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Undergraduate

Enhancement of Ferroelectrics: Strain-engineered Ferroelectric Thin Films

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In 1920, Joseph Valasek discovered that the polarization of the compound known as Rochelle Salt could be reversed by application of an external electric field. In effect, he was the first to recognize ferroelectric properties in a crystal. Ferroelectric materials are generally defined as those whose spountaneous polarization can be reversed through the application of an external electric field (Scott, 2007). (Fig. 1)

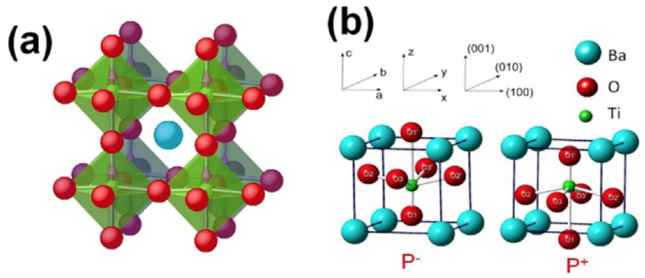

Figure 1: Perovskite oxides, of general formula ABO3 with a pseudocubic structure, where A and B are two different cations, furnish many interesting ferroelectrics. The B-type cation is octahedrally coordinated with oxygen. In the example shown, BaTiO3, it is the relative symmetry breaking displacement of the Ti atoms with respect to the O atoms which is responsible for the spontaneous polarization. BaTiO3 has three ferroelectric phases: tetragonal, orthorhombic and rhombohedral. (Oxides. (n.d.).

At first, ferroelectric devices were restricted to bulk materials, but in the 1980s, thin-film, a technology utilizing extremely thin layers of material, was developed. The focus of ferroelectric study has since moved from bulk properties to its thin-film properties, especially with the promise of using ferroelectric materials in computer microchips, a type of thin-film technology.

Ferroelectric materials with spontaneous polarization due to the special arrangement of atoms in a lattice structure exhibit interesting pyroelectric and piezoelectric properties and have, therefore, attracted a lot of scientific attentions.

> "Strain engineering is a strategy employed in exploring the special behavior of ferroelectric materials where a strained layer of ferroelectric epitaxially grown with respect to the crystalline substrate layer."

Strain engineering is a strategy employed in exploring the special behavior of ferroelectric materials where a strained layer of ferroelectric epitaxially grown with respect to the crystalline substrate layer.(Eom et al., 2008) (Fig. 2)

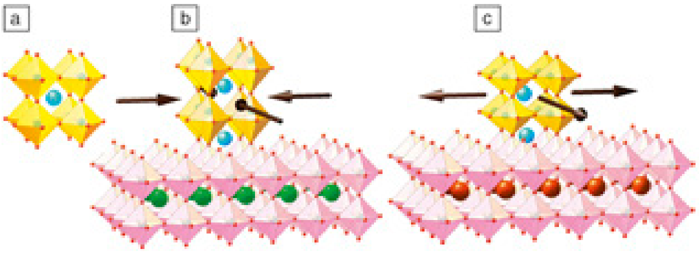

Figure 2: Before deposition, the structure is in an (a) unstrained state. When deposited on a substrate the energetic preference of the deposited atoms to follow the underlying substrate (epitaxy) can result in the film beginning in either (b) biaxial compression or (c) biaxial tension (Schlom, Chen, Fennie, Gopalan, Muller, Pan, Uecker, 2014)

This process creates a strained state. Under this strained state, the properties of the ferroelectric film differ greatly compared to the bulk ferroelectric, in a way that makes it suitable for use in applications such as memory storage on microchips. Before strain engineering, researchers used chemical alloying or doping to manipulate the properties of bulk ferroelectrics. A typical 0.1% strain--stretching of material to a length 0.1% greater than the original length--will cause bulk ferroic oxides to crack. Epitaxial strain has the advantage of resulting in a more durable and ideally disorder-free film. Strain field is the electric field that results from a strained lattice structure, and in strain engineering, differences in lattice parameters between the epitaxial film and the underlying substrate are what create the strain of the overall thin-film material.

Past decades have seen a rapid progress in algorithms and calculations for analyzing thin-film ferroelectrics. Some of the methods include first principles calculations(determining electronic structure by solving Schrodinger's equation), molecular dynamics(understanding how the molecules in the lattice structure move), phenomenological models based on Ginzburg-Landau theory(capturing salient features of the thermodynamic free energy for particular boundary conditions), and more, taking into account internal and/or external variables.(Schlom et al., 2014) These calculations are meant to predict electronic properties and structural characteristics of ferroelectric materials using computational methods. Predictions can then be verified and tested through experimental data to provide insight into ferroelectric investigations.

In strain engineered ferroics, the strain appearing in the film shifts the transition temperatures and can change the properties of the material such as the dielectric and piezoelectric constants and remanent polarization, or even can induce room temperature ferroelectricity in a non-ferroelectric material. (Haeni et al., 2004). Landau-Ginsburg-Devonshire (LGD) thermodynamic theory is the theoretical framework used for explaining and predicting equilibrium states and phase transitions in bulk materials. However, the order parameters (for ferroelectrics those are the electric dipole moment or polarization) used in regular LGD theory change considerably at the presence of the mechanical interactions between ferroic oxide and substrate. Thus, when applied to ferroelectric thin films with mixed mechanical conditions, the standard theoretical framework needs modification. A modified thermodynamic potential G is derived by an appropriate transformation. A minimization of such potential yields the equilibrium state of a film as a function of the temperature and misfit strain. One of the important predictions is proposed by Pertsev and Tagantsev using primitive free-energy theories. In the temperature–misfit strain phase diagram they generated, a new ac phase occurs with polarization lying between the a and c phase of $BaTiO_3$. However, the aforementioned methods are only applicable when the free-energy expansion is up to fourth order in order parameter(polarization). As pointed out in some later works on ferroelectric thin film, including works by Tagantsev in 2013, for perovskites ferroelectric a more common situation requires the potential to be expanded up to sixth order in polarization. Thus, higher order couplings should be taken into account. The missing higher order coefficients are calculated using ab initio methods. When high-order electromechanical coupling terms in thermodynamics of ferroelectric thin films are added and the new temperature-misfit strain phase diagram is drawn, the ac phase previously predicted disappears. This shows the power of ab initio modeling over primitive free-energy theories.(Scott 2007) (Fig. 3)

The thin-films discussed thus far have been homogeneous films with single composition. Novel behaviors can be predicted from modeling and observing experimental data for compositionally graded monodomain ferroelectric films. Compositionally graded ferroelectrics possess a spatial variation in chemical composition that breaks the symmetry of the system (Zhang et al., 2014). To account for the spatial asymmetries, a new LGD-based thermodynamic framework is needed. Possible modifications include additional energy terms, including flexoelectric, gradient, and depolarization energies (Karthik et al., 2013; Ban, Alpay & Mantese, 2003; Catalan, Sinnamon, & Gregg, 2004; Eliseev et al., 2014). These gradient and energy tend to change the polarization behavior of the material by stabilizing a ferroelectric phase in the otherwise paraelectric composition. Some of the behaviors that are special to graded thin-film include: self-poling(Mantese, Schubring, Micheli, & Catalan, 1995), built-in potentials(Mantese, & Alpay, 2005), asymmetric or shifted hysteresis loop(Karthik, Mangalam, Agar & Martin, 2013), (Fig. 4) and the potential for geometric frustration(Choudhury, N., Walizer, L., Lisenkov, S., & Bellaiche, L. 2011). As a consequence, such systems are potentially important for a range of devices.(Mantese, & Alpay, 2005).

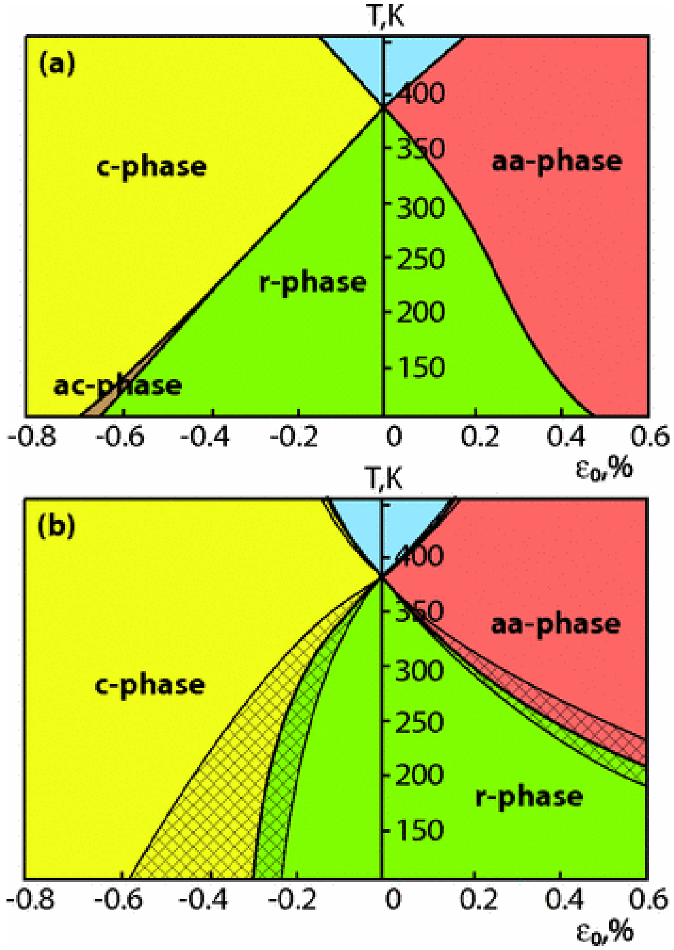

Figure 3: $BaTiO_3$ temperature-stress diagram with ab initio results (b) and results from Pertsev and Tagantsev in 1999 (a). (b) Developed with coefficient appended with the high-order coefficients. The hatched regions demonstrate the shift of the transition lines within the error bars of the coefficients. (Kvasov, & Tagantsev, 2013)

In 1976, Rotiburd predicted the polydomain phases of epitaxial layers theoretically. During the past years, experiments and simulations have proven the existence of polydomain structure on various crystalline substrates. Polydomain structure complicates the study by introducing

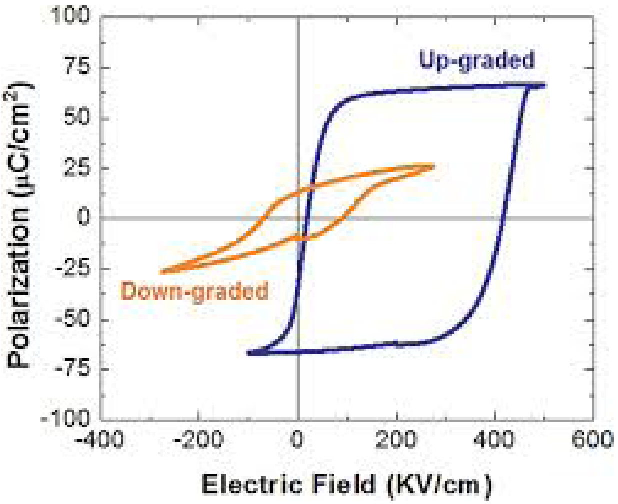

Figure 4: (Color online) Ferroelectric shifted hysteresis loops obtained at 1 kHz for compositionally up-graded and down-graded thin films. (Karthik, Mangalam, Agar & Martin, 2013)

internal mechanical stress caused by its inhomogeneity. The challenge can be solved by proposing new modeling to deal with existing stress at the film-substrate interface and the domain wall junctions. A rigorous nonlinear LGD thermodynamic theory has been developed for polydomain epitaxial films of perovskite ferroelectrics. The method makes it possible to determine polarizations, lattice strains, and mechanical stresses inside dissimilar domains forming dense laminar structures. Features of the theory demonstrate its great practical importance, because ferroelectric thin films have many possible applications in advanced microelectronic and micromechanical devices.(Koukhar, Pertsev, & Waser, 2001)

Thin-film technology made the development of high and novel electronic devices possible. The polarization of typical ferroelectric is reversed at a critical "coercive" field at about 50 kV/cm. In a bulk device, typically 1-mm in thickness, the voltage corresponding to this critical field is about 5-kV, which could not be put into mobile digital telephones. However, with submicrometer ferroelectric films, the voltage reduces drastically to less than 5V, permitting it to be integrated to microchips.(Scott 2007) Properties of ferroelectric thin-films are greatly enhanced by strained-engineering. With the distinctive electric field, thermal, and stress susceptibilities discovered by researchers through strain-engineering over the past decades, a range of devices such as transpacitors and transponents have been developed.(Mantese, & Alpay, 2005)

Over the past decades, the study of strained-engineering constantly present exciting new perspectives in epitaxial thin-film science and encourage novel physical solid-state devices. This field of study is practically useful if we can better modulate the theoretical background and predict how to control and engineer the thin-film structure with desired physical properties.

> "In strain engineered ferroics, the strain appearing in the film shifts the transition temperatures and can change the properties of the material such as the dielectric and piezoelectric constants and remanent polarization, or even can induce room temperature ferroelectricity in a non-ferroelectric material. "

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