

Molecular adsorbates and ferroelectric nanostructures: a 'memorable' combination

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Ferroelectric phase transitions of perovskite-based oxides represent an important class of structural phase transitions that bear significant technological implications. Ferroelectric perovskites exhibit a spontaneous electric polarization that can be reoriented by an external electric field. As the temperature increases and reaches a critical temperature, T_C , these oxides undergo a polar-to-centrosymmetric structural transformation and lose their ferroelectricity. The size-dependent evolution of T_C dictates the ultimate size limit of ferroelectric nonvolatile memory and has been the subject of numerous investigations. One of the most important factors determining the stability of nanoscale ferroelectricity is the compensation of polarization-induced surface charges. Incomplete screening of surface charges results in a depolarization field that opposes the bulk polarization, thereby suppressing ferroelectricity. In typical ferroelectric devices, the charge is screened by two metallic electrodes that sandwich the ferroelectric material. The observations of stable ferroelectricity in thin ferroelectric films and nanocrystalline materials in the absence of metallic electrodes suggest, however, that other types of screening mechanisms may also be operative in stabilizing nanoscale ferroelectricity.

We discuss combined experimental and theoretical investigations that characterize nanoscale ferroelectricity in single-crystalline BaTiO₃ nanowires and propose a new mechanism for the surface charge screening by atomic and molecular adsorbates. Variable-temperature scanned probe microscopy is used to probe temperature-induced phase transitions in individual single-crystalline BaTiO₃ nanowires lying on gold (Au) substrates, thereby removing the difficulties associated with ensemble averaging. The measurements show that the depression of the phase transition temperature T_C is inversely proportional to the nanowire diameter d_{nw} and that the smallest d_{nw} for which a nanowire exhibits room temperature ferroelectricity is ~ 3 nm. The extrapolation of our results indicates that the critical diameter at which the ferroelectricity is stable at low temperatures is ~ 0.8 nm, suggesting the persistence of polarization at a much smaller length scale than previously reported for BaTiO₃.

The observation of stable ferroelectricity in such small diameter nanowires in the absence of a top metallic electrode points to a new screening mechanism to reduce or eliminate depolarizing fields. Theoretical analyses based on density functional theory (DFT) calculations, phenomenological Landau theory and thermodynamic analyses indicate that the charge compensation is provided by molecular OH adsorbates. Surprisingly, the theoretical calculations show that the adsorbate-induced charge screening is even more effective than what is provided by metallic and oxide electrodes and stabilizes ferroelectricity in smaller BaTiO₃ structures. This finding suggests that perovskite-based ferroelectric devices may be miniaturized further than previously imagined by exploiting the new charge compensation mechanism.

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