Electron injection and polarization reversal processes in ferroelectrics analyzed with SEM: modelling of electron beam-stimulated effects

A V Pavelchuk, T K Barabash and A G Maslovskaya

Physics Engineering Department, Amur State University, 21 Ignatyevskoe Shosse, Blagoveshchensk 675000, Russia

E-mail: maslovkayaag@mail.ru

Abstract. The article is devoted to simulation of the injection and polarization switching processes arising in ferroelectrics analyzed with SEM techniques. Monte-Carlo simulation of electron trajectories was performed to estimate electron penetration depth depending on major scanning parameters. The charging kinetics caused by electron injection in ferroelectrics under nonequilibrium conditions of electron irradiation were also explored. The proposed model of polarization reversal process provides good agreement with experimental data.

1. Introduction

Recently the application of scanning electron microscope (SEM) techniques has become increasingly important in investigation of ferroelectrics owing to ability of getting specific responses and creating new modes of image formation. Indeed, the general modes usually used for SEM imaging are mostly considered to be the secondary electron image as well as the backscattered electron image modes. These modes permit one to explore a surface topography, composition inhomogeneity and field-induced contrast of ferroelectric and ferromagnetic materials. The earlier work [1] has reported the approach which allows a-c domains in BaTiO$_3$ crystals to be visualized due to a geometrical relief occurring on a sample surface covered by metal electrode. Afterwards numerous studies rapidly have shown the principal possibility of domain structure imaging on uncoated sample surface [2-3]. Moreover raised accelerating voltages (>10 keV) and injection of an electron beam into samples can be employed to observe evolution of domain structure with simultaneous registration of polarization switching current electron beam-induced [4]. Also the charging processes in ferroelectrics have been used to design controlled polarization switching method and create periodical submicron domain structures [5].

The theoretical studies of electron beam-material interaction and related phenomena usually consider numerous aspects. The basic approach consists in Monte-Carlo simulation of electron trajectories in irradiated target. This approach enables evaluating the geometry of electron trajectory distribution in the sample versus different values of energy of primary beam. In previous works methods, algorithms as well as numerical experiments have been discussed relative to mechanisms and principles describing electron beam interaction with irradiated materials [6-8]. In reality, multiple effects resulting from electron beam interaction with dielectric material can be analyzed by means of simulation, such as secondary electron emission, charging effect, heating process etc. [9-11]. In view....
of the importance of SEM advantages for analyzing as well as modifying ferroelectrics, there is a need for an improved understanding of the mechanisms and principles of electron beam interaction with ferroelectric materials in order to explain the registered processes. The following study was done to simulate electron injection and formation of polarization switching response focusing on conditions of observation of electron beam-induced polarization reversal processes in ferroelectrics being analyzed with SEM modes.

2. Monte-Carlo simulation of electron trajectories in irradiated target: overview of algorithm

The analysis of electron injection effect was based on conventional approach, which consists in Monte-Carlo simulation of large number \( N \) of single electron interaction with irradiated target. The procedure utilizes as basis the following principles. An electron with primary beam energy \( E_0 \) falls perpendicularly on surface of the sample. The landing position of the electron is determined to be \( P_0 \). The interactions between an electron and material are assumed to be separated into elastic and inelastic type. This implies that the random moving or energy loss can be realized. The type of interaction is specified stochastically. In order to evaluate the electron position at current point \( P_i \) scattering angle \( \varphi \) as well as azimuthal scattering angle \( \omega \) need to be calculated. Between the random scattering events each electron travels the distance \( s \) with energy \( E_i \). The distance can be calculated by the following equation [6]:

\[
s = -\lambda \ln(\xi), \quad \lambda = (1/(N_0 \cdot \rho))\sum_{k=1}^{M} (A_k \cdot \sigma_k / \sigma_k^M),
\]

where \( \lambda \) is mean free path in cm; \( \xi \in (0,1) \) is uniform distributed random quantity; \( A_k \) is atomic weight in g/mole; \( \omega_k \) is weight fraction of element \( k \); \( \sigma_k \) is cross-section for each element \( k \) in cm\(^2\); \( M \) is number of elements composed substance; \( N_0 \) is Avogadro’s number in mole\(^{-1}\) and \( \rho \) is layer density in g/cm\(^3\).

The total cross-section \( \sigma_k^M \) can be determined by means of Mott cross-section ratio [11]:

\[
\sigma_k^{Mott} = \frac{4.7 \cdot 10^{-18} (Z_k^{1.33} + 0.032Z_k^2)}{(E + 0.015Z_k^{1.33} \cdot E_i^{0.5}) \left(1 - 0.02Z_k^{0.3} \cdot \exp(-u_k^2)\right)}, \text{cm}^2,
\]

where \( u_k = \ln(8E_i \cdot Z_k^{1.33}) \), \( Z_k \) is atomic number of element \( k \) and energy \( E_i \) is expressed in keV.

In addition the algorithm groups all the electron energy loss events in a continuous energy loss function. In this way we can calculate the energy between collisions with use of the form of Bethe law:

\[
\frac{dE_i}{ds} = \frac{-75800}{E_i} \cdot \sigma_k \cdot Z_k \cdot \ln \left(\frac{1.16(E + 0.8J_k)}{J_k}\right), \text{keV/cm},
\]

where \( J_k = (9.76Z_k + 58.5Z_k^{0.19}) \cdot 10^{-3} \) is Seltzer-Berger expression, which is mean ionization potential of element \( k \) in keV [6].

Note that ordinary differential equation (3) augmented by initial condition determined as previous value of energy is solved numerically for each inelastic scattering event. Besides the calculation of electron position and energy loss should be performed till the energy is less than threshold energy \( E_{\text{thr}} \), which is set to be 0.5 keV. If electron escapes the sample surface it is recorded as backscattered electron. This procedure is repeated for each electron interaction. With this assumption the Monte-Carlo simulation requires initializing the initial parameters such as geometrical size of the sample, material element composition, start electron beam energy \( E_0 \) and number of incident electrons \( N \).

3. Simulation model of polarization reversal process electron beam-stimulated in ferroelectrics

The electron beam-induced polarization current (EBIC) mode is based on electron injection into ferroelectric sample at increased accelerating voltages (10–40 kV). This mode enables visualizing domain structure images and also exploring polarization switching response [4]. Injection of electron beam into sample leads to accumulation of charges in the irradiated layer, which stimulates
appearance of charges on the top and bottom electrodes. This causes the occurrence of fields $E_1$ and $E_2$ in irradiated and unirradiated parts of sample respectively. The field intensity $E_2$ can activate polarization reversal processes in domains “tail-to-beam” orientated and, on the contrary, can stabilize the domain structure with “head-to-beam” orientation of spontaneous polarization vector $P_S$. The diagram of charge and field distributions electron beam-induced in ferroelectric sample is shown in figure 1.

The electron beam irradiation of one of the sample surfaces results in drift of ferroelectric domain structure due to injection and charging-up effects. This gives rise to forming response of polarization switching. In order to express polarization switching current the Kolmogorov-Avrami model is generally applied [12]. Nevertheless this approach possesses a number of disadvantages regarding to electron beam-stimulated polarization current mode. Firstly this method can be referred to approximating one and it does not consider specifics of domain structure dynamics induced by an electron probe. Secondly the model does not include the operating parameters of the SEM modes and as a consequence it does not result in satisfactory fit with a form of current curves registered experimentally. The proposed model of polarization switching in ferroelectrics with 180° domain structure is based on main features of polarization reversal process experimentally observed. We assumed, that polarization switching is realized owing to growth of domains possessing wedgewise shape with the fixed base width $2y$ and the changing angle of domain boundary slope $\phi$ (figure 2 demonstrates the geometrical scheme).

The first stage of polarization switching process completes as long with the middle of a wedge $z(t)$ reaches the bottom electrode. The second stage suggests that the lateral domain growth is incorporated to mechanism of polarization switching. In general the repolarization process is due to growth of $n$ wedge-shaped domains with an identical speed and width of the base $2y/n$. The polarization switching current is determined by superposition of deposits which are given by separate switching areas. To specify the self-similarity dynamics of domain structure we found fractional order differential equation:

$$\frac{d^{\alpha}s}{dw^{\alpha}} = \exp \left\{ - \frac{\tau_2}{\tau_w + \tau_3 L s (1 + \cos^2 \phi)/(4l)} \right\}, \quad s(w_0) = 0, \quad 0 \leq s(w) \leq 2(1-l/L),$$

where $s=x/L$ and $w=t/\tau_1$ are dimensionless distance and time variables; $\tau_1=L/v_\infty$ is the characteristic time of boundary growth through a crystal in $s$; $\tau_2=\delta \varepsilon_{0} L/(j l)$ is the characteristic time (in $s$) of accumulation of charge generating the field $E_2 = \delta$ at given current density $j$ (in A/m$^2$); $\delta$ is activation field in V/m; $\tau_3 = 2P_S/j$ is the characteristic time period (in $s$) during which the charge density $\sigma$ is defined to be $2P_S$; $\alpha$ is fractal parameter; $v_\infty$ is maximal velocity of domain boundary movement in m/s.

In this way we can obtain the polarization switching current in following form:
The differential equation in (4) can be solved numerically using fractional derivative approximation by Grunwald-Letnikov formula.

4. Results and discussion
In order to perform the simulation of electron trajectories in irradiated target one needs to specify parameters: primary beam energy \( E_0 \), chemical composition of material, probe diameter \( d_{pr} \), threshold value of energy loss \( E_{th} \), number of electrons \( N \). The figure 2 demonstrates the results of modeling of electron transport in typical ferroelectrics. The analysis of similar computations suggests that the geometry of electron beam-ferroelectrics interaction can be characterized by hemispherical, semi-ellipsoidal (in preference for crystals of inorganic group – LiNbO\(_3\), LiTaO\(_3\), BaTiO\(_3\), etc.) and "pear-shaped" forms (for group of organic crystals – TGS, DTGS, thiourea, Rochelle salt) depending on element composition and beam energy. Depth of electron penetration \( l \) is defined by a chemical composition as well as primary beam energy and does not depend on size of irradiated area on the sample surface. For instance, depth of electron penetration for lithium niobate crystal was estimated to be: \( l=1.2 \, \mu m \) at \( E_0=15 \) keV, \( l=2.4 \, \mu m \) at \( E_0=25 \) keV, \( l=5 \, \mu m \) at \( E_0=40 \) keV.

\[
I(w) = \begin{cases} 
\frac{2PSS}{\tau_1}\frac{d^\alpha s}{dw^\alpha}, & 0 \leq s \leq 1 - \frac{l}{L}, \\
\frac{2PSS}{s^2\tau_1}L^2\left(1 - \frac{i}{N}\right)\frac{d^\alpha s}{dw^\alpha}, & 1 - \frac{l}{L} < s \leq 2\left(1 - \frac{l}{L}\right), i = 1, N.
\end{cases}
\]

\((5)\)

The following parameters should be also estimated to calculate the characteristics of polarization switching process: probe parameters (primary beam current \( I_{pr} \) and accelerating voltages \( V \)).
U), geometrical size of crystal (d, L, y), specific time parameters τ₁, τ₂, τ₃, spontaneous polarization $P_S$ and dielectric permittivity $\varepsilon$. The simulation was performed for TGS crystal according to experimental data [4]. The curve of polarization switching current reproduces features experimentally observed. Also the computed response enables the time moment $t_{st}$ of beginning of polarization reorientation to be evaluated. During the period $t_{st}$ start charge $q_{st}$ is accumulating in the irradiated layer and in the same time the field in unirradiated part of the sample reaches the coercive field value. The completing of polarization switching process corresponds to falling polarization current to zero level. The field in unirradiated part of the sample is more than coercive field for TGS at $\varepsilon=50$. The dependence of start time moment $t_{st}$ of polarization switching versus injection current density $j$ indicates that $t_{st}$ decreases exponentially with increasing $j$. The computation of maximum value of polarization current $I_{max}$ normalized by primary value of electron beam current $I_{pr}$ allows us to conclude that when current density increases ($j>0.8\times10^{-3}$ A/m²) the polarization current can exceed the value of probe current as presented in figure 4 a.

Figure 4. The dependence of relative of impulse current on current density – a (simulated polarization switching current compared with experimental data is shown in the insert figure), the start moment of polarization switching as a function of accelerating voltages (in log-log scale) – b.

Obviously, different values of accelerating voltages $U$ correspond to different values of electron penetration depth $l$. The field in unirradiated part of the sample can reach the coercive field if $q_{st}l=const$. Taking into account the power relation between $l$ and $U$: $q_{st}U^p=const$ the accumulated charge kinetics can be analyzed by means of calculation polarization switching start moment $t_{st}$ depending on accelerating voltages $U$: $t_{st}U^p=const$. The corresponding function is shown in figure 4 b. As a consequence we can obtain the index of power $p=1.7$ at given values $U=[10, 15, 25, 40]$ kV.

5. Concluding remarks

Finally, Monte-Carlo simulation of electron trajectories and computation of polarization switching current were performed to analyze the condition as well as characteristics of polarization reversal processes electron beam induced in ferroelectrics. The calculation of electron transport in ferroelectrics allows us to evaluate the electron penetration depth and features of geometry electron beam-material interaction region at given experimental parameters. Also the evidence indicates that the thickness of used metal electrode is approximately estimated to be less than 0.1 μm to observe polarization reversal process in ferroelectrics with EBIC mode of SEM. Also the characteristics of polarization switching processes in ferroelectrics were analyzed with use of proposed model of 180° domain structure dynamics and formation of polarization current. Our results theoretically support the experimental EBIC mode and permit us to study the effect of variation of probing parameters such as acceleration voltages and probe current on charging kinetics, start switching moment, the form and value of polarization current. The essential features of simulation results correspond to experimental data observed.
References
[1] Robinson G Y, White R M 1967 *Appl. Phys. Lett.* **10** 320
[2] Le Bihan R, Sella S 1970 *J. Phys. Soc. Japan.* **28** 377
[3] Ikeda S, Uchikawa Y J 1980 *Electron Microsc.* **29** 209
[4] Sograt A A, Maslovskaya A G, Kopylova I B 2006 *Ferroelectrics* **341** 29
[5] He J, Tang S H, Qin Y Q et al. 2003 *J. Appl. Phys.* **93** 9943
[6] Joy D C 1995 *Monte-Carlo modeling for electron microscopy and microanalysis* (New York: Oxford University Press)
[7] Napchan E 1992 *European Microscopy and Analysis* **2** 21
[8] Drouin D, Couture AR, Joly D et al. 2007 *Scanning* **29** 92
[9] Ohya K, Inai K, Kuwada H, Hayashi T, Saito M 2008 *Surface and Coating Technology* **202** 5310
[10] Maslovskaya A, Pavelchuk A 2015 *IOP Conf. Series: Materials Science and Engineering* **81** 012119
[11] Czyzewski Z, MacCallum D O, Roming A, Joy D C 1990 *J. Appl. Phys.* **68** 3066
[12] Ishibashi Y 1990 *Journal of the Physical Society of Japan* **59** 4158