Quantification of Defect-Defect Interactions in Ferroelectric Materials

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The ability to tailor response and performance of functional materials via careful manipulation of defect concentration can result in dramatic effects on material functionality. Semiconductor materials are a prime example of this, where modification of the type, charge, concentration, spatial distribution, and mobility of defects is used to manipulate material properties, resulting in the design of devices that we use and interact with on a daily basis, from modern *pn*-junction transistors to photovoltaic (PV) cells, to photoactive image sensing. Ferroelectrics are no exception – their advantageous dielectric, polarization, and electromechanical responses have made them excellent candidates for use in microelectromechanical systems (MEMS) sensors and actuators, logic elements, and environmental energy harvesting, all of which derive advantageous responses from some degree of defect-defect interactions in the ferroelectric material.

Chemical impurity doping has traditionally been employed to study the effects of defect concentrations in ferroelectric materials, but complications arising from compositional heterogeneity, such as phase separation and chemical instabilities, often make interpretation of results difficult. On the other hand, irradiation is a versatile means of evaluating defect-defect interactions in ferroelectric materials that avoids the compositional complexities of doping. Defects generated as a result of X-ray, proton, gamma and neutron irradiation can modify the motion of nonlinearly-mobile internal interfaces (e.g., domain walls and eventual phase boundaries), resulting in substantial changes to ferroelectric functional responses.

In this work, a phenomenological model is developed to quantify defect-defect interactions and compare material performance in ferroelectric materials as a function of radiation dose, relying on the pinning of the mobile internal interfaces within a ferroelectric volume as the primary means of response modification. Two coefficients arise from the model, i.e. the effective change in volume of defect-defect interactions per new defect created/activated in the material, and the effective rate of defect saturation. Leveraging such parameters, defect-defect interactions can be quantified, allowing for predictions of material behavior as a function of defect concentrations arising from irradiation.

The model is first demonstrated by comparing historical data from the literature on irradiation of ferroelectrics in both thin film and bulk form, in addition to showing good agreement with prior work on dopant concentration dependence of ferroelectric response. To further elucidate the effects of microstructure on defect-defect interactions, experimental trends in gamma-irradiated PZT thin films with columnar vs. equiaxed grain structures are quantified and studied, employing the phenomenological model. Results of comparing dielectric and electromechanical responses show nearly equivalent volumes affected by defect-defect interactions per new defect created; however, samples with columnar grains demonstrate lower rates of defect saturation for both dielectric and electromechanical responses. Incident gamma rays may intersect less with the boundaries of directional columnar grains, and thus create fewer defects. Additionally, the surface-area-to-volume ratio of columnar grains is greater, potentially increasing effective defect sinks for accumulation of response-robbing defects. Ultimately, the proposed model offers avenues toward more effective methods of defect engineering, not only in ferroelectric materials, but a broader class of functional metal oxides.