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RELAXATION OF EXCESS MINORITY CARRIER DISTRIBUTION IN MACROPOROUS SILICON

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Relaxation of the excess minority carrier distribution in macroporous silicon structure was calculated using the finite difference method. The initial distribution of the excess minority carriers has two maxima after carrier generation by electromagnetic wavelength 0.95 μm with small absorption depth. The first maximum of the initial distribution function is in macroporous layer, the second one is in monocrystalline substrate. Surface recombination leads to the diffusion of excess charge carriers to recombination centers and creates the non-homogeneity of the excess charge carrier distribution. A rapid maximum decrease of the excess carrier distribution function in a macroporous layer and near the boundary of a macroporous layer and monocrystalline substrate is found. The slow decrease of the distribution function in a monocrystalline substrate is evaluated. We observed one maximum of the excess minority carrier distribution after homogeneous carrier generation by electromagnetic wavelength 1.05 μm with big absorption depth. The rate of change in the concentration of excess minority carriers decreases in time in macroporous silicon layer due to high recombination and increases due to diffusion to the surface of silicon substrate after generation by the electromagnetic wave 0.95 μm with small absorption depth. The rate of change in the concentration of excess minority carriers decreases in time in the entire structure after generation by the electromagnetic wave 1.05 μm with big absorption depth and small non-homogeneity.

Keywords: *relaxation, carrier distribution, macroporous silicon*

INTRODUCTION

Macroporous silicon has found application in sensors, receivers, in integrated microchips [1]. Gas [2, 3] and biological sensors [1] are developed on the basis of porous silicon with CMOS-compatible manufacturing. Macroporous silicon [4, 5] and black silicon nano-textured by cones and pyramids [6] are used as a solar cell. A layer of macroporous silicon is used as a broad-band antireflective coating for silicon solar cells [7, 8]. The penetration of light into the pores and its multiple reflections from the pore walls increase the absorption of light. The scattering of light leads to an increase in the optical path, and so, to an increase in the light absorption [9]. If the pores are etched on the two silicon surfaces then we obtain a multiple reflection of light between these surfaces due to the fact that a part of the rays scattered by one surface falls onto another surface at the angles greater than the critical angle of the total internal reflection and will be completely reflected [10].

Effective conductivity and photoconductivity in macroporous silicon decrease with increasing of concentration and volume fraction of macropores and reduction in the thickness of the space charge region (SCR) at small macropore diameters [11]. An analytical model for the effective carrier lifetimes of surface-passivated macroporous silicon [12, 13] and black silicon nano-textured by cones and pyramids [6] allowed determining the effective minority carrier lifetime as a function of bulk lifetime, surface passivation and morphology. The numerical calculation of the distribution of excess minority carrier concentration in macroporous silicon in case of the spatially homogeneous generation of charge-carriers is made in [14]. The excess minority carrier concentration both between pores and in monocrystalline layer sharply decreases with increased depth macropores to 10 microns. The concentration of excess carriers between macropores does not change when the depth of macropores is from 100 to 200 microns in case of the spatially homogeneous generation of charge-carriers [14]. The calculation [15] has been performed for macroporous silicon with different depth of macropores and different thickness of the monocrystalline substrate. The influence of mechanisms of the charge carrier transport through the macropore surface barrier

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on the kinetics of photoconductivity at various temperatures is examined [16].

The aim of this work is to study the peculiarities of relaxation of the excess minority carrier distribution in macroporous silicon structures using numerical calculations by the finite difference method [17]. Carrier generation was implemented by the electromagnetic waves 0.95 and 1.05 μm; in this case absorption coefficients and absorption depths differ almost 10 times for comparable wavelengths of electromagnetic radiation. Two maxima of the initial excess minority carrier distribution, the rapid and slow maxima decrease, non-exponential carrier relaxation, the rate of change in the concentration of excess minority carriers have been studied.

DIFFUSION AND EFFECTIVE RELAXATION TIME OF EXCESS MINORITY CARRIERS IN SILICON PLATE AND IN MACROPOROUS SILICON

Diffusion equation and effective relaxation time of excess minority carriers. The minority carrier diffusion equation for the one-dimensional case under non-steady state conditions for macroporous *n*-silicon (Fig. 1 *a*) is:

$$\frac{\partial}{\partial t}\delta p(x,t) = D_p \frac{\partial^2}{\partial x^2}\delta p(x,t) - \frac{\delta p(x,t)}{\tau_b}. \tag{1}$$

Here $\delta p(x, t)$ is the distribution function of the excess minority carrier concentration in the *x*-direction, D_p is the diffusion coefficient of minority carriers, τ_b is the bulk minority carrier recombination lifetime. The boundary conditions are:

$$g_s(x_0,t) - s_p \delta p(x_0,t) = e^{-1} j_p(x_0,t). \tag{2}$$

Here: e – an elementary charge, $\delta p(x_0, t)$ – the concentration of excess minority carriers on a surface, $g_s(x_0, t)$ – the rate of surface generation of excess minority carriers on the surface, $j_p(x_0, t)$ – the current density of excess minority carriers near the surface, and s_p – the rate of surface recombination of excess minority carriers on the surface. Recombination predominates the generation in equation (2) if the diffusion current of the excess minority carriers j_p flows to the surface (the diffusion current j_p must be taken with a minus sign).

The general solution of the diffusion equation (1) for the periodic system is sought in the form of a Fourier series:

$$\delta p(x,t) = \sum_{n=-\infty}^{\infty} A_n^*(t)\exp(ina_s x), \tag{3}$$

where a_s is a parameter dependent on the cell size, $A_n^*(t) = A_n^* \exp(-t/\tau_n)$ are the time-dependent coefficients which should be defined by substituting terms $A_n^*(t)\exp(ina_n x)$ into equation (1) and solving a simple differential equation, τ_n, A_n^* are coefficients. If we assume that *p*(*x, t*) is an even function, since the unit cell of the macroporous silicon structure is symmetric, then this function can be represented as a trigonometric Fourier series containing only the cosine $\delta p(x,t) = \sum_{n=1}^{\infty} A_n \exp(-t/\tau_n)\cos(na_s x)$, where A_n is the coefficient. We substitute this Fourier series expansion in equation (1) and find the relation between τ_n and a_s, which will be written so:

$$\frac{1}{\tau_n} = \frac{1}{\tau_b} + D_p a_s^2 n^2. \tag{4}$$

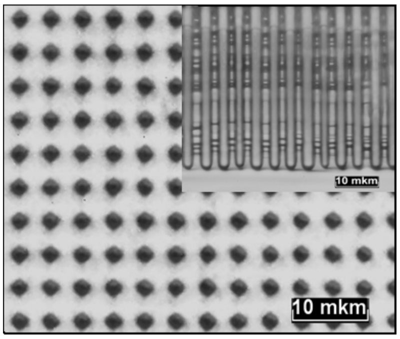
If $t >> \tau_1$ in (3), we leave the first term for $n = 1$ only, the other terms of the series can be neglected. Then equation (4) determines the effective lifetime τ_{eff} of minority carrier recombination:

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_b} + D_p a_s^2, \tag{5}$$

where $D_p a_s^2 = 1/\tau_s$ (τ_s is the surface recombination lifetime).

Let us consider a single-crystal sample of thickness H in the form of a rectangular plate (Fig. 1 *b*) and macroporous silicon structure (Fig. 1 *c*). Electromagnetic radiation falls on the surface of the plate, as shown in Fig. 1 *b, c*. The thickness of Si plate is much smaller than its length and width. We choose the direction of the *x* axis parallel to the propagation of the electromagnetic wave. Let us consider three sections perpendicular to the *x* axis: two cross sections are at the boundaries of the plate, and the third section passes through the maximum point of the distribution function of the excess minority carrier concentration. The beginning of coordinates is chosen at this maximum point (see Fig. 1 *c*). Using the boundary condition (2) and the general solution (3), we define the equation for the boundary conditions in each of the above planes. In the plane passing through the maximum point, the surface recombination rate is zero ($s = 0$), therefore:

$$\sin(a_s x_0)=0. \qquad (6)$$



a

Fig. 1 *a*. Microphoto of macroporous silicon structure

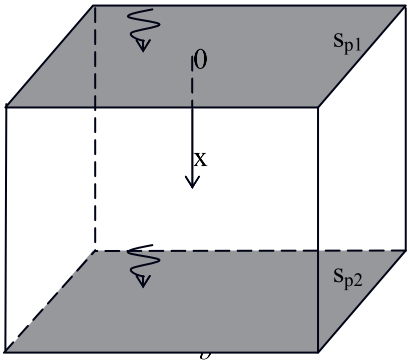


Fig. 1 *b*. Monocrystalline silicon

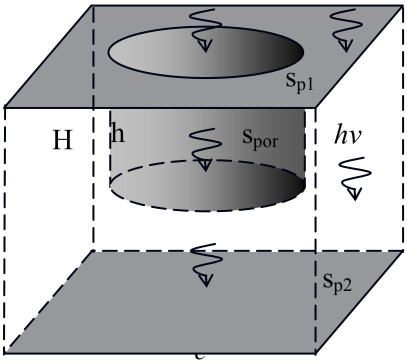


Fig. 1 *c*. Unit cell of macroporous silicon structure

The boundary conditions on two surfaces of the rectangular plate are:

$$a_s\tan(a_s x_1)=s_{p1}/D_p, \qquad (7)$$

$$a_s\tan(a_s x_2)=s_{p2}/D_p, \qquad (8)$$

where s_{p1} and s_{p2} are the rate of surface recombination on surfaces with coordinates x_1 and x_2. Assuming that $s_{p1}x_1/D_p<<1$, $s_{p2}x_2/D_p<<1$ and $s_{p1}=s_{p2}=s_p$ from the equations (7) and (8), we have:

$$D_p a_s^2 = \frac{1}{\tau_s} = \frac{s_{p1}+s_{p2}}{x_1+x_2} = \frac{2s_p}{H}. \qquad (9)$$

Initial distribution of excess minority carriers. The minority carrier diffusion equation for the one-dimensional case under steady state conditions for macroporous n-silicon in the x-direction (parallel to the pores) is

$$D_p\frac{\partial^2}{\partial x^2}\delta p(x) - \frac{\delta p(x)}{\tau_1} + g_{0\mathrm{p}}(\alpha)\exp(-\alpha x) = 0\ . \qquad (10)$$

Here α is the absorption coefficient of silicon, $g_{0p}(\alpha)$ is the generation rate of excess minority carriers at the illuminated surface, and τ_1 is taken from [14, 15].

The distribution functions of the steady-state excess minority carrier concentration in macroporous silicon and for the single crystal substrate are

$$\delta p_1(x) = C_1\cosh(X_1) - C_2\sinh(X_1) - \delta p_{g1}(x), \qquad (11)$$

$$\delta p_2(x) = C_3\cosh(X_2) - C_4\sinh(X_2) - \delta p_{g2}(x). \qquad (12)$$

Here $\delta p_{g2}(x) = \frac{g_0\alpha\tau_2\left[(1-P)\exp(-\alpha x) + P\exp(-\alpha(x-h_{por}))\right]}{(\alpha L_2)^2-1}$,

$\delta p_{g1}(x) = \frac{g_0\alpha\tau_1\exp(-\alpha x)}{(\alpha L_1)^2-1}$, $X = \frac{x}{L_p}$, C_1, C_2, C_3 and C_4 the unknown coefficients, $X_1 = \frac{x}{L_1}$, $X_2 = \frac{x}{L_2}$, $L_1 = \sqrt{D_p\tau_1}$, $L_2 = \sqrt{D_p\tau_b}$, h_{por} is the macropore depth and $P = \pi D_{por}^2/(4a^2)$ is the pore volume fraction, D_{por} is the pore diameter.

The unknown coefficients C_1, C_2, C_3 and C_4 can be found from the system that can be written more compactly as

$$\frac{d\delta p_1}{dx}(0) = s_1\delta p_1(0), \qquad (13)$$

$$\frac{d\delta p_2}{dx}(H) = s_2\delta p_2(H), \qquad (14)$$

$$(1-P)D\frac{d\delta p_1}{dx}(h_{por}) = D\frac{d\delta p_2}{dx}(h_{por}) - Ps_{por}\delta p_2(h_{por}), \qquad (15)$$

$$\delta p_1(h_{por}) = \delta p_2(h_{por}), \qquad (16)$$

where $\delta p_1(x, t)$ is the distribution function of the excess minority carriers in the macroporous layer, $\delta p_2(x, t)$ is in a monocrystalline substrate.

The relaxation of the distribution of excess minority carriers in macroporous silicon. The minority carrier time-dependent diffusion equation (1) for the one-dimensional case for macroporous *n*-silicon in the *x*-direction (parallel to the pores) is

$$\frac{\partial}{\partial t}\delta p(x,t) = D_p \frac{\partial^2}{\partial x^2}\delta p(x,t) - \frac{\delta p(x,t)}{\tau_1}. \qquad (17)$$

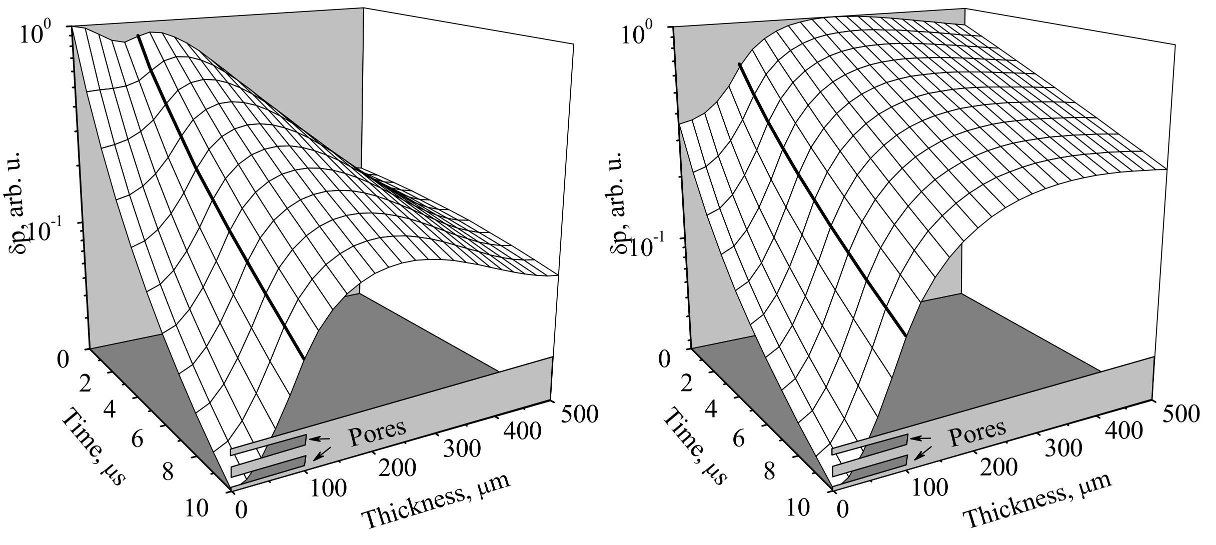
The boundary conditions for macroporous silicon are written in equations (13)–(15) but $\delta p = \delta p(x, t)$. Solving numerically the system of equations (10)–(17) by the finite difference method, we find the distribution of excess minority carriers in macroporous silicon after the certain time interval.

RESULTS AND DISCUSSION

The excess minority carrier distribution in macroporous silicon structure. We calculated the relaxation of the distribution of excess minority carriers in macroporous silicon structure [17] with boundary conditions (10)–(16) after the excess minority carrier generation by the electromagnetic waves 0.95 and 1.05 μm. The parameters of macroporous silicon are: the thickness of silicon substrate $H = 500$ μm; depth of macropores $h_p = 100$ μm; the average diameter of macropores – 2 μm, the average distance between pore centers – 4 μm. The bulk lifetime τ_b in monocrystalline silicon is equal to 10 μs.

Wavelength 0.95 μm corresponds to absorption coefficient of electromagnetic radiation 156 cm^{-1} in silicon [18] and absorption depth 64 μm $\geq h_p$. Absorption coefficient is 16 cm^{-1} and absorption depth 614 μm $\geq H$ for wavelength 1.05 μm in silicon structure. Thus, absorption coefficients and absorption depths differ almost 10 times for comparable wavelengths of electromagnetic radiation (0.95 and 1.05 μm).

Fig. 2 shows relaxation of the distribution of the normalized concentration of excess minority carriers with time in macroporous silicon after the generation of excess charge carriers by an electromagnetic wave of 0.95 (*a*) and 1.05 μm (*b*).



a *b*

Fig. 2. Relaxation of distribution of the normalized excess minority carrier concentration δp in macroporous silicon structure after the excess minority carrier generation by the electromagnetic wave: *a* – 0.95, *b* – 1.05 μm. The upper curve is 0 μs, the other curves are shown with an interval of 1 μs

The upper curves on Fig. 2 *a–b* correspond to the initial distribution of the concentration of excess minority carriers. Other curves show the carrier distribution with a time interval of 1 μs. Electromagnetic radiation propagated in the direction parallel to the pores and fell on the surface of macroporous silicon and on the bottom of pores. Generation of excess charge carriers was non-homogeneous (Fig. 2 *a*) due to the strong absorption electromagnetic radiation at wavelength 0.95 μm with absorption coefficient 156 cm^{-1}. The electromagnetic wave of 1.05 μm is absorbed weakly by silicon with absorption coefficient 16 cm^{-1}, so the generation of excess charge carriers by this electromagnetic wave is homogeneous. In addition, electromagnetic radiation created additional generation of excess charge carriers in macroporous silicon, since it fell on the surface of the bottom of the pores.

Surface recombination leads to the diffusion of excess charge carriers to recombination centers, creates the inhomogeneity of the distribution of excess charge carriers. In addition, the non-homogeneity of the generation of excess charge carriers creates a non-homogeneity of their distribution. Diffusion and recombination processes transform the distribution of excess minority carriers under non-homogeneous generation in their distribution without generating. Recombination occurs much faster in the bulk between pores than in a monocrystalline substrate, due to recombination on the pore surface. As a result, we see rapid decrease in the concentration of excess minority carriers: 500 times on the macropore surface and 7–8 times on the opposite side of silicon plate (Fig. 2 *b*), 12–15 times on the macropore surface and 2–4 times on the opposite side of Si plate (Fig. 2 *c*).

In addition, at the beginning of relaxation we have no exponential law of the relaxation of the distribution of the concentration of excess minority carriers. But with increasing time, the terms of the series with smaller coefficients in equation (3) of the relaxation time become very small. When time exceeds the effective relaxation time, then one exponent remains only and determines the effective relaxation time of the distribution of excess minority carriers, equation (5). The non-exponential part of the relaxation of the distribution of excess minority carriers, modeled by the sum of exponents, hides due to rapid recombination of excess charge carriers in the macroporous layer.

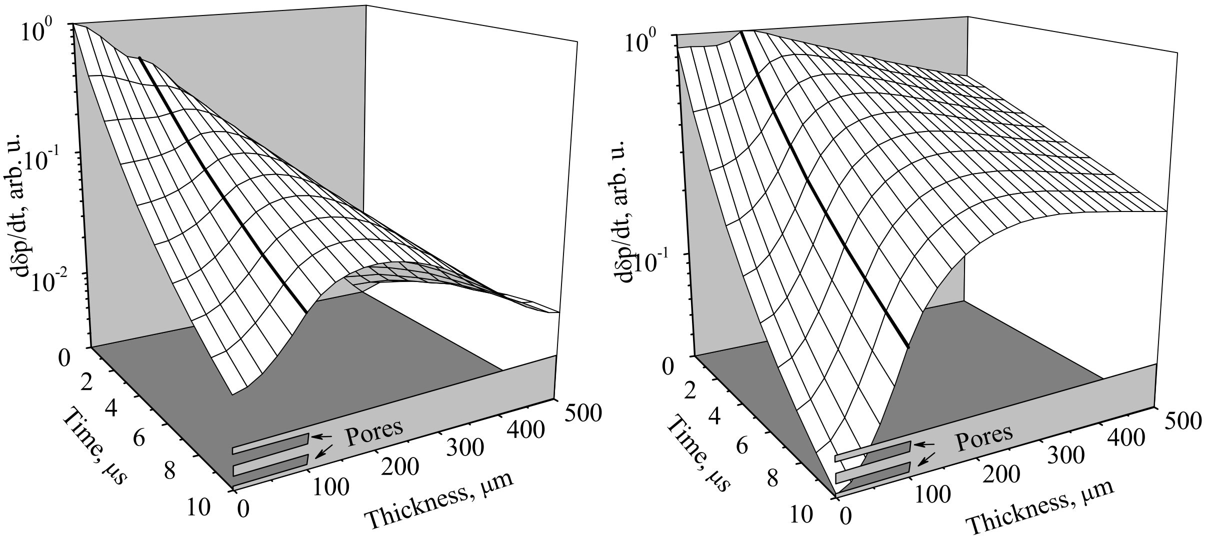
Two maxima in the distribution of excess minority carriers in macroporous silicon. It is evident from Fig. 2 *a* that at the beginning there are two maxima of distribution. With time, the first maximum decreases and after relaxation during 10 μs becomes the minimum. This minimum is due to the superficial recombination of excess charge carriers, which occurs both on the surface of the pores and on the surface of the sample. When the generation of excess charge carriers is switching off, the relaxation of the distribution of excess minority carriers in macroporous silicon is due to diffusion processes, bulk and surface recombination of excess charge carriers. The bulk recombination is homogeneous therefore it has little effect on the non-homogeneous of the distribution of excess minority carriers in macroporous silicon during generation and after switching off the generation of excess charge carriers. Surface recombination leads to the diffusion of excess charge carriers into recombination centers, creates the non-homogeneity of the distribution of excess charge carriers. In addition, the non-homogeneity of generation of excess charge carriers creates non-homogeneity of their distribution too. Diffusion and recombination processes transform the distribution of excess minority carriers under non-homogeneous generation in their initial distribution.

In macroporous layer, there is a strong recombination of excess charge carriers due to the large area of recombination on the surface of macropores. Thus, we observe a significant decrease in excess minority carriers after the termination of their generation (Fig. 2 *a*) near the boundary of a macroporous layer and a monocrystalline substrate. And we observe a small decrease in the concentration of excess minority carriers on the opposite side of substrate because the surface area of the substrate is an order of magnitude smaller than that of the macropores.

The second maximum is due to the generation of excess charge carriers by electromagnetic radiation which falls to the bottom of the macropores, as well as diffusion and recombination on the surface. And the generation of excess charge carriers shifts this distribution maximum toward of the bottom of the pores.

We observe one maximum of the excess minority carrier distribution of (Fig. 2 *b*), because homogeneous generation does not affect the distribution of excess minority carriers. Really, the electromagnetic wave of 1.05 μm is absorbed weakly by silicon and generation of excess charge carriers by this electromagnetic wave is homogeneous.

The relaxation of the distribution of the rate of change excess minority carriers in macroporous silicon. Fig. 3 shows the relaxation of the distribution of the normalized rate of change in the concentration of excess minority carriers in macroporous silicon structure at different time moment after the termination of the generation of excess charge carriers by an electromagnetic wave of 0.95 (*a*) and 1.05 μm (*b*).



a *b*

Fig. 3. The relaxation of the distribution of the normalized rate of change in the concentration of excess minority carriers dδp/dt in macroporous silicon after the termination of the generation of excess charge carriers by the electromagnetic wave *a* – 0.95, *b* – 1.05 μm. The upper curve is 0 μs, the other curves are shown with an interval of 1 μs. The pore depth is 100 μm

The rate of change in the excess minority carrier concentration dδp/dt is determined by the recombination of excess charge carriers in a structure volume and diffusion into or out of this volume. Fig. 3 *a, b* is constructed on a semi-logarithmic scale. As can be seen from Fig. 3 *a*, the rate of change in the concentration of excess minority carriers decreases with time in macroporous silicon layer (the left half of the sample) and increases in silicon substrate (in the right half of the sample) after generation by the electromagnetic waves 0.95 μm. The rate of change in the concentration of excess minority carriers decreases with time in macroporous silicon layer and increases in silicon substrate after generation by the electromagnetic waves 0.95 μm. Excess charge carriers move from the middle of the sample to the recombination surfaces. The recombination of excess charge carriers on the surface of the macropores is high, so all the excess charge carriers that are diffusing from the monocrystalline substrate to the surface of the macropores are recombined, their concentration decrease. Reduced concentration of excess minority carriers (Fig. 2 *a*) decreases the rate of change in the concentration of excess minority carriers. The rate of change in the concentration of excess minority carriers grows on silicon substrate surface due to generation by electromagnetic wavelength 0.95 μm with small absorption depth and diffusion to the surface of a monocrystalline substrate. Not all photocarriers recombine, their concentration varies very slowly. Thus, the rate of change in the concentration of excess minority carriers increases.

The rate of change in the concentration of excess minority carriers decreases in time in the entire structure after generation by the electromagnetic waves of 1.05 μm (Fig. 3 *b*) with big absorption depth and small non-homogeneity.

CONCLUSIONS

We calculated by the finite difference method the relaxation of the distribution of excess minority carrier concentration in macroporous silicon layer and silicon substrate after generation by the electromagnetic waves of 0.95 and 1.05 μm. In this case absorption coefficients and absorption depths differ almost 10 times for comparable wavelengths of electromagnetic radiation.

The function of the initial excess minority carrier distribution has two maxima after generation by electromagnetic wavelength 0.95 μm with small absorption depth 64 μm. The first maximum is in the macroporous layer, the second one is in the monocrystalline substrate. Surface recombination leads to the diffusion of excess charge carriers to recombination centers and creates a non-homogeneity of the excess charge carrier distribution. A rapid maximum decrease of the excess carrier distribution function in a macroporous layer and near the boundary of a macroporous layer and monocrystalline substrate are found. We observed a small decrease in the concentration of excess minority carriers on the opposite side of substrate due to the surface area of the substrate an order of magnitude smaller than the surface area of the macropores. In addition, the non-exponential part of the relaxation of the excess minority carrier distribution in macroporous silicon hides by the rapid recombination of excess charge carriers in a macroporous layer. After generation by electromagnetic wavelength 1.05 μm with big absorption depth 614 μm we observed one maximum of the excess minority carrier distribution, because homogeneous generation does not affect the distribution of excess minority carriers.

The rate of change in the concentration of excess minority carriers decreases in time in macroporous silicon layer and increases in silicon substrate after generation by the electromagnetic waves 0.95 μm with small absorption depth. The recombination of excess charge carriers on the surface of the macropores is high, it is concentration decrease. The rate of change in the concentration of excess minority carriers grows on the silicon substrate surface due to diffusion to the surface of a monocrystalline substrate. Not all photocarriers recombine, the rate of change in the excess minority carrier concentration increases. The rate of change in the concentration of excess minority carriers decreases in time in all structure after generation by the electromagnetic waves 1.05 μm with big absorption depth and small non-homogeneity.

Релаксація розподілу надлишкових неосновних носіїв заряду в макропористому кремнію

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Релаксація розподілу надлишкових неосновних носіїв заряду в структурі макропористого кремнію була розрахована методом кінцевих різниць. Початковий розподіл надлишкових неосновних носіїв заряду має два максимуми, після генерації носіїв заряду електромагнітної хвилею 0.95 мкм з малою глибиною поглинання. Перший максимум функції початкового розподілу знаходиться в макропористому шарі, другий - в монокристалічній підкладці. Поверхнева рекомбінація призводить до дифузії надлишкових носіїв заряду до центрів рекомбінації і створює неоднорідність їх розподілу. Виявлено швидке зменшення максимуму функції розподілу надлишкового носіїв заряду в макропористому шарі і поблизу межі між макропористим шаром і монокристалічною підкладкою. Виявлено повільне зниження функції розподілу в монокристалічній підкладці. Швидкість зміни концентрації надлишкових неосновних носіїв заряду з часом зменшується в шарі макропористого кремнію через високу рекомбінацію і збільшується за рахунок дифузії носіїв заряду до поверхні кремнієвої підкладки. Після генерації фотоносіїв електромагнітною хвилею 0.95 мкм з малою глибиною поглинання, швидкість зміни концентрації надлишкових неосновних носіїв заряду з часом зменшується в шарі макропористого кремнію через високу рекомбінацію і збільшується за рахунок їх дифузії до поверхні кремнієвої підкладки. Після однорідної генерації носіїв заряду електромагнітною хвилею 1.05 мкм з великою глибиною поглинання формується один максимум розподілу надлишкових неосновних носіїв заряду. Водночас швидкість зміни концентрації надлишкових неосновних носіїв заряду з часом зменшується у всій структурі.

***Ключові слова**: релаксація, розподіл носіїв заряду, макропористий кремній*

Релаксация распределения избыточных неосновных носителей заряда в макропористом кремнии

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Релаксация распределения избыточных неосновных носителей заряда в структуре макропористого кремния была рассчитана методом конечных разностей. Первоначальное распределение избыточных неосновных носителей заряда имеет два максимума после генерации носителей заряда электромагнитной волной 0.95 мкм с малой глубиной поглощения. Первый максимум функции начального распределения находится в макропористом слое, второй – в монокристаллической подложке. Поверхностная рекомбинация приводит к диффузии избыточных носителей заряда к центрам рекомбинации и создает неоднородность распределения избыточных носителей заряда. Обнаружено быстрое уменьшение максимума функции распределения избыточных носителей заряда в макропористом слое и вблизи границы макропористого слоя и монокристаллической подложки. Выявлено медленное снижение функции распределения в монокристаллической подложке. После генерации фотоносителей электромагнитной волной 0.95 мкм с малой глубиной поглощения скорость изменения концентрации избыточных неосновных носителей заряда со временем уменьшается в слое макропористого кремния из-за высокой рекомбинации и увеличивается за счет их диффузии к поверхности кремниевой подложки. После однородной генерации носителей заряда электромагнитной волной 1.05 мкм с большой глубиной поглощения формируется один максимум распределения избыточных неосновных носителей заряда. При этом скорость изменения концентрации избыточных неосновных носителей заряда со временем уменьшается во всей структуре.

***Ключевые слова**: релаксация, распределение носителей заряда, макропористый кремний*

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