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Preparation and characterization of rhombohedral PZT thin films

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Epitaxial ferroelectric PZT (lead zirconium titanate $Pb(Zr_{0.6}Ti_{0.4})O_3$) thin films, that display a second order phase transition, have been produced on (100) $SrTiO_3$ substrates. The films, grown by off-axis RF magnetron sputtering, are uniform over large areas. Different x-ray diffraction techniques (Θ–2Θ, rocking curve and Φ-scan) reveal the high crystalline quality and strong epitaxial character of the films. Transmission electron microscopy (TEM) is used to characterize the roughness of the PZT/$SrTiO_3$ interfaces as well as their epitaxial behavior. TEM will also be used to study the ferroelectric domain wall properties close to the Curie point.

Some ferroelectric materials such as rhombohedral lead zirconium titanate $Pb(Zr_{0.6}Ti_{0.4})O_3$ (PZT) display a second order ferroelectric to paraelectric phase transition. In the ferroelectric state, the material is divided into domains of uniform spontaneous polarization, separated by domain walls. It has been shown that close to a critical point, the behavior of interfaces of two-dimensional systems differs drastically from that of three-dimensional systems, in particular it has been shown [1] that, unlike in three or more dimensions of space, the critical exponent describing the divergence of the interfacial thickness at a critical point is a non-universal function of the external field in contrast to the commonly accepted view that in the critical region, the interfacial thickness is proportional to the spontaneous fluctuations in the coexisting bulk phase. Unfortunately, experimental results are only available for three-dimensional systems.

With the idea to study a two-dimensional case, we produced rhombohedral PZT thin films in which we want to measure the domain wall thickness as a function of temperature by different transmission electron microscope (TEM) techniques such as high resolution transmission electron microscopy, electron holography and convergent beam electron diffraction (CBED).

In a first step, we prepared the ferroelectric thin films and analyzed their crystalline quality and epitaxial behavior by x-ray diffraction and TEM. The films were grown on (100) $SrTiO_3$ substrates by 90° off-axis RF magnetron sputtering with a substrate temperature of 540°C in an atmosphere of 30% oxygen and 70% argon at 200 mTorr [2]. The deposition rate is approximately 350Å per hour and the deposition is homogeneous over an area of about 3 cm x 3 cm.

The films of 10-200 nm thickness where then examined by x-ray diffraction. On Θ–2Θ diffractograms, the (001) and (002) reflections of PZT can be seen along with the (100) and (200) reflections of the substrate. The PZT peaks are extremely intense and narrow. The lattice parameter of PZT is found to be about 4.08Å which is consistent with previously reported thin film data [3]. The rocking curve full width at half maximum (FWHM) around the (001) reflection of PZT is 0.19° in comparison to FWHM values of 0.08°-0.09° for the single crystal $SrTiO_3$ substrate. We performed Φ-scans (azimuthal scans) on off-axis planes to analyze the epitaxial character of the films. Figure 1 shows the (110) $SrTiO_3$ and (011) PZT reflections for an azimuthal angle χ of 45°. Both, the substrate and the PZT exhibit a fourfold symmetry, the peaks are respectively aligned and very narrow which reveals a 'cube on cube' growth of the PZT films on the substrate and demonstrates a strongly epitaxial behavior.

TEM diffractions confirm the orientation of the films in the (001) direction as well as the lattice parameter value for the PZT thin film (4.08Å). Bright field and dark field TEM images show that the thickness of the film is homogeneous. A structure of vertical lines going from the substrate to the surface of the film, appear in regular distances of about 10-40 nm (Figure 2). Those lines could be a first indication for ferroelectric domain boundaries, but no further evidence can be given at this point. Possible reasons for the wave-like contrasts that can be seen at the interface, might be interfacial strain, domain adaptation or charge accumulation. High resolution transmission electron micrographs reveal that the $SrTiO_3$/PZT interface is very sharp and confirm that the PZT film is well aligned on the substrate lattice in the (001) direction.

In conclusion we successfully prepared PZT thin films by RF magnetron sputtering. Extensive x-ray analysis reveal the high crystalline quality and demonstrate the epitaxial growth of the films. TEM analysis confirms the crystalline quality and give a first indication for the presence of ferroelectric domains.

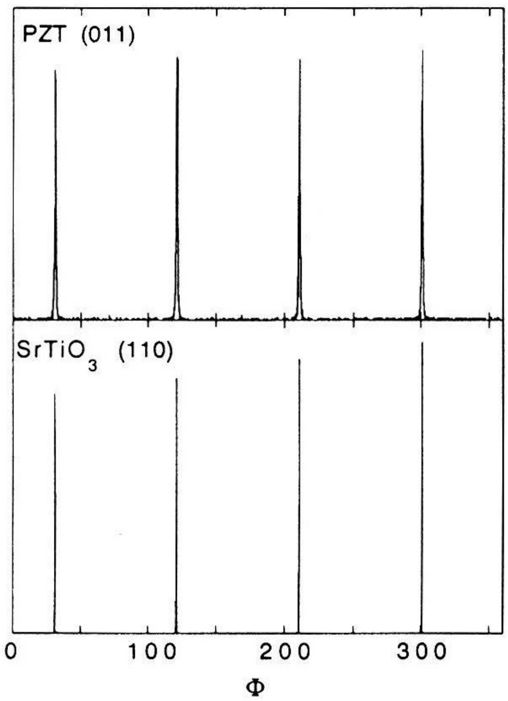

Figure 1: Φ-scan on PZT (011) and $SrTiO_3$ (110) planes

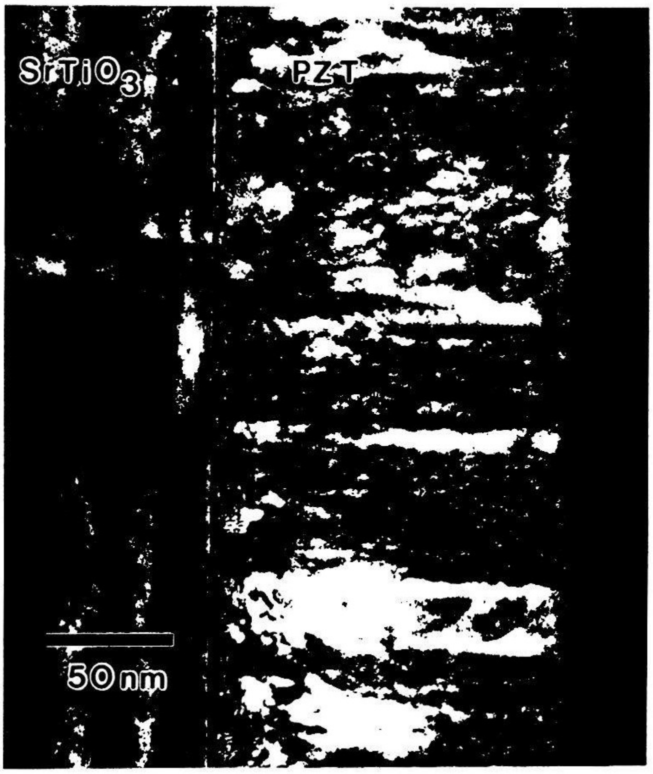

Figure 2: Dark field image of a PZT thin film on $SrTiO_3$

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