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(41, Nauky Ave., Kyiv 03028, Ukraine; e-mail: lakar@isp.kiev.ua)**CONDUCTIVITY AND PHOTO-INDUCED
CONDUCTIVITY OF TWO-DIMENSIONAL
MACROPOROUS SILICON STRUCTURES**

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The effective conductivity and the photoconductivity in two-dimensional macroporous silicon structures have been measured, and their dependences on the macropore concentration and diameter have been calculated. The effective conductivity of macroporous silicon structures is found to decrease as the concentration and the volume fraction of pores grow. A size effect was revealed, a significant reduction in the thickness of the space charge region at small macropore diameters (the surface charge) is observed. The effective relative photoconductivity is found to be governed by the charge recombination and accumulation on the pore surface. Theoretical dependences of the relative photoconductivity in the examined structures are found to correspond to a surface recombination rate of 90 cm/s.

Keywords: macroporous silicon structures, effective conductivity, photoconductivity.

1. Introduction

Two-dimensional structures of macroporous silicon fabricated by the photo-assisted anodic etching found applications in optics as photonic crystals, being promising in photoelectronics. This fact is associated with a possibility to manufacture structures with a required geometry, a large surface area of an order of 10^3 – 10^4 cm² per structure unit volume, an opportunity of their integration into microcircuits, as well as with their photo-electric characteristics. The latter are governed by processes running at the macropore surface [1, 2]. The photoconductivity kinetics in macroporous silicon has a non-exponential dependence, being a function of the surface potential and the surface recombination rate [3]. In particular, the temperature dependence of the photoconductivity relaxation time has an activation character in the temperature interval $T = 200 \div 300$ K, but this quantity does not depend on the temperature if the latter diminishes below this interval. Provided that the energy of photons is comparable with the energy of an indirect band-to-band transition, the temperature dependences of the photovoltage in two-dimensional structures of macroporous silicon at temperatures close to that of liquid nitrogen are driven by the process of electron accumulation at surface-induced levels with the energies located near the conduction band

[4]. The mechanisms responsible for the transport of photo-induced carriers in macroporous silicon structures through the barrier indium–macroporous silicon have been determined [5–7]. Photoelectric properties of two-dimensional macroporous silicon structures—in particular, the photoconductivity maximum—depend on the distance between pores and their diameter. The photoconductivity in macroporous silicon structures exceeds the corresponding value in single crystals, which is explained by a large area of the macropore surface and the modulation of a Schottky layer at illumination [8, 9].

In this work, the effective conductivity and photoconductivity of two-dimensional macroporous silicon structures were measured, and the dependences of those quantities on the concentration and the diameter of macropores were calculated. The effective conductivity of the silicon matrix in the direction parallel to macropores was calculated as a function of the ratio between the volume fraction occupied by the silicon matrix, $1 - P$, and the volume fraction of the space charge region. The thickness of the space charge region was determined depending on the diameter of macropores in studied macroporous silicon structures. We also determined the surface recombination rate.

2. Experimental Technique

Structures of macroporous silicon under study were fabricated on silicon wafers of the thickness

Parameters of specimens of macroporous silicon structures

No.	$D_p, \mu\text{m}$	$N_p, 10^6 \text{ cm}^{-2}$	$a - D_p, \mu\text{m}$	$S_p, \text{cm}^2/\text{cm}^3$	$\sigma, \Omega^{-1} \cdot \text{cm}^{-1}$	$\sigma_p, \Omega^{-1} \cdot \text{cm}^{-1}$	$\sigma_{\text{ph}}, \Omega^{-1} \cdot \text{cm}^{-1}$
1p	1	25	1	7854	0.1	0.04	0.6
2	1.8	7.5	1.6	4241	0.16	0.1	0.5
3p	2	6.25	2	3925	0.18	0.12	0.45
4	3	3	2.8	2827	0.19	0.13	0.27
5	6	1	4	1885	0.2	0.15	0.24
6	5	1	5	1570	0.2	0.15	0.2

$H = 400 \mu\text{m}$ and with conductivity of the n -type, the equilibrium concentration of electrons $n_0 = 10^{15} \text{ cm}^{-3}$, a specific resistance of $4.5 \Omega \cdot \text{cm}$, and the orientation [100]. Using the method of electrochemical etching at illuminating the rear side of the silicon single-crystalline substrate [1], cylindrical macropores of the depth $h_p = 40 \div 100 \mu\text{m}$ were formed. Macropores with the diameter $D_p = 1 \div 6 \mu\text{m}$ and the distance between them $a - D_p = 1 \div 4 \mu\text{m}$ were arranged both periodically and irregularly. The periodic arrangement of cylindrical macropores filled with air was provided by a corresponding periodic arrangement of etching pits. The latter were preliminarily formed with the use of the photolithographic procedure and the anisotropic etching in a KOH solution. The diameter, depth, and concentration of macropores were determined with the help of an optical microscope Carl Zeiss Jena NU. The concentration of macropores amounted to $N_p = (1 \div 6) \times 10^6 \text{ cm}^{-2}$; the volume fraction of pores, $P = \pi D_p^2 N_p / 4$, was equal to 0.2–0.3 rel. units; the specific area of the macropore surface, $S_p = 4P / D_p$, fell within the interval from 1900 to 7900 cm^2 per unit volume of the macroporous silicon structure (see Table). The notation in the table is as follows: σ is the specific conductance of the macroporous silicon specimen, σ_p the calculated effective specific conductance of the macroporous silicon layer, σ_{ph} the relative effective photoconductivity of macroporous silicon structures, specimens 1p and 2p have a periodic macropore arrangement.

Ohmic contacts Au/single-crystalline n -Si and Au/macroporous n -Si were formed by rubbing the Au/Si eutectic into fresh cleavages of macroporous silicon structures at a temperature of 450 K. In the course of specimen conductance measurements, the current flowed perpendicularly to the cylindrical macropores.

The stationary photoconductivity and the conductivity in macroporous silicon structures were measured with the use of a compensating circuit in the maximum sensitivity mode. For illumination, an IR light diode GaAlAs/GaAs with a wavelength of $0.95 \mu\text{m}$ was used.

3. Effective Conductivity in Two-Dimensional Structures of Macroporous Silicon

To analyze the effective conductivity in a silicon layer with macropores, let us take into account that, around every macropore, there is a space charge region with thickness w , which is characterized by the conductivity σ_s different from that in the quasineutral bulk between the macropores, σ_b . The effective specific conductance of the macroporous silicon layer in the direction parallel to the macropores was determine as a sum of conductivities of the space charge region and the quasineutral bulk, with the conductance of the space charge region being regarded as a parallel element, so that

$$\sigma_{p1} = P_b \sigma_b + P_s \sigma_s, \quad (1)$$

where $P_b = 1 - P - N_p \pi w (D_p + w)$ and $P_s = N_p \pi w (D_p + w)$ are the volume fractions of the quasineutral bulk and the space charge region, respectively. The effective conductivity of the macroporous silicon layer can also be found in terms of the volume fraction of the silicon matrix, $1 - P$,

$$\sigma_{p1} = (1 - P) \sigma_{sm1}, \quad (2)$$

where σ_{sm1} is the effective conductivity of the silicon matrix in the direction parallel to the pores. The conductivity in the direction perpendicular to the macropores, when calculated in the framework of the theory of effective medium, gives the approximate solution

$$\sigma_{p2} \approx \frac{1 - P}{1 + P} \sigma_{sm2}, \quad (3)$$

where σ_{sm2} is the effective conductivity of the silicon matrix in the direction perpendicular to the pores. At large distances between macropores, the conductance of the space charge region can be neglected, and $\sigma_{p2} \approx \sigma_b P_b / (2 - P_b)$.

The conductivity of the macroporous silicon structure on the silicon substrate in the direction parallel to the macropores, σ_1 , is calculated as a series connection of the macroporous layer and the silicon substrate. Then the conductivity of macroporous layer in this direction can be found as follows:

$$\sigma_{p1} = \sigma_b \left(1 - \frac{H}{h_p} \left(1 - \frac{\sigma_b}{\sigma_1} \right) \right)^{-1}. \quad (4)$$

The conductivity in the direction perpendicular to the pores, σ_2 , is determined as for the parallel connection of the macroporous layer and the silicon substrate. In this case, the conductivity of the macroporous layer equals

$$\sigma_{p2} = h_p \left(\frac{\sigma_2}{H} - \frac{\sigma_b}{H - h_p} \right). \quad (5)$$

The effective conductivity of the silicon matrix, provided that the distance between the pores exceeds the doubled thickness of the space charge region, can be written down as a sum of the space charge region and quasineutral bulk conductivities,

$$\sigma_{sm} = \sigma_b \left(1 - \frac{P_s}{1 - P} \right) + \frac{P_s}{1 - P} \sigma_s, \quad (6)$$

where $P_s / (1 - P)$ is the fraction of the space charge region in the silicon matrix.

Let us calculate the effective conductivity of the silicon matrix in the direction parallel to the macropores as a function of the ratio between the volume fractions of the silicon matrix, $1 - P$, and the space charge region, $N_p \pi w (D_p + w)$. The expression for the effective conductivity in the porous silicon layer looks like

$$\sigma_{sm1} \approx \frac{1 - P}{P_s} \sigma_s = \frac{(1 - P) \sigma_s}{\pi N_p w (D_p + w)}. \quad (7)$$

The effective conductivity of the material in the direction perpendicular to the macropores in the case where the depletion layers overlap equals

$$\sigma_{sm2} \approx \frac{(1 - P)^2}{P_s (1 + P)} \sigma_s = \frac{(1 - P)^2 \sigma_s}{\pi N_p w (D_p + w) (1 + P)}. \quad (8)$$

According to work [11], the first Poisson integral in the case of overlapping space charge regions looks like

$$\frac{dy}{dx} = L_D^{-1} \left[\left(\left(\frac{n_i}{n_0} \right)^2 + \frac{\Delta n}{n_0} \right) (e^{-y} - 1) + \left(1 + \frac{\Delta n}{n_0} \right) (e^y - 1) - y + \left(\frac{e L_D E_0}{kT} \right)^2 \right], \quad (9)$$

where $y = e\varphi / (kT)$ is the dimensionless surface potential, e the elementary charge, φ the surface potential, k the Boltzmann constant, T the temperature, n_i the concentration of charge carriers in the intrinsic semiconductor, Δn the nonequilibrium concentration of charge carriers, L_D the Debye screening length in the doped semiconductor, and E_0 the electric field strength in the middle between the pores. The conductivity of the space charge region, σ_s , can be calculated with the use of the first Poisson integral,

$$\sigma_s = (e \mu_{sn} n \int_y^0 \exp(y) F^{-1} dy + e \mu_{sp} p \int_y^0 (\exp(-y) F^{-1} dy) / \int_y^0 F^{-1} dy), \quad (10)$$

where $F = L_D dy / dx$; n and p are the concentrations of electrons and holes, respectively, in the quasineutral bulk; and μ_{sn} and μ_{sp} are their mobilities near the surface.

The required dependences for the effective conductivity in macroporous silicon structures on the single-crystalline substrate and without it (Fig. 1) were calculated using formulas (3), (5), (8)–(10), and (12), and the data listed in Table. Those data were measured for the current running perpendicularly to the pores. When calculating the conductivity in the macroporous silicon structure, we used formula (12), which involves the dependence of the thickness of the surface charge region around a cylindrical macropore on the macropore diameter, $w = w(D)$. Figure 1 also exhibits experimental data.

As one can see from Fig. 1, the effective conductivity in a macroporous silicon structure on a single-crystalline substrate is higher than that of a macroporous silicon layer without substrate if they are normalized to the identical specimen size. At an average distance between the macropore edges of 1.5–2 μm , the effective conductivity begins to diminish

drastically, because the average distance between the macropores becomes shorter than the doubled thickness of the space charge region. In this case, the reduction of the effective conductivity in the macroporous silicon structures is associated with the capture of electrons onto surface energy states (mainly, acceptor ones).

4. Space Charge Region Around a Cylindrical Macropore

In order to calculate the thickness of the space charge region around a cylindrical macropore, let us use the Poisson equation in the cylindrical coordinate system,

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial y}{\partial r} \right) = - \frac{\rho}{\varepsilon \varepsilon_0 kT}, \quad (11)$$

where r is the radial coordinate, and ρ the charge density. The boundary conditions for the space charge region with thickness w around a cylindrical pore of diameter D look like $E(D_p/2+w) = 0$, $y(D_p/2+w) = 0$, and $y(D_p/2) = y_s$, where E is the electric field strength, and y_s is the value of dimensionless potential on the pore surface. Integrating Eq. (11) and using the boundary conditions indicated above, we obtain the equation

$$\frac{16\varepsilon\varepsilon_0kyTw}{eqVD_p^2} - 1 + \left(1 + \frac{2w}{D_p}\right)^2 \left(1 - 2\ln\left(1 + \frac{2w}{D_p}\right)\right) = 0, \quad (12)$$

where the charge density ρ is determined either in terms of the bulk charge q_V , namely, $\rho = q_V/w$, or, in the case of the layer with total depletion, as $\rho = en_0$. This equation allows the thickness of the space charge region around a cylindrical pore to be determined. Notice that the Debye screening length in the intrinsic semiconductor equals $L_i = \sqrt{\varepsilon\varepsilon_0kT/(4\pi e^2n_i)}$, where ε is the electric constant, and $\varepsilon_0 = 11.68$ is the dielectric permittivity of silicon. In addition, $2\varepsilon\varepsilon_0kTy/(qVe) = 2yn_0eL_D^2/qV \approx w_0$, because $qV = \sqrt{2}en_iL_iF \approx en_0L_D\sqrt{-2y}$, where $F \approx \sqrt{-yn_0/n_i}$ in a semiconductor of the n -type.

In Fig. 2, the dependences of the space charge region around cylindrical macropores (panel *a*) and the volume fraction of macropores (panel *b*) on their diameter calculated for various values of dimensionless surface potential are plotted. The figure demonstrates the appearance of a size effect, namely, the

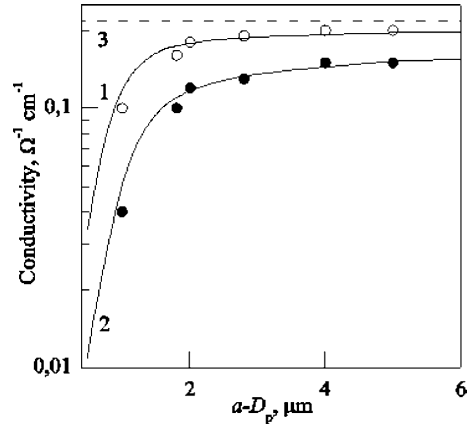


Fig. 1. Experimental data (symbols, see Table) and theoretical dependences of the effective conductivity in a macroporous silicon layer on the average distance between macropore edges: on a single-crystalline substrate (curve 1) and without substrate (curve 2). Curve 3 is the conductivity of a silicon single crystal, $\sigma_b = 0.22 \Omega^{-1} \cdot \text{cm}^{-1}$. The volume fraction of pores equals 0.2

substantial dependence of the space charge region thickness w on the macropore diameter at $D_p < 6 \mu\text{m}$, and the same behavior of the porosity at $D_p < 10 \mu\text{m}$. If the radius of a cylindrical macropore diminishes, the area of its surface also decreases, as well as the surface charge. Therefore, the thickness of the bulk charge that compensates the surface one becomes smaller.

5. Photoconductivity in Two-Dimensional Macroporous Silicon Structures

The distance $a - D_p$ between macropores is an important parameter for the determination of the photoconductivity in a macroporous silicon structure. In the examined specimens, the distance between the macropore edges, $a - D_p$, is smaller than the diffusion length of nonequilibrium charge carriers, $L_P \approx 100 \mu\text{m}$ (see Table). The penetration depth of light with a used wavelength of $0.95 \mu\text{m}$ amounts to $50 \mu\text{m}$. Under those conditions, the generation of photocarriers can be considered as occurring in the bulk. At the distances between macropores $a - D \leq 2w$, the concentration of equilibrium charge carriers depends on the distance and the surface recombination rate s (in the layer, the thickness of which is equal to the diffusion length). The diffusion length is governed by the lifetime of nonequi-

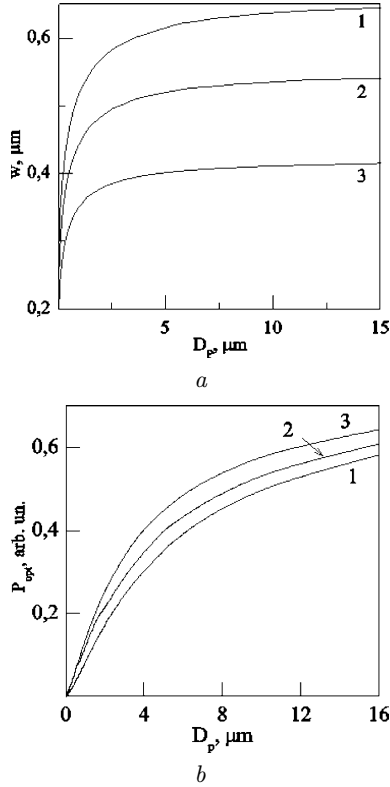


Fig. 2. Dependences of the thickness of the space charge region around a cylindrical macropore (a) and the volume fraction of macropores at $a - D_p = 2w$ (b) on the macropore diameter for various values of dimensionless surface potential: 12 (1), 8 (2), and 4 (3)

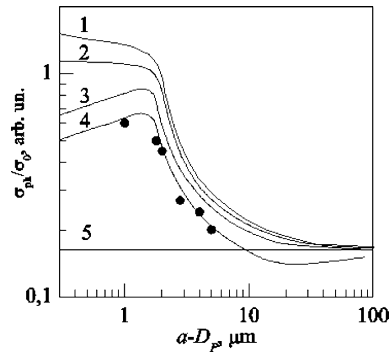


Fig. 3. Experimental data (symbols, see Table) and calculated dependences of the relative effective photoconductivity on the average distance between macropores at various surface recombination rates $s = 0$ ($N_t = 0$) (1), 0 (2), 50 (3), and 90 cm/s (4). For curves 2 to 4, $N_t = 10^{10} \text{ cm}^{-2}$. Curve 5 describes the relative photoconductivity in the silicon single crystal. Specimens were illuminated with light with a wavelength of $0.95 \mu\text{m}$ and the illumination intensity $I = 10^{15} \text{ quantum}/(\text{cm}\cdot\text{s})$

librium charge carriers in the substance bulk. The latter parameter can be determined from the photoconductivity kinetics [3]. Under the conditions specified above, the average concentration of photo-induced charge carriers in the quasineutral bulk at the stationary photoconductivity is determined by the formula

$$\Delta n = \beta \tau I \left(\frac{2s(n_0 + \Delta n, y)\tau}{a - D_p} + 1 \right)^{-1}, \quad (13)$$

where I is the illumination intensity, β the quantum yield (this parameter takes, in particular, the reflection of light from the surface of a silicon crystal into account and, by its order of magnitude, equals 1), and τ is the lifetime of nonequilibrium charge carriers. The surface recombination rate, in its turn, depends on the carrier concentration n and the surface potential y , which are affected by the illumination intensity,

$$s(n, y) = (C_p C_n N_t (n + p_0)) / (C_n (n \exp(y) + n_i \exp(\varepsilon_t)) + C_p (p \exp(-y) + n_i \exp(-\varepsilon_t))), \quad (14)$$

where N_t is the concentration of surface electron states; C_n and C_p are the coefficients of electron and hole capture, respectively, by surface levels; $\varepsilon_t = E_t/kT$; E_t is the surface level energy reckoned from the energy gap middle-point; and $\Delta y = y - y_0$ is a change of the dimensionless potential associated with photo-induced transitions between the valence band and the surface states. In the case of a depletion band bending at the macropore surface, the variation of the dimensionless potential can be obtained by solving the electro-neutrality equation; i.e. the charge of surface states must be equal to that of the space charge region in the semiconductor,

$$\Delta n_t(n, y) = \sqrt{2} n_i L_i \Delta F(n, y), \quad (15)$$

where Δn_t is a change of the electron concentration on the surface levels after illumination, and ΔF is a variation of the function from the first Poisson integral. The concentration of electrons on the surface levels equals

$$n_t(n, y) = (N_t (C_n n \exp(y) + C_p n_i \exp(-\varepsilon_t))) / (C_n (n \exp(y) + n_i \exp(\varepsilon_t)) +$$

$$+ C_p(p \exp(-y) + n_i \exp(-\varepsilon_t)). \quad (16)$$

The relative effective photoconductivity was calculated by solving the system of equations (12), (13), (15), (16).

In Fig. 3, the experimental data and the corresponding theoretical dependences of the relative effective photoconductivity in macroporous silicon structures on the distance between macropore surfaces are depicted for various surface recombination rates. The following parameters of surface levels were used in the calculations: the concentration of surface levels $N_t = 10^{10} \text{ cm}^{-2}$, the coefficient of hole capture on the surface level for holes $C_p = 10^{-11} \text{ cm}^3/\text{s}$, the same parameter for electrons $C_n = 10^{-5} \text{ cm}^3/\text{s}$, the dimensionless energy of surface center activation reckoned from the middle of the energy gap $\varepsilon = 5$.

Curve 1 corresponds to the case where there are no surface levels on the surface, so this curve has no maximum. Curve 2 makes allowance for surface electron states that accumulate charge. The accumulation of photoelectrons at the surface results in a reduction of their concentration in the bulk. Therefore, the growth of the photoconductivity slows down. There emerges a maximum in curves 3 and 4 at a distance of $1.5 \mu\text{m}$ between the macropore edges. The relative photoconductivity grows at that, as the distance between the macropores diminishes owing to a reduction of the dark conductivity, and the influence of Schottky layer thickness modulation at illumination increases with respect to the neutral bulk case. On the other hand, the relative photoconductivity decreases, because the influence of the surface recombination rate increases (the lifetime of photo-induced charge carriers decreases).

Curve 4 in Fig. 3 corresponds to a surface recombination rate of 90 cm/s in the examined macroporous silicon specimens. This value was obtained with regard for the concentration of surface centers at the given energy and the coefficients of electron and hole capture.

From Fig. 3, it is evident that the macroporous silicon structures have a minimum in the relative photoconductivity at $a - D_P > 10 \mu\text{m}$, which is less than the relative photoconductivity in the silicon single crystal. The minimum of the relative photoconductivity stems from a shorter lifetime of

charge carriers in the macroporous silicon structure in comparison with that in single crystals owing to an additional recombination through the macropore surface.

6. Conclusions

When the concentration of macropores and their volume fraction in macroporous silicon structure increase, the effective conductivity of the latter decreases. The calculation of the thickness of the space charge region around a cylindrical macropore revealed a size effect, namely, a substantial reduction in the thickness of the space charge region w , when the macropore diameter diminishes below $D_P < 6 \mu\text{m}$, and in the macropore volume fraction below $D_P < 10 \mu\text{m}$. The decrease of the cylindrical macropore radius gives rise to a reduction of the macropore area and, respectively, the surface charge. Therefore, the thickness of the bulk charge, which compensates the surface one, will be smaller.

The effective relative photoconductivity is driven by the charge recombination and accumulation on the pore surface. For the researched specimens of macroporous silicon, the calculated dependences of the relative photoconductivity correspond to a surface recombination rate of 90 cm/s . It is shown theoretically that, provided this surface recombination rate and $a - D_P > 10 \mu\text{m}$, the macroporous silicon structures must be characterized by a lower relative photoconductivity in comparison with that of single-crystalline specimens, which is associated with a shorter lifetime of charge carriers in the former objects.

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ПРОВІДНІСТЬ
ТА ФОТОПРОВІДНІСТЬ ДВОВИМІРНИХ
СТРУКТУР МАКРОПОРИСТОГО КРЕМНІЮ

Резюме

У двовимірних структурах макропористого кремнію виміряно ефективну провідність та фотопровідність, а також розраховано залежність цих величин від концентрації та діаметра макропор. Встановлено, що при збільшенні концентрації та об'ємної частки пор ефективна провідність структур макропористого кремнію зменшується. Виявлено розмірний ефект: суттєве зменшення товщини області просторового заряду w при зменшенні діаметра макропор (поверхневого заряду). Ефективна відносна фотопровідність визначається рекомбінацією та накопиченням заряду на поверхні пор. Для досліджених структур теоретичні залежності відносної фотопровідності відповідають значенню швидкості поверхневої рекомбінації 90 см/с.