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Recombination of non-equilibrium charge carriers injected into Ge through intermediate defective layer

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The recombination of non-equilibrium charge carriers injected into n-Ge sample through an intermediate defect layer has been studied in experiment as well as theoretically. The structure defects were formed by cyclic straining with simultaneous ultrasonic irradiation of the sample at 310 K. Distribution of defects in the sample depth was examined by metallography. The recombination of the injected carriers was studied by conductivity modulation in a point contact with the semiconductor surface. Two differently inclined segments have been found in plots of measuring pulse voltage decay against delay time in relation to the injecting pulse. These two segments are associated with recombination of surplus charge carriers in the subsurface defect layer and in depth of the crystal. The length and steepness of the segments at small delay time are rising with increase of the defect layer thickness and concentration of defects therein.

Экспериментально и теоретически исследован процесс рекомбинации неравновесных носителей заряда, инжектированных в образец n-Ge через промежуточный дефектный слой. Дефекты структуры вводились циклической деформацией сжатием с одновременным ультразвуковым облучением образца при 310 K. Распределение дефектов по глубине образца определялось металлографическим способом. Процесс рекомбинации инжектированных носителей исследовался методом модуляции проводимости в точечном контакте с поверхностью полупроводника. На графиках зависимости напряжения спада измерительного импульса от времени задержки относительно инжектирующего импульса обнаружены два отличающихся по крутизне участка, связанных с рекомбинацией избыточных носителей заряда в приповерхностном дефектном слое и в толще кристалла. Протяженность и крутизна участков при малых временах задержки увеличиваются с ростом толщины дефектного слоя и плотности дефектов в нем.

The low-temperature (in 77–300 K interval) straining of Ge and Si results in generation of dislocations, vacancy clusters and vacancy-impurity ones in a surface layer [1–3]. The occurrence of deep energy levels in the forbidden zone of semiconductor and lifetime (τ) reduction of non-equilibrium charge carriers are connected with such defects [1]. Method of conductivity modulation in a point contact with the crystal surface is often used to measure τ [4–6]. The method consists essentially in what follows.

The non-equilibrium charge carriers are injected into a sample by means of a rectangular current pulse. During the injection of charge carriers, the sample resistance drops. The voltage on the sample also goes down, because the pulse current is constant. Therefore, the voltage pulse (Fig. 1) does not repeat the shape of the current pulse but has a descending branch (decay) due to increasing charge carrier concentration. After the injecting current pulse is over, the carrier injection process into the sample stops, and concentration of non-equilibrium

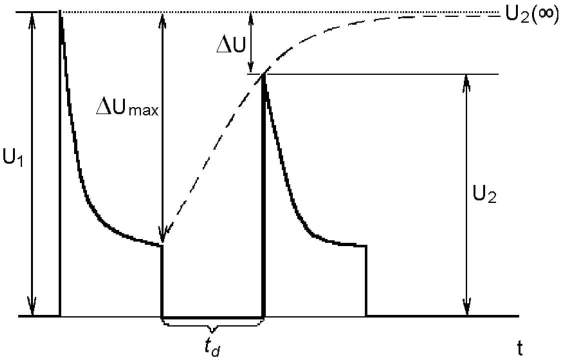

Fig. 1. Voltage pulses on the sample.

charge carriers starts to decrease due to recombination and diffusion. As a result, the sample resistance increases in time. So the voltage U_2 at the measuring pulse front rises also as its delay time t_d increases.

The law of $\ln\Delta U(t_d)$ value change makes it possible to determine the lifetime τ of the charge carriers injected into the sample. Theoretical and experimental investigation of the minor charge carriers lifetime measuring method in semiconductors based on the conductivity modulation in a point contact is described in [5]. Dependence of τ value obtained by this method for Ge on the injecting pulse parameters and on the delay time t_d of the measuring pulse has been investigated. It has been noted [5] that at low current of injecting pulse and its short duration T_p, the experimental τ values were underrated. At $T_p > (1.5–2)\tau$ and high currents, when an uniform distribution of charge carriers in the contact area takes place, the measured τ values become independent of the pulse parameters. However, in this case, τ also can be underrated if it is determined from $\ln\Delta U(t_d)$ relationship in the region of small delay times ($t_d < \tau$) of measuring pulse. Thus, in [5] the discrepancies were observed in τ values as compared to those measured by photoelectric method and calculated in the used theoretical model. The cause of that discrepancy was remained incomprehensible. However, it has been supposed [5, 6] that it was connected with recombination of injected charge carriers at the surface.

An n-Ge single crystal with resistivity 20 $\Omega \cdot$ cm and mean density of growth dislocations ~$4 \cdot 10^3$ cm^{-2} was used in this work. The samples were cut out in the shape of rectangular parallelepipeds of $3\times4\times10$ mm^3 size. The defect surface layer was removed by machining and chemical-dynamic polishing. The parallelepiped was strained along the largest measurement direction (10 mm) coinciding with the [110] direction. The side surfaces of the samples coincided with (111) and (112) planes. The samples were strained in the compression/unloading cycles at 310 K. The maximum reached stress was 200 MPa, the cycle duration was 2 h, and the whole test lasted 24 h. Simultaneously with the cyclic straining, the sample was irradiated with ultrasound of 22.5 kHz frequency and 5 W power.

The distribution of the defects caused by the straining in the crystal depth was studied by optical microscopy. The level-by-level removing of surface layers from the strained Ge crystal was carried out in aqueous HF and HNO_3 solution. The structure defects were visualized using the chromium etcher. Before each subsequent removing of the defect layer, the Ge sample was etched in boiling H_2O_2 solution, washed in distilled water, and dried. Then the recombination process of injected charge carriers was studied using the conductivity modulation in a point contact. The tungsten needle (probe) was fastened in the indenter holder of the microhardness gauge PMT-3. The measurements were conducted at dosed loads on the probe. There was a possibility of XY-movement of a sample. The area of its contact with the probe surface could be determined.

The character of ΔUt_d curves and τ values calculated according to these curves for unstrained Ge samples was found to depend only slightly on the spot where the probe was placed. The life time τ_p of injected holes in n-Ge was determined from the relation

$$\Delta U(t_d) = \text{const} \cdot \exp\left(-t_d/\tau_p\right). \qquad (1)$$

For samples with conductivity σ = 5 Sm/m (ρ = 20 $\Omega \cdot$ cm), the hole mobility of μ_p = 0.17 m$^2 \cdot$ V^{-1}s^{-1} at the injection current 10 mA and the pulse duration $T = t_d$ = 250 μs, the found values conformed to value $\tau_p \approx 250$ μs, indicated in the crystal certificate.

When crystal structure defects are introduced into the crystal subsurface layer by straining, the character of $\Delta U(t_d)$ curves changes substantially. The orientation of the sample subjected to the pressure p is shown in Fig. 2a. The distribution of the subsurface layer defects in the cross-section 1-2 revealed by structure observations can be seen in Fig. 2b. The distribution of de-

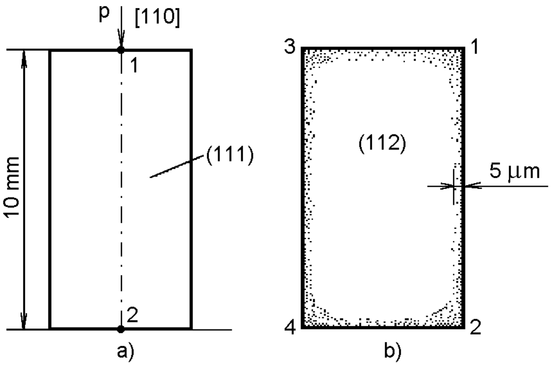

Fig. 2. Orientation of the sample under pressure (a) and distribution of defects of crystalline structure in the cross-section (b).

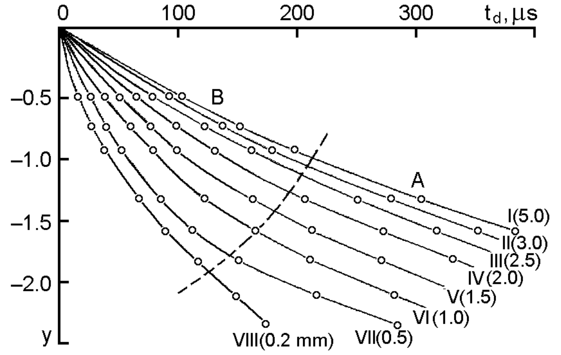

Fig. 3. Experimental dependences of the logarithm of normalized voltage $y = \ln(\Delta U/\Delta U_{max})$ in the measuring pulse on its delay time for different points along the sample height. The Ge sample is strained at $T = 310$ K.

fects (dislocations and clusters) is rather inhomogeneous, since the contact section does not vary due to a high rigidity of loading platforms and small plasticity at butt ends. So, a very complex stress distribution arises in the crystal [7]. The defect layer depth (Fig. 2b) is minimum (~5 μm) in the middle section of the side surface and increases near to butt ends and the side ribs, where reaches about 200 μm. In the thin subsurface layer along the directions 1–3 and 2–4, the defects are distributed in continuous manner.

In Fig. 3, the normalized dependences $y = \ln(\Delta U/\Delta U_{max})$ on the delay time t_d for different points on the sample surface along 1–2 direction are presented (ΔU_{max} is the voltage decay at the injecting pulse end moment shown in Fig. 1). When charge carriers are injected through the defect layer, the character of $y(t_d)$ dependence changes substantially. A segment of increased steepness appears in each curve of Fig. 3 in the area B (to the left of the broken line). The thicker is the defective layer and the higher is the defect concentration therein, the steeper will be the segment in the area of short delay time. So, the curve 1 was obtained when carriers were injected through the about 5 μm thick defect layer. The steepness in A and B areas for this curve is practically the same. This can be explained by the fact that the probe pierces the defect layer and holes are injected directly into the undisturbed bulk of the crystal where $\tau_p \approx 250$ μs.

For the defect layer depth of 200 μm (curve 7), the steepness difference between segments in areas A and B is considerable. After removal of the defect layer by chemical etching, the mentioned relations almost coincide with the initial ones obtained on the same crystals prior to straining. It follows from the experiments that the initial segments of curves in area B are characterized by the hole lifetime τ_s in the defect layer. The segments in area A which corresponds to longer delay time values are characterized by the hole lifetime τ_v in the undisturbed crystal bulk. The curve 8 corresponds to injection of holes into thick defect layer near the sample upper butt.

The defect layer depth can be increased by heat treatment of strained samples. When a crystal is cyclically strained by compression at low temperature, the non-equilibrium point defects interact with the initial structure disturbances as well as with each other due to changing in topology of the resulting stress field. After the unloading, new unstable complexes (concentrators) can arise. Those become sources of dislocations at high-temperature annealing [8]. Such effective sources of dislocations arise in large numbers in the subsurface layer, where the diffusion processes are most intense [3], as well as in the crystal volume.

The *n*-Ge single crystals strained by the procedure mentioned above were annealed during 5 h in vacuum ~$2 \cdot 10^{-4}$ Pa at 800 K and 900 K. After the appropriate chemical treatment of the surface (as mentioned above), the structure was examined and the injection process of charge carriers in the annealed samples was studied.

A very developed structure with dislocation density reaching ~10^6 cm^{-2} in the surface clusters was revealed using the level-by-level structure examinations. In deeper layers, the dislocation density decreases and their gettering effect is observed: the point

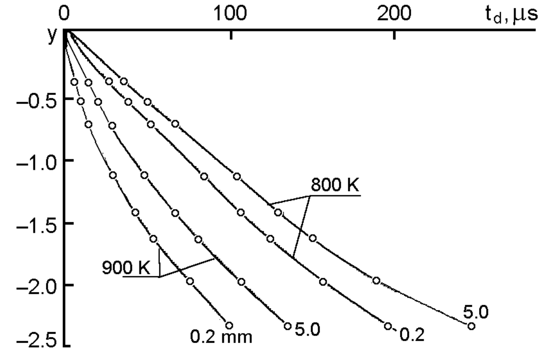

Fig. 4. Experimental dependences of the normalized voltage in the measuring pulse on its delay time for the samples strained at T = 310 K and then annealed in vacuum ~$2\cdot10^{-4}$ Pa during 5 h at $T = 800$ K and 900 K. The measurements were made at distances 0.2 mm and 0.5 mm from the sample upper butt.

defects migrating to the dislocations as to runouts making up an atmosphere. As a result, round pits are etched thereon as on growth dislocations. In the annealed crystals, accumulations of the introduced dislocations were observed on a depth exceeding 1 mm from the surface.

The defective layer depth increase becomes apparent also in dependences $y(t_d)$ (Fig. 4): their steepness is increased and the distinction between dependences taken in different points along the sample height becomes decreased. This is due to the increased homogeneity of the defect structure.

Theoretical analysis of the recombination of non-equilibrium charge carriers injected into Ge through an intermediate defect layer was carried out using the model shown in Fig. 5 (inset). The hemisphere of the metallic probe tip is inserted into the sample flat surface. The tip radius is r_0. Holes are injected into the crystal bulk through a hemispherical defect layer of the thickness h. The problem was solved for the same parameters of the sample and of the injecting pulse that were used in the experiment. The distribution of surplus holes in semiconductor along the radius r at the termination moment of the injecting pulse was found from the formula [6]:

$$\Delta p(r) = \Delta p(r_0)\ \exp\ [-\frac{2\pi\sigma}{3\mu_p IT}(r^3 - r_0^3\mathit{right}\ )\}], \quad (2)$$

where $\Delta p(r_0)$ is concentration of excess charge carriers in semiconductor at the interface with the probe; $\Delta p(r)$, the same concentration for the radius r. The formula (2)

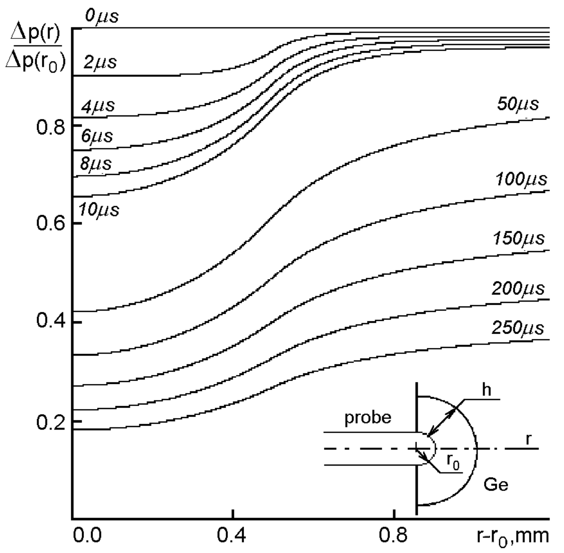

Fig. 5. Calculated curves of non-equilibrium hole distribution along the direction r in the sample at different values of measuring pulse delay time. A model for theoretical analysis of the problem of injected holes recombination in the sample is shown in the inset.

also was used to estimate the penetration depth of excess holes into the semiconductor. At $\sigma = 5$ Sm/m, $\mu_p = 0.17\ \mathrm{m^2V^{-1}s^{-1}}$, T = 300 μs, r_0 = 5 μm for $r < 1.5$ mm, the exponent power index in (2) is < Therefore, within the hemisphere of 1.5 mm radius, at the termination moment of the injecting pulse the concentration of excess holes is practically the same. The corresponding distribution plot in Fig. 5 is denoted 0 μs (time zero for the delay time of the measuring pulse).

The distribution of holes in the sample after the injection is over was found taking into account their recombination and diffusion. The differential diffusion equation [6] was used. In spherical coordinate system it has the form:

$$\frac{\partial \Delta p}{\partial t} = D_p\,\frac{\partial^2 \Delta p}{\partial r^2} + D_p\,\frac{2}{r}\cdot\frac{\partial \Delta p}{\partial r} - \frac{\Delta p}{\tau_p}. \quad (3)$$

From the condition of constancy in distribution Δp along the radius r at the termination moment of the injecting pulse, the initial condition can be written as

$$\Delta p(r)|_{t=0} = \Delta p(r_0). \quad (4)$$

It was supposed that there are no flows of excess charge carriers to the probe through the hemisphere of radius r_0 [9, 10] and from the probe through a hemisphere of radius 1.2 mm (the right-hand boundary in Fig. 5). For these surfaces, the boundary condition was taken in the form

$$\frac{\partial \Delta p(r)}{\partial r} = 0. \tag{5}$$

For the right-hand boundary, the time function also was used expressed as

$$\Delta p(t) = \Delta p(0)\exp\left(-\frac{t}{\tau_p}\right). \tag{6}$$

The equation (3) was being solved taking into account (4), (5) and (6) using the net method [11]. The defect layer thickness was taken to be h = 500 μm, lifetime of holes in the layer, τ_s = 20 μs and in the crystal bulk, τ_v = 250 μs. The set of the calculated hole distributions $\Delta p(r)/\Delta p(r_0)$ for different delay time values t_d of the measuring pulse is shown in Fig. 5.

The voltage decay conditioned by the excess charge carriers is

$$\Delta U = \frac{j_0 \cdot r_0^2 \cdot \Delta p(0)(b+1)}{e \cdot n^2 \cdot b^2 \cdot \mu_p} \int_{r_0}^{\infty} \frac{\Delta p(t)}{\Delta p(0) \cdot r^2} \cdot dr, \tag{7}$$

where j_0 is the current density at the probe surface; $b = \mu_n/\mu_p$; μ_n is the mobility of electrons, μ_p, that of holes; n, the equilibrium concentration of electrons in the semiconductor.

The voltage decay in the injecting pulse end when $\Delta p(t) = \Delta p(0)$ is

$$\Delta U_{\max} = \frac{j_0 \cdot r_0 \cdot \Delta p(0)(b+1)}{e \cdot n^2 \cdot b^2 \cdot \mu_p}. \tag{8}$$

The normalized voltage decay

$$\frac{\Delta U}{\Delta U_{\max}} = r_0 \int_{r_0}^{\infty} \frac{\Delta p(t)}{\Delta p(0)} \cdot \frac{dr}{r^2}. \tag{9}$$

The dependences $\Delta U/\Delta U_{max}$ on t_d in logarithmic scale are shown in Fig. 6 where $y = \ln(\Delta U/\Delta U_{max})$. The initial segments of high steepness correspond to recombination of injected holes in the defect layer with lifetime τ_s = 20 μs, and the low slop segments at long delay times correspond to recombination of holes in the crystal bulk where the lifetime τ_v = 250 μs.

The obtained calculated dependences $y = (t_d)$ take into account the recombination of injected charge carriers and their diffusion from the crystal bulk towards the defect layer. The calculated curves (Fig. 6) conform qualitatively to experimental curves shown in Fig. 3 and Fig. 4. But in each $y(t_d)$ set, there are its own features connected with distinctions in structural state of the defect layer and its thickness. So, when calculating theoretical relations (Fig. 6), the defect structure with hole lifetime τ_p = 20 μs was supposed to be homogeneous in depth. The tangents to each curve of the set drawn from the origin will have the same slope determining τ_s = 20 μs. Only the extent of sections in the field of short delay time values t_d increases for larger layer thickness h.

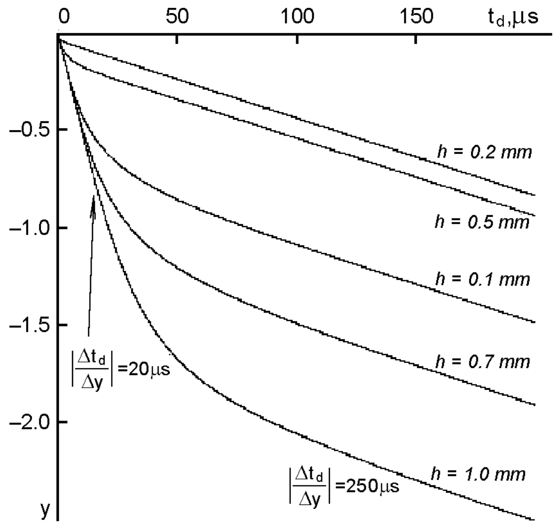

Fig. 6. Calculated dependences of the logarithm of injecting pulse normalized voltage $y = \ln(\Delta U/\Delta U_{max})$ on its delay time t_d for different thickness values h of the defect layer.

In experimental curves of Fig. 3 (area B) an increase of depth and concentration of defects in the near-surface layer was exhibited in the sequence 1–8. Therefore, the steepness of initial segments is augmented together with the increase of their extension, that corresponds to a decreasing τ_s in the layer. The distribution of defects in depth is not uniform. Their density reduces from the surface to the crystal depth. In this case, a certain effective lifetime can be determined from the slope of tangents to the initial segments. It would be incorrect to connect it with only one defect type, since at low-temperature straining, the clusters of point defects are formed in the near-surface layer in addition to dislocations.

After high-temperature processing of strained crystals, the defect layer becomes more homogeneous, its thickness is increased up to ~1 mm, and majority of point defects are annealed [8] due to diffusion to runouts (mainly to the surface and to dislocations). Therefore, the lifetime of non-equilibrium charge carriers in the defect layer is defined by their recombination on dislocations. The lifetime τ_s has been found from the data of Fig. 4. The dislocation density in the probe sites was determined metallographically. A correlation $\tau_s(s) = 2.5/N_d(\mathrm{cm}^{-2})$ was established between the measured values τ_s and the dislocation density within limits $N_d = (10^4$–$10^6)$ cm^{-2}, in agreement with [12]. For relations shown in the Fig. 4, in the sequence of their increasing steepness, the τ_s and N_d were equal to 90 μs ($2.8 \cdot 10^4$ cm^{-2}), 77 μs ($3.2 \cdot 10^4$ cm^{-2}), 48 μs ($5.2 \cdot 10^4$ cm^{-2}) and 13.3 μs ($1.9 \cdot 10^5$ cm^{-2}), respectively. For the annealed samples, also the diffusion length L_p of minor charge carriers has been measured by the mobile light probe method [6]. The lifetime of holes τ_p was found from the formula $\tau_p = L_p^2/D_p$. The diffusivity of holes for Ge $D_p = 44$ cm^2/s. The difference between τ_p values calculated using two reviewed methods did not exceed 15 %.

Thus, it was shown in this work that underrated life time values for carriers at short delay times are due to recombination processes in near-surface layers, as it was supposed in [5, 6]. The offered solution method of the problem and designed computer program can be used in solving a problem under changed initial conditions, for example, when a certain distribution of τ_p in the defect layer depth is preset. The results obtained in this work can be useful also in estimating the defect concentration in the subsurface layer of semiconductor after various technological processings.

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Рекомбінація нерівноважних носіїв заряду в Ge, інжектованих через проміжний дефектний шар

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Експериментально і теоретично досліджено процес рекомбінації нерівноважних носіїв заряду, інжектованих у зразок n-Ge через проміжний дефектний шар. Дефекти структури вводилися циклічною деформацією стиском з одночасним ультразвуковим опроміненням зразка при 310 К. Розподіл дефектів за глибиною зразка вивчався металографічним способом. Процес рекомбінації інжектованих носіїв досліджувався методом модуляції провідності в точковому контакті з поверхнею напівпровідника. На графіках залежності напруги спаду вимірювального імпульсу від часу затримки відносно імпульсу інжекції виявлено дві ділянки різної крутості, пов'язані з рекомбінацією надлишкових носіїв заряду у приповерхневому дефектному шарі й у товщі кристала. Довжина і крутість ділянок при малих термінах затримки збільшуються зі зростанням товщини дефектного шару і густини дефектів у ньому.