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

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(Received 19 November 2010; accepted 3 December 2010; published online 29 December 2010)

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 Pb$_x$Sr$_{1-x}$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 Pb$_x$Sr$_{1-x}$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. 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.

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, 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. 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 parameters [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. Most importantly, only if the strain can be tuned continuously, we will be able to access the theoretically predicted phases and/or properties, 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 Pb$_x$Sr$_{1-x}$TiO$_3$, as well as the Curie temperatures $T_C$, vary linearly between the two end members of the solid solution [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 tetragonal phases of PbTiO$_3$. In this way we can use a phenomenological Landau–Devonshire (LD) approach to calculate the phase diagram of Pb$_x$Sr$_{1-x}$TiO$_3$ epitaxial thin films on (110)-DyScO$_3$. The substrate was chosen because the strain state of Pb$_x$Sr$_{1-x}$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...
out-of-plane,²⁵ whereas the polarization of epitaxial SrTiO₃ films on DyScO₃ is in the plane of the film.⁴,⁶,²⁶

The phase diagram of PbₓSr₁₋ₓTiO₃ on (110)-DyScO₃ 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 PbₓSr₁₋ₓTiO₃ have been constructed as a linear combination of the well-known Landau coefficients of the end members, PbTiO₃ and SrTiO₃, 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 a₁ = a₁(T - Tc), the composition dependences of Tc and a₁ 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 PbTiO₃ and SrTiO₃ are almost equal,³² the thermal expansion of PbₓSr₁₋ₓTiO₃ is assumed to be that of PbTiO₃. The thermal expansion of DyScO₃ does significantly differ from that of PbₓSr₁₋ₓTiO₃.¹⁷ The small anisotropy of 0.05% in the lattice parameters of the (110) DyScO₃ 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 PbTiO₃ and Pb₀.₃₅Sr₀.₆₅TiO₃ films give no qualitative difference in the phase diagram after including a substrate anisotropy as small as that of DyScO₃.³³ Since the oxygen rotations present in SrTiO₃ below 105 K are not included in the calculations, our results are not expected to be valid for x < 0.5.²⁵ 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 PbₓSr₁₋ₓTiO₃ on DyScO₃ is shown in Fig. 2. The misfit strain goes from a very small compressive strain for pure PbTiO₃ to a tensile strain that increases with increasing Sr-content. The different strain values stabilize polarizations along different directions. For large x, PbₓSr₁₋ₓTiO₃ is predicted to be a c-phase ferroelectric, with the electrical polarization P perpendicular to the film plane, similar to that of PbTiO₃. At lower x an aa-phase, with P||[100], should be stabilized. In between these two, an intermediate r-phase is expected, in which the polarization points somewhere in between (001) and (110). The addition of Sr gives rise to the decrease in Tc.

To test our predictions, a series of PbₓSr₁₋ₓTiO₃ thin films with a thickness of 50 ML (20 nm) was grown on (110)-DyScO₃ using molecular beam epitaxy. The films were grown at a substrate temperature of 650 °C, with an adsorption controlled growth mechanism as described for PbTiO₃.³⁴–³⁶ Sr substitution is obtained by providing a constant flux of atomic Sr for a certain amount of time tSr 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 DyScO₃ (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 PbTiO₃. The polarization is expected to be along the symmetry axis, so this corresponds to a c-ferroelectric phase, with P||[001]. At x ≈ 0.83, there is a discontinuous decrease in the out-of-plane lattice parameter to a value smaller than that of DyScO₃, 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. 2. Phase diagram vs composition for PbₓSr₁₋ₓTiO₃ strained on DyScO₃ as calculated using LD theory. The top axis defines the “isostrain” lines in the composition vs temperature diagram.](image-url)
dependent measurements indicate that the Curie temperatures of the strained films are also in agreement with the calculated ones. However, the assumption of uniform polarization throughout the film is most likely not valid, since domains are expected to form, modifying the phase diagram. Reciprocal space maps in our films reveal, indeed, the presence of domains. 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.

We are grateful to Sergey Art’yukhin for useful discussions. This work is part of the research program of the Foundation for Fundamental Research on Matter (FOM), which is part of the Netherlands Organisation for Scientific Research (NWO).

18Values are given in SI units (T=K, \( a_{ij}=J \ m^{-2}, a_{i}=J \ m^{-3}, a_{ij}=J \ m^{-2}, Q_{ij}=m^{2}, a_{ij}^{1}=m^{2}-J^{-1} \)). PbTiO\(_{3}\): \( a_{1}=3.8 \times 10^{-5} \) (T-752), \( a_{1}=7.3 \times 10^{-5}, a_{1}=5 \times 10^{-5}, a_{1}=6.1 \times 10^{-5}, a_{1}=3.7 \times 10^{-5}, Q_{1}=0.008, a_{1}=0.026, Q_{4}=0.075, a_{1}=3.7 \times 10^{-12}, a_{1}=2.5 \times 10^{-12}, a_{4}=9 \times 10^{-12}, a_{1}=7.06 \times 10^{-3} \) (T-355) (approximation only valid above 100 K), \( a_{1}=1.04 \times 10^{-5}, a_{1}=7.46 \times 10^{-7}, a_{1}=0, a_{1}=0, a_{4}=0, Q_{1}=0.004, a_{4}=0.0131, Q_{4}=0.019, a_{1}=3.52 \times 10^{-12}, a_{1}=8.5 \times 10^{-12}, a_{4}=7.87 \times 10^{-12}.