INTERACTION OF RELATIVISTIC PARTICLES WITH CRYSTALS AND MATTER

MECHANISMS OF LUMINESCENCE OF AMORPHUS DIELECTRICS EXPOSED TO HIGH-ENERGY ELECTRONS

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Main features of cathodoluminescence (CL) of amorphous dielectrics exposed to pulsed beam of accelerated electrons are described. On the basis of a simplified two-level model of electron traps in the prohibited zone, it has been shown, that CL has got the prompt and delayed components determined by dynamics of filling the deep traps with the quasi-free electrons generated by irradiation. At great values of the absorbed dose and time after EOB, the recombination radiation can become apparent as well. The analytical expressions obtained for dynamics of the CL intensity are qualitatively agreed with the available experimental data. The conditions to use a CL signal induced in the technical materials for on-line diagnostics of a product processing regime at a radiation-industrial installation with an electron accelerator are studied.

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INTRODUCTION

Effect of optical radiation excitation at interaction of accelerated electrons with various materials (cathodoluminescence (CL)) is known since development of first electronic tubes [1]. At present CL is used in elemental analysis, mineralogy, analysis of nanostructures, scanning electron microscopy etc. (see e.g. [2, 3]). A new area is the study of CL arising in the coats of the spacecrafts exposed to electron flux of a solar wind [4]. This time CL reveals an unwanted effect as a background light for the on-board optical telescopes [5, 6].

CL is used in the devices for beam profile diagnostics at the electron accelerators as the specially designed luminescent screens [7], and also as the monitors of optical transient radiation (see e.g. [8]).

In this work, analysis is conducted on the pathways and dynamics of the CL signal formation in the amorphous dielectrics exposed to a pulse electron beam, and also on the conditions of such a signal application for diagnostics of regime of the radiation processing of technical materials.

1. INTERACTION OF NON-EQUILIBRIUM ELECTRONS WITH TRAPS

It is adopted to describe the electrophysical effects in the amorphous dielectrics revealed under the influence of ionizing radiation within the framework of a quasi-zone theory considering the presence of electron traps with high concentration in the prohibition zone. For instance, the intermolecular cavities, macromolecule tipping, side groups in polymers, as well as the anionic vacancies and positive ions in the interstitial sites of inorganic materials can act the part of those traps. Besides, the admixtures, and also the structure defects generated under the influence of the high-dose ionizing radiation, in the first place, the free radicals, can play the role of traps in all types of the materials [9].

Depending on the level depth relative to the bottom of the conduction band, it is accepted to subdivide the traps into shallow (ST) and deep (DT) ones [4]. It is considered also, that the shallow trap's depth ε_{ST} makes ~ kT, where k – is the Boltzmann constant, T – is the temperature (K), when those deep have the depth ε_{DT} ~ eV. It should be noted, that the division of the traps into the shallow and deep ones is rather relative, because their actual depth distribution seems to be quasi-continuous [10].

Optical radiation excited in amorphous dielectrics by accelerated electrons belongs to incoherent type of CL [11]. It is caused by interaction of the irradiation induced non-equilibrium charge carriers in the conduction band with the electron traps. Those processes can be schematically presented in the form shown in Fig. 1. So the electrons of a primary beam lose their energy in the inelastic collisions with the atoms of a dielectric followed by ionization of atoms. As a result, the non-equilibrium charges the electrons in the conduction zone CB and the holes in the valence band VB are generated. For a period of $<10^{-11}$s, the electrons are thermalized, and a mayor part of them recombines with the holes through the radiationless transitions. The remained quasi-free electrons drift nearly the conduction-band bottom interacting with the traps [9].

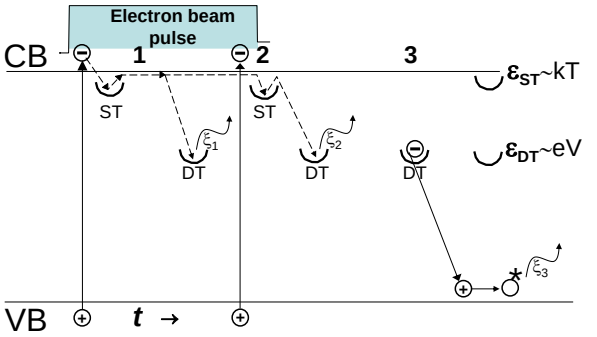

Fig. 1. CL mechanisms in amorphous dielectrics

As it is seen from Fig. 1, CL of dielectrics in the optical region can take place via the next main pathways:

1 – as a result of the quasi-free electron transitions into the deep traps straight during irradiation process (a prompt component of CL);

2 – in consequence of the thermally induced transitions of electrons, remained at the shallow traps after

EOB, into the conduction band followed by the capture of them at the deep traps (a delayed component of CL);

3 – when radiative recombination of electrons localized at the deep traps with the positive centers.

The two first mechanisms are connected with the presence of non-equilibrium electrons in the conduction band resulting from irradiation of dielectrics. An electro-physical manifestation of those processes is an increase of material electro-conductivity having the prompt and delayed components as well [9].

It is adopted to describe the dynamics of radiation conductivity of the disordered solids within the framework of a Rouse-Fowler-Weisberg model – see e.g. [12]. The model considers mainly the prompt processes of the electron transitions mostly contributing to the radiation induced conductivity: generation of electrons into the conduction band, interaction of quasi-free electrons with the shallow traps and holes etc.

2. PROMPT COMPONENT OF CL

The above mechanisms of CL are characterized with the considerably different period of the reveal. Therefore we will analyze them separately. So the photon flux connected with the first mechanism and reduced to the unit of volume of a region of electron beam interaction with a dielectric, ξ_1, is determined with the rate of the deep traps filling with the electrons from the conduction band

$$\xi_1 = \frac{dn_{DT}}{dt}, \qquad (1)$$

where n_{DT} – is the electron concentration at the deep traps, t – is the exposure. The dependence ξ_1 on t is determined by the equation

$$\xi_1(t) = n_{CB}\bar{v}_e S_{DT} N_{DT}(t), \qquad (2)$$

where n_{CB} – is the electron concentration in the conduction band; S_{DT} – is the cross-section of their capture with the deep traps; $\bar{v}_e$ – is the average velocity of the quasi-free electrons; N_{DT} – is the concentration of vacant deep traps.

For conducting the radiotechnology processes, the electron accelerators operating in a pulse mode at a pulse duration of $10^{-6}\ldots10^{-5}$ s, particle energy of up to 10 MeV and average beam power of about tens kilowatt are used [13]. Commonly, the required dose of the product processing makes tens kilogrey (for instance, at radiation sterilization of medical devices [14]). Whence, the radiation exposure makes ~ s or less. For that period, the electrons localized at the deep traps can be considered frozen. Besides, in that dose range the effect of radiation defects on the electro-physical characteristics of a material, and consequently on the CL yield can be neglected [12]. Hence it follows, that the dependence of vacant deep trap concentration on the exposure can be written in the form

$$N_{DT}(t) = N^0_{DT} - n_{DT}(t). \qquad (3)$$

By solution of equations (1) - (3), one can obtain the expression for the dependence of filled deep traps concentration on the exposure

$$n_{DT}(t) = N^0_{DT}\left[1 - \exp(-n_{CB}\bar{v}_e S_{DT} t)\right]. \qquad (4)$$

It should be noted, that within the considered model the n_{DT} value corresponds to the reduced photon fluence of prompt CL component, Φ^1_{ph}.

Under irradiation of a dielectric, the electron concentration in its conduction band n_{CB} is determined by the equation

$$n_{CB} = \frac{\sigma_{rs}}{e\mu_0}, \qquad (5)$$

where e – is the electron charge; μ_0 – is the microscopic mobility of the electrons; σ_{rs} – is the radiation conductivity (RC) of a dielectric. In the absence of a strong electric field, its value σ^0_{rs} makes

$$\sigma^0_{rs} = K\dot{D}, \qquad (6)$$

where K – is the so-called coefficient of the prompt component of RC, $\dot{D}$ – is the absorbed dose rate [9]. Taking into account the formulae (5) - (6), the expression (4) takes the form

$$\Phi^1_{ph} = N^0_{DT}\left[1 - \exp(-\frac{\bar{v}_e S_{DT} K\dot{D}}{e\mu_0} t\right]. \qquad (7)$$

In case of a thin target

$$\dot{D} = \dot{\Phi}_e \frac{dE_e}{dz}, \qquad (8)$$

where $\dot{\Phi}_e$ – is the electron flux density, $\frac{dE_e}{dz}$ – is the average ionization loss of electrons with energy E_e per mass unit of their range in a material.

3. DELAYED COMPONENT OF CL

The thermally activated transitions of electrons from the shallow traps into the conduction band are revealed in the influence of temperature on the RC value and the CL yield observed in the experiments [4, 9]. Those transitions are described by an activation law with time constant

$$\tau_{ST} = F^{-1}_{e,ph}\exp(\varepsilon_{ST}/\mathrm{kT}), \qquad (9)$$

where $F_{\mathrm{e,ph}}$ – is the frequency of the electron–phonon interaction. It becomes the most apparent immediately after EOB, when the direct electron injection from VB into CB is over, and this phenomenon determins the CL and RC delayed components.

The equation for the electron concentration in CB in time t' after EOB can be presented in the form

$$\frac{dn_{CB}(t')}{dt'} = \frac{n_{ST}(t')}{\tau_{ST}} - \frac{n_{CB}(t')}{\tau_{CB}}, \qquad (10)$$

where n_{ST} – is the electron concentration at the shallow traps, τ_{CB} – is the life time of a quasi-free electron in CB until their capture with a deep trap. Taking into account the formula (9), the dependence of n_{ST} on time has the form

$$n_{ST}(t') = n_{ST,0}\exp(-t'/\tau_{ST}), \qquad (11)$$

where $n_{ST,0}$ – is the electron concentration at the shallow traps at EOB (t'=0).

In its turn, the life time of the quasi-free electrons until their capture with the deep traps

$$\tau_{CB} = (\bar{v}_e S_{DT} N'_{DT,0})^{-1}, \qquad (12)$$

where $N'_{DT,0}$ – is the deep trap concentration at EOB. Considering a typical dose value imparted to a material in a radiotechnology process we obtain

$$N'_{DT,0} \approx N^0_{DT}. \quad (13)$$

Hence, the dependence of CL delayed component on the time, $\xi_2(t')$, can be presented in the form

$$\xi_2(t') \approx n_{CB}(t')\bar{v}_e S_{DT} N^0_{DT}. \quad (14)$$

The expression for $n_{CB}(t')$ can be derived by the solution of equation (10) with an allowance for the formula (11)

$$n_{CB}(t') = \left(n_{CB,0} + \frac{n_{ST,0}\tau_{CB}}{\tau_{CB}-\tau_{ST}}\right)\exp\left(-t'/\tau_{CB}\right) - \frac{n_{ST,0}\tau_{CB}}{\tau_{CB}-\tau_{ST}}\exp\left(-t'/\tau_{ST}\right), \quad (15)$$

where $n_{CB,0}$ – is the electron concentration in the conduction band at EOB. E.g., in case of rectangular form of the beam pulse, the $n_{CB,0}$ value is determined by the formal (5).

4. RECOMBINATION RADIATION

In the dielectric materials, the charge screening length providing the energy of electrostatic interaction exceeding the heat energy, makes

$$r_{SC} = \frac{e^2}{4\pi\varepsilon\varepsilon_0 kT}, \quad (16)$$

where ε – is the dielectric permittivity, ε_0 – is the electric constant.

It means that if the electron concentration at the deep traps meets the condition

$$n_{DT} \approx r_{SC}^{-3}, \quad (17)$$

a charge recombination is exhibited. Its rate is described with a Langevin low

$$\frac{\partial n_{DT}}{\partial t'} = -\beta n_{DT} p, \quad (18)$$

where p – is the concentration of positive recombination centers (the holes, cations, cation-radicals etc. [15]), β – is the recombination rate constant

$$\beta = \frac{e(\mu_+ + \mu_-)}{\varepsilon\varepsilon_0}, \quad (19)$$

where μ_+ и μ_- – are the macroscopic mobility of charge of the corresponding sign, respectively. Commonly, in the polymers, $\mu_+ << \mu_-$. So it is believed that the positive charges are immobile. As a result of the electron-hole recombination, an exciton is formed (see Fig. 1), which can deactivate through the radiative or radiationless transitions depending on its spin state [15].

The intensity of recombination radiation reduced to the unit of the volume, ξ_3, is determined by the expression

$$\xi_3(t') = \beta' n_{DT} p, \quad (20)$$

where β' – is the coefficient of radiative recombination.

If the recombination centers of only the holes, then from the condition of electrical neutrality it follows

$$n_{DT} = p. \quad (21)$$

By the solution of equation (20) with an allowance for condition (21), we obtain

$$\xi_3(t') = \frac{\beta' n^2_{DT,0}}{(1+\beta' n_{DT,0} t')^2}, \quad (22)$$

where $n_{DT,0}$ – is the concentration of deep traps at EOB.

If the concentration of positive centers in a material is large, $p >> n_{DT,0}$, the dependence of recombination radiation on the time takes the form

$$\xi_3(t') \approx \frac{\beta' n_{DT,0} p}{1+\beta' p t'}. \quad (23)$$

5. APPLICATION OF CL FOR DIAGNOSTICS OF RADIATION PROCESSING MODE

Commonly, the beam parameters are sustained invariable under a product treatment. To provide a required absorbed dose, the processed objects are moved via irradiation zone using a conveyor with established velocity. Alongside with the conveyor velocity and electron energy, the distribution of electron flux density on an object's surface $\dot{\Phi}_e$, is one of the crucial process parameters [14].

Practically, any material processed with an electron beam can be considered as a luminescence radiator. For instance, cellulose – a natural polymer being the basis of such widely-spread package material as carton has got this property [16].

It was shown in work [17], that when irradiation of technical materials (polystyrene, polypropylene, carton etc.) under the conditions of an industrial processing, a CL signal matches with a beam pulse, i.e. a delayed component of radiation is faintly revealed. Therefore, with an allowance for the formulae (1), (4) - (6), the volumic luminescence intensity can be re-written in the form

$$\xi_1(t) = \frac{K\dot{D}}{e\mu_0} S_{DT} \bar{v}_e N^0_{DT} \exp\left(-\frac{K\dot{D}}{e\mu_0} S_{DT} \bar{v}_e t\right). \quad (24)$$

So if the beam pulse duration τ_p, meets the condition

$$\tau_p << \frac{N_{DT}}{n_{CB}} \tau_{CB}, \quad (25)$$

the prompt CL intensity appears proportional to the dose rate $\dot{D}$ (the electron flux density $\dot{\Phi}_e$) on the surface of an irradiated object. In its turn, the $\dot{D}t$ value corresponds to the absorbed dose in a material. So at the fulfillment of condition

$$g\rho D << N^0_{DT}, \quad (26)$$

where g – is the radiation-chemical yield of charge carriers, ρ – is the material density, the dose can be determined by the fluence of CL prompt component Φ^1_{ph} – [17]. It is believed, that in a laboratory polymer pattern the N^0_{DT} value makes ~ 10^{18}cm^{-3}. One can expect that in the technical materials with an allowance for their defect structure and admixtures, that value is still more. The g value makes ~1. So at an industrial dose span of about 10 kGy, n_{DT}~10^{17}cm^{-3}, and the condition (26) is satisfied.

The intensity of CL with wavelength λ generated in an elementary layer *dz* disposed at a depth z of a radiator makes

$$dI(\lambda) = R_\lambda \cdot \xi_i \exp(-a_\lambda \cdot z)dz\,, \qquad (27)$$

where R_λ – is the coefficient of reflection of the luminescence radiation from the material interface, a_λ – is the radiation absorption coefficient. Hence the total radiation intensity escaping a radiator by *d* in thickness makes

$$I(\lambda) = \begin{cases} \dfrac{\xi_\lambda \cdot d}{2}\left(1 - R_\lambda^2\right), \quad d << a_\lambda^{-1} & (28a) \\ (\textit{thin radiator}) \\ \dfrac{\xi_\lambda \cdot \left(1 - R_\lambda^2\right)}{2a_\lambda}, \quad d >> a_\lambda^{-1}. & (28b) \\ (\textit{thick radiator}) \end{cases}$$

6. DISCUSSION

The three examined pathways of luminescence of an amorphous dielectric exposed to electron radiation act simultaneously. At the same time, depending on the intensity and duration of the electron irradiation, the period after EOB, and also a material and its temperature, the contribution of every process to the total CL yield is considerably different (Fig. 2). So the first mechanism provides the prompt luminescence component concurrent with an activating radiation. The second one is responsible for the delayed CL component. It seems that in the technical materials the latter process is faintly exhibited.

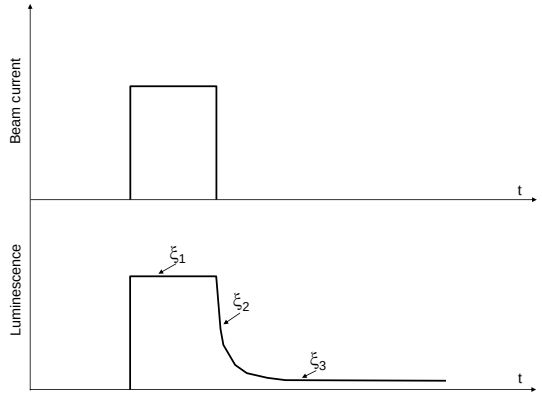

Fig. 2. The pathways of CL induced by pulse beam

Recombination radiation arises when a considerable concentration of localized charges (great absorbed dose – see formulae (17), (26)) and is characterized by a large delay time [12, 18]. So its contribution into the prompt component of CL can be neglected.

The obtained analytical expressions for the second and third mechanisms of CL are agreed with the following empirical dependence for the intensity of luminescence on the period after EOB proposed in a number of works (see e.g. [18])

$$I(t') = A_1 \exp(-t'/\tau 1) + A_2 \exp(-t'/\tau 2) + A_3(1 + \alpha t')^m, \quad (29)$$

where 1<m<2.

As it follows from the proposed model, one can to connect the two first terms of the dependence (29) with the processes of redistribution of electrons from the shallow traps into the deep ones, when the last term – with the charge recombination. The index of its hyperbolic dependence on time after EOB is determined by the ratio of concentrations of inherent recombination centers and the holes induced by irradiation. In particular, the index is close to unity when the inherent centers prevail and in a contrary case to two.

CONCLUSIONS

The fulfillment of conditions (25), (26) makes it possible to determine the distribution of current density of the scanned electron beam in the on-line mode on the CL intensity, as well as the dose and its rate over the surface of an irradiated object At the same time, a preliminary calibration of a measuring channel with due respect to the properties of a material of a luminescent radiator is needed. The sensitivity of such a channel can be adjusted both by the selection of radiator's material and by the variation of its optical thickness – see formula (28a).

The results obtained in the work can be considered as some extension of the luminescence techniques into the domain of industrial dosimetry. In this case, a sufficient level of induced optical signal in the common technical materials is achieved due to high intensity of an electron beam at a relatively low yield of CL. At the same time, .the use of a special material provides also the possibility measuring the absorbed dose in an off-line mode using the photo- and thermo-stimulated luminescence (see e.g. [19, 20]).

REFERENCES

1. W.Crookes. Contributions to Molecular Physics in High Vacua // *Philos. Trans. of the Royal Soc*. 1879, v. 170, p. 641-662.
2. M. Pagel, V. Barbin, P. Blanc and D. Ohnensteller// *Cathodoluminescence in Geosciences*. 2000.
3. D. Strikoska, J. Arbiol, A. Gustafsson, et al. Structural and Optical Properties of High Quality Zinc-Blende / Wurtzite GaAs Nanowire Heterostructures // *Phys. Rev*. 2009, v. B80, p. 245325.
4. J. Dekany, J. Christiansen, J.R. Dennison, et al. Variations in Cathodoluminescent Intensity of Spacecraft Materials Exposed to Energetic Electron Bombardment // *IEEE Trans on Plasma Scien*. 2015, v. 40(2), p. 305-310.
5. J.R. Denninson, A.E. Jensen, J. Dekany, et al. Diverse Electron-induced Optical Emissions from Space Observatory Materials at Low Temperatures // *Proc. SPIE Cryogenics Optical Systems and Instr. Conf.* 2013, v. 8863, p. 886330B1-88630B15.
6. D. Ball. Electron Induced Luminescence in Insulating Polymeric Materials // *Senior Theses and Projects*. 2011, Paper 5. http://digitalcommons.usu.edu /mp- seniorthesesprojects/5
7. F. Decker. Beam Size Measurement at High Radiation Levels // *Proc. PAC*. 1991 (SLAC-PUB-5481).
8. M. Ross, S. Anderson, J. Frish, et al. A Very High Resolution Optical Transition Radiation Beam Profile Monitor // *SLAC-PUB-9280*. July 2002.
9. A.P. Tyutnev, A.V. Vannikov, G.S. Mingaleyev, V.S. Sayenko. *Electrical phenomena under irradiation of polymers.* M.: "Energoatomizdat", 1985, 185 p. (in Russian).

10. R.J. Fleming, L.F. Pender. Electron trap distribution in organic polymers- an additional set of characterisation parameters // *J. Electrostatics*. 1977, v. 3, p. 139-148.
11. B.J.M. Brenny, T. Coenen, A. Polman. Quantifying Coherent and Incoherent Cathodoluminescence in Semiconductors and Metals // *J. Appl. Phys*. 2014, v. 115, p. 244307.
12. I.P. Bezrodnyh, A.P. Tyutnev, V.T. Semenov. *Radiation Effects in Space.* Pt. 2, 2016, p. 9-12 (in Russian). *www.cosmic-rays.ru/articles/02/201604.pdf*
13. N.J. Hackensack. *Review of Accelerator Science and Technology.* Singapore; World Scien. Pub. Co. 2011, 291 p.
14. ISO 11137-1. Sterilization of Health Care Products-Radiation-Part 1: Requirements for Development, Validation and Routine control of a Sterilization Process for Medical Devices.
15. N.I. Voronkina, V.G. Senchishin, V.K. Milinchuk, et al. Recombination Luminescence in Plastic Scintillators // *Problems of Atomic Science and Technology. Series "Nuclear Physics Investigations" (89)*. 2006, № 4, p. 228.
16. M.Z. Gavrilov, I.N. Ermolenko. A study of cellulose luminescence // *J. Appl. Spectroscopy*. 1966, v. 5, p. 542-544.
17. S.K. Romanovsky, V.A. Shevchenko, A.Eh. Tenishev, et al. Dinamics of Amorphus Dielectric Luminescence Induced by Pulse Electron Beam // *Problems of Atomic Science and Technology. Series "Nuclear Physics Investigations"*, 2017, № 6, p. 152-156.
18. V. Griseri, L.A. Dissado, J.C. Fothergill, et al. Photoluminescence, Recombination Induced Luminescence and Electroluminescence in Epoxy Resin // *J. Phys. D. Appl. Phys.* 2001, v. 34, p. 2534-2540.
19. M. Reitzig, T. Hartling, M. Winkler, et al. Time-resolved luminescence measurements on upconversion phosphors for electron beam sterilization monitoring // *Proc. SPIE 8693, Smart Sensor Phenomena, Technology, Networks, and System Integration*. 2013, 86930R (April 11, 2013).
20. A.S. Pradhan. Thermoluminescence Dosimetry and its applications // *Radiat. Prot. Dosimetry*. 1981, v. 1(3), p. 153-167.

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МЕХАНИЗМЫ ЛЮМИНЕСЦЕНЦИИ АМОРФНЫХ ДИЭЛЕКТРИКОВ ПОД ВОЗДЕЙСТВИЕМ ВЫСОКОЭНЕРГЕТИЧНЫХ ЭЛЕКТРОНОВ

С.К. Романовский, В.Л. Уваров

Описаны основные закономерности катодолюминесценции (КЛ) аморфных диэлектрических материалов под воздействием импульсного пучка ускоренных электронов. На основе упрощенной двухуровневой модели ловушек электронов в запретной зоне показано, что КЛ имеет мгновенный и задержанный компоненты, определяемые динамикой заполнения глубоких ловушек квазисвободными электронами, генерируемыми облучением. При больших значениях поглощенной дозы и на больших временных интервалах может проявляться также рекомбинационное излучение. Полученные аналитические выражения для динамики интенсивности КЛ качественно согласуются с имеющимися экспериментальными данными. Исследованы условия применения сигнала КЛ технических материалов для on-line диагностики режима обработки продукции на радиационно-технологических установках с ускорителями электронов.

МЕХАНІЗМИ ЛЮМІНЕСЦЕНЦІЇ АМОРФНИХ ДІЕЛЕКТРИКІВ ПІД ДІЄЮ ВИСОКОЕНЕРГЕТИЧНИХ ЕЛЕКТРОНІВ

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Описані основні закономірності катодолюмінесценції (КЛ) аморфних діелектричних матеріалів під дією імпульсного пучка прискорених електронів. На основі спрощеної дворівневої моделі пасток електронів у забороненій зоні показано, що КЛ має миттєвий та затриманий компоненти, які визначаються динамікою заповнення глибоких пасток квазівільними електронами, що генеровані опроміненням. При великих значеннях поглинутої дози, та на великих проміжках часу може також проявлятися рекомбінаційне випромінювання. Одержані аналітичні вирази щодо динаміки інтенсивності КЛ якісно погоджуються з наявними експериментальними даними. Досліджено умови використання сигналу КЛ технічних матеріалів для on-line діагностики режиму обробки продукції на радіаційно-технологічних установках з прискорювачами електронів.