

Using Rouse-Fowler model to describe radiation-induced electrical conductivity of nanocomposite materials

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Abstract. Using the Rouse-Fowler (RF) model this work studies the radiation-induced electrical conductivity of a polymer nanocomposite material with spherical nanoparticles against the intensity and exposure time of gamma-ray, concentration and size of nanoparticles. The research has found the energy distribution of localized states induced by nanoparticles. The studies were conducted on polymethylmethacrylate (PMMA) with CdS nanoparticles.

1. Introduction

Nanocomposite materials are materials formed by inclusion of nanoparticles into some matrix material. As a result, we can create a new functional material with unique electro physical properties. PMMA+CdS or CdSe nanocomposite allows creation of new types of photo galvanic and optoelectronic devices [1-2]. It is important to consider the possibility of using these devices under increased radiation (space, nuclear engineering, etc.). Therefore, the study of the nanocomposite radiation resistance is an important and relevant task [3]. Particular attention is given to spherical semiconductor nanoparticles such as CdS or CdSe due to the fact that their fluorescence band covers whole visible, near-IR and near-UV bands depending on the particle size. It is known that such size dependent properties are related to quantum confinement effects that are more pronounced with the smaller nanoparticle size. Thus nanocomposites with the nanoparticle size less than 10 nm possess the most interesting electrophysical properties. The maximal realization of electrophysical properties of CdS and CdSe nanoparticles requires their isolation from each other, that is why the nanoparticle concentration normally does not exceed 10 vol.%.

Using the Rouse-Fowler (RF) model, this work studies the radiation-induced electrical conductivity of the polymer nanocomposite exposed to gamma-rays. According to works [4-6], phenomena related to the radiation-induced electrical conductivity of polymers are best described by the Rouse-Fowler model. There are analytic and numerical solutions [7-11] for the model variations where either the spectrum of localization centers (traps) in the bandgap has only one or two states or the distribution of trap energy states follows the exponential law. Nanocomposite materials are characterized by existence of additional centers of localization in the bandgap. The energy distribution of these centers depends on the shape, size and concentration of nanoparticles. Thus the need to describe electrophysical properties of nanocomposites requires the RF model generalization for a certain energy distribution of localization centers in the bandgap.



2. Localization centers

It is known that dielectrics and semiconductors have intrinsic localized states (intrinsic traps) due to various structure defects [7]. Trap properties of many polymers are well understood. For example, such polymers as polymethylmethacrylate (PMMA) have the p-type conductivity and the trap energy distribution follows the exponential law:

$$N(E) = (N_0/kT_1) \exp[-E/kT_1],$$

where N_0 is the full concentration of traps, T_1 is the characteristic temperature of distribution, E is the trap energy calculated from the valence band top.

Free charge carrier trapping on the energy level (E) is characterized by the capture coefficient $k_E = \nu \sigma_a(E)$, where ν is the free charge carrier velocity, $\sigma_a(E)$ is the capture cross-section on the relevant level [7]. The thermal release time of trapped charge carriers follows the formula $\tau_E = \nu_0^{-1} \exp(E/kT)$, where ν_0 is the frequency factor. k_E, ν_0 values for a variety of polymers are estimated in works [7-11].

Due to differences in the Fermi levels of materials, the introduction of nanoparticles into matrix materials forms the potential well with additional localized centers just as impurities in semiconductors lead to formation of acceptor and donor states. Following this line of reasoning, localized centers induced by nanoparticles shall be designated as impurity localized centers (impurity traps).

Let us denote the Fermi energies and work functions of the matrix and the particle by $F_M, W_M, F_{pat}, W_{pat}$, respectively. When $F_M < F_{pat}$ ($W_M > W_{pat}$), electrons flow from the nanoparticle to the matrix tending to the energy minimum. As a result, the nanoparticle acquires positive charge $q_{pat} = C_{pat} U_0$, where C_{pat} is the nanoparticle capacitance, $U_0 = W_M - W_{pat}$. Electrons held by the field of the positively charged nanoparticle become localized in the potential well the depth of which is $-U_0$ from the conductivity band bottom of the matrix. These inclusions are of donor-type. In the opposite case, when $F_M > F_{pat}$ ($W_M < W_{pat}$), the hole potential well forms with the depth U_0 measured from the valence band top. These inclusions are of acceptor-type.

To find the energy distribution of traps it is necessary to solve the steady Schrodinger equation for subatomic particles with the effective mass in the inclusion field. For definiteness let us consider the donor-type inclusion. The potential energy can be written as:

$$U(r) = -U_0 \text{ at } r \leq R_{pat} \text{ and } U(r) = -(U_0 R_{pat}/r_D) \cdot \exp[-(r - R_{pat})/r_d] \text{ at } r > R_{pat}.$$

Here r_D is the Debye shielding radius at the particle, which is determined so that the number of localized centers is not less than $q_{pat}/2e$ including spin. The Schrodinger equation is solved in spherical coordinates for two areas: $r \leq R_{pat}$ and $r > R_{pat}$. Since the problem is one-dimensional, the WKB-method is used to solve the wave equation. For the acceptor inclusion the trap spectrum is sought the same way.

The frequency factor for impurity traps can be estimated in the form: $\nu_0 = A_v \nu_E / 2r_E$, where A_v is the probability of absorbing a phonon by an electron, ν_E is the average velocity of a trapped charge carrier, r_E is the radius of the potential well with the given energy found from the terms: $U(r_E) = E$.

Let us consider the nanocomposite based on PMMA ($W_{PMMA} = 4,68$ eV) with CdS nanoparticles ($W_{CdS} = 6,05$ eV). In this nanocomposite, the potential well depth for holes is $U_0 = 1,37$ eV.

Increase of the nanoparticles size leads to increase in the number of energy levels in the potential well and the proportion of deep traps with the large lifetime ($\tau_E \geq 10^4$ s). Charge carrier release from deep traps by the thermal motion at $T = 300$ K is not possible, but under external exposure, such as

ionizing radiation or nanocomposite heating, the deep trap influence on the electrical conductivity increases.

It is important to note that compared to intrinsic localized centers the energy spectrum of impurity centers belongs to a certain particle. Thus, holes trapped on impurity centers and tending to the energy minimum always tend to go to a deeper energy level if it has a vacancy.

3. Ionization of nanocomposite material

To describe the radiation-induced electrical conductivity of materials it is necessary to set the volumetric generation rate of charge carrier pairs (S).

The volumetric generation rates in the matrix and inclusions can be written in the form:

$$S = (1 - f_{pat}) \rho D / w_i, \quad S_{pat} = f_{pat} \cdot (\rho D / w_i)_{pat},$$

where ρ is the mass density of matter, D is the radiation energy absorbed by unit mass of substance per unit time, f_{pat} is the volume fraction, w_i is the average energy of electron-hole pair generation, the values with the pat index in the brackets are defined for nanoparticles. Generally, for a solid dielectric the value w_i makes several hundreds of eV [7] to exclude pair generation with the small recombination time (less than 10^{-12} s) from consideration.

The charge carrier generation rate in the matrix (S) determines the generation speed of electrons in the conduction band and holes in the valence band. As a rule, ionization of a nanometer-sized inclusion is accompanied by secondary electron removal from it. Such a conclusion can be based on the experimental and theoretic studies of the attenuation length (the distance at which an electron flux is weakened by e times) of low energy electrons in different materials [12]. For metals, where the free electron concentration is large and, therefore, the share of electron-electron interaction is large too, the minimal attenuation length makes 3-4 nm and is observed in the range of the secondary electrons energy 10-30 eV. The one in dielectrics is substantially greater due to a low probability of inelastic collision between a low energy electron and bound electrons.

As an inclusion is a localization center, electron release from this center leads to occupancy change of the localized state.

In case of the donor inclusion, electron removal leads to increase of its positive charge that results in electron capture by this inclusion from its impurity trap. Thus, ionization of the donor inclusion forms S_{pat} of free electrons and the same number of vacancies on impurity electron states in unit volume per unit time.

In case of the acceptor inclusion, electron removal from it leads to electron transfer with the minimal energy from the matrix to the inclusion, that is hole generation with the energy close to the valence band top. Thus, ionization of the acceptor inclusion forms S_{pat} of free electrons and the same number of holes localized on high states in unit volume per unit time.

The dose rates (D) absorbed by materials of the matrix and the inclusion were calculated for exposure by deceleration radiation quanta generated by electrons with the initial energy of 1 MeV in the wolfram absorber with the thickness of 260 μm . Transfer of electrons is calculated by the method [13]. Using the attenuation coefficient tables [14], transfer of deceleration quanta in the absorber is described by the kinetic equation excluding scattering. At the current density of the electron beam 0.1 kA/cm^2 in the PMMA layer located behind the wolfram target, the absorbed dose rate near the contact boundary is $D_{PMMA} = 1.9 \cdot 10^8 \text{ W/kg}$. For the CdS layer, it makes $D_{CdS} = 5.58 \cdot 10^8 \text{ W/kg}$. The considered irradiation mode at the average energy per ion pair formed $w_i = 100 \text{ eV}$ and $f_{pat} = 0.05$ the volumetric generation rates are $S_{PMMA} = 1.29 \cdot 10^{28} \text{ m}^{-3} \text{ s}^{-1}$ and $S_{CdS} = 8.4 \cdot 10^{27} \text{ m}^{-3} \text{ s}^{-1}$. Thus, CdS nanoparticle ionization contributes to PMMA+CdS nanocomposite ionization even more than matrix ionization.

4. The Rouse-Fowler equation system for nanocomposite material

As at this stage of the work only the local conductivity is interesting to us. We assume that ionization is homogeneous in volume, loading effects [6] are not significant and drift of charge carriers can be neglected. It should be noted, that the considered here model and method of its realization are easily generalized to heterogeneous irradiation, loading and drift of charge carriers, and a multidimensional case.

Let us denote the concentrations of free electrons and holes by n, p ; n_m, p_l – the concentrations of electrons and holes localized by traps, where $1 \leq m \leq m_0, 1 \leq l \leq l_0$, m_0, l_0 – the numbers of electron and hole states. Let states $1 \leq m \leq \tilde{m}_0, 1 \leq l \leq \tilde{l}_0$ be related to localized states of the matrix (intrinsic localized traps) and $\tilde{m}_0 + 1 \leq m \leq m_0, \tilde{l}_0 + 1 \leq l \leq l_0$ be related to impurity traps. The other denotations: α – the recombination coefficient, $K_m = k_m(M_m - n_m)$, $K_l = k_l(P_l - p_l)$, k_m, k_l – the capture coefficients on electron and hole traps, M_m, L_l – the concentrations of electron and hole traps, $\tau_{m,l} = \exp(E_{m,l}/kT)/\nu_0$ – the life times of charge carriers on electron and hole traps with the energy $E_{m,l}$, respectively [7].

The equation system describing the dynamics of free and trapped charge carriers has the forms:

$$\dot{n} = S + S_{pat} - \alpha n \left[p + \sum_{l=1}^{l_0} p_l \right] - n \sum_{m=1}^{m_0} K_m + \sum_{m=1}^{m_0} \frac{n_m}{\tau_m}; \quad (1)$$

$$\dot{p} = S + (S_{pat} - S'_{pat}) - \alpha p \left[n + \sum_{m=1}^{m_0} n_m \right] - p \sum_{l=1}^{l_0} K_l + \sum_{l=1}^{l_0} \frac{p_l}{\tau_l}; \quad (2)$$

$$\dot{n}_m = K_m n - \frac{n_m}{\tau_m} - \alpha p n_m - S'_{pat} \delta_{m, \tilde{m}_0}, \quad 1 \leq m \leq m_0; \quad (3)$$

$$\dot{p}_l = K_l p - \frac{p_l}{\tau_l} - \alpha n p_l + (S_{pat} - S'_{pat}) \delta_{l, \tilde{l}_0 + 1}, \quad 1 \leq l \leq l_0, \quad (4)$$

where $S'_{pat} = S_{pat}$ for donor inclusions, $S'_{pat} = 0$ for acceptor ones.

At the initial time moment, the concentrations of charge carriers have the equilibrium (without irradiation) values n^0, p^0, n_m^0, p_l^0 . They can be found by the solving system (1)-(4) with the zero initial conditions for the concentrations of free and trapped charge carriers and without vacancies on impurity traps at $S = S_T$, $S_{pat} = 0$, where S_T is the thermal ionization rate.

The general idea of the system solving (1)-(4) is finding the approximate analytical solution for a certain time interval $\Delta t = t_{k+1} - t_k$ that is chosen to minimize bias of the found analytical solution.

5. Test calculations

The system solving (1)-(4) suggested in this work was tested by comparing our results with the results of the analytic solution of the problem of the dielectric radiation-induced conductivity for the two-trapped model (the Van-Lint model) [7], and with the numerical results for the exponential distribution of traps [9].

Our results fully coincide with the Van-Lint model results, and this fact indicates the adequacy of our model for two traps.

For the exponential distribution of traps, we compared our results with those reported in [9] (figure 1) at the following parameters: $T = 300$ K; $N_0 = 10^{25} \text{ m}^{-3}$; $k = 10^{-16} \text{ m}^3/\text{s}$; $\alpha = 10^{-14} \text{ m}^3/\text{s}$; $\nu_0 = 10^4 \text{ s}^{-1}$; $S = 6,25 \cdot 10^{19} \text{ m}^{-3} \text{ s}^{-1}$ at continuous irradiation. Here, as well as in [9], we consider the dielectric material, which has the p -type conductivity with the hole mobility $\mu_p = 10^{-6} \text{ m}^2/\text{V}\cdot\text{s}$. It is

clear that the obtained results for the intrinsic radiation-induced conductivity of the polymer coincide well with the results [9].

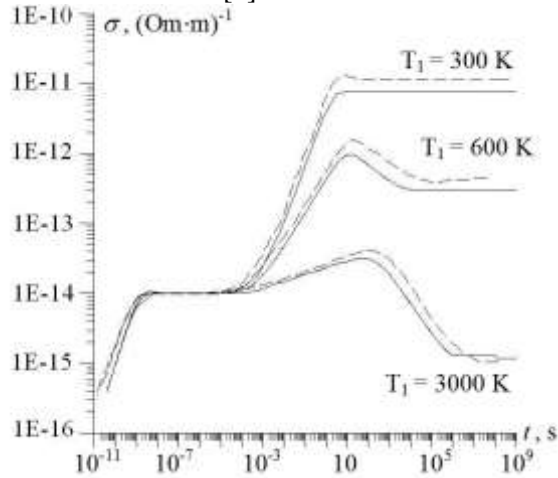


Figure 1. Radiation-induced conductivity σ ($\Omega\cdot\text{m}^{-1}$) of the polymer matrix with the exponential distribution of traps and various distribution parameters T_1 (K). “—” indicates the results from the work [9]; “—” plots our results.

6. Radiation-induced conductivity of nanocomposite material

The calculation of the radiation-induced conductivity for pure PMMA and PMMA with CdS nanoparticles against their size, concentration and absorption dose rate is shown in figure 2.

Intrinsic localized centers of PMMA have the exponential distribution with the distribution parameter $T_1 = 2150$ K at room temperature [11]. The full concentration of intrinsic localized centers is 10^{25} m^{-3} .

The dark conductivity of pure PMMA does not exceed $10^{-20} (\Omega\cdot\text{m})^{-1}$. The nanoparticle inclusion leads to formation of additional centers and increase of the nanocomposite dark conductivity. The resulting equilibrium condition is used as initial for the calculation of the radiation-induced conductivity.

During irradiation, when a process of generation dominates over processes of capture and recombination, the radiation-induced conductivity increases to a certain value. This value is kept constant until the end of irradiation by the equilibrium between processes of generation, recombination and capture on traps. After irradiation, the equilibrium is disturbed and active capture of charge carriers by localized centers takes place. As a result, the conductivity drops drastically by four orders. Further behavior of the conductivity is caused by release of localized charge carriers from traps and recombination of these charge carriers.

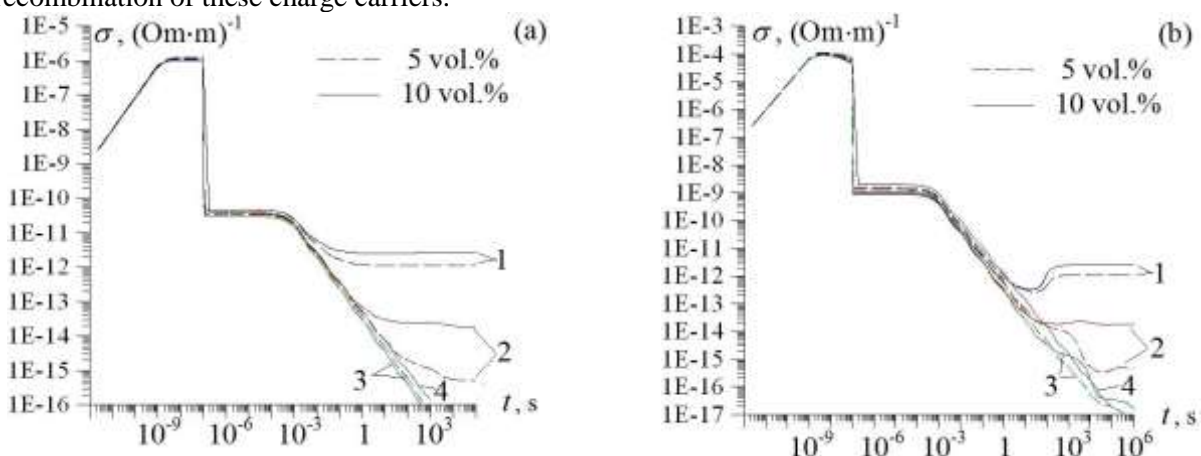


Figure 2. Radiation-induced conductivity of PMMA+CdS nanocomposite with the CdS radius: 2 nm (1); 5 nm (2); 10 nm (3); pure PMMA (4). The absorbed dose rate of the matrix is $D = 10^8$ (a) and 10^{10} W/kg (b). The duration pulse is $\tau_{rad} = 100$ ns.

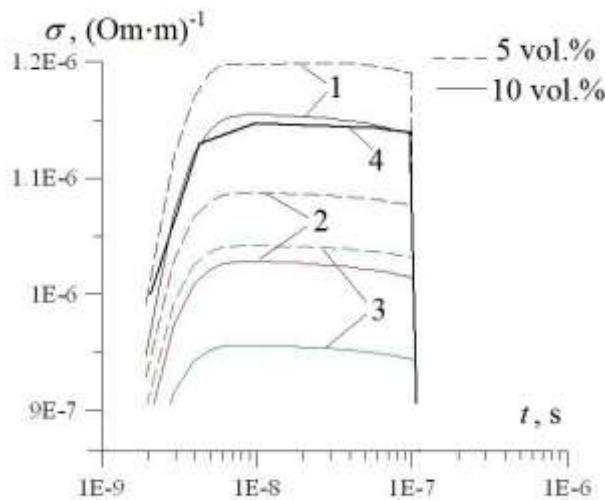


Figure 3. Radiation-induced conductivity of PMMA+CdS nanocomposite during irradiation $t < \tau_{rad} = 10^{-7}$ s against the size and concentration of CdS. The CdS radius is 2 nm (1); 5 nm (2); 10 nm (3); pure PMMA (4). The absorbed dose rate is $D = 10^8$ W/kg.

During irradiation the conductivity of nanocomposite with CdS nanoparticles with 2 nm in radius exceeds the value of pure PMMA (figure 3). While for nanoparticles with 5 or 10 nm in radius, the electrical conductivity is less than the one of pure PMMA. It is caused by growth of the capture cross-section on impurity centers with increase of the nanoparticles size. Because inclusion of nanoparticles leads to formation of impurity centers, the nanocomposite conductivity decreases with increase of the nanoparticle concentration.

After irradiation, the conductivity returns to its original state of the equilibrium and the relaxation rate depends on the nanoparticle size. Decrease of the relaxation rate with increase of the nanoparticle radius is caused by increase in the number of deep traps. For CdS nanoparticles with 2 nm in radius at $\dot{D}_\gamma \leq 10^8$ W/kg, the relaxation time does not exceed 1 s, but for the nanoparticle radius of 5 and 10 nm, it reaches 10^4 s.

7. Conclusion

The test calculations have demonstrated that the suggested method is efficient for solving the Rouse-Fowler equation system for a certain spectrum of traps.

The developed model of nanocomposite ionization considers both matrix ionization and inclusion ionization. Our research has shown that ionization of inclusions changes the concentration of free charge carriers and the occupation of energy states.

Inclusion of CdS nanoparticles into PMMA leads to generation of additional charge carriers and increase of the nanocomposite dark conductivity. The number of impurity centers in PMMA+CdS nanocomposite grows with increase of the nanoparticle size, at that the number of deep traps, charge carrier release from which is possible only under external exposure (ionization, heating), grows too.

During irradiation, the radiation-induced conductivity of nanocomposite depends on the size and concentration of nanoparticles. For CdS nanoparticles with $R_{pat} = 2$ nm, the electrical conductivity exceeds the value of pure PMMA. While for CdS nanoparticles with $R_{pat} > 5$ nm, the electrical conductivity is less than the one of pure PMMA caused by growth of the capture cross-section on impurity centers with increase of the nanoparticle size.

After irradiation, the conductivity returns to its original state of the equilibrium and the relaxation rate depends on the size and concentration of inclusions. The equilibrium time for the nanocomposite conductivity grows with increase of the nanoparticle radius due to increase in the number of deep traps.

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