Investigation and analysis of Insulating layer charging of Nanomaterials by Electron Bombardment

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ABSTRACT

The processes of charging of near-surface layers of nanomaterials under electron bombardment have been investigated using computer simulation. A physical model, an algorithm and a program for calculation of the charging parameters of bulk insulating materials have been modified taking into account the features of nanostructured materials such as changes of the band gap energy and the energy trap depth, and scattering of electrons by boundaries of nanoparticles. The current density, the charge value, the electric field intensity as a function of the dielectric layer depth and the irradiation time have been simulated with verified parameters of an electron beam in nanoscale layers of SiO_2.

1.Introduction

The electrical, optical, and emission properties of dielectric nanomaterials considerably change under the action of different types of radiation, leading to charging of these nanomaterials. The surface and near-surface layers of dielectrics are charged especially high under electron bombardment. The calculations of the processes of charging of dielectric layers in materials exposed to electron bombardment were made and described in [1-3]. A computer simulation of charging of a crystalline silica film on a silicon substrate after electron irradiation at an energy of 1-10 keV was performed, and, also, the effect of the parameters of the exciting electron beam and the irradiation time on the value of a localized charge, the induced internal electric field, and the potential at the dielectric surface was shown in [4, 5].
A considerable challenge to simulation of the processes of charging of near-surface layers in nanomaterials consists in taking into account their real structure. The size and the shape of particles in a nanostructured sample are inhomogeneous. The present work deals with charging of model nanostructures, which approximately correspond to the real structure of nanoscale silica selected for the study.

2.PHYSICAL MODEL OF CHARGING OF CRYSTALLINE DIELECTRICS

A mathematical description of the physical model of the processes of charging of dielectrics under electron bombardment is based on the calculations of currents arising upon exposure to an electron beam. They include currents of primary (PE) and secondary (SE) electrons, Pool-Frenkel (PF) current, Fowler-Nordheim (FN) current, and hole (H) and inverse (G) currents. The densities of these currents are defined by the relationships given in [4]. The density of the total current is calculated from the formula:

$$j(x) = j_{PE}(x) + j_{SE}(x) + j_{PF}(x) - j_{FN}(x) - j_H(x) + j_G(x), \qquad (1)$$

where x is the depth of a near-surface layer of the sample.

The electric field intensity F is calculated using a numerical iterative method by solving an integro-differential equation deduced from a transformation of the Poisson equation and the continuity equation in a differential form [6]:

$$F_n(x,t) = F(x,t-\Delta t) - \frac{\Delta t}{\varepsilon_0 \cdot \varepsilon} \cdot \left[j_n\left(x, \left\{F'_{n-1}(x')\right\}\right) - j_n\left(x=0, \left\{F'_{n-1}(x')\right\}\right)\right], \qquad (2)$$

where $F'(x')$ is an electric field throughout the dielectric layer ($0< x' <d$), d is the layer thickness, t is the time of exposure to electrons, Δt is a small time interval, ε is the permittivity of the material, and ε_0 is the absolute permittivity. The iterations were performed until a steady state was established; that is, until the intensity changed less than 1% or a preset time t was reached.

The density ρ of a space charge localized in the bulk of a dielectric is determined from the Poisson equation [4, 5]:

$$\varepsilon_0 \varepsilon \nabla \vec{F} = \varepsilon_0 \varepsilon \frac{d}{dx} F = \rho. \qquad (3)$$

3.SPECIFIC FEATURES OF CHARGING OF NANOSTRUCTURED DIELECTRICS

When one studies charging of nanostructured dielectric layers after their electron bombardment, he should take into account specific features of the nanocrystalline state of solids, which affect the processes of charge transfer, including scattering of electrons by nanoparticle boundaries, variation of the energy gap width, and the energy depth of trapping centers.

Processes of electron scattering by nanoparticle boundaries. A difference in the properties of nanostructured and crystalline samples is due to a small size of crystallites and highly developed interfaces in nanomaterials. While moving in a nanostructure, electrons collide repeatedly with these interfaces, leading to a loss of the electron energy. For an electron to pass to another nanoparticle, its energy E should be higher than a potential barrier at the nanoparticle boundary, χ_B, taking into account a scattering angle θ. If the energy is insufficient for surmounting a barrier at a nanocrystal boundary, the electron bounces from the boundary, is scattered by phonons, and is thermalized. The probability that an electron passes across the boundary, W_B, is defined by the formula [7]:

$$W_B = \frac{4\left(1 - \frac{\chi_B}{E \cdot \cos^2 \theta}\right)^{1/2}}{\left[1 + \left(1 - \frac{\chi_B}{E \cdot \cos^2 \theta}\right)^{1/2}\right]^2}, \; E \cdot \cos^2 \theta \geq \chi_B, \quad (4)$$

Variation of the energy gap width. The energy of electron excitation of an isolated molecule usually is larger than the energy gap width in a bulk material. Hence it follows that the transition of a material to the nanocrystalline state should be accompanied by a shift of the fundamental absorption band to the high-frequency region. For this reason, unlike in their crystalline analogs, the energy gap width in nanostructures changes according to the formula [8-10]:

$$\Delta E = E'_g - E_g = \frac{\hbar^2 \cdot \pi^2}{2 \cdot \mu \cdot R_C^2}, \quad (5)$$

where E'_g and E_g denote the energy gap width in a dimensionally limited structure and a bulk crystal, R_C is the nanocrystal radius, and μ is the effective mass of an electron-hole pair equal to $\mu = \frac{m_e \cdot m_h}{m_e + m_h}$. Here m_e is the effective mass of an electron and m_h is the effective mass of a hole.

It follows from formula (5) that as the size of nanoparticles diminishes, ΔE will increase, and, hence, the energy gap width in a dimensionally limited structure will grow, too. For example, the energy gap width in a nanostructured $BaSO_4$ powder with nanoparticles 30-50 nm in size increased 3% as compared with its value in a crystalline sample [11]. The energy gap width in CdTe with nanoparticles of diameter 4 and 2 nm increased from 1.5 eV to 2.0 and 2.8 eV, respectively [12].

Variation of the energy depth of trapping centers. The concentration of surface electron trapping centers considerably increases in nanostructured materials, and this increase is due to a growth of the number of nanoparticle boundaries with a high defect content [6]. A considerable proportion of electrons will be captured at these centers under electron bombardment. The energy of surface states differs from the energy of bulk solids. One of the reasons is a disruption of the three-dimensional periodicity on the surface. The formula, which is given below, can be used to evaluate a change in the energy of surface trapping levels as compared to their bulk analogs [10]:

$$\Delta E_S = (1 - \beta) \cdot E_g / 2, \quad (6)$$

where $\beta = M_S / M_V$ is a ratio between the surface and bulk Madelung constants. According to the experimental data, ΔE_S for E'-centers in silica is approximately 0.45-0.6 eV [13]; that is, the surface traps have a larger energy depth as compared to those in the crystal.

4.OBJECTS OF STUDY AND SIMULATION PARAMETERS

The calculations of the processes of charging were performed for a dielectric-semiconductor structure with a thin film of crystalline or nanostructured SiO_2 as the insulator. The semiconductor was a silicon substrate. The model structure of a nanoscale sample was a set of hexagonal nanocrystals, which were tight against each other with their faces [7]. A nanoparticle boundary was viewed as infinitely thin

surfaces, and, while crossing these surfaces, an electron lost some of its energy for surmounting a potential barrier at a nanoparticle boundary.
The calculations were made taking the following parameters: the thickness *d* of the SiO_2 film was 100 nm; the primary electron energy E_0 = 10 eV; the beam current density $j_0 = 10^{-5}$ A/cm^2; the temperature *T* of the sample was assumed to be 300 K. The constants were as follows: $\varepsilon = 3.84$; the effective electron mass $m_e = m_0$; the effective hole mass $m_h = 10m_0$. The energy gap width E_g and the energy depth of a trap, E_d, in crystalline SiO_2 were taken to be 9 eV and 1.1 eV, respectively. The trap depth, which was selected for the calculations, corresponded to the energy for ionization of the center, which was responsible for a characteristic peak of the thermally stimulated emission in SiO_2. In the case of nanostructured silica with particles 1 nm in size, these parameters were calculated from the formulas (5) and (6): E_g = 10.65 eV and E_d = 1.55 eV. The maximum duration of the electron bombardment corresponded to establishment of a steady total current in a near-surface layer (a steady state).

5.Results of Simulation and Discussion

The charging parameters, which were simulated at different exposures to the electron bombardment, included the density of the total current, the space charge density, and the electric field intensity in a near-surface layer of crystalline silica (Figs. 1 to 3). As can be seen from Fig. 1, when the exposure time was short ($t < 300$ ms), the density of the total current changed considerably in a layer up to 10 nm deep, and then it decreased gradually as the film-substrate interface was approached and was zero about 25 nm deep in the near-surface layer. When the electron bombardment time was long ($t > 300$ ms), the current density changed insignificantly with the depth of the dielectric layer and passed to a steady state at $t > 1$ s (curve 5). A principal contribution to the total current at the selected simulation parameters was due to the currents of primary and secondary electrons, as well as hole and inverse currents.

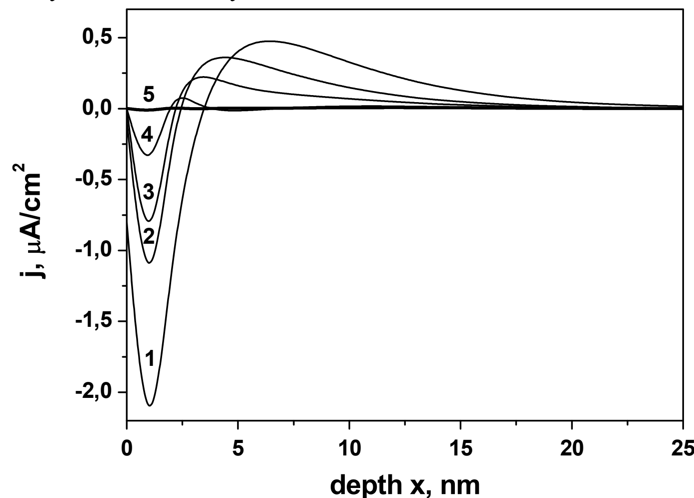

Figure 1. Dependence of the total current density on the depth of a layer of crystalline SiO_2 at different values of the irradiation time *t*: (1) 5 ms, (2) 50 ms, (3) 100 ms, (4) 300 ms, (5) 1 s.

Figure 2 shows the process of formation of the injected charge region. A "minus-plus" charge structure with a negatively charged near-surface region, which is formed by

the currents of primary and secondary electrons, appears in a near-surface layer of crystalline SiO_2. A positively charged region, which is formed by the hole current, appears at a depth of 1-3 nm. At the selected energy of bombarding electrons (10 eV), they are localized near the surface in the dielectric. This is because electrons with these energies are considerably scattered by phonons, and, as a result, they are quickly thermalized in the bulk of the dielectric and are captured in traps. The space charge density increases with the electron bombardment time. At the irradiation time t = 1 s the charge density reaches a steady state.

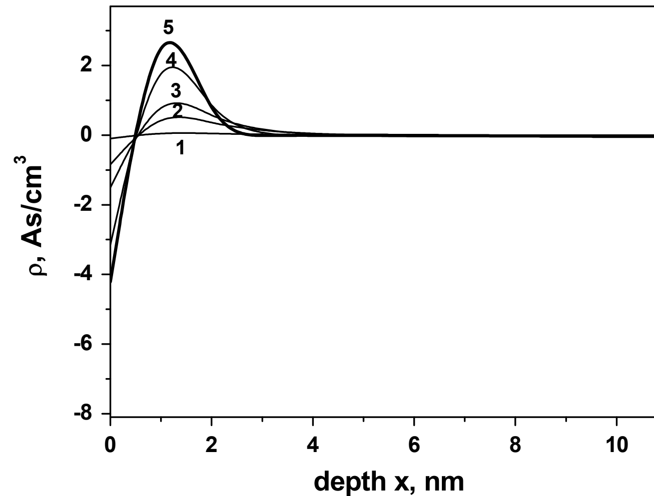

Figure 2. Distribution of the space charge density in a near-surface layer of crystalline SiO_2 at different values of the irradiation time t: (1) 5 ms, (2) 50 ms, (3) 100 ms, (4) 300 ms, (5) 1 s.

The buildup of an injected charge is accompanied by formation of an internal electric field (Fig. 3). When the irradiation time is short, the electric field is practically absent (curve 1). An increase in the electron bombardment time is followed by a growth of the electric field intensity. A region of a high electric field, which is produced by a negative charge and has an intensity of up to 0.5 MV/cm with a maximum at a depth of 2 nm, appears near the surface. One more region of an electric field, which is produced by a positive internal charge, is observed at a depth of 3-30 nm. Its intensity drops to zero with distance from the surface of the sample.

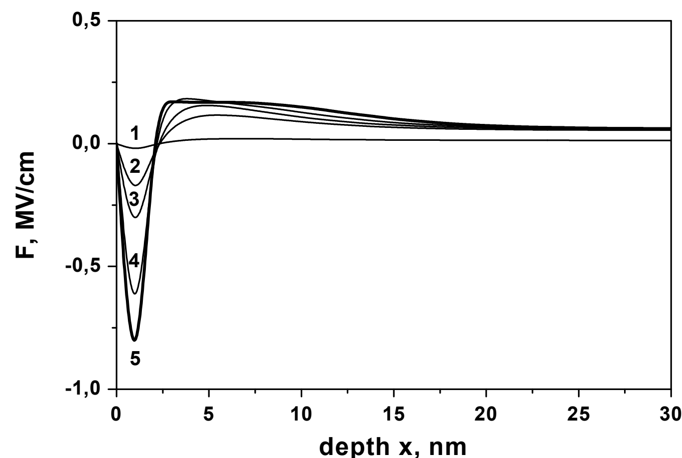

Figure 3. Distribution of the electric field intensity in a near-surface layer of crystalline SiO_2 at different values of the irradiation time t: (1) 5 ms, (2) 50 ms, (3) 100 ms, (4) 300 ms, (5) 1 s.

To compare the processes of charging of near-surface layers in the nanostructured and crystalline materials, we calculated the densities of the injected charge (Fig. 4) and the internal electric field (Fig. 5) for the crystal and nanostructured SiO_2 with particles 1 nm in size in the steady state, that is, at the irradiation time $t = 1$ s. The calculations were made considering two specific features of the nanostructured state, namely, changes in the energy gap width and the energy depth of trapping centers of charge carriers. The charge density formed in nanostructured silica increases as compared to the charge density in the crystalline sample. It is worth noting that the nanostructured sample has a region of a negative internal charge at a depth of more than 3 nm, which is absent in the crystalline film. A growth of the space charge density in the nanostructure is due to an increase in the current of secondary electrons and the hole current, which form negative and positive charges in the bulk of the dielectric as the energy gap width grows. The intensity of the internal electric field produced in nanostructured SiO_2 is also higher across the whole depth of the dielectric layer than it is in the crystalline film (Fig. 5). A sufficiently high electric field having an intensity of up to 1.1 MV/cm is produced near the surface. Notice also that a negative charge existing in the nanostructured sample at a depth more than 3 nm induces an electric field, which grows with the depth. Oppositely, the electric field induced by a positive charge in crystalline SiO_2 decreases with the depth.

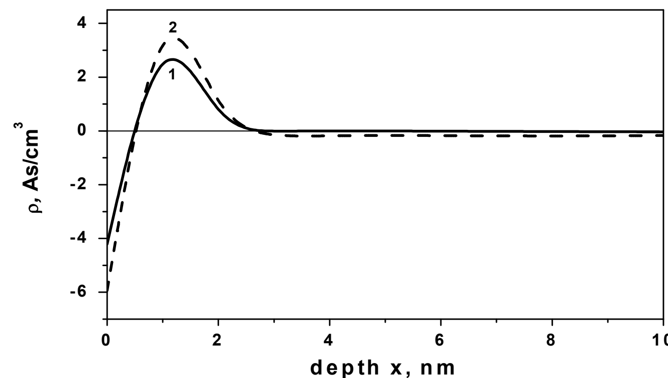

Figure 4. Profile of a charge in a near-surface layer in the steady state: (1) crystalline SiO_2; (2) nanostructured SiO_2.

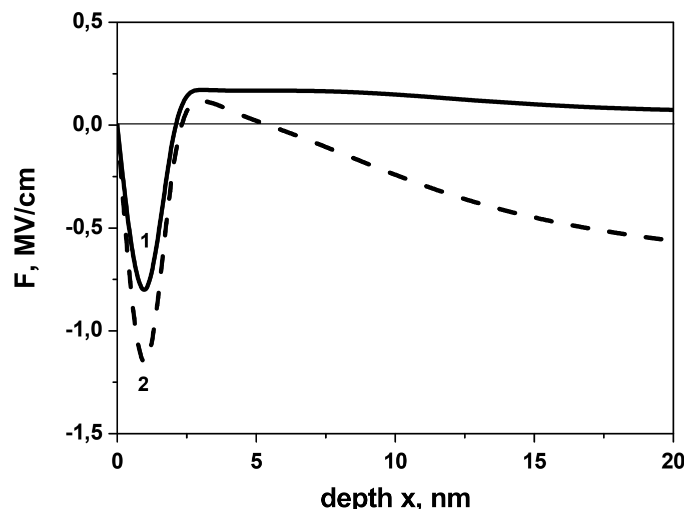

Figure 5. Distribution of the electric field intensity in a near-surface layer in the steady state: (1) crystalline SiO_2; (2) nanostructured SiO_2.

6.Conclusion

A physical model for computer simulation of processes of charging of dielectric materials taking into account basic specific features of the nanostructured state, which influence the transfer of charge carriers, has been refined. The total current density, the internal charge, and the electric field intensity at different exposures to electron bombardment have been calculated for crystalline silica. A comparison of the injected space charge density and the intensity of the internal electric field in crystalline and nanostructured SiO_2 with particles 1 nm in size demonstrated that the charge density and the field intensity were much higher in the nanostructured sample than in crystalline silica.

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