Monte Carlo simulations of imprint behavior in ferroelectrics

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In this letter, Monte Carlo simulation methods were used to investigate the influence of the defect orientation and concentration on the hysteresis loop in ferroelectric thin films. The hysteresis loops were calculated by an existing Monte Carlo model. For a certain type of defect orientation, the simulations revealed an asymmetric hysteresis loop behavior, similar to hysteresis curves recorded by imprint measurements. Though these results may not directly offer a new explanation for the imprint mechanism in ferroelectric thin films, they still provide insight information about the often observed phenomenon of imprinted hysteresis loops of as-prepared thin-film capacitors. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2140076]

PZT thin films are very promising candidates for ferroelectric random access memory applications. To be chosen for such devices, this material has to fulfill requirements due to reliability aspects. The most important failure mechanisms of ferroelectric capacitors are fatigue[1] and imprint.[2] The fatigue effect is solved technologically by introducing oxide electrode materials, but a physical understanding of this process is still open.

Several models have been proposed to explain the imprint behavior of ferroelectric thin films. Currently, there are two principle types of reasonable models. The first one is correlated with defect dipoles. The second type deals with interface-related mechanisms, such as stress-induced interface layer[3] or a nonferroelectric interface layer between the film and the electrode.[4] This nonferroelectric interface layer leads to an insufficient screening of the polarization charges on the electrodes and therefore reveals a depolarizing field that is able to separate and trap charges within this region.[5]

In this letter, the influence of defect concentration and its orientation on the shape of the hysteresis curves will be analyzed using Monte Carlo methods and discussed in the eye of the imprint scenario. The two-dimensional Monte Carlo simulation used to calculate the hysteresis loops was based on a model published by Potter *et al.*[6] and was further improved by Bolten.[7] This model takes into account the dipole-dipole interaction, the gradient energy, and the energy of the dipoles in an external electric field. A simulation volume of 100×100 unit cells is used to calculate a hysteresis loop. Each unit cell is represented by a tetragonal lattice point with a fixed dipole moment. The dipole moment remains constant during the whole simulation procedure. The simulation is started with a completely random configuration of the dipoles. For each simulation step, the minimum of the energy is calculated for the total lattice. 400 single Monte Carlo steps are performed per spin (MCS/spin). After each spin, the lattice configuration was allowed to relax for 200 MCS/spin, after which the configuration was saved to a file, and the current polarization value was recorded. After this initialization, an external electric field was applied along the *y* direction of the simulation volume and charged stepwise to trace the single points of a complete hysteresis loop. Free boundary conditions were employed by simply truncating the lattice. No compensating charges were introduced on the "surface" of the lattice to simulate screening charges. Details of the applied model and its implementation can be found elsewhere.[7]

In this simulation model, three different kinds of defect types were introduced. At first, voids were implemented as lattice cells which exhibit no spontaneous polarization at all. This kind of defect can describe nonferroelectric inclusions, voids, or other defects that locally suppress the ferroelectric spontaneous polarization and is labeled as defect type 0. Second, stationary nonferroelectric defect dipoles were installed that were not allowed to switch. They remain in their initially assigned orientation. The dipole moment of these defects is set to the double value of the regular dipoles in the neighborhood. The defect dipoles were oriented parallel to the external field (along the *y* axis). The local distribution of the defect dipoles was chosen to be random. This type of defect was labeled as defect type 1. These defects may describe defect dipoles in the ferroelectric film resulting, e.g., from acceptor doping which were held responsible for aging effects. The last defect (defect type 3) describes the same kind of defect dipoles as defect type 1, but here the dipoles are randomly oriented and randomly aligned inside the film.

Simulating hysteresis curves with these kind of defects with a high concentration of 10%, one can clearly see that all defect types lead to a decrease of polarization and a slant of the hysteresis loop except for defect type 1. In this case, a significant shift of the hysteresis curve along the voltage axis was observed combined with an asymmetric deformation of the loop. All simulated hysteresis curves are displayed in Fig. 1. The polarization values are calculated in arbitrary units. The shift and deformation behavior of defect type 1 is very similar to results observed for imprint measurements. To achieve more details about this interesting feature, a series of hysteresis simulations was started where the doping concentration of defect type 1 was varied from 0.0% to 20.0%. Several hysteresis of this measurements were shown in Fig. 2. By increasing the defect concentration, the shift of the curve along the voltage axis is enforced. For high concentration values, the simulated hysteresis loops show a drastic deformation which is hardly observed experimentally. The dipole configuration shows that areas with a high number of

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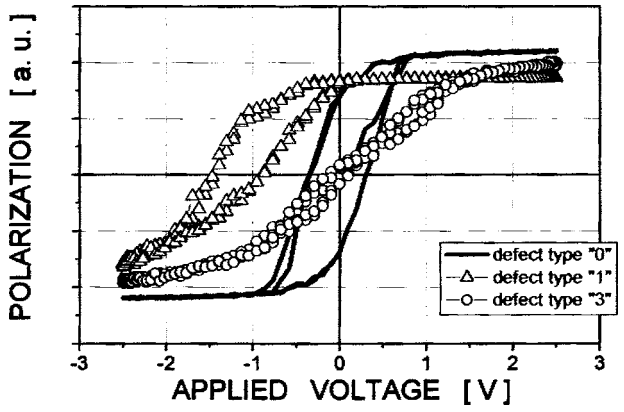

FIG. 1. Hysteresis loops for different types of defects varying in orientation and their local distribution. The simulations were calculated with a 50 $\times$ 50 cell sized, lattice free boundary conditions, and a defect concentration of 10%.

defects forced the orientation onto the surrounding normal dipoles which were thus effectively prevented from switching back. Though the simulation routine itself only calculates single hysteresis loops, the results shown in Fig. 2 reveal a qualitative impression of the correlation between the imprint effect and an increase of the defect dipole concentration. The imprint characteristics in real measurements is described by the shift of the mean coercive voltage over time.

If one normalizes the values of polarization for the single hysteresis curves at different states of imprint and symmetrizes the values of the saturated polarization, the coercive voltages are given by

$$\Delta V_{C,\mathrm{shift}} = \frac{1}{2}(V_{C,+} + V_{C,-}). \tag{1}$$

The correlation between the obtained shift margins and the defect concentration is displayed in Fig. 3. With increasing defect concentration, the mean coercive voltage shift became higher, too. The run of the mean coercive voltage over the defect concentration can be described empirically by a logarithmic growth function given by

$$\Delta V_{C,\mathrm{shift}}(\mathrm{conc.}) = \alpha + \beta \ln(\gamma \cdot \mathrm{conc.} + \delta). \tag{2}$$

With this equation, the parameters of this curve are α=0.144, β=1.555, γ=0.107, and δ=0.900. The curve of the fitted parameters is shown in Fig. 3, too, showing a good

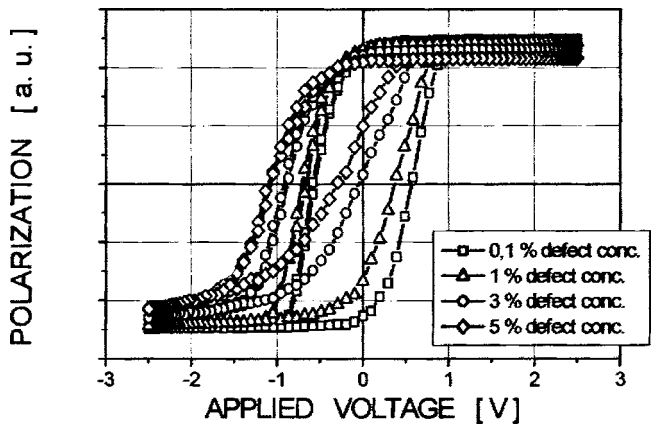

FIG. 2. Hysteresis loops for different amounts of defect concentrations type 1 varying from 0.1% to 5.0% calculated with a 100$\times$100 lattice cells.

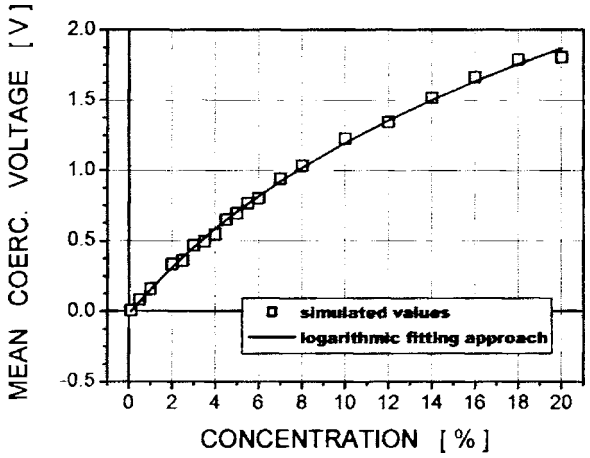

FIG. 3. Correlation between the mean coercive voltage shift and the defect concentration for all simulated hysteresis loops fitted by an exponential curve.

match between the fitting approach and the calculated data points.

If we now try to combine the results of our Monte Carlo simulations with experimental results, we have to find a feasible fit function for the measured voltage shift behavior over time. In earlier publication, it could be clearly shown that the imprint behavior is not a linear function of the elapsed time (on a logarithmic scale) as commonly assumed.[8] To achieve a sufficient fit approach, several dependencies were performed and compared by their minima values of nonlinear least squares. So qualitatively, this behavior has to be approximated by a slight exponential growth fit.

The voltage shift of a real thin film is given in Fig. 4. Here, a 140 nm thick PZT film is investigated by hysteresis loops with an applied voltage amplitude of 5.0 V at a frequency of 1 kHz. In between these single hysteresis curves, a constant bias voltage of 2.5 V was applied to the sample in order to enforce the voltage shift. Here, the shift of the mean coercive voltage is plotted over the logarithmic values of the elapsed time. The slight exponential behavior can be fitted by

$$\Delta V_{C,\mathrm{shift}}[\log(t)] = \Delta V_{C,0} + b \exp[c \cdot \log(t) + d], \tag{3}$$

where b, c, and d are constants, and $\Delta V_{c,0}$ represent the initial voltage asymmetry. By fitting the run of the curve in Fig. 4 with the equation above, one obtains values of

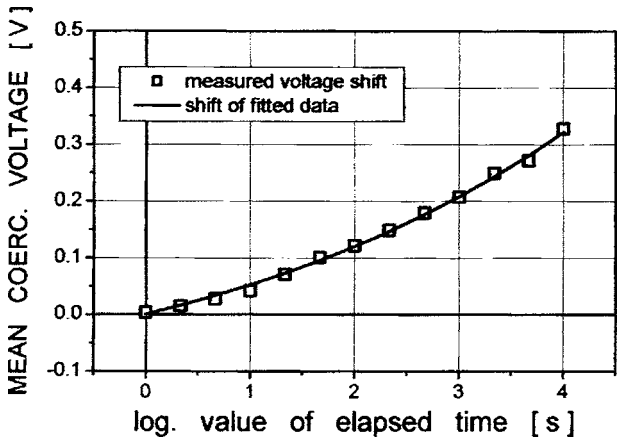

FIG. 4. Shift of the mean coercive voltage of a regular measured PZT thin film plotted over the logarithmic value of the elapsed time revealing a nonlinear shift behavior.

$\Delta V_{c,0}=-0.17$, $b=0.05$, $c=0.26$, and $d=1.25$. The curve of the calculated parameters nicely covers the scattered data points in Fig. 4.

If we now combine the results of our Monte Carlo simulations with the experimental results, we assume that the voltage shift due to the defect concentration can be interpreted as a qualitative quantity of the measured shift behavior. Therefore, the voltage shift in Eqs. (2) and (3) is set equal. With this assumption, we obtain a time-dependent equation of the amount of defect dipole concentration for a typical imprint behavior. So, Eq. (4) below gives the temporary development of the defect concentration for equivalent imprint rates:

$$\text{Conc.}(t) = A \cdot \exp(B \cdot t^C) - D. \tag{4}$$

This equation describes the voltage shift behavior as an exponential growth of defect concentration over time (on a linear scale!) resulting in an appropriate hysteresis shift behavior. The revealed parameters are $A=7.64$, $B=0.112$, $C=0.113$, and $D=8.41$. The numerical results have to be taken with care because these calculations are only valid for short times and low defect concentrations. High concentration values of more than 14% would reveal a drastic hysteresis shift and deformation behavior which is rarely observed for even very long measurement times in the area of months. It should be explicitly mentioned that all demonstrated results above should only give a qualitative impression of temporary creation of defects due to the imprint scenario. The fit parameters in Eqs. (2)–(4) depend on each other and therefore Eq. (4) could also be expressed by the combined parameters of Eqs. (2) and (3):

$$A = \frac{1}{\gamma}\exp\left(\frac{a-\alpha}{\beta}\right), \quad B = \frac{b}{\beta}\exp(d),$$

$$C = \frac{c}{\ln(10)}, \quad \text{and } D = \frac{\delta}{\gamma}.$$

In conclusion, it was found that the increased concentration of defect dipoles, randomly aligned but oriented along the y axis, can describe the imprint behavior in ferroelectrics quite well. From a detailed simulation series, a correlation between voltage shift and defect concentration could be determined. In comparison with imprint measurements, a time dependence of the voltage shift behavior was calculated. So, the experimentally observed imprint behavior can be clearly dedicated to a development of defect dipoles of type 1 inside the sample that were generated over time described by Eq. (4). The current imprint model suggests a nonferroelectric interface layer between the ferroelectric film and the electrode material where charges were separated and trapped.[4,5] The perception of creating defects of type 1 in a slightly exponential growing number is in complete agreement with this model. It should be mentioned that the presented simulation studies are not able to distinguish whether the defect dipoles are generated inside the ferroelectric film or at the interface. To describe the whole imprint effect in ferroelectrics, several extensions have to be introduced. But nevertheless, Monte Carlo simulations have shown that the creation of defects oriented in direction of the external electric field can cause a shift of the hysteresis curve along the voltage axis, which is comparable with the imprint behavior in ferroelectrics.

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