-angle side of the rocking curve, the antinodes start approximately on the Ti planes. As the crystal is rocked through the (001) reflection, the antinodes travel inward towards the Pb planes. Thus, the Ti signal peaks on the low-angle side and the Pb peaks on the high-angle side of the rocking curve. Based on the direct relationship between the phase of the XSW and the phase of the structure factor, it can be shown that the antinodes should pass through the Ti planes but not the Pb planes for the "up" case. Thus, the opposite should be true for the "down" case. The theoretical fitted curves in Figure 2 for the two models clearly show this behavior and indicate that the 400 Å as-grown PTO film is polarized up.

Acknowledgements

The technical support of the BESSRC-CAT and DND-CAT staffs is gratefully acknowledged. DND-CAT is supported in part by the State of Illinois under contract No. IBHE HECA NWU 96. This work was supported by the DOE under contracts W-31-109-ENG-38 to ANL and DE-F02-96ER45588 to M.J.B. and by NSF under contracts DMR-9632472 to the MRC and DMR-9632593 to M.J.B. at Northwestern University.

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