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Radiation-induced processes and their influence on the functional properties of dielectrics for different types of irradiation

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Abstract

The effect of ionizing and displacive components of irradiation on structural changes in ceramics is considered. The ionizing component of irradiation results in partial recrystallization in ceramics. Relaxation of radiation-induced electric charge carriers in structural defects causes selective character of atomic diffusion and radiation annealing of structural defects in the materials. The effect of displacive constituent of irradiation is due to energy release in local cascade regions of the materials accompanied by phase transitions and changes in the chemical composition of the materials. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Among the effects arising in dielectrics under irradiation are the radiation-induced conductivity (RIC), luminescence (RIL), transient optical absorption and structural changes. The latter is responsible for irreversible changes in all properties (electrical, optical, mechanical) of materials. The electrical and optical properties of dielectrics under irradiation of different types are caused by electric charge carrier production and electron–hole trap recharging due to ionization.

According to experimental data on RIC in wide bandgap dielectrics (Al_2O_3 , BN, etc.), the estimated ionizing efficiency for RIC is in the range of $(2\text{--}60) \times 10^{-14} \text{ s}/(\text{Gy } \Omega \text{ m})$ [1]. At a dose rate lower than 10^{12} Gy/s the localization of free charge carriers in traps predominates the electron–hole recombination, and electrical conductivity depends on the charge carrier mobility over traps.

Recharging of structural defects is responsible for changes in optical properties of dielectrics. For example, sharpening the absorption band at 400 nm of Al_2O_3 is

due to electron trapping in V_{OH} -centres [1], whereas recharging deep levels of F-centres results in an increase of the RIL band at 415 nm [2].

Ionization also results in electric charge partitioning in the bulk of the dielectrics, which also affects optical properties. The cause of the radiation-induced electrical charging in local regions in the bulk of dielectrics is concentration inhomogeneity in the trap system. Formation of electrically charged regions is caused by a difference in the hopping mobility of charge carriers over traps. It was shown in the study [3] that the local charge density is determined by the second-order derivative of the total trap concentration over coordinate. The sign and magnitude of the local charge depend on the ratios of trap concentration and hopping mobilities. Formation of negatively charged regions during irradiation results in an intensity increase for F-centre band (415 nm) in RIL spectra of single crystal Al_2O_3 with increasing dose [3]. This behaviour is attributed to a special mechanism according to which F-centre formation occurs after an electron is trapped in the neighbourhood of an oxygen vacancy. The increase of F-centre concentration is a response to both general and local electrical charging in the bulk of the material.

In ceramic $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$, the radiation-induced excess of electrical charge in grain boundaries with respect to the grain bulk occurs. In a previous study [3] the local

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electrical charge arising under irradiation in $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ was estimated with the help of data on the intensity of Cr^{3+} ion RIL band (690 nm), taking into account that the elementary luminescence process occurs after the electron is trapped by Cr^{4+} ion. The estimated excess of the positive charge in grains of ceramic $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ (charge excess was corresponding to calculated Cr^{4+} ion concentration) exceeded 10^4 Q/m^3 . The corresponding electric field exceeded 10^6 V/m .

Structural changes in dielectrics depend on the chemical composition and, to a great extent, the microstructure of the materials. A review on the types of radiation defects in dielectrics is given in [4]. Defect aggregates are three-dimensional entities and, in Al_2O_3 , can reach 90 Å in size (neutron irradiation $2.1 \times 10^{26} \text{ n/m}^2$, 1100 K) [5]. Formation of $\gamma\text{-Al}_2\text{O}_3$ from $\alpha\text{-Al}_2\text{O}_3$ under oxygen ion irradiation was observed in [6]. With the help of NMR for Al_2O_3 after neutron irradiation the aluminum colloids were observed [7]. Aggregate formation under irradiation also leads to higher swelling of the ceramic materials with respect to single crystals, because (according to testing of microstructure [4]) the aggregates appear preferentially in boundary grains. Swelling tests showed a swelling of 2.1% for Al_2O_3 ceramics after irradiation with a dose of $3.3 \times 10^{25} \text{ n/m}^2$ at a temperature of 540 K and a value of 1.1% for single crystals [1].

Peculiarities of structural damage in dielectrics are difficult to explain by formation and evolution of radiation point defects. The contribution from the ionizing component of irradiation of various types is much higher than the contribution of irradiation to displacements. In wide bandgap dielectrics electron–hole relaxation results in a high local energy release (several eV) at the structural defects. So, it is necessary to take into account the effect of ionizing component of irradiation on kinetics of activated processes in dielectrics. Also, it is important to revise the relevance of conventional dpa units as a measure of irradiation dose.

2. Microscopic non-equilibrium in solids

It was shown in [8,9], that resulting from collisions or nonradiative recombination of electron excitations in solids, a state of microscopic non-equilibrium arises under irradiation, which is due to the deflection of the distribution function of atoms over energy of vibrations out of the thermodynamically equilibrium one. The deflection depends on the parameter of non-equilibrium, $\alpha = \tau\kappa/(1 + \tau\kappa)$, where κ is the frequency of the energy transfer accompanied by an excitation of atomic vibrations and τ is the characteristic time of thermalization of the vibrations in solids. Under microscopic non-equilibrium (i.e., $\alpha \exp(W/T) > 1$) the probability of an atom to overcome an energetic barrier W weakly depends

on the temperature and exceeds the probability in local thermodynamic equilibrium.

A non-equilibrium distribution function of atoms, so interacting with the radiation flow I , that the energy transfer to particles of a subsystem in the range of $(\varepsilon, \varepsilon + d\varepsilon)$ depends on the differential cross-section $d\sigma = \kappa(\varepsilon) d\varepsilon$, is as follows:

$$f(E) = (1 - \alpha) \sum_{n=0}^{\infty} \left(\frac{\alpha}{\sigma}\right)^n \int \kappa(\varepsilon_1) \cdots \kappa(\varepsilon_n) \times U(E - \varepsilon_1 - \cdots - \varepsilon_n) \times f_0(E - \varepsilon_1 - \cdots - \varepsilon_n) d\varepsilon_1 \cdots d\varepsilon_n, \quad (1)$$

where

$$U(x) = \begin{cases} 0, & x < 0, \\ 1, & x > 0, \end{cases}$$

$f_0(E)$ is an equilibrium distribution function and $\sigma = \int \kappa(\varepsilon) d\varepsilon$ is the total interaction cross-section, $\alpha = \tau\sigma I / (1 + \tau\sigma I)$.

Under the condition

$$\kappa(\varepsilon) = \sigma/\varepsilon_0 \quad (2)$$

($0 < \varepsilon < \varepsilon_0$, σ is the total scattering cross-section, ε_0 is the maximal energy transferable to atoms), which takes place in solids under irradiation by high energy particles (electrons, ions, neutrons, gammas), the frequency of transitions of an atom over the energetic barrier W is given by

$$\omega = \omega_0 \left\{ 1 + \alpha \exp(W/T) \frac{\varepsilon_0 - W + T}{\varepsilon_0} \right\}, \quad (3)$$

where ω_0 is the frequency in the equilibrium.

Taking the expression (1) for the non-equilibrium function one can show that the mean energy of a system in the non-equilibrium to be equal to

$$\langle E \rangle = \langle E \rangle_0 + \langle \varepsilon \rangle \frac{\alpha}{1 - \alpha}, \quad (4)$$

where $\langle E \rangle_0 = \int E \cdot f_0(E) dE$ is the mean energy (temperature) of the equilibrium system and $\langle \varepsilon \rangle = \int \varepsilon \cdot \kappa(\varepsilon) d\varepsilon / \sigma$ is the mean energy transferred to the particles of the system.

The entropy is given by

$$S = S_0 - \ln(1 - \alpha) - \frac{\alpha}{1 - \alpha} \ln \alpha, \quad (5)$$

where S_0 is an oscillator entropy in the equilibrium.

One can distinguish two cases. The magnitude of α is low, so $S \approx S_0$ and $\langle E \rangle \approx \langle E \rangle_0$. The entropy and the mean energy of the system, and also all other thermodynamic functions, do not change. In this case the kinetics of activated processes can change to a great extent without violation of the thermodynamic equilibrium. That is, kinetic restrictions on the occurrence of the

processes leading to thermodynamic equilibrium are eliminated.

At high α , under considerable microscopic non-equilibrium, the entropy and mean energy differ to a great extent from those for the equilibrium, and the thermodynamic approach for phase equilibrium, phase transitions and chemical reactions in solids is not relevant.

Typical values of α for irradiation in fast fission reactors are about of 10^{-15} . Under ion irradiation, that is when the dose rate K can be equal to 10^{-4} – 10^{-2} dpa/s, the parameter α is equal to 10^{-12} – 10^{-10} . That is why, under reactor or ion irradiation the mean values of the energy, entropy and all other thermodynamic functions do not change significantly, but activated processes such as diffusion and chemical reactions accelerate. Microscopic non-equilibrium during under-threshold irradiation is responsible for under-threshold radiation-stimulated diffusion.

Strong violation of microscopic equilibrium arises in cascades of atomic displacements. High values of α (up to 10^{-1}) in cascades under these conditions are resulted from the transfer of energy up to hundreds of keV (almost the total energy of the primary recoil atom) into the energy of atomic vibrations in the region of size up to 10 nm, as for neutron irradiation. The lifetime of the microscopic non-equilibrium state in the cascades (up to 10^{-10} s) depends on the characteristic times of the transfer of energy into vibrations during development of displacement cascades, relaxation of the electron subsystem, and also, on the time of energy transfer from the cascade region to its neighbourhood. The latter is concerned with the excitation of both plasmons at the time of the order of the period of plasmon vibration (for metals) and acoustic waves at much longer times (for dielectrics). In the cascades, structural phase transitions or chemical reactions may occur.

It is important, that under over-threshold irradiation the frequency of diffusion processes in solids is more than an order of magnitude higher than the frequency of dynamic displacements of atoms during development of collision cascades. In fact, the parameter α under microscopic non-equilibrium can be defined as a ratio of the total energy transferred into solid minus the energy of defect formation to the mean energy of atomic vibration excitation $\varepsilon_0/2$. Under over-threshold conditions the following expression is valid

$$\alpha \cong 2[E_m - g(V_i + V_v)] \frac{I\sigma\tau}{\varepsilon_0}, \quad (6)$$

where I is the intensity of irradiation flow, $V_{i,v}$ the vacancy and interstitial formation energy, E_m the energy transferring from the particles of irradiation flow to atoms, $g \sim E_m/2E_d$ a mean number of displaced atoms related to one primary recoil atom and E_d is an energy

threshold of atomic displacements. Substituting the expression of dose rate (number of displacements per unit time $K = \sigma Ig$) of the frequency of dynamic displacements of atoms, into Eq. (6) we can obtain

$$\alpha \cong 4K\tau \frac{E_d}{\varepsilon_0}. \quad (7)$$

From the equation

$$\omega \approx v\alpha, \quad (8)$$

where v is a frequency of atomic vibrations, we can obtain the frequency of atomic vibrations ω exceeding the frequency of dynamic displacements of atoms K . It means that the cascade region can be considered as the region with high density of energy release, neglecting atomic displacements.

This discussion can be illustrated by some results on BN ceramics, where effects of ionizing and displacive components of irradiation on structural transformation are revealed most distinctly.

3. Radiation structural transformations in BN ceramics

It was shown in the papers [10–12], that due to irradiation at fast fission reactor and proton irradiation with the energy of 8 MeV, the structural transformations in grain boundaries, partial recrystallization grains, stoichiometry change and structural defect formation (stacking faults) occur in pyrolytic BN.

Pyrolytic BN is a small grain material. Aggregates of the size up to 2000 nm consist of grains of size 120–180 nm and wide boundaries. In the grains, there is a network of tiny cells (with weak misalignment of grains) of the size 20–40 nm and narrow boundaries. Decrease in the number of boundaries can be monitored by the decrease of RIL intensity, because luminescence centres in graphite-like BN materials occupy positions in boundaries or near-boundary regions [11]. RIL spectra of pyrolytic BN and changes of their intensity with the dose of irradiation are shown in Fig. 1. Up to a dose of $1.88 \times 10^{16} \text{ cm}^{-2}$ RIL intensity decreases linearly, and at the dose of $2.88 \times 10^{16} \text{ cm}^{-2}$ the saturation occurs.

After irradiation up to a dose of $5.2 \times 10^{15} \text{ cm}^{-2}$ the changes of the shape of Raman band of high frequency E_{2g} vibration along the range of protons is revealed (Fig. 2) [12]. At the same position of the maximum (1365 – 1367 cm^{-1}) gradual narrowing of the Raman band occurred with the increasing of the dose. It was shown that the narrowing is caused by a decrease of the density of boundaries in the material. Also, significant narrowing of X-ray reflection bands (100), (101) and (102) was observed. A significant shift of the band (002) towards higher angles was revealed for the samples after higher doses of irradiation (Fig. 3).

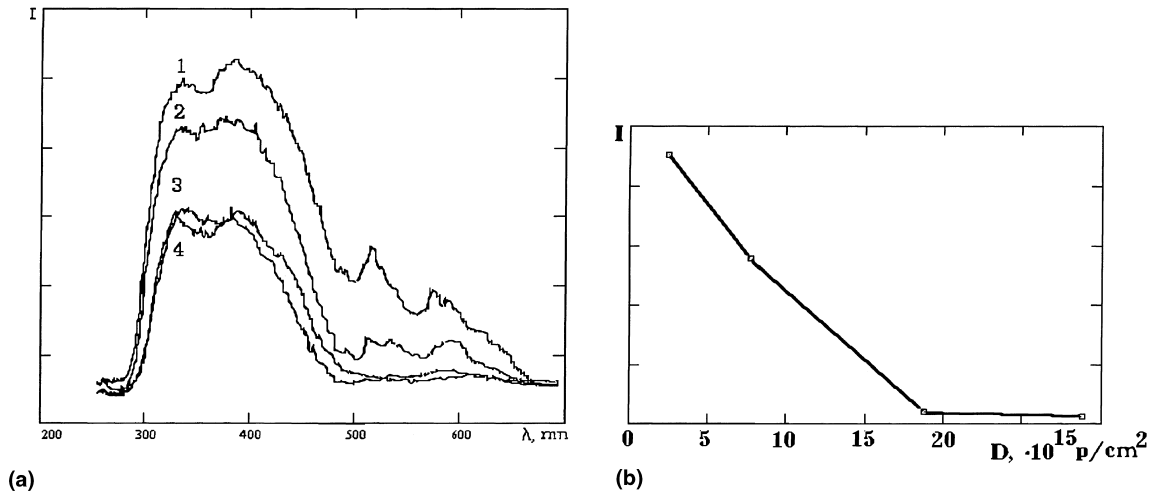


Fig. 1. (a) RIL spectra of BN under 8 MeV proton irradiation (flux $3.00\text{--}3.37 \times 10^{-12} \text{ pair/cm}^2 \text{ s}$) with the dose of: (1) $2.5 \times 10^{-15} \text{ pair/cm}^2$; (2) $7.7 \times 10^{-15} \text{ pair/cm}^2$; (3) $1.88 \times 10^{-16} \text{ pair/cm}^2$; (4) $2.88 \times 10^{-16} \text{ pair/cm}^2$. (b) Dose dependence of the intensity of RIL band at 390 nm of BN.

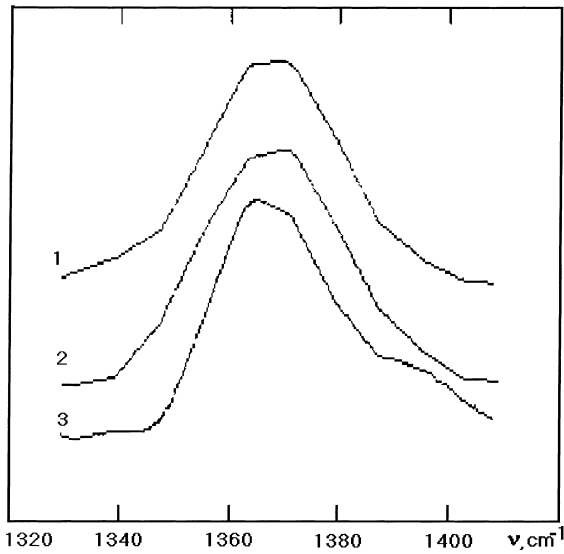


Fig. 2. Raman spectra of BN after 8 MeV proton irradiation with the ionizing dose: (1) $4.9 \times 10^7 \text{ Gy}$; (2) $5.1 \times 10^7 \text{ Gy}$; (3) $5.7 \times 10^7 \text{ Gy}$.

Similar changes of the structure occur during reactor irradiation with the dose of $1.5 \times 10^{21} \text{ n/cm}^2$. Due to recrystallization the band (102) appears, which is absent in the spectra of as-obtained materials. Difference is caused by the structural transformation accompanied by stoichiometry change. Mass spectrometry of the irradiated ceramics revealed considerable decrease of nitrogen contents: almost the order of magnitude in the near-surface region and approximately two orders in the bulk [10].

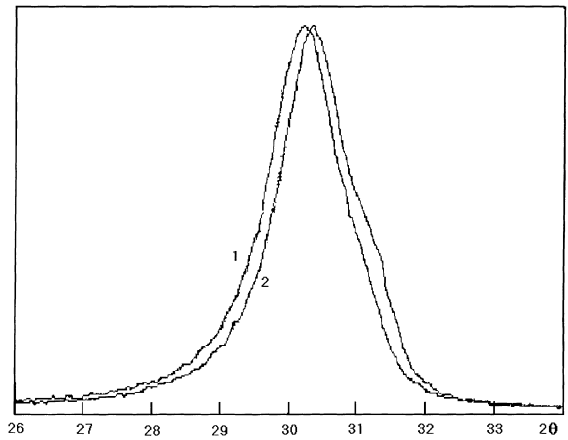


Fig. 3. X-ray reflection band (002) of BN, after 8 MeV proton irradiation with the ionizing dose: (1) $5.1 \times 10^7 \text{ Gy}$; (2) $5.7 \times 10^7 \text{ Gy}$.

Radiation-induced recrystallization in BN is caused by selective acceleration of the diffusion in grain boundaries. Taking into account that more than 99% of the energy is spent for electric charge carrier formation, the following mechanism of radiation stimulation of the diffusion during relaxation of produced electrons and holes can be considered. The energy released due to electron-hole relaxation transfers into the energy of atomic vibrations. Taking Eq. (3) one can derive

$$v \approx v_0 n \tau, \tag{9}$$

where n is the number of vibration excitations per unit time and τ is the characteristic time of thermalization of

atomic vibrations (10^{-11} – 10^{-12} s). In the steady state the rate of charge carrier production is equal to the relaxation rate. Production rate (10^{20} pair/cm³ s) can be estimated taking into account the dose rate, proton projective range (0.38 mm) and the energy gap. Electron–hole relaxation mainly occurs in the grain boundaries, because of luminescence centres and, obviously major part of traps localized in the boundaries. That is why, considering the content of the atoms in grains up to 10% ($\sim 10^{22}$ cm⁻³) in respect to the total number of atoms in pyrolytic BN with grain size of 10–40 nm, one can estimate a value of the frequency n ($\sim 10^{-2}$ s⁻¹), calculate the value of ν ($4 \times (1-10^{-1})$ s⁻¹) from Eq. (9) and obtain the frequency of radiation-induced diffusion processes for atoms in boundaries. The effective temperature of diffusion corresponding to these values of frequencies is in the range of 1450–1540 K. This temperature corresponds to the temperature of recrystallization in BN materials.

Change in stoichiometry of BN ceramics under reactor irradiation is caused by displacement cascades. At the energy of a primary recoil atom equal to 270 keV (corresponding to irradiation conditions) the effective temperature in the region of the size of about 10 nm is equal to $2-4 \times 10^3$ K. Taking into account the temperature of BN decomposition equal to 3000 K and the size of cascade regions corresponding to the lowest grain size in ceramics, one can conclude that decomposition of the BN material is connected with nitrogen release from tiny grains. The effect of displacive component of irradiation is due to energy release in the local cascade regions of the material.

4. Conclusions

Ionizing component of irradiation, along with RIC, RIL, transient optical absorption and electrical charging, determines to a great extent the structural changes in dielectrics. These structural changes are connected with the state of microscopic non-equilibrium (difference of distribution function of atoms over the vibration energy from the function in the thermodynamic equilibrium), which is the cause of under-threshold radiation-induced stimulation of activated processes, in particular, recrystallization of ceramics. Relaxation of radiation-induced charge carriers in structural defect

(impurities, boundaries, etc.) results in a selective stimulation of atomic diffusion and radiation annealing of structural defects in materials. A method of calculation of structural changes in wide gap dielectrics under ionizing irradiation has been introduced.

The recently found dependence of radiation damage of dielectrics on the ratio of ionizing to displacive component of irradiation (for instance see [13]) indicates the non-applicability of dpa units as a measure of damage. The effect of displacive component of irradiation reduces to release the ionization energy in the local cascade regions of the materials, which may be a cause of phase transitions and changes of chemical composition in local regions of the materials. As a measure of the irradiation effect, from the point of view of comparison of different types of irradiation, it is necessary, along with the total absorbed energy (Gy), to take the values of the concentrations of high energy cascades of displacements and the density of the energy release in cascades.

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