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Fine tuning epitaxial strain in ferroelectrics: $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ on DyScO_3

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Epitaxial strain can be efficiently used to modify the properties of ferroelectric thin films. From the experimental viewpoint, the challenge is to fine-tune the magnitude of the strain. We illustrate here how, by using a suitable combination of composition and substrate, the magnitude of the epitaxial strain can be controlled in a continuous manner. The phase diagram of $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ films grown epitaxially on (110)- DyScO_3 is calculated using a Devonshire–Landau approach. A boundary between in-plane and out-of-plane oriented ferroelectric phases is predicted to take place at $x \approx 0.8$. A series of $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ epitaxial films grown by molecular beam epitaxy shows good agreement with the proposed phase diagram. © 2010 American Institute of Physics. [doi:10.1063/1.3532103]

Modifying the properties of crystalline thin films using the epitaxial strain induced by the substrate as an adjustable parameter is known as *strain engineering* or *strain tuning*.¹ This has captured the interest of several condensed matter communities because ordering temperatures can be increased, physical responses can be enhanced, and even extra functionalities can be added to thin films utilizing epitaxial strain.^{2–4}

Ferroelectric materials are especially suitable for such strain studies due to their strong coupling between strain and electrical polarization. However, despite some very impressive experimental results,^{5–9} the realization of strain engineering in ferroelectrics lags behind the predictions and it is difficult to fully employ the wealth of interesting possibilities suggested by the theorists.^{10–16} The limited number of suitable substrate materials is an important factor in this. Two substrates that have a good lattice match with many functional perovskites are SrTiO_3 and DyScO_3 , but there is more than a percent difference between their (pseudo)cubic lattice parameters¹⁷ [see Fig. 1(a)]. This difference is too large if one aims to establish an experimental temperature-strain (T-u) phase diagram. Moreover, a too large mismatch between film and substrate will induce various relaxation mechanisms that will prevent elastic strain accommodation.^{18,19} Most importantly, only if the strain can be tuned continuously, we will be able to access the theoretically predicted phases¹⁶ and/or properties,^{20,21} which exist only for a narrow region of strain values.

In this letter we combine the epitaxial strain imposed by the substrate with compositional variations of the film in order to change the magnitude of the strain in a continuous manner. For that we use Sr-substituted PbTiO_3 thin films grown on DyScO_3 substrates. Various reasons led us to choose these materials. The lattice parameters of $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$, as well as the Curie temperatures T_C , vary linearly between the two end members of the solid solution^{22–24} [see Fig. 1(b)]. Moreover, above room temperature, the bulk solid solution does not show other phases than the well-known paraelectric cubic and ferroelectric tetrago-

nal phases of PbTiO_3 .²⁴ In this way we can use a phenomenological Landau–Devonshire (LD) approach to calculate the phase diagram of $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ epitaxial thin films on (110)- DyScO_3 . The substrate was chosen because the strain state of $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ films epitaxially grown on (110)- DyScO_3 can be changed from (slightly) compressive to tensile by varying the Sr-content. This is in agreement with other reports showing that the polarization of epitaxial PbTiO_3 films on (110)- DyScO_3 is predominantly

FIG. 1. (a) Comparison of the lattice parameter of SrTiO_3 and DyScO_3 substrates and $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ thin films. (b) Transition temperature of $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ vs the Pb content x . The dotted line is calculated from LD theory. The data points are taken from various literature sources (Refs. 22–24).

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FIG. 2. Phase diagram vs composition for $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ strained on DyScO_3 as calculated using LD theory. The top axis defines the “isostrain” lines in the composition vs temperature diagram.

out-of-plane,²⁵ whereas the polarization of epitaxial SrTiO_3 films on DyScO_3 is in the plane of the film.^{4,6,26}

The phase diagram of $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ on (110)- DyScO_3 was calculated including the epitaxial strain in the LD free energy expansion, as described by Pertsev *et al.*¹⁶ The composition-dependent Landau coefficients of $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ have been constructed as a linear combination of the well-known Landau coefficients of the end members, PbTiO_3 and SrTiO_3 , similar to Refs. 27–29. The Landau coefficients of the end members are those of Refs. 30 and 29, respectively.³¹

For the temperature dependent coefficient $a_1 = \alpha_1(T - T_C)$, the composition dependences of T_C and α_1 are treated separately. The misfit strain depends on both composition and temperature, because of differences in thermal expansion between film and substrate. As the thermal expansions for PbTiO_3 and SrTiO_3 are almost equal,³² the thermal expansion of $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ is assumed to be that of PbTiO_3 . The thermal expansion of DyScO_3 does significantly differ from that of $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$.¹⁷ The small anisotropy of 0.05% in the lattice parameters of the (110) DyScO_3 plane (3.945 Å versus 3.947 Å at room temperature) was neglected, and the average of the a and b lattice parameters was used as the in-plane lattice parameter in the calculations. This is justified by the results in Ref. 33 showing that Landau simulations on single domain PbTiO_3 and $\text{Pb}_{0.35}\text{Sr}_{0.65}\text{TiO}_3$ films give no qualitative difference in the phase diagram after including a substrate anisotropy as small as that of DyScO_3 .³³ Since the oxygen rotations present in SrTiO_3 below 105 K are not included in

the calculations, our results are not expected to be valid for $x < 0.5$.²⁹ Finally, the LD approach used here considers uniform polarization throughout the film; thus possible domain formation and polarization gradients are not taken into account in this approximation. The resulting free energy expansion was minimized with respect to the Cartesian components of the polarization (along the axes of the perovskite unit cell) to obtain a phase diagram as a function of Pb content (x).

The calculated phase diagram of $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ on DyScO_3 is shown in Fig. 2. The misfit strain goes from a very small compressive strain for pure PbTiO_3 to a tensile strain that increases with increasing Sr-content. The different strain values stabilize polarizations along different directions. For large x , $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ is predicted to be a c -phase ferroelectric, with the electrical polarization P perpendicular to the film plane, similar to that of PbTiO_3 . At lower x an aa -phase, with $P \parallel \langle 110 \rangle$, should be stabilized. In between these two, an intermediate r -phase is expected, in which the polarization points somewhere in between $\langle 001 \rangle$ and $\langle 110 \rangle$. The addition of Sr gives rise to the decrease in T_C .

To test our predictions, a series of $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ thin films with a thickness of 50 ML (20 nm) was grown on (110)- DyScO_3 using molecular beam epitaxy. The films were grown at a substrate temperature of 650 °C, with an adsorption controlled growth mechanism as described for PbTiO_3 .^{34–36} Sr substitution is obtained by providing a constant flux of atomic Sr for a certain amount of time t_{Sr} at each monolayer. Figure 3 shows the out-of-plane lattice parameter c , obtained from x-ray diffraction (XRD) 2θ - ω scans, versus the Pb content x . The lattice parameters were determined through simulation of the experimental data similar to Ref. 37. At large x , a lattice parameter larger than the pseudocubic lattice parameters of DyScO_3 ($c = 3.945$ Å) is observed in the films. For fully strained films and neglecting the small difference between the two in-plane lattice parameters of the substrate, this leads to a tetragonal structure similar to that of bulk PbTiO_3 . The polarization is expected to be along the symmetry axis, so this corresponds to a c -ferroelectric phase,¹⁶ with $P \parallel [001]$. At $x \approx 0.83$, there is a discontinuous decrease in the out-of-plane lattice parameter to a value smaller than that of DyScO_3 , leading to a structure with larger in-plane lattice parameters. Here the polarization is expected to lie in the plane of the film.

The experimental observations are in reasonable agreement with the proposed phase diagram. In particular, the boundary between the in-plane and out-of-plane polarizations is well reproduced experimentally. Temperature-

FIG. 3. (Color online) Out-of-plane XRD results for, respectively, (a) a $\text{Pb}_{0.53}\text{Sr}_{0.47}\text{TiO}_3$ and (c) a PbTiO_3 film grown on DyScO_3 . The solid lines show the simulation result, used to extract the lattice parameters. (b) shows the evolution of the c lattice parameter with composition x .

dependent measurements indicate that the Curie temperatures of the strained films are also in agreement with the calculated ones.³⁸ However, the assumption of uniform polarization throughout the film is most likely not valid, since domains are expected to form,^{25,26} modifying the phase diagram. Reciprocal space maps in our films reveal, indeed, the presence of domains.³⁸ Next we plan to look into the mechanisms of domain formation as well as to grow similar films with bottom and top electrodes in order to investigate the ferroelectric properties across the phase diagram. These experiments will also help elucidate if the predicted *r*-phase is experimentally accessible.

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