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INVESTIGATION OF RECHARGING PROCESSES FOR THE VOLUME LOCALIZED STATES IN POLYCRYSTALLINE SEMICONDUCTORS

The influence of recharging processes for the volume localized states in semiconductor component of polycrystalline structure on the kinetics of isothermal depolarization current is theoretically studied. The equation of continuity of electric induction on the borders of the insulator-semiconductor together with a first integral of the equations for the spatial charge is used as a model. Kinetic equations are recorded on the basis of the Shockley - Red - Hall statistics. The current density of depolarization, induced recharge of surface and volumetric local electronic states are determined as a result of the decision. The spectral characteristics of the current are obtained with using the Fourier transformation. In the spectra there are two clearly distinct maxima. The low-frequency maximum corresponds to the surface states, and the high-frequency one corresponds to the volume localized states. The values of parameters that are typical for the metal-oxide varistor ceramics based on ZnO are taken in the calculations. It is shown that the kinetic and spectral dependences of depolarization current at different temperatures can be used to evaluate the ionization energy and temperature dependences of the capture ratios of the electron states.

Keywords: polycrystalline semiconductor, isothermal depolarization current, localized electronic states, kinetics, spectrum, potential.

Теоретически исследуется влияние процессов перезарядки объемных локализованных состояний в полупроводниковой компоненте поликристаллической структуры на кинетику тока изотермической деполяризации. В качестве модели используется уравнения непрерывности электрической индукции на границах изолятор-полупроводник вместе с первым интегралом Пуассона для областей пространственного заряда. Кинетические уравнения записываются на основе статистики Шокли - Рида - Холла. В результате решения определяется плотность тока деполяризации, обусловленного перезарядкой поверхностных и объемных локальных электронных состояний. С использованием преобразования Фурье получаются спектральные характеристики тока. В спектрах явно выделяются два максимума: низкочастотный, соответствующий поверхностным и высокочастотный, соответствующий объемным локализованным состояниям. При расчетах принимаются значения параметров, характерные для металлооксидной варисторной керамики на основе ZnO. Показано, что кинетические и спектральные зависимости тока деполяризации при разных температурах можно использовать для оценки энергии ионизации и температурных зависимостей коэффициентов захвата электронных состояний.

Ключевые слова: поликристаллический полупроводник, ток изотермической деполяризации, локализованные электронные состояния, кинетика, спектр, потенциал.

Теоретично досліджується вплив процесів перезарядки об'ємних локалізованих станів в напівпровідниковій компоненті полікристалічної структури на кінетику струму ізотермічної деполяризації. В якості моделі використовується рівняння неперервності на межах ізолятор-напівпровідник сумісно з першим інтегралом Пуассона для областей просторового заряду. Кінетичні рівняння записуються на основі статистики Шоклі - Ріда - Холла. В результаті рішення визначається щільність струму деполяризації, обумовленого перезарядкою поверхневих і об'ємних локальних електронних станів. З використанням перетворення Фур'є одержуються спектральні характеристики струму. В спектрах явно виділяються два максимуми: низькочастотний, що відповідає поверхневим і високочастотний, що відповідає об'ємним локалізованим станам. При розрахунках приймаються значення параметрів, характерні для металоксидної варисторної кераміки на основі ZnO. Показано, що кінетичні і спектральні залежності струму деполяризації при різних температурах можна використовувати для оцінки енергії іонізації і температурних залежностей коефіцієнтів захвату електронних станів.

Ключові слова: полікристалічний напівпровідник, струм ізотермічної деполяризації, локалізовані електронні стани, кінетика, спектр, потенціал.

Introduction

Electron exchange processes for localized states in polycrystalline semiconductors with intercrystallite potential barriers can be studied by analyzing the isothermal depolarization (ID) current kinetics [1].

The known basic theoretical model of the ID current kinetics in polycrystalline semiconductors is based on the concept of recharging surface localized electronic states (LES) at the boundaries of the semiconductor crystallites and the matrix of the insulating phase [2]. The influence of volumetric LES in such structures has not been studied theoretically up to now.

At the same time, for several polycrystalline structures, in particular, metal oxide varistor ceramics, contribution of volumetric LES to the ID current can be considerable.

The presence of deep energy LES filled with electrons at the boundaries of semiconductor crystallites (e.g., ZnO) leads to the formation of surface charges and near-surface potential barriers (up to 1 eV or more) between the semiconductor crystallites [3]. The change of the filling of such LES by applying real (not admitting breakdown) polarizing voltage is usually insignificant, and needs more time for their discharge. Therefore, a significant contribution to the formation of the observed (fast) component of the ID current [1, 4] can be provided by volumetric LES of semiconductor crystallites.

In this paper a model of the kinetics of ID current, which takes into account the recharging processes for the volume LES in semiconductor crystallites is proposed. The effect on the value of its polarizing voltage and temperature is also studied; and the analysis of the information value of the model to obtain data on the characteristics of bulk LES is performed.

Element of the polycrystalline semiconductor structure

The element of the polycrystalline structure for the one-dimensional model is a layer of semiconductor material located in surface region. The region is isolated from both sides by dielectric thin films of intergranular phase.

Applying the polarizing voltage produces the additional filling and, accordingly, the devastation of surface and bulk LES that are energetically near the Fermi level and spatially located in the border areas of both the semiconductor layer.

After the decline of the applied voltage to zero, the sample depolarization starts. This process ends with relaxation to the initial filling of LES. The dependence of depolarization current versus time provides information on the nature of mentioned electrical transients [1, 4-6].

In order to concretize model, we consider a one-dimensional structure, characteristic for a metal-oxide varistor ceramics [3]. It includes a semiconductor layer ZnO with a thickness of $d_s \sim 10 \mu\text{m}$ located between two thin films of thickness $d_d \sim 20 \text{ \AA}$ of the dielectric intergranular phase. It is assumed that the charging occurs mainly for electron transitions between LES and the conduction band of ZnO.

It is necessary to solve two problems in the simulation. The first problem is to find the potential distribution and function of electron filling of surface and bulk LES in the crystallites in a steady state of polarization (for different values of voltage $V = V_{POL}$). The second one is to determine the dependence of these functions on time for the transition of the initially polarized object in equilibrium with its short-circuit ($V = 0$) using the kinetics of the ID current.

The model equations

The polarization state

Equations, that determine a steady-state polarization, are the equations of continuity of the electric charge displacement at the boundaries of a single insulator-semiconductor structure element (coordinates of the boundaries of the semiconductor layer $x = \mp d_s/2$, point $x = 0$ corresponds to the middle layer)

$$\varepsilon_0 \varepsilon_d \frac{V_d}{d_d} = \varepsilon_0 \varepsilon_s \frac{d}{dx} \Big|_{x=-d_s/2} + e N_S f_S \Big|_{x=-d_s/2} \quad (1)$$

$$\varepsilon_0 \varepsilon_s \frac{d}{dx} \Big|_{x=d_s/2} = \varepsilon_0 \varepsilon_d \frac{V_d}{d_d} + e N_S f_S \Big|_{x=d_s/2} \quad (2)$$

with the first integral of the Poisson equation for the space charge region of the form

$$\frac{d}{dx} = \frac{kT}{eL} F(Y) = \frac{kT}{eL} \text{sign}(-Y) \times \left\{ \int_0^Y \left\{ \frac{N_V}{n_{V0}} [(f_V(y) - f_V(0) + \exp(y) - 1)] - \frac{p_{V0}}{n_{V0}} [\exp(-y) - 1] \right\} dy \right\}^{1/2}, \quad (3)$$

where N_q – surfactant concentration (index $q = S$) and bulk (index $q = V$) donor LES, composite index q is used in a similar manner, and then to describe the surface and volumetric parameters; f_q – the electron distribution function in the LES (at equilibrium Fermi function); $Y = e(\varphi - \varphi_0)/kT$, φ_0 – level of capacity in the semiconductor; n_{V0} and p_{V0} – the concentration of free electrons and holes in a semiconductor crystal; ε_d and ε_s – the relative dielectric permittivity of the dielectric intergranular phase and a semiconductor; ε_0 – electric constant; e – the absolute value of the electron charge; k – Boltzmann constant; T – temperature; $V_d = V - [(d_s/2) - (-d_s/2)]$; $V = V_{POL}$, V_{POL} – the value of the polarizing voltage applied to the unit cell of a polycrystalline structure; x – coordinate along the axis orthogonal to the layers of a single structural element.

The numerical solution of the set of nonlinear equations (1) – (3) provides the potential distribution $Y^{(POL)}(x)$ and the distribution functions of electrons on surface $f_S^{(POL)}(\pm d_s/2)$ and bulk $f_V^{(POL)}(x)$ LES for the polarized structure element of polycrystalline semiconductor.

Kinetics of depolarization

Kinetic equations describing the recharging LES during depolarization written on the basis of the Shockley-Read-Hall statistics [7] have the form

$$df_q(x, t)/dt = c_{nq} \left\{ (1 - f_q(x, t)) \cdot n(x, t) - f_q(x, t) n_{1q} \right\} \quad (4)$$

where $n_{1q} = N_C \exp(-\Delta E_q/kT)$ – the concentration of electrons in the conduction band, reduced to the level of E_q , ΔE_q – ionization energy, N_C – effective density of states in the conduction band of the semiconductor; $Y(x, t)$ and $n(x, t) = n_{V0} \exp[Y(x, t)]$ – potential

profile (band bending) and the concentration of free electrons in the space charge of the structural element of the semiconductor crystallites; c_{nq} - coefficient of electron capture LES ($c_{nq} = \sigma_{nq} \cdot \bar{v}_T / g$, σ_{nq} - the effective capture cross section, \bar{v}_T - average thermal velocity of the electrons, g - the degeneracy of LES).

The initial conditions for the surface and bulk LES are

$$\begin{aligned} f_S(\mp d_s / 2) &= f_S^{POL}(\mp d_s / 2), \\ f_V(x, 0) &= f_V^{POL}(x). \end{aligned} \quad (5)$$

The dependencies $Y(x, t)$ are found by the equation integrating $\frac{x}{L} = \int_{Y_{POL}(x)}^{Y(x, t)} dy / F[y(t)]$

where $Y_{POL}(x)$ is the solution of the set (1)–(2) with using the expression (3) for the first integral of the Poisson equation, L - Debye screening length of an intrinsic semiconductor. The depolarization current density caused by the recharging of the surface and bulk LES can be written as

$$\begin{aligned} j_{ID}(t) &= j_{ID}^{(S)}(t) + j_{ID}^{(V)}(t) = eN_S d[f_S(-d_s/2, t) - f_S(d_s/2, t)]/dt + \\ &+ eN_V \int_0^{L_{SC}^{(1)}} \{d[f_V(x, t)]/dt\} dx - eN_V \int_0^{L_{SC}^{(2)}} \{d[f_V(x, t)]/dt\} dx, \end{aligned} \quad (6)$$

where $L_{SC}^{(1)}$ и $L_{SC}^{(2)}$ are thicknesses of space charge regions located near the left and right edges of the semiconductor layer.

Overall analysis of the expression (6) is complicated and can be carried out only approximately with using numerical methods. However, given the idea that the near-surface space-charge region is formed deep ("slow") levels [3] (LES with the long relaxation times, which, in particular, also confirmed by the study of thermally stimulated depolarization currents [8]), can be considered as the potential distribution in the crystallites during depolarization $Y(x, t) \approx Y(x)$. This allows obtaining the analytical solution of the kinetic equation (4) and equation (6) for the surface and volume ID currents explicitly

$$j_{ID}(t) = j_{ID}^{(S)}(t) + j_{ID}^{(V)}(t) = j_0^{(S)} \cdot \exp(-t/\tau_S) + j_0^{(V)} \cdot \exp(-t/\tau_V) \quad (7)$$

where $\tau_S = [c_{nS}(n_{1S} + n_S)]^{-1}$; $\tau_V = [c_{nV}(n_{1V} + n_{V0})]^{-1}$;

$$j_0^{(S)} = -eN_S \tau_S^{-1} \cdot [f_S^{(POL)}(-d_s/2) - f_S^{(POL)}(d_s/2)];$$

$$j_0^{(V)} = -eN_V \tau_V^{-1} \cdot \int_0^{L_{SC}} [f_{V.1}^{(POL)}(x) - f_{V.2}^{(POL)}(x)] dx;$$

$$L_{SC} = \max(L_{SC}^{(1)}, L_{SC}^{(2)});$$

$L_{SC}^{(1)}$ and $L_{SC}^{(2)}$ are the thicknesses of the left and right areas of the space charge polarization in the semiconductor crystallite.

Functions $f_{V,1}^{(POL)}(x)$ и $f_{V,2}^{(POL)}(x)$ correspond to the LES charge on one side and their discharge on the other side of the semiconductor layer.

For the equation (7) it is accepted that the resulting volumetric component of the depolarization current $j_{ID}^{(V)}(t)$ can be approximately determined by its maximal component. This component is caused by LES. Its energy level is crossing the Fermi level [9]. It's supposed that $n_V(x) \approx n_{V1}$ and $\tau_V(x) \approx \tau_{VF}$.

The kinetic and spectral dependences of depolarizing current

Theoretical kinetic dependence of the isothermal depolarization current $j_{ID}(t)$ of the polycrystalline semiconductor element of structure obtained on the basis (7) is presented in Fig. 1. The corresponding spectral dependences $J_{ID}(\omega)$, as shown in this figure, are found using the direct sine-transform of Fourier:

$$J_{ID}(\omega) = \frac{2}{\pi} \int_0^{\infty} j_{ID}(t) \sin(\omega \cdot t) dt = J_{ID}^{(S)}(\omega) + J_{ID}^{(V)}(\omega) \quad (8)$$

where ω - cyclic frequency ($\omega \in [0, \infty]$), a $J_{ID}^{(q)}(\omega) = (2j_0^{(q)}/\pi) \times \omega / [\omega^2 + (1/\tau_q)^2]$.

The left (low-frequency) maximum of spectrum corresponds to the surface LES, and the right (high-frequency) one – to bulk LES. In the calculations, the values of the parameters are for metal oxide varistor ceramics based on ZnO: $\Delta E_V = 0.2$ eV; $N_V = 10^{17}$ sm⁻³; $c_{nV} = 10^{-12}$ sm³/s and $\Delta E_S = 0.5$ eV; $N_S = 10^{14}$ sm⁻²; $c_{nS} = 10^{-14}$ sm³/s; $n_{V0} = 10^{17}$ sm⁻³; $n_{V0} \gg p_{V0}$ [8]. As can be seen, there are two relaxation areas in the kinetics $j_{ID}(t)$. They are characterized by times τ_V and τ_S depending on the capture coefficients c_{nq} and ionization energies ΔE_q of LES. The first area (fast) is associated with the recharging of bulk LES, and the second (slow) one – with recharging surface LES, i.e. $\tau_V \ll \tau_S$. If $\tau_V \sim \tau_S$, then these areas are overlapped.

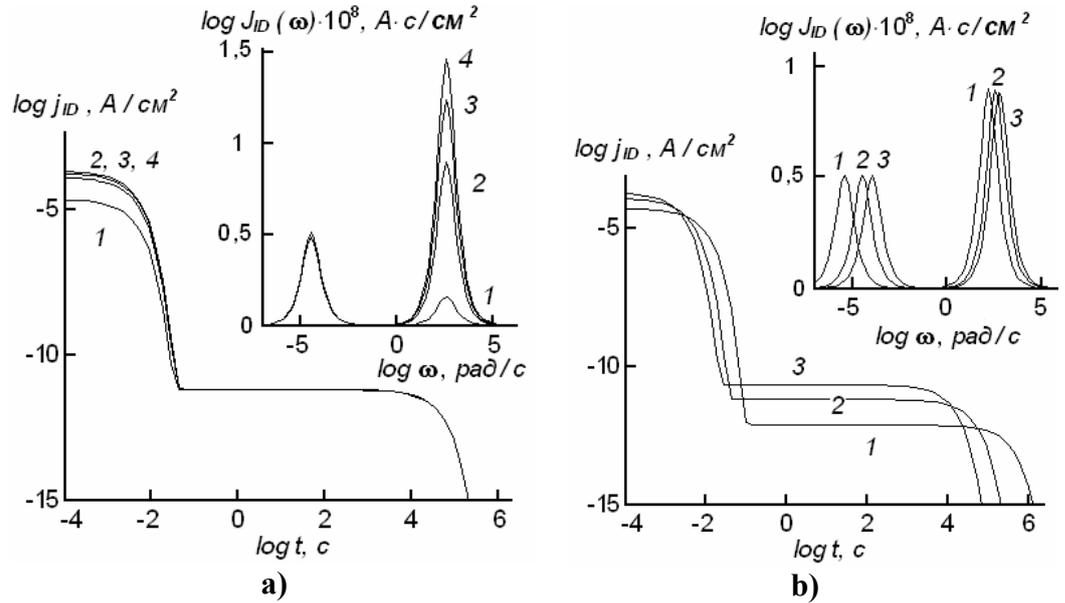


Fig. 1. Time $j_{ID}(t)$ and spectral $J_{ID}(\omega)$ dependences of isothermal depolarization current of structural element on V_{POL} , V: 1 – 0.5; 2 – 5; 3 – 10; 4 – 15 at $T=300$ K (a) and temperature T , K: 1 – 270; 2 – 300, 3 – 330 at $V_{POL} = 3$ V (b)

According to this in the spectra $J_{ID}(\omega)$ there are two dispersion areas: high-frequency region is associated with recharging volume LES and the low frequency one is due to the recharge of surface LES. For the frequencies of their maxima we have in accordance with (8)

$$\omega_{\max}^{(q)} = 1/\tau_q . \quad (9)$$

With increasing polarization voltage V_{POL} the dependences $j_{ID}^{(s)}(t)$ and $J_{ID}^{(s)}(\omega)$ are lifted up (current increases in absolute value) to a limiting value corresponding to full charge of surface LES on one side of the semiconductor layer and full discharge on the other. With increasing of polarization voltage V_{POL} the absolute value of the bulk component of the current density of depolarization $j_{ID}^{(v)}(t)$ and its maximum range $J_{ID}^{(v)}(\omega)$ increases. However, the saturation is not observed.

The growth temperature T increases the amount of ID current and speed depolarization. The temperature dependence of the frequency $\omega_{\max}(T)$ are straighten the coordinates $(\log(\omega_{\max}), 1/T)$. The activation energies conform to the calculation of ionization energies of the bulk and surface LES.

Parameters of localized states

The model gives the relationship between the parameters of bulk LES, relaxation times and ID current in a form similar to that in [2] for surface LES:

$$\ln \tau_q = -\ln c_{nq} N_C + \Delta E_q / (kT) . \quad (10)$$

The temperature dependences $\tau_q(T)$ or $\omega_{\max}^{(q)}(T)$ can be found from the spectral curves for the depolarizing current obtained at different temperatures. From Eq. (10) the formula follows for determining an ionization energy and capture coefficient of free electrons for the bulk (and surface) local electronic states:

$$\Delta E_q = \ln(10) \cdot k \cdot \Delta [\lg \tau_q(T) \times T^2] / \Delta(1/T) ; \quad (11)$$

$$c_{nq}(T) = [\tau_q(T) \cdot N_C(T)]^{-1} \cdot \exp[\Delta E_q / (kT)] . \quad (12)$$

Conclusions

In polycrystalline semiconductors with relatively high intercrystallite potential barriers isothermal depolarization currents depends on the recharging of both bulk and surface localized electronic states.

It is determined:

- the presence of two relaxation areas in the current spectrum and kinetics of isothermal depolarization due to charging volume and surface localized states, with the fast or, correspondingly, high frequency region is associated with charge of bulk LES, and slow or low-frequency region – with recharging surface LES;

- increasing the time and spectral dependencies to some "marginal" for the surface and the absence of "limit" for the volume dependencies of LES with increasing polarization voltage in the operating voltage range.

It is shown that the kinetic and spectral dependencies of the isothermal depolarization current obtained at different temperatures can be used to estimate the ionization energy and the temperature dependence of the capture coefficient of bulk (and surface) LES in semiconductor crystallites.

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