Giant Enhancement of Ferroelectricity

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Enormous strains can exist in thin films when one material is deposited on another due to differences in crystal lattice parameters and thermal expansion behavior between the film and the underlying substrate. As a result, the properties of thin films can be dramatically different than the intrinsic properties of the corresponding unstrained bulk materials. Biaxial compressive strain has been used to dramatically 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 environmentally benign lead-free ferroelectric for non-volatile memories and electro-optic devices.

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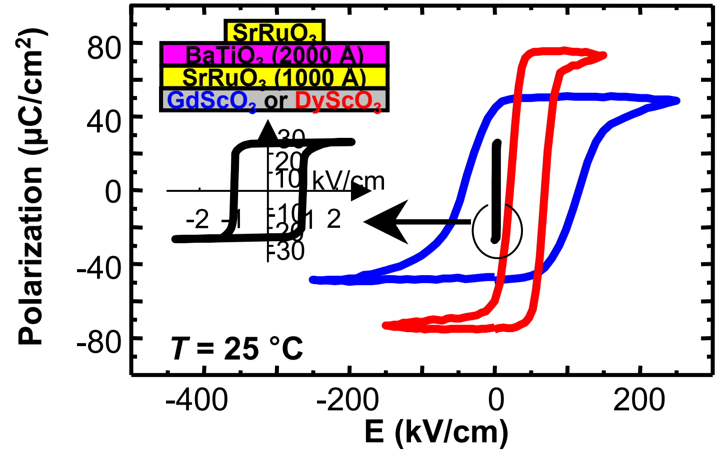

Figure 1. Polarization-electric field hysteresis loops of strained $BaTiO_3$ thin films and bulk single crystal

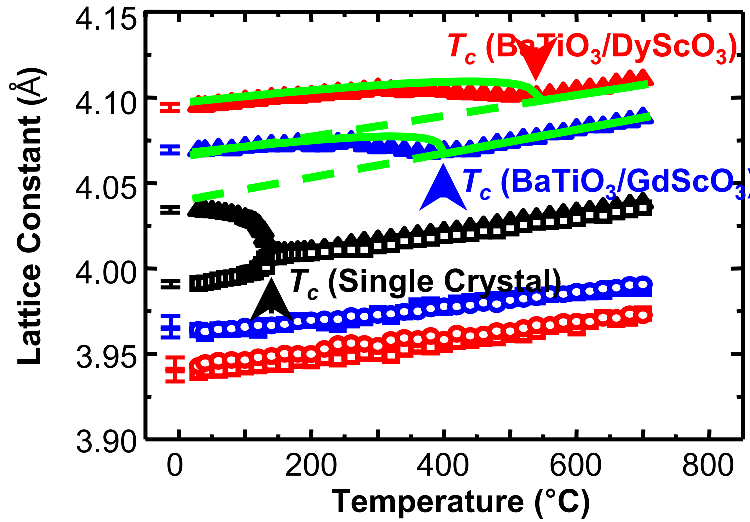

Figure 2. Temperature dependence of the lattice parameters of single crystal $BaTiO_3$ and strained $BaTiO_3$ thin films

Aim of the project:

Strain engineering could facilitate the introduction of more environmentally benign ferroelectric random access memories (FeRAM). Large shifts in the transition temperature (*Tc*) and remanent polarization (*Pr*) are expected and have been observed 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, Pb(Zr,Ti)O3 and SrBi2Ta2O9, are (i) the volatility of the lead and bismuth constituents of these materials that complicates their introduction into semiconductor fabrication facilities and (ii) environmental issues associated with the toxicity of lead. We demonstrate that the ferroelectric properties of BaTiO3 can be enhanced using strain to make them viable for ferroelectric memory and high speed electro-optic device applications.

Research results:

Epitaxial BaTiO3 thin films were grown on (110) GdScO3 and (110) DyScO3 substrates which have appropriate lattice constants to impart lattice mismatch of about –1.0% and –1.7%, respectively, on coherent (001) BaTiO3 films.

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 (2-D) area detector. The in-plane and out-of-plane lattice parameters of the strained BaTiO3 films are plotted as a function of temperature in Fig. 2. 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. Furthermore, The *Tc* of the coherent BaTiO3 thin films shown in Fig. 2 are ~400 °C on GdScO3 and ~540 °C on DyScO3.

Figure 1 shows the ferroelectric hysteresis loops measured on the ferroelectric stacks grown on GdScO3 and DyScO3 substrates with 2000 Å thick BaTiO3 layers, together with results from a BaTiO3 single crystal. The *Pr* and coercive field (*Er*) 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 *Pr* value is almost 270% of the 26 μC/cm2 of single crystal BaTiO3, 250% higher than the switched charge density assumed in the scaling analysis of FeRAM, and comparable to the *Pr* of unstrained Pb(Zr,Ti)O3 films.

Significance of this work:

We have demonstrated that the ferroelectric properties of $BaTiO_3$ can be dramatically enhanced through strain engineering. These strain-engineered heteroepitaxial thin film provide a broad range of operating temperature 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 $BaTiO_3$ films is high-speed electro-optic modulators, where the sizeable electro-optic coefficients of $BaTiO_3$ 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, whose ferroic order parameter has a strong coupling to strain.