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Limiting thickness of pore walls formed in processes of anode etching of heavily doped semiconductors

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With a decrease in the thickness of the walls separating the space of pores in porous semiconductors, the potential energy of interaction between an electron and a donor (or a hole and an acceptor) can become greater than the kinetic energy of a free charge carrier. As a consequence, such interlayers lose their conductivity and transit into the dielectric state (Mott phase transition). With regard to the conditions of electrochemical pore formation, this means that as the pore channels approach each other during anodic etching to a distance at which the current flow through the wall that separates them stops, the potential of its surface ceases to be determined by the external electric bias and the electrochemical process, that leads to a further decrease in the thickness of such a wall, stops. Expressions are obtained for the limiting thickness of the walls of pores formed in degenerate semiconductors of *n*- and *p*-type conductivity. In contrast to the well-known model that relates the loss of conductivity by pore walls to the combination of space charge layers, the proposed model allows a consistent explanation for the experimental data for both n- and p-type silicon with doping levels above $10^{18} \, cm^{-3}$.

Keywords: thickness limitation, pore formation, silicon, donor, acceptor.

Introduction

The process of electrochemical pore formation observed in silicon crystals and other sufficiently high-energy-gap diamond-like semiconductors for more than sixty years stays the subject of ongoing discussions with various and often contradictory interpretations [1–8]. The essence of the phenomenon is that when a not too high anode bias is applied to a single-crystal semiconductor electrode located in an electrolyte with a suitable anionic composition, the electrochemical etching process develops not on the entire surface of the electrode, but in a variety of spontaneously arising discrete regions of nano- or micrometer sizes, then deepening into the bulk of the crystal and giving rise to a system of extended branching channels — pores. With a sufficiently long course of this process, a stationary discrete etching front is formed in the crystal, leaving behind a macroscopically homogeneous layer of porous material, characterized by certain transverse pore sizes and separating them by partitions made of unreacted semiconductor material. Pores, as a rule, also retain some of the products of the electrochemical reaction that took place. The physicochemical properties of the porous media obtained in this way can radically differ from the properties of the initial materials. The resulting differences directly depend on the thickness of the pore walls, their specific surface area, and the nature of the adsorption coating, which determine the contribution of the surface energy to the chemical potential of the modified crystal. In those cases when the pore partitions reach nanometer sizes, at which quantum size effects begin to affect the structure of the energy bands of the semiconductor, the porous semiconductors acquire unique characteristics that are not inherent characteristic of the initial materials (for example, silicon that luminesces and explodes in contact with oxidizers [9–11]). Therefore, it is so important to understand the nature of self-organizing pores formation processes and the criteria that determine the stationary dimensions of pores and the partitions remaining between them.

As for the stationary size of the pore walls in the layers formed in the established etching mode, after the completion of the stage of intensive branching of the primary channels growing from the surface, this size, by consensus, regardless of views on the pore formation mechanism, should coincide with the size at which no free charge carriers remain in the pore walls. In this case, when a bias is applied from an external source, neither the holes transfer to the surface of the retained crystalline interlayers, nor the shift of their potential relative to the electrolyte existing in the pores turn out to be impossible. The most obvious of the probable reasons for the loss of
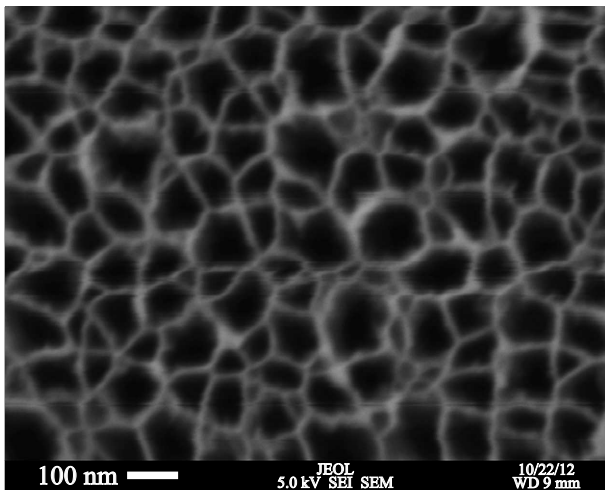
Figure 1. The structure of the surface of detachment from the substrate of layer of porous silicon $\sim 150\,\mu$m thick formed on (001) Si p-type plate with hole concentration of $2 \cdot 10^{19}\,\mathrm{cm}^{-3}$.

conductivity of the pore walls is the closure of the space charge regions that arise near their surface from the side of neighboring pores. Indeed, in meso- and macroporous layers formed in moderately doped silicon crystals and other n-type semiconductors, there is usually an approximate correspondence of the estimated pore wall thicknesses to double thickness of the space charge layer near the surface of the initial crystal with a given doping level [6]. However, this model does not comply with the fact that homogeneous mesoporous layers with pore wall thicknesses from a few to tens of nanometers are also formed in heavily doped degenerate silicon of both n- and p-type conductivity, as well as in degenerate n^+GaAs and n^+InP. In this case, near the surface of such metallized semiconductor crystals, a space charge layer without free charge carriers should not practically exist, since the entire potential drop at the interface should be localized in the Helmholtz layer [12]. If for the degenerate n-semiconductor, anode-polarized in the electrolyte one can also speak about the existence of a Debye screening region near the surface with thickness $L_D = (\varepsilon kT/2e^2n)^{1/2}$ (where ε — static permittivity of silicon, k — Boltzmann constant, T — temperature, e — electron charge, n — electron concentration), then for the degenerate p-type semiconductor the surface charge carriers depletion under these conditions is in principle impossible. Nevertheless, even in degenerate p-type silicon, during anodization in HF electrolytes, uniform mesoporous layers with minimum pore wall thicknesses of a few nanometers are formed (Fig. 1), which brings into question the generality of the pore wall model as area of closed up space charge layers.

Moreover, it is known that in HF-containing solutions the silicon surface is either hydrogenated [13] or termed by chemisorbed fluorine atoms under anode polarization conditions. Thus, in any case, the silicon surface, regardless

of the type and level of doping, is passivated by more electronegative atoms that close up the broken bonds of silicon. Consequently, Fermi level pinning on surface states lying in the forbidden band of the etched silicon crystal should not occur, and, accordingly, the associated band bending should not exist. Even if we suppose that uncompensated broken bonds and the corresponding surface states periodically arise during etching, stopping or slowing down etching lead to their disappearance and conductivity restoration of the outer layer of the crystal.

Besides, the very fact of uniformly distributed discrete etching of crystals of degenerate semiconductors of both types of conductivity contradicts the main condition of all presented until recently models of anode pore formation which requires selective delivery of holes in the valence band of the semiconductor from the bulk of the crystal to the bottom of the pores or equally selective generation of them at the interface with electrolyte.

In the papers [14–16] we proposed an alternative model of anode processes leading to pore formation in semiconductors, which does not require the direct participation of valence band holes in discrete etching of crystal. Such etching is considered as a consequence of the occurrence of multiparticle, cooperative reactions that develop with the participation of anions chemisorbed by the crystal surface when the threshold value of the potential jump in the Helmholtz layer, determined for a given semiconductor−anion combination, is exceeded. In this case, the threshold value of the potential jump for the beginning of cooperative reactions of nucleophilic substitution, with a synchronous attack of compact groups of chemisorbed anions-nucleophiles on antibonding or non-bonding (depending on the position of their levels in the semiconductor conduction band) orbitals of coordination-saturated atoms of the near-surface layer of the crystal, turns out to be below the potential jump that initiates the start of the usual anode etching process with the holes capture by lattice atoms separated from the surface. However, even in this case, the question of the physical reason for the conductivity loss by interlayers remaining between the pores growing deep into the crystal of the degenerate semiconductor remains open.

1. Conditions for the electrical conductivity absence in thin layers of degenerate semiconductors

Let us consider degenerate silicon using a donor impurity as an example. If the electron is localized at a donor site, then it is described by a hydrogen-like wave function and has a certain binding energy E_D. If the concentration of impurities is continuously increased, then starting from a certain concentration, the wave functions of electrons localized on donors begin to overlap. This means that the electrons localized at the sites begin to interact with each other. As a result, the bound state of the electron on the

donor disappears and the electrons are pushed into the conduction band. This state corresponds to the case of a heavily doped semiconductor, and the conductivity has a metallic nature, and depends weakly on temperature [17–19].

In this case, how many electrons are in the conduction band (holes in the valence band), the same number of randomly located ionized donor (acceptor) sites is. These randomly located charged centers create a fluctuating potential in the lattice that affects the movement of electrons. At low temperatures it turns out that the greater the concentration of impurities in a degenerate semiconductor is, the less the impurity field affects the conductivity of charge carriers. The determining role in this case is played by the ratio between the kinetic energy of electrons $K_{e,h}$ and their potential energy in the impurity field $U = e^2/(\varepsilon r)$, where r — distance to the nearest site. If $K_{e,h} \gg U$, then the electrons do not feel the field of charged impurities and move almost freely. Since the charge carriers are degenerate, they fill the states in the conduction band up to the level of the chemical potential μ. In this case, the maximum kinetic energy of an electron is approximately equal to the Fermi energy: $K_{e,h} \approx E_{Fe,h}$. In the case of heavy doping, the distance to the nearest site is $r \sim N^{-1/3} = n^{-1/3}$, where N — impurity concentration, n — electron concentration [17]. If the impurity concentration is such that $r \sim N^{-1/3} < d$, where d is the wall thickness, then in the expression for the potential energy U we can replace r by d:

$$U = \frac{e^2}{\varepsilon d}. \tag{1}$$

The Fermi energy depends on the concentration of charge carriers and is equal to

$$E_{Fe,h} = \frac{\hbar^2}{2m_{e,h}}(3\pi^2 n_{e,h})^{2/3}. \tag{2}$$

Here $\hbar$ — Planck's constant, $m_{e,h}$ — effective electron (hole) mass, $n_{e,h}$ — concentration of electrons (n_e) and holes (n_h). Expression (2) is valid for a strongly degenerate semiconductor when $\mu \gg kT$ and the particle distribution function $f(\varepsilon)$ are replaced by a step [17].

In the process of electrochemical etching of silicon, with a decrease in the spatial dimensions of the silicon layer, in our case with a decrease in the thickness of the pore walls, the binding energy of the electron with ionized donors increases with a decrease in the wall thickness d. For some wall thickness d_{cr} the potential energy of the electron (hole) in the impurity field is equal to the kinetic energy

$$\frac{e^2}{\varepsilon d_{cr}} = \frac{\hbar^2}{2m_{e,h}}(3\pi^2 n_{e,h})^{2/3}. \tag{3}$$

When the wall thickness is $d < d_{cr}$, the potential energy of interaction between the electron and the donor in the pore walls becomes greater than the kinetic energy of charge carriers. Under these conditions, a metal−dielectric
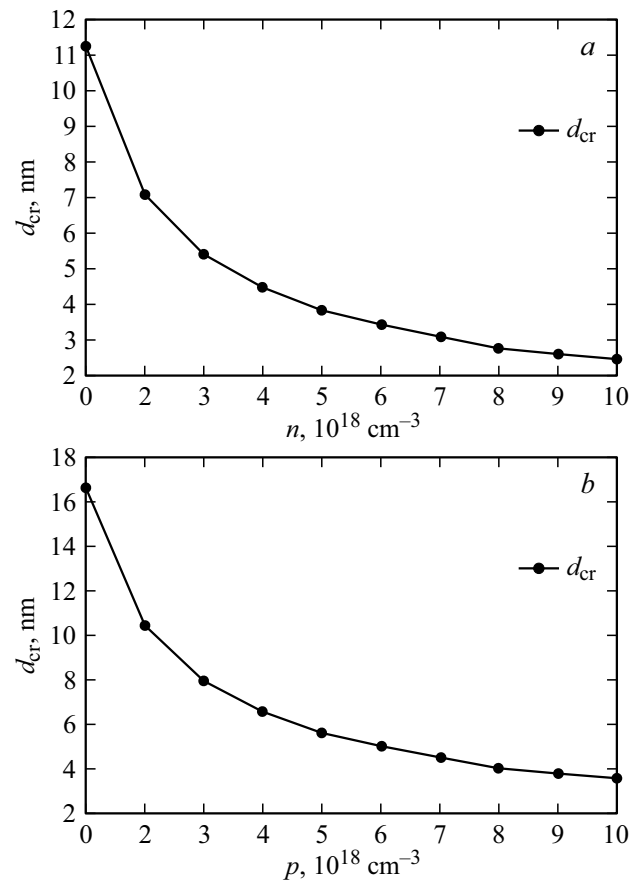
Figure 2. Minimum pore wall thickness d_{cr} vs. the concentration of electrons (donors) (*a*) and vs. the concentration (of acceptors) in the initial silicon (*b*).

phase transition (Mott phase transition) occurs in the system [17–19]. As a result, the electric current in the system is blocked, and the etching processes in the space between the approaching pores stop. The arguments presented here about the interaction of electrons and charged donors in pore walls are obviously also valid for holes and acceptor impurities.

Note that for electrons in silicon the energy minimum is located almost at the edge of the Brillouin zone, and the energy spectrum is not spherically symmetric. The effective mass of the electron along the symmetry axis $\Delta(m_{\|})$ differs from the effective mass in the transverse direction $(m_{\perp})$. Expressions (2) and (3) for electrons include the effective mass of the density of states $m_d = (m_{\|}m_{\perp}^2)^{1/3}$.

It follows from condition (3) that the critical wall thickness d_{cr} depends on the concentration of charge carriers, i.e. on the initial concentration of impurities in silicon; dcr decreases with dopant concentration increasing.

Fig. 2 shows the minimum possible pore wall thickness d_{cr} vs. the donor concentration (Fig. 2, *a*) and vs. the acceptor concentration in the initial silicon (Fig. 2, *b*). As follows from the Figures, in both cases the stationary wall thickness decreases with impurity concentration increasing.

Moreover, with equal concentration of free charge carriers in the range $10^{18}-10^{19}\,\text{cm}^{-3}$ the minimum thickness of the pore walls for *p*-type silicon should be by one and a half times larger than for *n*-type silicon. Indeed, experience shows that at the level of doping of initial silicon crystals $\sim 10^{19}\,\text{cm}^{-3}$ the porous layers with high porosity ($> 70\%$) obtained on *p*-substrates remain mechanically stable upon drying in air, while the layers obtained on *n*-type substrates are destroyed upon drying under the action of surface tension forces.

The following parameters were used when plotting the graphs [20]: $m_h = 0.5m_0$, $m_{\parallel} = 0.98m_0$, $m_{\perp} = 0.19m_0$, $\varepsilon = 11.7$.

Conclusion

The dependences of the minimum thicknesses of the pore walls growing into crystals of degenerate semiconductors during their stationary electrochemical etching on the concentration of the dopant are identified.

When the space between the pore channels moving deep into the crystal is reduced, the potential energy of the electron interaction with the donor (or the energy of the hole interaction with the acceptor) in the pore walls can become greater than the kinetic energy of charge carriers. Under these conditions, a metal−dielectric phase transition (Mott phase transition) occurs in the system [17–19]. As a result, the electric current in the system is blocked, and the etching processes in the space between the approaching pores stop.

Expressions are obtained for the critical thickness of pore walls in semiconductor materials of *n-* and *p*-type conductivity, in the presence of degeneracy of the gas of free charge carriers (3).

The proposed concept of pore wall thickness limitation in the process of electrochemical pore formation complements the well-known model of closure of space charge regions from neighboring pores, and makes it possible to consistently explain the formation of porous layers in heavily doped degenerate semiconductors.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] X.G. Zhang. *Electrochemistry of Silicon and Its Oxide* (Kluwer Academic Publishers NY., Boston-Dordrecht-London-Moscow,, 2004)

[2] Ed. by G. Korotcenkov. *Porous Silicon. From Formation to Aplication* (CRC Press, 2020), v. 1, 440 p.

[3] L. Santinacci, T. Djenizian. Comptes Rendus Chimie, **11** (9), 964 (2008). https://doi.org/10.1016/j.crci.2008.06.004

[4] V. Parkhutik, Sol. St. El., **43**, 1121 (1999).

[5] J.-N. Chazalviel, R.B. Wehrspohn, F. Ozanam. Mater. Sci. Eng. B, **69−70**, 1 (2000).

[6] V. Lehmann, R. Stengl, A. Luigart. Mater. Sci. Eng. B, **69**, 11 (2000).

[7] K.W. Kolasinski. Surf. Sci., **603**, 1904 (2009). DOI:10.1016/j.susc.2008.08.031

[8] H. Föll, M. Christophersen, J. Carstensen, G. Hasse. Mater. Sci. Eng., R39, 93−141 (2002).

[9] P.M. Fauchet, J. von Behren. Phys. Stat. Sol. (b), **204**, R7 (1997).

[10] A.G. Cullis, L.T. Canham, P.D.J. Calcott, J. Appl. Phys., **82**, 909 (1997).

[11] D. Kovalev, V.Y. Timoshenko, N. Künzner, E. Gross, F. Koch. Phys. Rev. Lett., **87** (6), 068301/1 (2001).

[12] Yu.Ya. Gurevich, Yu.Ya. Pleskov. *Fotoelektrokhimiya poluprovodnikov* (Nauka, M., 1983) (in Russian)

[13] G.S. Higashi, Y.J. Chabal, G.W. Trucks, K. Raghavachari. Appl. Phys. Lett., **56**, 656 (1990).

[14] V.P. Ulin, S.G. Konnikov. FTP, **41** (7), 854, 867 (2007) (in Russian).

[15] V.P. Ulin, N.V. Ulin, and F.Yu. Soldatenkov, FTP, **51**, 481 (2017). (in Russian)

[16] V.M. Freiman, G.G. Zegrya, V.P. Ulin, A.G. Zegrya, N.V. Ulin, Yu.M. Mikhailov. ZhTF, **89** (10), 1575 (2019) (in Russian). DOI: 10.21883/TP.2023.02.55482.224-22

[17] G.G. Zegrya, V.I. Perel. *Osnovy fiziki poluprovodnikov* (Fizmatlit, M., 2009) (in Russian)

[18] B.I. Shklovsky, A.L. Efros. *Elektronnye svojstva sil'nolegirovannykh poluprovodnikov* (Fizmatlit, Moscow, 1979) (in Russian)

[19] V.F. Gantmakher. *Elektrony v neuporyadichennykh sredakh* (Fizmatlit, Moscow, 2003) (in Russian)

[20] *New Semiconductor Materials. Biology systems. Characteristics and Properties.* http://www.matprop.ru/Si