A strained thin film structure includes a substrate layer formed of a crystalline scandate material having a top surface, and a strained layer of crystalline ferroelectric epitaxially grown with respect to the crystalline substrate layer so as to be in a strained state and at a thickness below which dislocations begin to occur in the crystalline ferroelectric layer. An intermediate layer may be grown between the top surface of the substrate layer and the ferroelectric layer wherein the intermediate layer carries the lattice structure of the underlying substrate layer. The properties of the ferroelectric film are greatly enhanced as compared to the bulk ferroelectric material, and such films are suitable for use in applications including ferroelectric memories.
Fig. 1

- Range of transition
- Ferroelectric
- GdScO₃
- DyScO₃

Temperature (°C) vs. In-plane strain $\varepsilon_s$ (%)
FIG. 2

<table>
<thead>
<tr>
<th>Temperature</th>
<th>30 °C</th>
<th>120 °C</th>
<th>130 °C</th>
<th>600 °C</th>
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BaTiO$_3$ on GdScO$_3$

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BaTiO$_3$ on DyScO$_3$

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<td>42 &amp; 48</td>
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</tr>
</tbody>
</table>

FIG. 3
FIG. 4

Lattice Constant (Å)

Temperature (°C)

theory

with $T_c$

without $T_c$

$\sim$-BaTiO$_3$(Δ) // DyScO$_3$

$\sim$-BaTiO$_3$(Δ) // GdScO$_3$

$T_c$ (Single Crystal)

0 100 200 300 400 500 600 700 800
FIG. 8


FIG. 9  FIG. 10  FIG. 11
1

STRAIN-ENGINEERED FERROELECTRIC
THIN FILMS

STATEMENT OF GOVERNMENT RIGHTS

This invention was made with United States government support awarded by the following agencies: NSF 0296021, 0103354 and 01222638. The United States government has certain rights in this invention.

FIELD OF THE INVENTION

This invention pertains generally to the field of semiconductor and related device manufacturing and particularly to thin film structures.

BACKGROUND OF THE INVENTION

Very large strains can exist in thin films of one material deposited on another material due to differences in crystal lattice parameters and thermal expansion behavior between the thin film and the underlying substrate, or arising from defects formed during film deposition. As a result, the properties of such thin films can be dramatically different than the intrinsic properties of the corresponding unstrained bulk materials. Such strain may be undesirable and lead to degraded film properties, but in appropriate cases and at appropriate strain levels, the strain in the thin film can actually enhance the properties of the thin film for use in certain applications. One example is in the production of more environmentally benign ferroelectric random access memories (FeRAM). Large shifts in the transition temperature \( T_c \) and remanent polarization \( P_r \) are expected and have been observed in various ferroelectric materials. The two materials most widely being investigated for use for FeRAM devices are Pb(Zr, Ti)O\(_3\) and SrBi\(_2\)Ta\(_2\)O\(_6\). The major disadvantages in the use of these two materials are the volatility of the lead and bismuth constituents of these materials, which complicates their introduction into semiconductor fabrication facilities, and environmental issues associated with the toxicity of lead. Thus, it would be desirable to have other suitable thin film ferroelectric materials with constituents that are not as volatile and which do not impose potential environmental risks.

SUMMARY OF THE INVENTION

In accordance with the present invention, the properties of ferroelectric materials are enhanced using appropriate control of the strain in thin films of such material for use in various applications including ferroelectric memories and electro-optical modulators. The thin films of ferroelectrics can have relatively non-volatile and non-toxic constituents which are well suited for semiconductor fabrication facilities and which are compatible with existing processing of silicon based devices. By control of the strain in the ferroelectric thin films in accordance with the present invention, much higher ferroelectric transition temperatures and much greater remanent polarizations can be achieved as compared to bulk single crystals of the same materials.

A strained thin film structure in accordance with the invention includes a substrate layer formed of a crystalline rare earth scandate material having a top surface. A strained layer of crystalline ferroelectric material is epitaxially grown with respect to the crystalline substrate layer so as to be in a strained state and at a thickness below which dislocations begin to occur in the crystalline ferroelectric layer. Preferably, the thickness of the ferroelectric layer is less than 5 \( \mu \)m, and most preferably between 1 \( \mu \)m and 50 \( \AA \). An intermediate layer may be grown between the top surface of the substrate layer and the ferroelectric layer wherein the intermediate layer carries the lattice structure of the underlying substrate layer. An appropriate intermediate layer is epitaxially grown on the top surface of the substrate and on which the strained layer of crystalline ferroelectric is epitaxially grown. An additional layer can be formed over the ferroelectric layer such that the layers separated by the ferroelectric layer function as plates of a capacitor. Such capacitor structures can be utilized in ferroelectric capacitive memory cells and in other applications. Further, the substrate layer may be formed on a crystalline silicon base so as to allow the devices in accordance with the present invention to be integrated with circuitry formed on the silicon base.

Examples of preferred materials include GdScO\(_3\) and DyScO\(_3\) for the rare earth scandate substrate layer, BaTiO\(_3\) for the ferroelectric layer, and SrRuO\(_3\) for the intermediate layer.

Further objects, features and advantages of the invention will be apparent from the following detailed description when taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings:

FIG. 1 is a diagram showing the expected \( T_c \) of (001) BaTiO\(_3\) by biaxial in-plane strain (\( \varepsilon_{xx} \)), based on thermodynamic analyses, with the data points showing the observed \( \varepsilon_{xx} \) and \( T_c \) values for coherent BaTiO\(_3\) films grown by MBE (circles) and by PLD (squares) on GdScO\(_3\) and DyScO\(_3\) substrates.

FIG. 2 is a simplified diagram showing a film of BaTiO\(_3\) grown on a substrate of GdScO\(_3\) or DyScO.

FIG. 3 are two-dimensional images at selected temperatures of the x-ray diffraction peaks from a BaTiO\(_3\) single crystal and from strained BaTiO\(_3\) thin films.

FIG. 4 are graphs showing the temperature dependence of the lattice parameters of single crystal BaTiO\(_3\) (c-axis triangles and a-axis squares) and strained BaTiO\(_3\) thin films grown by MBE on DyScO\(_3\) substrates (triangles for out-of-plane BaTiO\(_3\), circles for in-plane BaTiO\(_3\), and circles for in-plane DyScO\(_3\)) and on GdScO\(_3\) substrates (triangles for out-of-plane BaTiO\(_3\), squares for in-plane BaTiO\(_3\), and circles for in-plane GdScO\(_3\)) wherein the changes in slope at high temperature signal a phase transition.

FIG. 5 are graphs showing optical SHG signals from a BaTiO\(_3\) single crystal (open circles for heating and closed circles for cooling) and from the same strained BaTiO\(_3\) film on GdScO\(_3\) as in FIG. 4 (open squares for heating and closed squares for cooling), with the inset showing polar plots of SHG intensity (radius) versus fundamental polarization (azimuth), with circles representing experimental data and solid lines representing calculations from theory.

FIG. 6 are graphs showing polarization-electric field hysteresis loops of BaTiO\(_3\) thin film (2000 \( \AA \)) capacitors grown by PLD on GdScO\(_3\) and DyScO\(_3\) with SrRuO\(_3\) top and bottom electrodes, with the inset showing the hysteresis loop of an unstrained bulk BaTiO\(_3\) single crystal for comparison purposes.

FIG. 7 are graphs showing temperature dependence of the lattice parameters of strained SrRuO\(_3\)/BaTiO\(_3\)/SrRuO\(_3\) capacitor structures grown by PLD on DyScO\(_3\) substrates (closed triangles for out-of-plane BaTiO\(_3\), open circles for in-plane BaTiO\(_3\), open circles for in-plane DyScO\(_3\) and on GdScO\(_3\) substrates (closed triangles for out-of-plane BaTiO\(_3\), open circles for in-plane BaTiO\(_3\), open circles for in-plane DyScO\(_3\), and on GdScO\(_3\) substrates (closed triangles for out-of-plane BaTiO\(_3\), open circles for in-plane BaTiO\(_3\), open circles for in-plane DyScO\(_3\), and on GdScO\(_3\) substrates (closed triangles for out-of-plane BaTiO\(_3\)).
open squares for in-plane BaTiO₃, and open circles for in-plane GdScO₃, with the change in slope at high temperature indicating a phase transition.

FIG. 8 is a bright-field TEM image showing a 200 nm thick BaTiO₃ film grown on a (110) GdScO₃ substrate with a (110) SrRuO₃ bottom electrode layer.

FIG. 9 is a selected area electron diffraction pattern corresponding to the BaTiO₃ layer.

FIG. 10 is a selected area electron diffraction pattern corresponding to the SrRuO₃ layer.

FIG. 11 is a selected area electron diffraction pattern corresponding to the GdScO₃ substrate.

FIG. 12 is a high resolution TEM image showing the BaTiO₃/SrRuO₃ interface with a dashed line marking the position of the interface.

FIG. 13 is a high resolution TEM image showing the SrRuO₃/GdScO₃ interface with a dashed line marking the position of the interface.

FIG. 14 is a schematic diagram of the geometry of the SHG measurement (not to scale), showing wavevectors $k^0$ and $k^{2\omega}$ for the fundamental frequency ($\omega$) and the second harmonic frequency ($2\omega$), and the incidence and refraction angles $\phi$, with the subscripts i, s, f, and t corresponding to incidence, substrate, film, and transmitted, respectively.

**DETAILED DESCRIPTION OF THE INVENTION**

The present invention utilizes detailed investigations of the properties of ferroelectric thin films to achieve significantly improved ferroelectric properties compared to the bulk ferroelectric. The present invention may be used with various crystalline ferroelectrics, examples only of which are BaTiO₃, lead zirconium titanate (PZT), BiFeO₃, and lead magnesium niobate-lead titanate (PMN-PT). For purposes of illustration, the invention is exemplified below with respect to BaTiO₃, a preferred ferroelectric material, but it is understood that the invention is not limited thereto.

To predict the $T_c$ enhancement and temperature dependence of the lattice parameters of BaTiO₃ thin films under large biaxial strain using Landau thermodynamic theories, we determined a new set of phenomenological coefficients, since existing ones are only applicable to small compressive strains ($\sim 0.4\%$). FIG. 1 shows the $T_c$ enhancement predicted from thermodynamic analysis for a BaTiO₃ thin film under biaxial strain

$$\Delta T_c = \frac{a_{11} - a_{01}}{a_{01}}$$

where $a_{01}$ is the lattice parameter of free-standing cubic BaTiO₃ and $a_{11}$ is the in-plane lattice parameter of a biaxially strained (001) BaTiO₃ film. The dark shaded range of transition region shows the range in predicted $T_c$ due to the range of reported property coefficients for BaTiO₃ that enter into the thermodynamic analysis. FIG. 1 implies that a biaxial compressive strain of only $\sim 1\%$ should be sufficient to produce strained (001) BaTiO₃ films with a $T_c$ comparable to or higher than unstrained Pb(Zr,Ti)O₃ films.

Although FIG. 1 might seem to imply that $T_c$ can be enhanced without bound, there are limits to strain engineering. The driving force for film relaxation increases with strain and film thickness. When films are grown to thicknesses greatly exceeding their critical values, relaxation toward a zero-strain state by the introduction of dislocations begins. Thus, it is important to grow films below, or at least close to, their critical thickness for relaxation. As the critical thickness at which dislocations begin to form varies approximately inversely with lattice mismatch, lower mismatch is desired to allow strained BaTiO₃ films that are thick enough to allow their ferroelectric properties to be conveniently probed or utilized in devices. FIG. 1 only applies to thick strained ferroelectrics; as ferroelectrics get thin (below 100 Å), their ferroelectric properties can be drastically diminished by finite-size effects. Optimizing the tradeoff between strain and film thickness depends on the particular application. For FeRAMs, films several hundred angstroms in thickness are needed. Based on the equilibrium critical thickness for BaTiO₃, this would constrain $\epsilon_s$ to be less than about 0.5%; however, we have found that it is possible to grow 500 Å thick coherent BaTiO₃ films at $\epsilon_s = 1.7\%$.

Single crystal substrates of GdScO₃ and DyScO₃ were used because they are structurally, chemically, and thermally compatible with BaTiO₃, and they have appropriate lattice constants to impart $\epsilon_s$ of about $-1%$ and $-1.7\%$, respectively, on coherent (001) BaTiO₃ films. As illustrated in FIG. 2, BaTiO₃ thin films were epitaxially grown on (110) GdScO₃ and (110) DyScO₃ substrate layers by reactive molecular beam epitaxy (MBE) and by pulsed laser deposition (PLD) with in situ high-pressure reflection high-energy electron diffraction, as discussed in further detail below.

The lattice parameters of the strained (001) BaTiO₃ thin films are summarized in Table 1. These films are epitaxial, purely c-axis oriented (the c-axis of all BaTiO₃ domains is perpendicular to the wafer surface as illustrated in FIG. 2) and, with the exception of the 2000 Å thick BaTiO₃ film on DyScO₃, are fully coherent with the substrates, without any resolvable lattice relaxation.

**TABLE 1**

<table>
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<tr>
<th>Material</th>
<th>plane</th>
<th>FWHM(°)</th>
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<tr>
<td>BaTiO₃ (1000 Å)</td>
<td>GdScO₃</td>
<td>3.946</td>
</tr>
<tr>
<td>BaTiO₃ (500 Å)</td>
<td>GdScO₃</td>
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<tr>
<td>BaTiO₃ (2000 Å)</td>
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<tr>
<td>BaTiO₃ (1000 Å)</td>
<td>DyScO₃</td>
<td>3.944</td>
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<tr>
<td>BaTiO₃ (2000 Å)</td>
<td>DyScO₃</td>
<td>3.944</td>
</tr>
<tr>
<td>BaTiO₃ (1000 Å)</td>
<td>SrRuO₃</td>
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<tr>
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<tr>
<td>BaTiO₃ (2000 Å)</td>
<td>SrRuO₃</td>
<td>3.947</td>
</tr>
</tbody>
</table>

To identify the ferroelectric phase transition, the temperature dependence of the in-plane and out-of-plane lattice parameters of the films and substrates was measured using a variable-temperature four-circle x ray diffractometer equipped with a two-dimensional (2D) area detector with an angular resolution of $\sim 0.02°$. Unstrained BaTiO₃ undergoes a
ferroelectric transition at about 130°C from the high-temperature cubic (Pm3m) to the low-temperature tetragonal (P4mm) phase. Fig. 3 shows 2-D images of the 002 and 006 diffraction peaks at selected temperatures from a BaTiO3 single crystal as well as from coherent BaTiO3 thin films grown on (110) GdScO3 and (110) DyScO3 substrates. There is no significant change in the diffraction peaks of the BaTiO3 films at or above Tc ~130°C. As expected, the single diffraction spot of the BaTiO3 single crystal splits into two below 130°C, corresponding to a and c domains of the tetragonal (P4mm) ferroelectric phase.

The in-plane and out-of-plane lattice parameters of the strained BaTiO3 films grown by MBE were determined from the 002 and 006 diffraction peaks and are plotted as a function of temperature in Fig. 4. The in-plane lattice parameters of the BaTiO3 layer are coherent to the underlying substrates over the entire temperature range (25-700°C). There are striking differences in the evolution of the lattice parameters with temperature between the unstrained BaTiO3 single crystal and the strained BaTiO3 thin films. Notably, the BaTiO3 thin films never become cubic; they remain tetragonal due to the biaxial substrate constraint. The predicted dependence of the c lattice parameter of biaxially strained BaTiO3, with and without a ferroelectric phase transition, was calculated from thermodynamic analysis and is shown by the solid curve and dashed curve, respectively, in Fig. 4. As the BaTiO3 film is clamped-in-plane, all structural changes due to the phase transition and thermal expansion are accommodated through changes in the out-of-plane lattice parameter only. The agreement between the prediction and the measured c-axis lattice parameters in Fig. 4 is strong evidence that the change in slope of the c-axis parameter at high temperature corresponds to a ferroelectric phase transition. Analogous lattice constant behavior has been observed in other constrained ferroelectric films (E. D. Specht, et al., Phys. Rev. Lett. 80, 4317 (1998); S. K. Streiffer, et al., Phys. Rev. Lett. 89, 067601 (2002)), consistent with theory (M. Sepiarsiak, et al., J. Appl. Phys. 91, 3165 (2002); S. K. Streiffer, et al. (2002), supra), and has been used to determine Tc. The Tc of the coherent BaTiO3 thin films shown in Fig. 4 are ~400°C on GdScO3 and ~540°C on DyScO3.

To confirm the huge shifts in Tc, measurements were made of polarization hysteresis loops on a 2000 Å thick coherent BaTiO3 film grown by PLD on a coherent SrRuO3 bottom electrode on (110) GdScO3. At temperatures up to about 200°C, hysteresis loops were clearly seen, but at higher temperatures the dielectric losses in the films became too high for reliable measurements. Second harmonic generation (SHG) measurements were made as a function of temperature on this PLD-grown BaTiO3/SrRuO3/GdScO3 sample as well as the MBE-grown BaTiO3/GdScO3 sample whose lattice constants vs. temperature behavior is shown in Fig. 4. An SHG signal is only exhibited by materials that lack inversion symmetry. All ferroelectrics must lack inversion symmetry, but there are many materials that lack inversion symmetry and are not ferroelectric. This makes SHG a necessary but insufficient probe for ferroelectricity. Nonetheless, Fig. 5 shows that the phase that is known from hysteresis loops to be ferroelectric at room temperature remains non-centrosymmetric to the same high temperature where x-ray diffraction indicates a phase transition. The interpretation consistent with all of these analyses—x-ray diffraction, SHG, and hysteresis measurements—is that biaxial compressive strain increases the Tc of BaTiO3.

Hysteresis measurements were made on 200 μm diameter capacitors, shown for illustration at 25 in Fig. 6, of a strained BaTiO3 thin film 26 sandwiched between epitaxial top and bottom electrodes 27 and 28 of the conducting perovskite oxide SrRuO3 which was grown epitaxially on substrate layers 30 of GdScO3 and DyScO3. High-resolution x-ray diffraction measurements (summarized in Table 1) revealed the BaTiO3 ferroelectric layers as well as the 1000 Å thick SrRuO3 bottom electrodes to be fully coherent with the underlying substrates. No relaxation was observed even for BaTiO3 films as thick as 500 Å on DyScO3 and 2000 Å on GdScO3. The critical thicknesses of BaTiO3 thin films grown on coherent SrRuO3 bottom electrodes on GdScO3 and DyScO3 are higher than those of BaTiO3 films grown directly on GdScO3 and DyScO3. This observation is consistent with critical thickness theory, where the difference arises from strain partitioning between the layers as well as the altered geometry of misfit dislocations in a single layer versus a bilayer. Because the leakage in the coherent stack containing a 500 Å thick BaTiO3 layer on DyScO3 was too high for good ferroelectric hysteresis measurements, a SrRuO3/BaTiO3/SrRuO3/DyScO3 stack was grown with a 2000 Å thick BaTiO3 layer. This latter stack had low leakage; however, it was partially relaxed.

Fig. 6 shows the ferroelectric hysteresis loops measured on the ferroelectric stacks grown on GdScO3 and DyScO3 substrates 30 with 2000 Å thick BaTiO3 layers, together with results from a BaTiO3 single crystal for comparison. The hysteresis loops are shifted in the positive voltage direction. This imprint effect is probably due to the asymmetric interfacial properties of the top and bottom electrodes to the BaTiO3 films. Even though SrRuO3 was used for both electrodes, the growth temperature (350°C) of the top electrode was much lower than that of the bottom electrode (680°C), which might lead to poor crystallinity of the top electrode and asymmetric interfaces. The Pc and coercive field (Ec) were determined to be ~50 μC/cm2 and 80 kV/cm for the fully coherent BaTiO3/GdScO3 sample and ~70 μC/cm2 and 25 kV/cm for the partially relaxed BaTiO3/DyScO3 sample, respectively. This Pc value is almost 270% of the 25 μC/cm2 of single crystal BaTiO3, 250% higher than the switched charge density assumed in the scaling analysis of FeRAM, and comparable to the Pc of unstrained Pb(Zr,Ti)O3 films. As this Pc of ~70 μC/cm2 was observed in a partially relaxed sample with Ec of ~1.3%, a coherently strained BaTiO3/DyScO3 sample with Ec of ~1.7% can have an even higher Pc.

Another important feature for the application of ferroelectric capacitors to memory devices is the loss of switched polarization after repeated switching, i.e., fatigue. Fatigue measurements were performed by applying 8.6 μs wide pulses with a repetition frequency of 10 kHz to the top and bottom SrRuO3 electrodes of the SrRuO3/BaTiO3/SrRuO3/GdScO3 structure at Vmax =4 V (200 kV/cm). The switched polarization decreased by 10% of its original value after 1010 cycles, but recovered its original value after 1010 cycles. This is consistent with previous observations of fatigue-free behavior when conducting oxide electrodes are used.

As a verification that the enhancement of Tc observed in coherently strained BaTiO3 thin films grown by MBE (see Fig. 4) is inherent and applicable to a device structure with a conductive bottom electrode, high-temperature x-ray diffraction measurements were performed on the coherent BaTiO3 thin films with SrRuO3 bottom electrodes grown by PLD. Fig. 7 shows the evolution of the in-plane (a) and out-of-plane (c) lattice parameters of the BaTiO3 film and the GdScO3 and DyScO3 substrates as a function of temperature. The in-plane lattice parameters reveal that both the BaTiO3 and SrRuO3 layers are coherently strained to the underlying substrates over the entire temperature range. This is consis-
tent with the absence of misfit dislocations along the interface between GdScO$_3$ and SrRuO$_3$ and along the interface between SrRuO$_3$ and BaTiO$_3$ as shown by the cross-sectional transmission electron microscope images. The transition behavior of the PLD samples was found to be quite similar to those grown by MBE. T$_{\text{c}}$ was determined to be $-420^\circ$C and $-680^\circ$C for samples grown on GdScO$_3$ and DyScO$_3$, respectively. The solid and dashed lines in Fig. 7 are theoretical predictions of c-lattice parameters with and without the ferroelectric phase transition, which are fairly consistent with the experimentally measured values. The agreement in the results for films grown by MBE and PLD indicates that the observed shifts in ferroelectric properties with strain represent the intrinsic behavior of strained BaTiO$_3$. Note also that this experimental dependence of T$_{\text{c}}$ on $\varepsilon$ is consistent with the expectations shown in Fig. 1. It is understood that other film growth processes may be used in addition to MBE and PLD, including sputtering and chemical vapor deposition (CVD and MOCCVD).

The foregoing examples demonstrate that the properties of ferroelectric can be dramatically enhanced through strain engineering. These strain-engineered heteroepitaxial thin films provide a broad range of operating temperatures as well as higher remanent polarization for improved noise immunity and the ability to scale FeRAM to smaller cell sizes. The ability to withstand huge strains gives thin films a degree of freedom that is not available in the bulk material. This can be exploited to enhance the ferroelectric properties of any ferroic system, including multilayers, whose ferroic order parameter has a strong coupling to strain.

The (110) GdScO$_3$ and (110) DyScO$_3$ substrates used in the examples above are two of a series of rare-earth scandates with pseudo-cubic lattice constants that range from 3.93 Å to 4.05 Å in roughly 0.01 Å increments as the rare earth species is varied. These rare earth scandates have the GdFeO$_3$-type orthorhombic structure (space group: Pbnm). GdScO$_3$ has lattice constants $a=5.488$ Å, $b=5.754$ Å, and $c=7.934$ Å and DyScO$_3$ has lattice constants $a=5.440$ Å, $b=5.715$ Å, and $c=7.887$ Å. In these structures the (100) plane, spanned by [010] and [001] directions, provides a nearly square base with $c/2=3.967$ Å and $(a^2+b^2)/2=3.973$ Å for the in-plane surface mesh of (110) GdScO$_3$ and $c/2=3.943$ Å and $(a^2+b^2)/2=3.944$ Å for (110) DyScO$_3$. Thus, (110) GdScO$_3$ and (110) DyScO$_3$ substrates provide $\varepsilon$ of about $-1.0\%$ and $-1.7\%$, respectively, for the epitaxial growth of (1001) BaTiO$_3$ films. The pseudo-cubic lattice parameters of other rare earth scandates are given in Table 2 below.

### Table 2

<table>
<thead>
<tr>
<th>Material</th>
<th>a(Å)</th>
<th>b(Å)</th>
<th>c(Å)</th>
<th>c/2(Å)</th>
<th>c(2Å)</th>
<th>2(Å)</th>
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<th>$\beta(\varepsilon)$</th>
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<tbody>
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<td>LaScO$_3$</td>
<td>5.678</td>
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<td>5.727</td>
<td>7.915</td>
<td>3.958</td>
<td>3.958</td>
<td>87.344</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DyScO$_3$</td>
<td>5.440</td>
<td>5.713</td>
<td>7.887</td>
<td>3.944</td>
<td>3.944</td>
<td>87.212</td>
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<tr>
<td>HoScO$_3$</td>
<td>5.427</td>
<td>5.714</td>
<td>7.895</td>
<td>3.947</td>
<td>3.940</td>
<td>87.065</td>
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</table>

The epitaxial BaTiO$_3$ thin films were grown on (110) GdScO$_3$ and (110) DyScO$_3$ substrates by both MBE and PLD. For the films grown by MBE, molecular beams of the constituent elements were supplied to the surface of unmixed (110) GdScO$_3$ and (110) DyScO$_3$ substrates held at 700°C. A mixture of 90% O$_2$ and 10% ozone at a background pressure of 5x10$^{-6}$ Torr was used as the oxidant, incident upon the substrate via a directed inert nozzle. The BaTiO$_3$ was deposited by the sequential deposition of BaO and TiO$_2$ monolayers, where each monolayer dose was controlled in real time by feedback from reflection high-energy electron diffraction (RHEED) intensity oscillations. To grow BaTiO$_3$ films by PLD, unmixed (110) GdScO$_3$ and (110) DyScO$_3$ substrates were attached to a resistive heater and positioned 5.0 cm from the target. A KrF excimer laser (248 nm) beam was focused on a stoichiometric BaTiO$_3$ target to an energy density of 2.0 J/cm$^2$ and pulsed at 5 Hz. BaTiO$_3$ films were grown at substrate temperatures ranging from 650 to 800°C and oxygen pressures of 100-150 mTorr. The PLD system is equipped with high-pressure RHEED, which enabled the layer-by-layer growth of the thin films to be monitored in situ during growth.

The three-dimensional strain state of the films was determined using high-resolution four-circle x-ray diffraction. The crystalline perfection of the films was assessed by measuring the full width at half maximum (FWHM) in $\omega$ (rocking curve) of the 002 BaTiO$_3$ reflection. The microstructure and interfacial structure of the BaTiO$_3$ thin films grown on both GdScO$_3$ and DyScO$_3$ substrates were characterized by cross-sectional transmission electron microscopy (TEM). Fig. 8 is a bright-field TEM image showing a 200 nm thick BaTiO$_3$ film grown on a (110) GdScO$_3$ substrate with a (110) SrRuO$_3$ bottom electrode layer. The corresponding selected area electron diffraction patterns for each film layer and the substrate are shown in Figs. 9-11. It was found that the BaTiO$_3$ film grows epitaxially and is purely c-axis oriented normal to the substrate through the whole film. No misfit dislocations are seen along the interface between GdScO$_3$ and SrRuO$_3$ or along the interface between SrRuO$_3$ and BaTiO$_3$. This indicates that both the SrRuO$_3$ and BaTiO$_3$ films are strained to the lattice spacing of the substrate by coherent epitaxial growth, which is consistent with the x-ray data shown in Fig. 7 and Table 1. The change in the diffraction contrast of the BaTiO$_3$ film indicates that the film is highly strained. High-resolution TEM images of the BaTiO$_3$/SrRuO$_3$ and SrRuO$_3$/GdScO$_3$ interfaces are shown in Figs. 12-13. Sharp interfaces are seen both between GdScO$_3$ and SrRuO$_3$ and between SrRuO$_3$ and BaTiO$_3$. The position of the interfaces is indicated by dashed lines.

To measure the polar plots shown in the inset of Fig. 5, incident light at frequency $\omega$ (wavelength 900 nm) was polarized at an angle of 0° to the x-y plane and $\phi_v=23^\circ$ to the surface normal (z) of the GdScO$_3$ substrate. The incident fundamental polarization was p-polarized and the output SHG polarization ($\phi_{2\omega}$) at frequency $2\omega$ (wavelength of 450 nm) was p-polarized (0°-90°) for the film and s-polarized (0°-90°) for the single crystal.
The general expression for this SHG intensity is given by

\[ P_{\text{out}} = K_1 \cos \theta + K_2 \sin \theta + K_3 \sin^2 \theta + K_4 \sin^2 \theta \]

where \( K_1, K_2, \) and \( K_3 \) are constants that depend on nonlinear coefficients \( d_{11}, d_{15}, \) and \( d_{12} \); geometric factors involving Fresnel coefficients, the angles shown in FIG. 14, and microstructural parameters involving the relative area fraction of various polarization variants (domains) in the BaTiO3 film.

No SHG signal was detected for normal incidence on the film system (q = 0°) in FIG. 5, confirming that the strained BaTiO3 film is indeed predominantly c-axis (001) oriented. X-ray diffraction measurements revealed that following the temperature cycling of the SHG measurement shown in FIG. 5, the film contained ~0.8% by volume of a-domains. These domains have polarization \( P_{\text{a}} \) along the c-axis and \( \pm \)z directions.

The first term in the equation above involving the constants \( K_1 \) and \( K_2 \) arises predominantly from domains with polarization \( P_{\text{a}} \) along the \( \pm \)z directions, and possibly a small amount of contribution from domains with \( P_{\text{a}} \) along the c-axis. The second term arises from a small SHG contribution from domains with polarization \( P_{\text{a}} \) along the \( \pm \)z directions. The ratio, \( P_{\text{out}}^2 / P_{\text{in}}^2 \), corresponding to the ratio of p-to-s polarized SHG intensity from the film, is related purely to intrinsic nonlinear coefficients of the film \( d_{11}, d_{33}, \) and \( d_{12} \) and fixed geometric factors, and is independent of the film domain microstructure. Numerical fitting of the polar plots yields the constant \( K_1 = 2.2 \times 10^{-7} \), which is therefore related to intrinsic BaTiO3 material properties. This constant is found to remain constant between 50° C and 400° C in the polar plots, but decreases thereafter in polar plots up to 700° C. This indicates a discontinuity in the intrinsic material property beyond the \( T_c \) in the strained BaTiO3 film.

It is understood that the invention is not confined to the particular embodiments set forth herein as illustrative, but embraces all such forms thereof as come within the scope of the following claims.

What is claimed is:

1. A strained thin film structure comprising:
   (a) a substrate layer formed of a crystalline rare earth scandate material and having a top surface;
   (b) a strained layer of crystalline ferroelectric material epitaxially grown with respect to the crystalline substrate layer so as to be in a strained state and at a thickness below which dislocations begin to occur.

2. The thin film structure of claim 1 wherein the ferroelectric layer has a thickness of 5 \( \mu \)m or less.

3. The thin film structure of claim 1 including an intermediate layer of material grown between the top surface of the substrate layer and the ferroelectric layer wherein the intermediate layer carries that lattice structure of the underlying substrate layer.

4. The thin film structure of claim 3 wherein the intermediate layer comprises SrRuO3 between the top surface of the substrate layer and the layer of ferroelectric and epitaxially grown on the substrate layer.

5. The thin film structure of claim 4 wherein the layer of SrRuO3 is 1 \( \mu \)m or less in thickness.

6. The thin film structure of claim 4 further including an additional layer of SrRuO3 formed over the ferroelectric layer whereby the layers of SrRuO3 can function as plates of a capacitor separated by the layer of ferroelectric acting as a dielectric.

7. The thin film structure of claim 1 further including a base of crystalline silicon on which the substrate layer is formed.

8. The thin film structure of claim 1 wherein the thickness of the ferroelectric layer is at least 50 \( \AA \).

9. The thin film structure of claim 8 wherein the thickness of the ferroelectric layer is less than 5 \( \mu \)m.

10. The thin film structure of claim 1 wherein the substrate layer is formed of a material selected from the group consisting of GdScO3 and DyScO3, and the strained layer ferroelectric material comprises BaTiO3.

11. The thin film structure of claim 10 wherein the strained layer is formed of (001) BaTiO3 and the substrate layer is formed of (110) GdScO3 or (110) DyScO3.

12. The thin film structure of claim 1 wherein the strained layer is grown epitaxially by molecular beam epitaxy.

13. The thin film structure of claim 1 wherein the strained layer is grown epitaxially by pulsed laser deposition.

14. The thin film structure of claim 1 wherein the substrate layer is DyScO3.

15. The thin film structure of claim 14 wherein the strained layer of BaTiO3 has a thickness of 500 \( \AA \) or less.

16. The thin film structure of claim 1 incorporated into an electro-optical modulator.

17. The thin film structure of claim 18 formed as a single layer of crystalline ferroelectric material grown.

18. A strained thin film structure comprising:
   (a) a substrate layer formed of a crystalline material selected from the group consisting of GdScO3 and DyScO3 and having a top surface;
   (b) a strained layer of crystalline BaTiO3 epitaxially grown with respect to the crystalline substrate layer so as to be in a strained state and at a thickness below which dislocations begin to occur.

19. The thin film structure of claim 19 wherein the BaTiO3 layer has a thickness of 5 \( \mu \)m or less.

20. The thin film structure of claim 19 including an intermediate layer of SrRuO3 between the top surface of the substrate layer and the layer of BaTiO3 and epitaxially grown on the substrate layer.

21. The thin film structure of claim 20 wherein the layer of SrRuO3 is 1 \( \mu \)m or less in thickness.

22. The thin film structure of claim 20 further including an additional layer of SrRuO3 formed over the BaTiO3 layer whereby the layers of SrRuO3 can function as plates of a capacitor separated by the layer of BaTiO3 acting as a dielectric.

23. The thin film structure of claim 19 further including a base of crystalline silicon on which the substrate layer is formed.

24. The thin film structure of claim 19 wherein the thickness of the layer of BaTiO3 is at least 50 \( \AA \).

25. The thin film structure of claim 19 wherein the thickness of the layer of BaTiO3 is less than 5 \( \mu \)m.

26. The thin film structure of claim 19 wherein the strained layer is formed of (001) BaTiO3 and the substrate layer is formed of (110) GdScO3 or (110) DyScO3.

27. The thin film structure of claim 19 wherein the strained layer is grown epitaxially by molecular beam epitaxy.

28. The thin film structure of claim 19 wherein the strained layer is grown epitaxially by molecular beam epitaxy.

29. The thin film structure of claim 19 wherein the strained layer is grown epitaxially by pulsed laser deposition.

30. The thin film structure of claim 19 wherein the substrate layer is DyScO3.

31. The thin film structure of claim 19 wherein the substrate layer is GdScO3 and the strained layer of BaTiO3 has a thickness of 2000 \( \AA \) or less.

32. The thin film structure of claim 19 wherein the structure is located outside of a deposition system in which the strained layer of crystalline ferroelectric material is grown.

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