Deep-level recombination spectroscopy in GaP light-emitting diodes

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Deep-level parameters determined from an analysis of the differential coefficients of the forward-bias current-voltage curves are compared in the example of commercial GaP LEDs. It is shown that these parameters are suitable for deep-center diagnostics. The proposed measurements can be performed on semiconductor wafers in the industrial environment without sealing or dividing into individual crystals. © *1999 American Institute of Physics.*
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Recombination in a space-charge region, theoretically grounded in the classical work of Shockley, Noyce, and Sah,[1] has received far less attention than it deserves. Charge injection into the space-charge region induces deep-level charge exchange accompanied by a change in the recombination rate.[2,3] This effect creates anomalous features in the forward-bias current-voltage (*I-V*) characteristics. These distinctive features are faint against the background of the exponential growth of the forward current and have therefore been ignored for a long time. A series of previous papers[4–6] has been devoted to the elucidation of these features and their utilization for determining the parameters of deep levels.

In this paper we compare various differential parameters of the forward-bias *I-V* characteristics and estimate their suitability for deep-center diagnostics in the example of commercial GaP light-emitting diodes (LEDs), in which nonradiative recombination channels lower the emission efficiency. To understand the recombination channels, it is necessary to determine the parameters of the defects which participate in nonradiative recombination and which lower its fraction in recombination processes. This problem is of utmost importance in LED technology.

The samples of GaP-based *p-n* junctions had standard parameters for commercial nitrogen-doped green-light LEDs. The epitaxially grown junction was sharp, asymmetric, and characterized by a density of electrons in the base $(3-9.5)\times10^{15}\,\mathrm{cm}^{-3}$. The *I-V* curves were measured on an automated apparatus described in Ref. 5. The current was set by means of a V7-42É electrometer in the range from 10^{-12} A to 10^{-2} A, and the voltage was set by means of a V7-46 voltmeter with a step of 0.01 V. The data were entered into computer memory. A total of 15 diodes were investigated. Selected parameters of one of them are shown in Table I.

At a low injection level the recombination currents in the space-charge region of a wide-gap semiconductor *p-n* junction are generally higher than the diffusion currents. In this case the *I-V* curve is described by a characteristic equation of the form

$$J=A(U)\exp(qU/\beta kT), \tag{1}$$

where β assumes values from 1 to 2 ($\beta=1$ for the diffusion currents). The physics of the process is described in detail in Refs. 1–5. The proportionality factor $A(U)$ depends on the parameters of the deep centers, which can be determined under certain assumptions.

The recombination current in the space-charge region of a *p-n* junction with the participation of several, simple, doubly charged deep levels is described by the equation[5]

$$j_r=\sum_{m=1}^{s}\frac{qw(U)c_{nm}c_{pm}n_i^2(e^{qU/kT}-1)N_{tm}}{2n_i\sqrt{c_{nm}c_{pm}}e^{qU/kT}+c_{nm}n_{1m}+c_{pm}p_{1m}}\times\frac{2kT}{q(V_d-U)}, \tag{2}$$

where q is the electron charge, $w(U)$ is the width of the space-charge region, s is the number of deep levels

$$n_{1m}=N_c\exp\left(-\frac{E_{tm}}{kT}\right);\quad p_{1m}=N_v\exp\left(-\frac{E_{tm}}{kT}\right);$$

c_n and c_p are the electron and hole capture coefficients for the given center, averaged over all states, N_t is the density of deep levels, E_t is the position of a deep level in the band gap,

$$E_{tn}=E_c-E_t;\quad E_{tp}=E_1-E_v,$$

and V_d is the diffusion potential.

TABLE I. Deep-level activation energies determined by different methods for a GaP LED.

Method	E_7, eV	E_6, eV	E_5, eV	E_4, eV	E_3, eV	E_2, eV	E_1, eV	E_8, eV	E_9, eV	E_{10}, eV
TSCAP	⋯	0.35	⋯	⋯	⋯	0.53	0.63	0.66	0.81	1.0
R_{np}	0.29	0.33	⋯	⋯	0.48	0.56	0.61	⋯	⋯	⋯
$\frac{d\beta}{dU}$	0.27	0.32	0.38	0.42	0.48	0.52	0.61	⋯	⋯	⋯
γ	0.26	0.30	0.37	0.41	0.46	0.54	0.61	⋯	⋯	⋯

Note: E_i denotes the deep-level thermal activation energies calculated from Eq. (5) and determined by the TSCAP technique. Other methods used to determine E_i are described in the text.

Equation (2) differs somewhat from the expressions in Ref. 1. This difference has already been analyzed in detail,[6] and we shall not discuss it further. The limits of applicability of Eq. (2) have been established previously.[2–5]

To analyze the *I-V* characteristics, it is convenient to introduce a different physical variable: the normalized recombination rate

$$R_{np}=\frac{i}{qwSn_i[\exp(qU/2kT)-1]}\,\frac{q(V_d-U)}{2kT}, \tag{3}$$

where i is the current, and S is the area of the *p-n* junction. This quantity is related to the deep-center parameters by an equation taken from Refs. 2 and 3:

$$R_{np}=\frac{c_nc_pn_iN_t[\exp(qU/2kT)+1]}{2n_i\sqrt{c_nc_p}\,\exp(qU/2kT)+n_1c_n+p_1c_p}. \tag{4}$$

The latter can be used to expand the total recombination process into individual components, using algorithms in Refs. 4–6. An example of such a partition for the investigated diodes is shown in Fig. 1. For each recombination process through a doubly charged deep center we can determine the voltage ($U_{0.5}$) at which the normalized recombination rate (4) decreases by one-half relative to saturation. Assuming that the deep center lies above the middle of the band gap (i.e., $c_pp_1\ll c_nn_1$), we find

$$E_{tn}=\frac{E_g-qU_{0.5}}{2}+\delta, \tag{5}$$

where

$$\delta=\frac{kT}{2}\ln\left(\frac{1}{4}\,\frac{c_nN_c}{c_pN_v}\right).$$

This quantity, like the capture coefficients, is unknown as a rule. However, the ratio of the capture coefficients can be determined by measuring the temperature dependence of the forward current.[2,3] The systematic error introduced when δ is disregarded does not exceed 0.06 eV for a ratio $c_n/c_p=100$. The activation energies calculated from Eq. (5) are given in Table I.

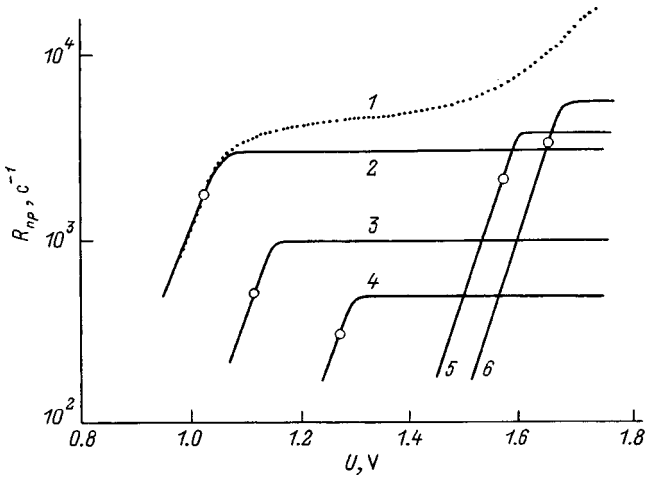

FIG. 1. Separation of recombination processes into components on the basis of the function $R_{np}=f(U)$. (*1*) Experimental; activation energies: (*2*) $E=0.61$ eV; (*3*) 0.56 eV; (*4*) 0.48 eV; (*5*) 0.33 eV; (*6*) 0.29 eV.

The deep-level activation energy can be determined from the extrema of the derivative of the differential slope of the *I-V* characteristic (β):

$$\beta=\frac{qJ_r}{kT}\left(\frac{\partial J_r}{\partial U}\right)^{-1}. \tag{6}$$

Equation (5) can also be used to determine deep-level activation energies from the maxima of the function $d\beta/dU=f(U)$, but the expression for δ will not contain the factor 1/4 in this case.[4] If we assume that $c_n/c_p=10^2$, the systematic error at $T=300$ K is then $\delta\approx0.04$ eV for GaP.

The function $d\beta/dU=f(U)$ for one sample is plotted in Fig. 2. There is a noticeable correlation between the maxima of curve *2* and the features of the normalized recombination rate (see Fig. 1). Every time a new level enters into the recombination process, the derivative of the differential slope of the *I-V* characteristic acquires a maximum.

A drawback of the method is the need to calculate the second derivative of the experimental data, which requires special numerical methods. In this regard, it is more practical to use another differential coefficient, whose determination requires only the calculation of the first derivative:[4]

$$\gamma=\left(\frac{\partial R_{np}}{\partial U}\right)\frac{2kT}{q}\,\frac{1}{R_{np}}. \tag{7}$$

The voltage at which the coefficient (7) is a minimum (Fig. 2) can be used to find the deep-center activation energy from Eq. (5). Certain conditions formulated in Ref. 4 must be satisfied. An approximate estimate shows that these conditions are usually met for deep levels formed in the fabrication of commercial semiconductor devices.

A function of the form (7) has minima at points U_{0m}; the amplitude of each minimum differs according to the contribution of the specific deep level to the total recombination current. The quantities U_{0m}, which depend on $c_{n(p)m}$ and N_{tm}, can be determined experimentally. Assuming that the deep level is situated above the middle of the band gap (i.e., $c_{pm}p_{1m}\ll c_{nm}n_{1m}$), we obtain an expression analogous to (5). The results obtained by this method for the investigated diode are also shown in Table I.

To refine the deep-center energies, we have determined them by the well-known thermally stimulated capacitance (TSCAP) technique, which is described, for example, in Refs. 7 and 8. In this technique the capacitance of the sample (C) is measured as the sample is heated at a constant rate. Deep levels in the space-charge region have been previously filled with electrons. The derivative of the capacitance with respect to the temperature is described by an expression whose one and only fitting parameter is the deep-level activation energy (E_t):

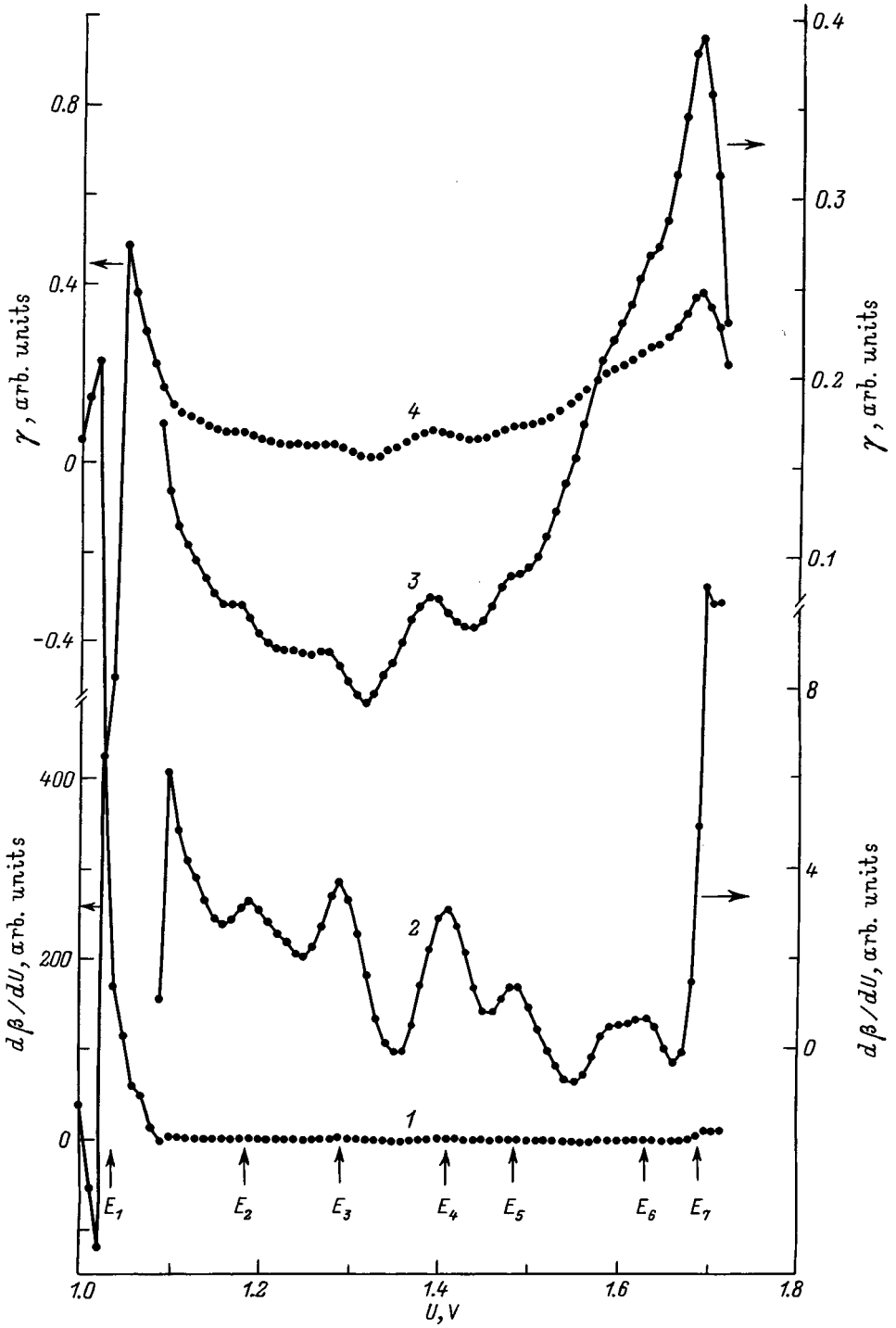

FIG. 2. Differential coefficients of the *I-V* characteristic. The extrema correspond to the levels in Table I.

$$\frac{dC}{dT}=A\left(\frac{T}{T_m}\right)^2 \exp\left[\frac{E_t}{k}\left(\frac{1}{T_m}-\frac{1}{T}\right)\right]$$
$$\times\exp\left\{1-\left(\frac{T}{T_m}\right)^2 \exp\left[\frac{E_t}{k}\left(\frac{1}{T_m}-\frac{1}{T}\right)\right]\right\}. \quad (8)$$

A certain difficulty is encountered in that the experimental curve comprises the superposition of ionization processes of the individual levels, each providing its own contribution to the capacitance. These processes can be separated by means of Eq. (8). It is more convenient to begin the breakdown in the high-temperature region, specifying the temperature of the maximum and the amplitude of the TSCAP peak. If the choice of E_t is smaller than the true value, the analytical curve is broader than the experimental curve. If the chosen energy E_t is greater than the true value, the curve calculated from Eq. (8) is narrower than the experimental curve. The energy can be selected very accurately with good agreement between the experimental and analytical curves. Figure 3 shows a graph plotted by the TSCAP technique, and Table I gives the activation energies determined from it.

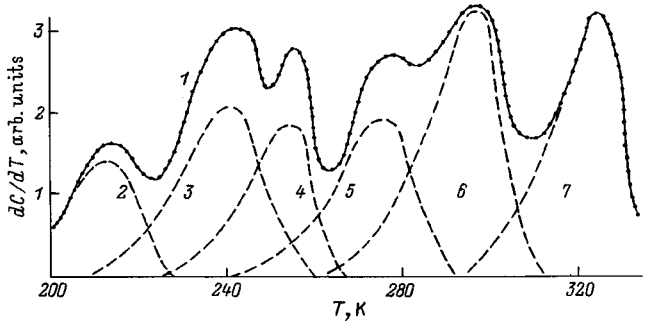

FIG. 3. Separation of deep levels on the basis of the function $dC/dU = f(T)$. (*1*) Experimental; activation energies: (*2*) $Et = 0.35$ eV; (*3*) 0.53 eV; (*4*) 0.63 eV; (*5*) 0.66 eV; (*6*) 0.81 eV; (*7*) 1.0 eV.

A comparison of the tabulated results shows that all the methods used here yield good agreement of the thermal activation energies. The differential parameters of the *I-V* characteristics are now measured at a fixed temperature — room temperature in our case, simplifying the experimental procedure. The measurements can be performed on semiconductor wafers in the industrial environment without having to seal them or divide them into individual crystals. The experiment itself can be easily automated in the part associated with measurement and processing.

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