Grain-size effects in ferroelectric switching

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A model of ferroelectric switching that describes crystals composed of a large number of relatively small grains is presented. It is shown that, if the grain boundaries stop or significantly affect domain-wall growth, then the observed switching current transients will deviate from those predicted by the infinite-grain model of Ishibashi and Takagi. The model accounts for constant nucleation rate throughout the switching period and for constant domain-wall velocity. It is shown that at some time dependent only on the size of the grains and the domain-wall velocity, the switching-current transient changes from its small-time infinite-grain behavior to an exponential decay. The results are applied to two-dimensional Ising-model simulations.

I. INTRODUCTION

This paper is an extension of the previous work of Ishibashi and Takagi[1] (also see E. Fatuzzo,[2] and M. Avrami[3]). In that paper they presented a model of ferroelectric switching which occurs by means of nucleation and growth of opposite-polarity domains. The purpose of this paper is to examine the consequences of one of the assumptions that they made—that domains can grow without bound—and to present a model of switching for ferroelectrics whose grain boundaries stop domain-wall motion. Unlike the infinite-grain model of Ishibashi and Takagi, this new finite-grain model allows the possibility of indirectly obtaining microscopic parameters from bulk measurements. This theory should be relevant for the switching of thin-film ferroelectrics such as sol gel deposited lead zirconate titanate (PZT) in which the grain size is on the order of 1000 Å.[4]

Since all of the models assume that polarization reversal is due to formation and growth opposite polarity nuclei, in Sec. II we provide a review of classical nucleation theory. Section III provides a review of the results of the infinite crystal (Ishibashi) model. The finite-size grain model is presented in Sec. IV. Current transients generated by two-dimensional Ising simulations are analyzed using the above models in Sec. V.

II. CLASSICAL NUCLEATION THEORY (CNT)

We will assume that the ferroelectric is being switched by means of nucleation and growth of domains, and so we provide a brief review of classical nucleation theory. See J. D. Gunton *et al.*[5] for a more complete review of the theory of Becker and Döring.[6,7]

Let the system initially be in the "up" state, and apply a switching field in the "down" direction. If the field is sufficiently large it will be energetically favorable for each unit cell to be in the down state, regardless of the state of the surrounding ferroelectric. In this case the system is unstable and will switch immediately after the field is applied. The current transient will have the form of an exponential decay, as each unit cell changes to the down state without regard to the state of its neighbors. On the other hand, if the field is small, interactions with surrounding unswitched cells make it energetically unfavorable for a cell to switch. Immediately after the field is applied the ferroelectric will reach metastable equilibrium, and it will not switch to the down state until nuclei overcome a free energy barrier and begin to grow.

For the following assume that the system is isotropic and d dimensional. If the volume of a hyperspherical domain is V, define its radius by $C_d r^d \equiv V$, where $C_d = 2, \pi, 4\pi/3$ for $d = 1,2,3$, respectively. The surface area of the domain is given by $\gamma d C_d r^{d-1}$, where the parameter γ is a measure of the roughness of the surface. The energy associated with the creation of a domain of volume V is given by

$$U = 2[(\gamma d C_d r^{d-1}) U_S - h C_d r^d] , \tag{1}$$

where h is the applied field and U_S is the energy per unit area due to the surface. Assuming that the entropy associated with the domain is proportional to its surface area the free energy of the domain is

$$\begin{aligned} A &= U - TS \\ &= 2\Gamma r^{d-1} - 2h C_d r^d , \end{aligned} \tag{2}$$

where Γ is the free energy per unit area. The critical nucleus size occurs when the free energy reaches a maximum:

$$r_c = \frac{(d-1)\Gamma}{d C_d} . \tag{3}$$

Domains smaller than this will tend to shrink, and those larger will tend to grow. At low temperatures and for small fields the rate at which domains of this size are formed will be proportional to the formation free energy:

$$R \propto \exp(-A_c/kT) , \tag{4}$$

$$A_c = \frac{2\Gamma^d}{d} \left[\frac{d-1}{dhC_d} \right]^{d-1} . \tag{5}$$

This relationship has been verified in Ising simulations.[8]

III. MODEL I: INFINITE-GRAIN MODEL (IGM)

Four parameters are required to describe the polarization reversal. The probability of nucleation per unit volume per unit time is given by R, the initial radius of a nucleus by r_c, the domain-wall velocity by v, and the dimensionality of growth by d. In addition, crystals are divided into two categories—category-I crystals do not contain latent nuclei and the nucleation rate R is a constant, while category-II crystals contain latent nuclei and no new nuclei form after the field is applied. In this paper, only category-I crystals will be studied.

In both the infinite- and finite-grain models it is assumed that domains grow with uniform wall velocity. This is clearly an approximation—the critical radius of a nucleus is defined to be the radius at which it is as likely to shrink as grow. One expects that the wall velocity is a function of, among other things, the size of the domain. The velocity should approach a fixed value as the domain becomes appreciably larger than the size of the nucleus. This is illustrated in Sec. V.

Three-dimensional growth occurs when the nuclei are spheres of radius r_c. The domains grow isotropically, and the volume of a domain formed at time t_f is given by $S(t,t_f)=(4\pi/3)[r_c+v(t-t_f)]^3$. If the ferroelectric under study is a thin film, this implies that the nuclei form in the bulk of the material, away from the surfaces, and that before the surfaces stop the growth of a significant number of domains the film has essentially switched. Two-dimensional growth occurs when the ferroelectric is highly anisotropic. The nuclei form either in the bulk or at a surface, followed by rapid growth across the crystal. If this is the case, the nuclei can be considered cylinders of radius r_c, and the axes of all nuclei are assumed to be parallel. Therefore the crystal can be viewed as a sheet, and the area of a domain formed at time t_f is given by $S(t,t_f)=\pi[r_c+v(t-t_f)]^2$. In this case R is the nucleation probability per unit area. The crossover from three-dimensional to two-dimensional growth occurs when $vt_0 \approx W$, where t_0 is the time at which half the crystal has switched, and W is the film thickness. Similarly, one-dimensional growth occurs if domains grow rapidly from one surface to the other and the film is anisotropic with respect to the two directions parallel to the film. Domains can be assumed to form and grow on a line, with "volume" given by $S(t,t_f)=2[r_c+v(t-t_f)]^1$, and R representing nucleation rate per unit length. The volume for all three cases can be written as

$$S(t,t_f)=C_d[r_c+v(t-t_f)]^d , \tag{6}$$

where $C_d=2,\pi,4\pi/3$ for $d=1,2,3$, respectively.

The objective is to calculate $q(t)$, the probability that a given point P in the crystal is not inside a switched domain. The fraction of switched volume to total volume is given by $Q(t)=1-q(t)$, and the switching current is then found by

$$i(t)=2P_s\frac{dQ(t)}{dt}=-2P_s\frac{dq(t)}{dt} , \tag{7}$$

where P_s is the spontaneous polarization per unit volume. For category-I crystals Ishibashi and Takagi obtained the result

$$\ln q(t)=-R\int_0^t S(\tau,0)d\tau$$
$$=-\frac{C_dR}{v(d+1)}[(r_c+vt)^{d+1}-r_c^{d+1}] . \tag{8}$$

The current for category-I crystals is then given by

$$i(t)=2P_sC_dR(r_c+vt)^d$$
$$\times\exp\left[-\frac{C_dR}{v(d+1)}[(r_c+vt)^{d+1}-r_c^{d+1}]\right] . \tag{9}$$

If the size of a nucleus is negligibly small on the scale of the system, as is usually the case, then the current transient is of the form

$$i(t)=2P_s\theta t^d\exp\left[-\frac{\theta}{d+1}t^{d+1}\right] , \tag{10}$$

where $\theta=C_dRv^d$. The values of θ and d can be obtained by fitting the above equation to the experimental current transients—however, the nucleation rate or the wall velocity cannot be extracted separately from measurements of θ. As will be shown in the next section, this can be overcome by considering the switching of finite-size grains.

This model has been applied to actual data with varying degrees of success. For example, Dimmler *et al.*[9] applied the model to thin-film KNO_3 and found that the apparent dimensionality of domain growth seemed to depend on the film thickness. For a brief review of additional literature, and for techniques of applying the model and interpreting the results, see Ishibashi and Takagi.[1]

IV. MODEL 2: FINITE-GRAIN MODEL (FGM)

This model is used to describe thin-film ferroelectrics which often consist of a very large number of small grains. The basic assumption of this model is that domains which form and grow inside a given grain cannot cross grain boundaries. The problem is solved for both two- and three-dimensional growth, but only for category-I crystals.

Two simplifications have been made in order to avoid making the calculation unnecessarily complicated. First, the grains are assumed to be identical hypercubes of size L^d. Second, in order to avoid complicated boundary conditions on the integrals, the grains are assumed to have periodic boundary conditions. This implies that every point in the grain is equivalent to every other point, and that the surfaces do not affect the nucleation rate as they would if free surfaces were considered. This effect will be included in later work.

Let $V=L^d$ be the number of possible nucleation sites in a single grain, and R be the probability that a nucleus will form at a given nucleation site per time step. Divide the time t into N increments of size $\Delta t, N\Delta t=t$. For now, set $\Delta t=1$. The probability that exactly n nuclei form during a given time step is the probability that n nuclei form and $(V-n)$ do not, multiplied by the number of

ways of distributing n nuclei on V nucleation sites,

$$W_n = \frac{V!}{(V-n)!n!} R^n (1-R)^{V-n} . \tag{11}$$

Define $V_D(N,N_f)$ to be the volume of a domain which forms at time step N_f,

$$V_D(N,N_f) = \begin{cases} C_d[r_c + v(N-N_f)]^d \text{if } N < N_f + N_s \\ V \text{ if } N \geq N_f + N_s , \end{cases} \tag{12}$$

where N_s is approximately the time required for one domain to grow to include the whole grain,

$$N_s = \frac{1}{v}\left[\left(\frac{V}{C_d}\right)^{1/d} - r_c\right] . \tag{13}$$

Let n_m be the number of nuclei which form in a given grain during time step m. Imagine placing each domain at random in the grain one at a time, completely without regard to the location of previously placed domains. Then the probability that a given point in the grain is not inside a switched domain at time step N is given by

$$q(N) = \prod_{m=1}^{N} \left[1 - \frac{V_D(N,m)}{V}\right]^{n_m} . \tag{14}$$

The ensemble average $\langle q(N)\rangle$ is the value of $q(N)$ averaged over the probabilities W_n:

$$\begin{aligned} \langle q(N)\rangle &= \left[\sum_{n_1=0}^{V} W_{n_1}\left[1-\frac{V_D(N,1)}{V}\right]^{n_1}\right]\left[\sum_{n_2=0}^{V} W_{n_2}\left[1-\frac{V_D(N,2)}{V}\right]^{n_2}\right]\cdots \\ &\quad \left[\sum_{n_N=0}^{V} W_{n_N}\left[1-\frac{V_D(N,N)}{V}\right]^{n_N}\right] \\ &= \prod_{m=1}^{N}\left[\sum_{n_m=0}^{V} W_{n_m}\left[1-\frac{V_D(N,m)}{V}\right]^{n_m}\right] . \end{aligned} \tag{15}$$

The problem must be solved for two different time ranges, $N < N_s$ and $N \geq N_s$. For the lower time range no domain has had time to grow and cover the entire grain, and the answer should reduce to the IGM, while for the upper time range we expect the answer to reduce to an exponential decay. For the lower time range,

$$\begin{aligned} \langle q(N)\rangle &= \prod_{m=1}^{N}\left[(1-R)^V \sum_{n_m=0}^{V} \frac{V!}{(V-n_m)!n_m!}\left[\frac{R[V-V_D(N,m)]}{V(1-R)}\right]^{n_m}\right] \\ &= \prod_{m=1}^{N}\left\{(1-R)^V\left[1+\left[\frac{R}{1-R}\right]\left[1-\frac{V_D(N,m)}{V}\right]\right]^V\right\} \\ &= \prod_{m=1}^{N}\left[1-R\frac{V_D(N,m)}{V}\right]^V \\ &\approx \prod_{m=1}^{N}[1-RV_D(N,m)] . \end{aligned} \tag{16}$$

This reduces to Eq. (8), the result obtained for the IGM. Following the same procedure for the upper time range, obtain

$$\begin{aligned} \langle q(N)\rangle &= (1-R)^{V(N-N_s)} \prod_{m=N-N_s+1}^{N}\left[1-R\frac{V_D(N,m)}{V}\right]^V \\ &= (1-R)^{V(N-N_s)} \prod_{m=1}^{N_s}\left[1-R\frac{V_D(N_s,m)}{V}\right]^V \\ &\approx e^{-RV(N-N_s)}\langle q(N_s)\rangle . \end{aligned} \tag{17}$$

It is fairly easy to set up and solve differential equations from the above. For the lower time range,

$$\langle q(N+1)\rangle-\langle q(N)\rangle=\prod_{m=1}^{N+1}[1-RV_D(N+1,m)]-\prod_{m=1}^{N}[1-RV_D(N,m)]$$
$$=\prod_{m=0}^{N}[1-RV_D(N,m)]-\prod_{m=1}^{N}[1-RV_D(N,m)]$$
$$=-RV_D(N,0)\prod_{m=1}^{N}[1-RV_D(N,m)] \tag{18}$$

and for the upper time range,

$$\langle q(N+1)\rangle-\langle q(N)\rangle\approx(1-RV)\langle q(N)\rangle-\langle q(N)\rangle=-RV\langle q(N)\rangle\ . \tag{19}$$

With the identification $\langle q(N)\rangle\rightarrow q(t)$,

$$\frac{dq}{dt}=\begin{cases}-RC_d(r_c+vt)^d q(t) & \text{if } t<t_s\\ -RVq(t) & \text{if } t\geq t_s\ ,\end{cases} \tag{20}$$

$$t_s=\frac{L}{v}\left[\left[\frac{1}{C_d}\right]^{1/d}-\frac{r_c}{L}\right]\ . \tag{21}$$

Note that for $t\geq t_s$ the differential equation is independent of the dimensionality of domain growth. The solutions for the two equations are required to match at $t=t_s$, obtaining

$$q(t)=\begin{cases}\exp\{-[C_dR/v(d+1)][(r_c+vt)^{d+1}-r_c^{d+1}]\} & \text{if } t<t_s\\ q(t_s)\exp[-RV(t-t_s)] & \text{if } t\geq t_s\ .\end{cases} \tag{22}$$

The key result of this paper can be summarized as follows. If growing domain walls cannot cross grain boundaries then at some time determined only by the grain size and the wall velocity (and possibly the size of the nuclei) the dependence of the switching current transients on time will change from $i(t)\sim t^d\exp(\beta t^{d+1})$ to $i(t)\sim\exp(\beta' t)$.

Define $t_{\max}$ to be the same at which the current transient described by the IGM reaches a maximum,

$$t_{\max}=\frac{1}{v}\left[\left[\frac{dv}{C_dR}\right]^{1/(d+1)}-r_c\right] \tag{23}$$

and define $V_{\max}$ to be the size a domain would reach if it formed at time $t=0$ and grew without obstruction to time $t=t_{\max}$:

$$V_{\max}=C_d\left[\frac{dv}{C_dR}\right]^{d/(d+1)}\ . \tag{24}$$

If $t_s\gg t_{\max}$ then the crystal has switched before one domain has had time to cover a given grain—the wall velocity is low enough and the nucleation rate great enough for the effect of the grain boundaries to be negligible. This is equivalent to saying that, at time $t=t_{\max}$, the grains are much larger than the largest possible domains, $V\gg V_{\max}$, and the switching of each grain is due to a large number of domains. If this is the case, the FGM reduces to the IGM.

On the other hand, if $t_s\ll t_{\max}$ then the wall velocity is large enough and the nucleation rate low enough for the polarization reversal of each grain to be due to a single domain, and in this case the dimensionality of domain growth predicted by the IGM will be much lower than that predicted by the FGM.

V. ISING-MODEL SIMULATIONS

The two-dimensional Ising model was chosen to simulate ferroelectric switching for a number of reasons. First, it is the simplest model which exhibits nucleation and growth phenomena. Second, it is trivial to impose periodic boundary conditions which ensures that the nuclei form in the bulk of the system and not at the surfaces. Third, we can ensure two-dimensional, isotropic growth by imposing isotropic coupling constants. Finally, by keeping track of the growth of individual domains, a direct measure of the domain-wall velocity can be obtained. This can be used to verify the value obtained by fitting the current transients to the FGM.

The systems to be studied consist of a large number of grains, each grain consisting of $L\times L$ psuedospins. Since the grains are assumed to be noninteracting the Hamiltonian of each grain can be written separately:

$$H=\sum_{i,j=1}^{L}[-J(S_{ij}S_{i,j+1}+S_{ij}S_{i+1,j})-pES_{ij}]\ , \tag{25}$$

where $S_{ij}=\pm1$, E is the applied electric field, and p is the maximum polarization of a unit cell. Periodic boundary conditions are imposed by setting $S_{i,L+1}=S_{i,1}$, $S_{L+1,j}=S_{1,j}$. During a given simulation each grain is allowed to reach equilibrium in the spin-up state, after which the switching field is applied.

Four grain sizes were used: The systems consisted of 2000 20×20 grains, 1000 30×30 grains, 400 50×50 grains, and 20 200×200 grains. The values of $K=J/kT$ and $h=pE/kT$ were chosen so that the polarization reversal of a 20×20 grain was almost always due to a single domain, while that of a 200×200 grain was due to several. After some trial and error, it was found that

$K=0.7$ (corresponding to $T\approx 0.63T_c$) and $h=-0.26$ gave good results. Figure 1 shows the polarization curves resulting from these simulations. Note that as the grain size increases, the polarization for each grain approaches that of the ensemble average.

Current transients were then generated from the average polarization curves $i(N)=P(N-1)-P(N)$. As Fig. 3(a) illustrates, the critical nucleus consists of about 11 spins for the above values of K and h, and so we set $r_c=0$ when fitting the current transients to both models, since $r_c \ll L$ even for the smallest grains used in the simulations. With this approximation the IGM has only two independent parameters, and reduces to

$$q(t)=\exp(-\delta t^{d+1}) , \tag{26}$$

$$\delta=\frac{C_d R v^d}{d+1} . \tag{27}$$

The physical interpretation of δ is not clear since the effects of the wall velocity cannot be separated from the effects of the nucleation rate. Since a two-dimensional system is being modeled the FGM becomes

$$q(t)=\begin{cases}\exp(-(\pi R v^t/3)t^3) & \text{if } t<t_s \\ \exp(-(\pi R v^2/3)t_s^3)\exp[-RL^2(t-t_s)] & \text{if } t\geq t_s\end{cases} , \tag{28}$$

where

$$t_s=\frac{L}{v\sqrt{\pi}} . \tag{29}$$

In this case the FGM also has only two independent parameters, R and v. It should be pointed out that in systems where the dimensionality of domain growth is not known *a priori* the FGM will have one more parameter than the IGM.

As Fig. 2 illustrates, the IGM does well describing the current transients of the two systems with the largest grains. The model predicts the dimensionality of growth greater than 2 for both large-grain systems due to the fact that the wall velocity depends on the size of domain. However, the IGM does very poorly at predicting d for the two small-grain systems. In addition, since δ decreases with increasing grain size, it might be inferred (incorrectly) that either the wall velocity or the nucleation rate has decreased. The IGM predicts nothing about either the wall velocity or nucleation rate for any of the systems, and requires different values of d and δ for each system.

On the other hand, with the FGM the same values for R and v fit all four current transients reasonably well given the relatively small systems used for the simulations. Using $R=9.3\times10^{-6}$ and $v=0.24$ it is found that $V_{\max}\approx 2100$, and so, following the arguments of the preceding section, the polarization reversal of the 400

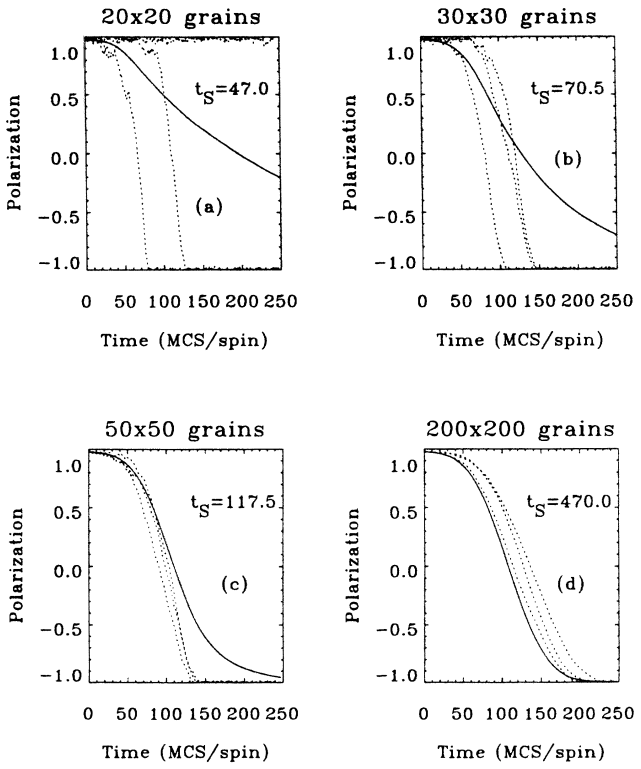

FIG. 1. Polarization curves for the four different systems. The solid lines are the ensemble average of all the grains in each system, while the dotted lines are polarization curves for single grains chosen at random. The unit of time is Monte Carlo steps per spin (MCS/spin).

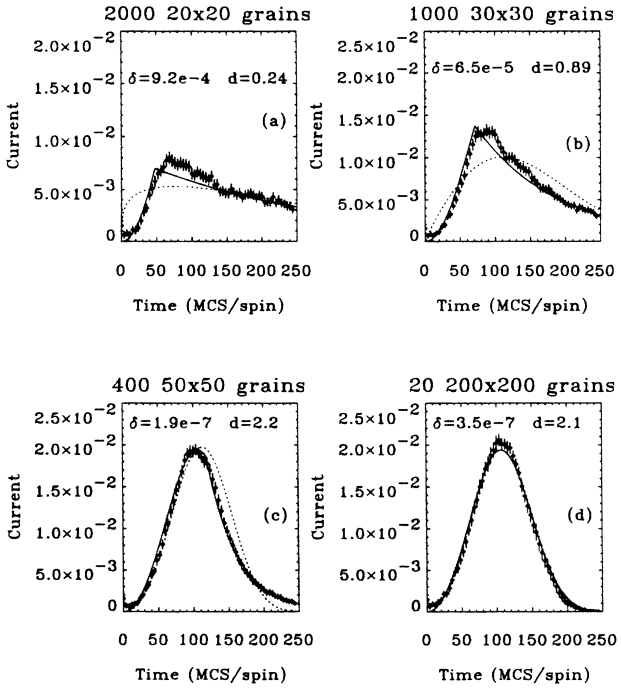

FIG. 2. Current transients generated from the polarization curves of the preceding figure. The dashed lines, and the values of d and γ, are the best fit to the IGM for each grain size. The solid line is the fit to the FGM, using $R=9.3\times10^{-6}$ and $v=0.24$ for all four grain sizes. These values of R and v yield $\delta=5.6\times10^{-7}$.

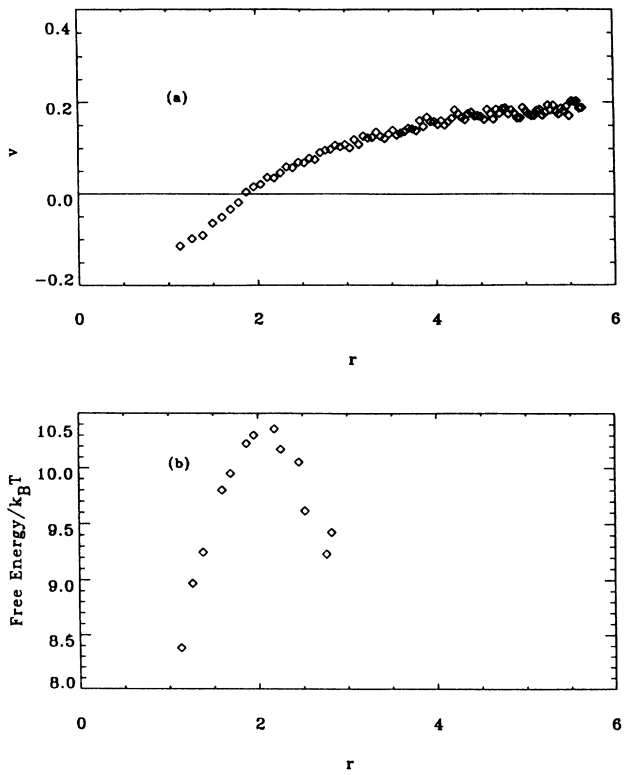

FIG. 3. The results of an independent simulation to generate data on the growth of Ising domains. The velocity and radius were determined by the equation $\Delta V_D = 2v\sqrt{\pi V_D}$ and $r = \sqrt{V_D/\pi}$, where V_D is the number of spins in the domain and ΔV_D is the average growth of the domain. Part 3(b) shows that the peak of the free energy occurs at r_c, as expected by classical nucleation theory.

and 900 spin grains will be dominated by single domains, while that of the 40 000 spin grains will be due several. The current transients for the two small-grain systems show clearly the point at which they change from low-time $i(t) \propto t^2 \exp(-\beta t^3)$ behavior to an exponential decay. This makes small-grain systems useful for determining R and v: If it is known that $t_s < t_{\max}$ then t_s is the time at which the current reaches its maximum, and the domain-wall velocity is found using this value in Eq. (28). Similarly, a value for R can be found by looking at the slope of the semilog plot of $i(t)$ versus t for $t > t_s$—the nucleation rate R is given by this slope divided by L^d.

The most accurate method of determining the wall velocity of Ising domains is to keep track of the growth of individual domains. A second simulation was performed to do this and to study the entropy and energy of the domains as they nucleated and grew. Figure 3(a), a plot of wall velocity versus domain radius, illustrates that while the wall velocity is zero at $r = r_c$, for large domains it does approach a constant. The value of v obtained in this manner is roughly 20% greater than that obtained by fitting the current transients to the FGM—this is because the model assumed that the wall velocity is independent of the size of the domain. Figure 3(b) was included to show that the peak of the free energy occurs at approximately the size of the critical nucleus, as assumed by classical nucleation theory. The entropy was found from measurements of the energy fluctuations of the domains.

VI. SUMMARY

We have presented a new model of ferroelectric switching which specifically accounts for the presence of grain boundaries. We have shown that the infinite-grain model of Ishibashi and Takagi can lead to incorrect assumptions about the dimensionality of domain growth if a ferroelectric is in fact composed of a large number of small grains.

The two models were applied to Ising-model simulations. Current transients for four different grain sizes were accurately fit by the FGM using the same values for R and v for all grain sizes.

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