Enhancement of Ferroelectricity in Strained BaTiO3 Thin Films
K. J. Choi et al.
Science 306, 1005 (2004);
DOI: 10.1126/science.1103218

This copy is for your personal, non-commercial use only.

If you wish to distribute this article to others, you can order high-quality copies for your colleagues, clients, or customers by clicking here.

Permission to republish or repurpose articles or portions of articles can be obtained by following the guidelines here.

The following resources related to this article are available online at www.sciencemag.org (this information is current as of May 21, 2013):

Updated information and services, including high-resolution figures, can be found in the online version of this article at:
http://www.sciencemag.org/content/306/5698/1005.full.html

Supporting Online Material can be found at:
http://www.sciencemag.org/content/suppl/2004/11/03/306.5698.1005.DC1.html

This article cites 29 articles, 4 of which can be accessed free:
http://www.sciencemag.org/content/306/5698/1005.full.html#ref-list-1

This article has been cited by 318 article(s) on the ISI Web of Science

This article has been cited by 8 articles hosted by HighWire Press; see:
http://www.sciencemag.org/content/306/5698/1005.full.html#related-urls

This article appears in the following subject collections:
Materials Science
http://www.sciencemag.org/cgi/collection/mat_sci
from the donors), there is a relaxation of acceptor molecules on the near side of the silver film (primarily excited by donor layer, and that the total emission from the structure can be strongly enhanced by recovering coupled SPP emission from both donor and acceptor through scattering from the grating microstructure.

A direct application of the strategy outlined above would be to top-emitting organic light-emitting diodes. Such devices are attractive for display applications where emission occurs through a metallic cathode. We have shown that depositing a dielectric layer on the surface of the device may lead to greater efficiency (7), and by dye-doping this layer SPP-mediated energy transfer could increase the spectral coverage of the output. Another potential area of application is synthetic light harvesting structures; SPP modes could act to channel energy from absorbing species to reaction centers and more generally in photochemistry near surfaces.

Enormous strains can exist in thin films when one material is deposited on another (1), resulting from differences in crystal lattice parameters and thermal expansion behavior between the film and the underlying substrate or arising from defects formed during film deposition (2, 3). As a result, the properties of thin films can be markedly different from the intrinsic properties of the corresponding unstrained bulk materials (4–9).

Although such strain often leads to degraded film properties, if judicious use is made of substrates and growth parameters, strain offers the opportunity to enhance particular properties of a chosen material in thin film form, namely strain engineering.

Strain engineering could facilitate the introduction of more environmentally benign ferroelectric random-access memories (FeRAM). Large shifts in the paraelectric-to-paraelectric transition temperature in thin film BaTiO$_3$ for nonvolatile memories and electro-optic devices.

Fig. 4. Dispersion data for the sample containing both donors and acceptors with structure Alq$_3$:PMMA|60 nm Ag|R6G:PMMA deposited onto a corrugated substrate. Data were obtained by recording the transverse-magnetic polarized (A) transmittance and (B) PL emission as a function of the in-plane wave vector of light, $k_{2\pi}/2\pi$. Both are plotted with a logarithmic gray scale, where for (A), transmittance ranges from $T = 0.001$ (black) to $T = 0.1$ (white), whereas for (B), white represents minimum and black maximum PL emission. In each case, the data are dominated by the scattered features corresponding to the excitation and emission of both symmetric and antisymmetric coupled SPPs.

Enhancement of Ferroelectricity in Strained BaTiO$_3$ Thin Films

K. J. Choi,1 M. Biegalski,2 Y. L. Li,2 A. Sharan,2 J. Schubert,3 R. Uecker,4 P. Reiche,4 Y. B. Chen,2 X. Q. Pan,2 V. Gopalan,2 L.-Q. Chen,2 D. G. Schlom,2 C. B. Eom1*

Biaxial compressive strain has been used to markedly enhance the ferroelectric properties of BaTiO$_3$ thin films. This strain, imposed by coherent epitaxy, can result in a ferroelectric transition temperature nearly 500°C higher and a remanent polarization at least 250% higher than bulk BaTiO$_3$ single crystals. This work demonstrates a route to a lead-free ferroelectric for nonvolatile memories and electro-optic devices.

References and Notes

2. S. M. Nie, S. R. Emery, Science 275, 1102 (1997).
27. P. Andrew, W. L. Barnes, data not shown.
28. We thank M. J. Jory for the R6G absorption spectrum data presented in Fig. 1D and the UK EPSRC and the EC (under project FP6 NMP4-CT-2003-505699) for financial support.

\*To whom correspondence should be addressed.

1Department of Materials Science and Engineering, University of Wisconsin–Madison, Madison, WI 53706, USA. 2Department of Materials Science and Engineering, Pennsylvania State University, University Park, PA 16802, USA. 3Institut für Schichten und Grenzflächen ISG1-IT, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany. 4Institute for Crystal Growth, Max-Born-Straße 2, D-12489 Berlin, Germany. 5Department of Materials Science and Engineering, The University of Michigan, Ann Arbor, MI 48109, USA.

E-mail: eom@engr.wisc.edu

www.sciencemag.org SCIENCE VOL 306 5 NOVEMBER 2004 1005

Downloaded from www.sciencemag.org on May 21, 2013
ferroelectric transition temperature ($T_c$) and remanent polarization ($P_r$) are expected (10–14) and have been observed (15–17) in ferroelectrics, signaling the viability of a strain-engineered advance for FeRAM. The major disadvantages of the two materials most widely being pursued for FeRAM (18), PbZr$_x$Ti$_{1-x}$O$_3$ and SrBi$_2$Ta$_2$O$_9$, are (i) the volatility of the lead and bismuth constituents of these materials, which complicates their introduction into semiconductor fabrication facilities, and (ii) environmental issues associated with the toxicity of lead. We demonstrate that the ferroelectric properties of BaTiO$_3$ can be enhanced with the use of strain to make them viable for ferroelectric memory applications. The widespread use of (Ba,Sr)TiO$_3$ in semiconductor fabrication facilities for dynamic random-access memories (DRAM) greatly simplifies the introduction of this related material into silicon-based devices.

To predict the $T_c$ enhancement and the temperature dependence of the lattice parameters of BaTiO$_3$ thin films under large biaxial strains with the use of Landau thermodynamic theories (10), we determined a new set of phenomenological coefficients, because existing ones are only applicable to small compressive strains ($< -0.4\%$) (11). Figure 1 shows the $T_c$ enhancement predicted from thermodynamic analysis for a BaTiO$_3$ thin film under biaxial strain $\varepsilon_{ab} = \varepsilon_a - \varepsilon_b$, where $\varepsilon_a$ is the lattice parameter of free-standing cubic BaTiO$_3$ and $\varepsilon_b$ is the in-plane lattice parameter of a biaxially strained (001) BaTiO$_3$ film. The green region shows the range in predicted $T_c$ resulting from the range of reported property coefficients for BaTiO$_3$ that enter into the thermodynamic analysis (19–21). Figure 1 implies that a biaxial compressive strain of only $\approx 1\%$ should be sufficient to produce strained (001) BaTiO$_3$ films with a $T_c$ comparable to or higher than unstrained Pb(Zr,Ti)O$_3$ films.

Table 1. Results from high-resolution x-ray diffraction measurements on the films. The in-plane (a) and out-of-plane (c) lattice constants and full width at half maximum (FWHM) of rocking curves of various peaks (002 of BaTiO$_3$, 200 pseudo-cubic of SrRuO$_3$, and 200 pseudo-cubic of GdScO$_3$) at room temperature are given. The a- and c-lattice parameters of single-crystalline BaTiO$_3$ are 3.992 and 4.036 Å, respectively (20).

<table>
<thead>
<tr>
<th>Material</th>
<th>Parameter</th>
<th>FWHM (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTiO$_3$ (1000 Å) on GdScO$_3$</td>
<td>a (0.002)</td>
<td>0.080</td>
</tr>
<tr>
<td>GdScO$_3$</td>
<td>a (0.0005)</td>
<td>0.009</td>
</tr>
<tr>
<td>BaTiO$_3$ (500 Å) on DyScO$_3$</td>
<td>c</td>
<td>0.120</td>
</tr>
<tr>
<td>BaTiO$_3$</td>
<td>c</td>
<td>0.009</td>
</tr>
<tr>
<td>DyScO$_3$</td>
<td>c</td>
<td>0.009</td>
</tr>
</tbody>
</table>

Pulsed-laser deposition

Table 1. Results from high-resolution x-ray diffraction measurements on the films. The in-plane (a) and out-of-plane (c) lattice constants and full width at half maximum (FWHM) of rocking curves of various peaks (002 of BaTiO$_3$, 200 pseudo-cubic of SrRuO$_3$, and 200 pseudo-cubic of GdScO$_3$) at room temperature are given. The a- and c-lattice parameters of single-crystalline BaTiO$_3$ are 3.992 and 4.036 Å, respectively (20).

Fig. 1. Expected $T_c$ of (001) BaTiO$_3$ under biaxial in-plane strain ($\varepsilon_{ab}$), based on thermodynamic analysis (10, 21). The green region represents the range (error bars) in the predicted $T_c$, resulting from the spread in reported property coefficients (20, 21) for BaTiO$_3$ that enter into the thermodynamic analysis. The data points show the observed $T_c$ and $\varepsilon_{ab}$ values of coherent BaTiO$_3$ films grown by MBE on GdScO$_3$ (blue circle) and DyScO$_3$ (red circle) substrates and by PLD on GdScO$_3$ (blue square) and DyScO$_3$ (red square) substrates.
sult of the biaxial substrate constraint. The predicted dependence of the c-lattice parameter of biaxially strained BaTiO$_3$ with and without a ferroelectric phase transition, was calculated from thermodynamic analysis (10) and is shown by the green solid and dashed curves in Fig. 2B, respectively. Because the BaTiO$_3$ film is clamped in-plane, all structural changes resulting from the phase transition and thermal expansion are accommodated through changes in the out-of-plane lattice parameter only. The agreement between the solid green prediction and the measured c-axis lattice parameters in Fig. 2B is strong evidence that the change in slope in the c-axis lattice parameter at high temperature corresponds to a ferroelectric phase transition. Analogous lattice constant behavior has been observed in other constrained ferroelectric films (15, 17), and has been used to determine $T_c$. The $T_c$ of the coherent BaTiO$_3$ thin films shown in Fig. 2B is ~400°C on DyScO$_3$ and ~540°C on DyScO$_3$.

To confirm the huge shifts in $T_c$, we attempted to measure polarization hysteresis loops on a 2000-A-thick coherent BaTiO$_3$ film grown by PLD on a coherent SrRuO$_3$ bottom electrode on (110) GdScO$_3$. 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. We made second harmonic generation (SHG) measurements as a function of temperature on this PLD-grown BaTiO$_3$/SrRuO$_3$/GdScO$_3$ sample as well as the MBE-grown BaTiO$_3$/GdScO$_3$ sample, whose lattice constants versus temperature behavior is shown in Fig. 2B (21). 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, SHG (Fig. 2C) shows that the phase we know from hysteresis loops to be ferroelectric at room temperature remains noncentrosymmetric to the same high temperature (29, 30) at which x-ray diffraction indicates a phase transition. The interpretation consistent with all our analyses—x-ray diffraction, SHG, and hysteresis measurements—is that biaxial compressive strain increases the $T_c$ of BaTiO$_3$.

Hysteresis measurements were made on 200-μm-diameter capacitors of strained BaTiO$_3$ thin films sandwiched between epitaxial top and bottom electrodes of the conducting perovskite oxide SrRuO$_3$ (37). High-resolution x-ray diffraction measurements (summarized in Table 1) revealed the BaTiO$_3$ ferroelectric layers as well as the 1000-A-thick SrRuO$_3$ bottom electrodes to be fully coherent with the underlying substrates. No relaxation was observed even for BaTiO$_3$ films as thick as 500 Å on DyScO$_3$ and 2000 Å on GdScO$_3$. The critical thicknesses of BaTiO$_3$ thin films grown on coherent SrRuO$_3$ bottom electrodes on DyScO$_3$ and GdScO$_3$ are higher than those of BaTiO$_3$ films grown directly on GdScO$_3$ and DyScO$_3$. This observation is consistent with critical thickness theory, in which 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 (26). Because the leakage in the coherent stack containing a 500-A-thick BaTiO$_3$ layer on DyScO$_3$ was too high for good ferroelectric hysteresis measurements, a SrRuO$_3$/BaTiO$_3$/SrRuO$_3$/GdScO$_3$ stack was grown with a 2000-A-thick BaTiO$_3$ layer. This latter stack had low leakage; however, it was partially relaxed.

Figure 3A shows the ferroelectric hysteresis loops measured on the ferroelectric stacks grown on GdScO$_3$ and DyScO$_3$ substrates with 2000-A-thick BaTiO$_3$ layers, together with results from a BaTiO$_3$ single crystal (32). 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 BaTiO$_3$ films. Even though we used SrRuO$_3$ 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

---

**Fig. 2.** (A) 2D images at selected temperatures of the x-ray diffraction peaks from a BaTiO$_3$ single crystal and strained BaTiO$_3$ thin films. (B) Temperature dependence of the lattice parameters of single-crystal BaTiO$_3$, and strained BaTiO$_3$ thin films grown by MBE on DyScO$_3$ substrates and GdScO$_3$ substrates. The in-plane (\(I\)) and out-of-plane (\(0\)) lattice constants of the BaTiO$_3$ thin films and underlying substrates are shown. The change in slope at high temperature signals a phase transition. The error bars (±SD) of the measured lattice constants are shown to the left of each curve. The measured values of the out-of-plane lattice constant of biaxially strained BaTiO$_3$ are compared with theoretical predictions (10, 21) with and without a ferroelectric transition. (C) Optical SHG signals from a BaTiO$_3$ single crystal [heating (black open circles) and cooling (black filled circles)] and the same strained BaTiO$_3$ on GdScO$_3$ film as (B) [heating (blue open squares) and cooling (blue filled squares)]. The fundamental wave (wavelength 900 nm, 65-fs laser pulses) is incident on the sample at an angle of $\phi = 23^\circ$ on the substrate side of the thin film and at normal incidence ($\phi = 0^\circ$) for the BaTiO$_3$ single crystal. SHG signals of 1 arbitrary unit (a.u.) or lower are at the noise level of our lockin-based measurement system. The inset shows polar plots of SHG intensity (radius) versus fundamental polarization (azimuth). Circles are experiment and solid lines are theory (21, 35).
asymmetric interfaces. The $P_c$ and coercive field ($E_c$) 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 $P_c$ value is almost 270% of the 26 μC/cm² of single crystal BaTiO₃. 3.5 times higher than the maximum switching charge density (20 μC/cm²) assumed in the scaling analysis of FeRAM (18), and comparable to the $P_c$ of unstrained Pb(Zr,Ti)O₃ films (33). As this $P_c$ of ~70 μC/cm² was observed in a partially relaxed sample with $e_r$ of ~1.3%, a coherently strained BaTiO₃/DyScO₃ sample with $e_r$ of ~1.7% could have an even higher $P_c$.

Another important issue for the application of ferroelectric capacitors to memory devices is the loss of switched polarization after repeated switching, i.e., fatigue. We performed fatigue measurements 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 $V_{\text{max}} = 4$ V, where $V_{\text{max}}$ is the amplitude of the pulse voltage. $V_{\text{max}} = 4$ V corresponds to 200 kV/cm of the electric field. The switched polarization decreased by 10% of its original value after 10⁶ fatigue 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 (34, 35).

As a check that the enhancement of $T_{\text{r}}$ observed in coherently strained BaTiO₃ thin films grown by MBE (Fig. 2B) is inherent and applicable to a device structure with a conductive bottom electrode, we performed high-temperature x-ray diffraction measurements on the coherent BaTiO₃ thin films with SrRuO₃ bottom electrodes grown by PLD. Figure 3B 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 consistent with the absence of misfit dislocations along the interface between GdScO₃ and SrRuO₃ and along the interface between SrRuO₃ and BaTiO₃, as shown by the cross-sectional transmission electron microscope images in Figs. S1 and S2 (21). As seen in the figure, the transition behavior of the PLD samples is quite similar to those grown by MBE. $T_{\text{c}}$ was determined to be ~420°C and ~680°C for samples grown on GdScO₃ and DyScO₃, respectively. The green solid and dashed lines in Fig. 3B 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 BaTiO₃. This experimental dependence of $T_{\text{r}}$ on $e_r$ is also consistent with the expectations shown in Fig. 1.

In summary, we have demonstrated that the ferroelectric properties of BaTiO₃ can be markedly 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. Another application of strain-engineered BaTiO₃ films is high-speed electro-optic modulators, in which the sizeable electro-optic coefficients of BaTiO₃ can be enhanced by appropriate strain engineering. The ability to withstand huge strains gives thin films a degree of freedom absent from bulk. This can be exploited to enhance the ferroelectric properties of any ferroic system, including multiferroics (8, 22, 36), whose ferroic order parameter has a strong coupling to strain.

References and Notes

19. For biaxial tensile ($e_{11} > 0$) or biaxial compressive ($e_{11} < 0$) strains, $T_{\text{r}}$ is expressed as follows: $T_{\text{r}} = \frac{T_{\text{r0}} + 2c_2 c \alpha T_{\text{c}}}{2c_2 + \alpha}$. $T_{\text{r0}}$, $e_{11}$, and $\alpha$ are the Curie temperature, strain, and the Curie constant, respectively. $Q_{t1}$ and $Q_{t2}$ are electrostrictive coefficients, and $s_{11}$ and $s_{12}$ are elastic compliances. The breadth of the green region in Fig. 1 for $T_{\text{r}}$ is due to the variation in what are considered the most accurate reported values of these constants for BaTiO₃ single crystals (20, 21). Because $Q_{t1}$ and $Q_{t2}$ are not measured, $T_{\text{r}}$ is predicted to increase for both positive and negative strains.
21. Materials and methods are available as supporting material on Science Online.
25. This thickness is a result of the low operational voltage of FeRAM (about 1.2 V in 2007) coupled with the need for a ferroelectric layer with low leakage. For reliable switching, the FeRAM operational voltage divided by the thickness of the ferroelectric should be several times larger than the coercive field of the ferroelectric. Thin film ferroelectrics have coercive fields of 10 to 100 kV/cm. This is true for our films as
Cation Exchange Reactions in Ionic Nanocrystals

Dong Hee Son, Steven M. Hughes, Yadong Yin, A. Paul Alivisatos

Cation exchange has been investigated in a wide range of nanocrystals of varying composition, size, and shape. Complete and fully reversible exchange occurs, and the rates of the reactions are much faster than in bulk cation exchange processes. A critical size has been identified below which the shapes of complex nanocrystals evolve toward the equilibrium shape with lowest energy during the exchange reaction. Above the critical size, the anion sublattice remains intact and the basic shapes of the initial nanocrystals are retained throughout the cation exchange. The size-dependent shape change can also be used to infer features of the microscopic mechanism.

Chemical transformations from one solid to another via insertion and exchange of atoms can be used to modify the properties of crystalline materials (1). Recent developments have enabled the production of many technologically important crystalline materials in nanometer sizes, with a wide range of size- and shape-tunable properties (2–8). Of particular interest is the creation of nanocrystals with nonequilibrium shapes and with higher structural and compositional complexity (9–13). In extended solids, reactions involving chemical transformation are in general very slow because of high activation energies for the diffusion of atoms and ions in the solid. For this reason, typical solid-phase reactions require very high temperatures or pressures (14–16) and therefore would seem to be incompatible with kinetically controlled nonequilibrium nanostructures.

However, in crystals only a few nanometers in size, both the thermodynamics and kinetics of reactions can change with size. For example, a large surface-to-volume ratio can be accompanied by a lowering of phase transition temperatures (17, 18). With the decrease in the volume, statistical averaging of the kinetics and mechanisms over a distribution of heterogeneous reaction sites intrinsic to the bulk solid is also reduced, leading to more homogeneous molecule-like reaction kinetics and even different reaction mechanisms in nanocrystals (19). The optimal use of various chemical transformation methods to broaden the range of nanocrystalline materials depends on an understanding of how chemical transformations in a crystalline solid will be affected by a reduction in size. We show that cation exchange reactions can occur completely and reversibly in ionic nanocrystals at room temperature with unusually fast reaction rates. We also show that the crystal structure and morphology of the reaction products are strongly dependent on the size and shape of the nanocrystals.

The prototypical semiconductor nanocrystal system of CdSe reacts with Ag⁺ ions to yield Ag₂Se nanocrystals by the forward cation exchange reaction, and vice versa for the reverse cation exchange reaction. We chose to work with CdSe nanocrystals because of the high degree of control over size and shape that has been achieved (2, 3). The conversion to Ag₂Se is strongly favored by a thermodynamic driving force of about \(-1000\) kJ/mol in the bulk (20, 21). Ag₂Se also exhibits an interesting temperature-dependent polymorphism: The superionic conducting phase transition occurs at a relatively low temperature of 133°C in the bulk phase (22). Thus, it may be possible to prepare Ag₂Se with unusually high cation mobility. These two factors favor complete cation exchange in nanocrystals and may prove sufficient to overcome the fact that the exchange reaction is completely kinetically hindered at ambient temperature and pressure in the bulk.

We investigated the reaction by mixing a solution of CdSe nanocrystals (diameter 4.2 nm) in toluene with a small amount of methanolic solution of AgNO₃ under ambient conditions. The volume fraction of methanol in the solution mixture is about 1%; the solution contains Ag⁺ ion in a slightly larger amount than necessary to replace all the Cd²⁺ ions in the nanocrystals. Methanol more strongly binds to any free binary cations in solution and thus favors the forward reaction. A rapid (\(<1\) s) change of solution color and complete disappearance of fluorescence is observed upon mixing the solutions. Measurements of the x-ray diffraction (XRD) patterns and optical absorption spectra confirm that the reaction product is Ag₂Se (Fig. 1). The reverse reaction is done under ambient conditions by mixing Ag₂Se nanocrystals with an excess amount (typically 50 to 100 times the initial Cd²⁺ content) of Cd(NO₃)₂ in a mixture of toluene and methanol in the presence of tributylphosphine (volume fraction <3%). A slower color change back to that of CdSe nanocrystals and the reappearance of fluorescence are observed over a period of 1 min. XRD patterns, optical absorption, and fluorescence spectra all indicate that CdSe is recovered from the reverse cation exchange. The XRD linewidths of the initial and recovered case are nearly identical. Moreover, the absorption and fluorescence peak positions, which show strong size dependence due to the quantum confinement effect (2), are also nearly identical for the initial and recovered CdSe nanocrystals. Finally, transmission electron micrograph (TEM) images of the initial and recovered