Formation of channel silicon to create filter layers

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The features of the formation of porous layers on substrates of low doped silicon of *n*-type conductivity by anodic etching using illumination are considered. The formation of microporous silicon layer on the walls of macropores was found. It is shown that the illumination modes strongly influence the morphological parameters of the obtained layers. After exposure to alkali, macroporous layers with pore diameters up to 550 nm were obtained, which can be used to create filter layers.

Keywords: porous silicon, electrochemical etching, gas filters, scanning electron microscopy.

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Macroporous silicon is a promising material for the production of various devices due to the opportunity of varying the morphology and properties of porous layers. Based on macroporous silicon (pore size > 50 nm), devices such as lithium-ion batteries, gas and biosensors, as well as filters and sorbents [1–3] are created.

Important characteristics for filter layers are throughput, adsorption capacity, and mechanical strength [4]. Filtering gas-permeable membranes should selectively retain toxic or explosive gases, i. e. combine high throughput for some gases and high adsorption capacity for others. Gas transport properties are determined by the diameters of through pores (channels) and porosity. Adsorption capacity increases with increasing specific surface area, porosity, decreasing pore sizes, and creating adsorption centers [5]. Membranes based on macroporous silicon with through channels $\sim 1\,\mu$m have high gas transport properties, but have a low specific surface area [6] and weak adsorption capacity. The gas transport properties of membranes with channel diameters < 100 nm have low throughput due to the comparability of pore diameters with the mean free path of molecules in air under normal conditions (~ 70 nm) and capillary effects [7]. Macroporous silicon with through channels of intermediate sizes ($100-1000$ nm) combines the morphological characteristics required for filter layers.

On silicon substrates *p*-type conductivity, using electrochemical etching, it is possible to create either mesoporous layers with a low pore density $10^6-10^7\,\mathrm{cm}^{-2}$ and pore diameters $> 1\,\mu$m, or mesoporous layers with pores with a diameter < 50 nm. At the same time, both microporous layers and layers with pores up to 200 nm in size can be formed on silicon substrates of the *n*-type conductivity. The porosity of layers obtained on lightly doped silicon of electronic conductivity type without additional generation of holes is extremely small and amounts to $< 10\%$, which limits its use in many areas [8].

Illumination is an effective way to generate holes in silicon of the *n*-type conductivity, which allows the porosity and pore diameter to be varied over a wide range. Previous studies have shown the opportunity of forming porous membranes based on macroporous silicon with pore diameters in a layer of $100-300$ nm, sorbing nitrogen dioxide [9]. This work examines the features of the formation of channel silicon using illumination to create filter layers with pores with a diameter of up to 550 nm.

Porous silicon samples were formed on plates of monocrystalline silicon doped with phosphorus with a resistivity of $1\,\Omega\cdot$cm. Porous layers were obtained by the method of anodic etching in the electrolyte of the composition $HF:C_2H_5OH$ 1 : 1. The etching process took place in a double-tank electrochemical cell equipped with a sapphire window for silicon illumination. The silicon plate was illuminated from the front side[10]. The current density during etching for all samples was 100 mA/cm^2, the etching duration was — 15 min. The influence of the intensity of the light flux from an incandescent lamp with a power of 300 W was studied. The intensity of the light flux varied with changes in the distance between the lamp and the silicon wafer, as well as by applying different voltages to the lamp. After preparation, the samples were kept in 0.1 M NaOH solution for 5 min. The morphology of the samples was studied using a scanning electron microscope (SEM) JEOL JSM-6610-L and software packages SmileView and Origin 6.1. Pore density was measured from SEM images of the sample surface. The pore diameter at various depths was determined from SEM-images of the cross section of a porous silicon layer. The pore diameter values were averaged over at least 30 measurements at each depth.

From the SEM images (Figure 1) it is clear that the surface of the porous silicon samples before exposure to NaOH is rough. The average pore diameter at the surface does not exceed 200 nm, and also gradually increases with depth. The pores propagate along the crystallographic direction $\langle 100\rangle$, there is no branching of the side pores (Figure 1, *c*). After exposure to an alkali solution, the

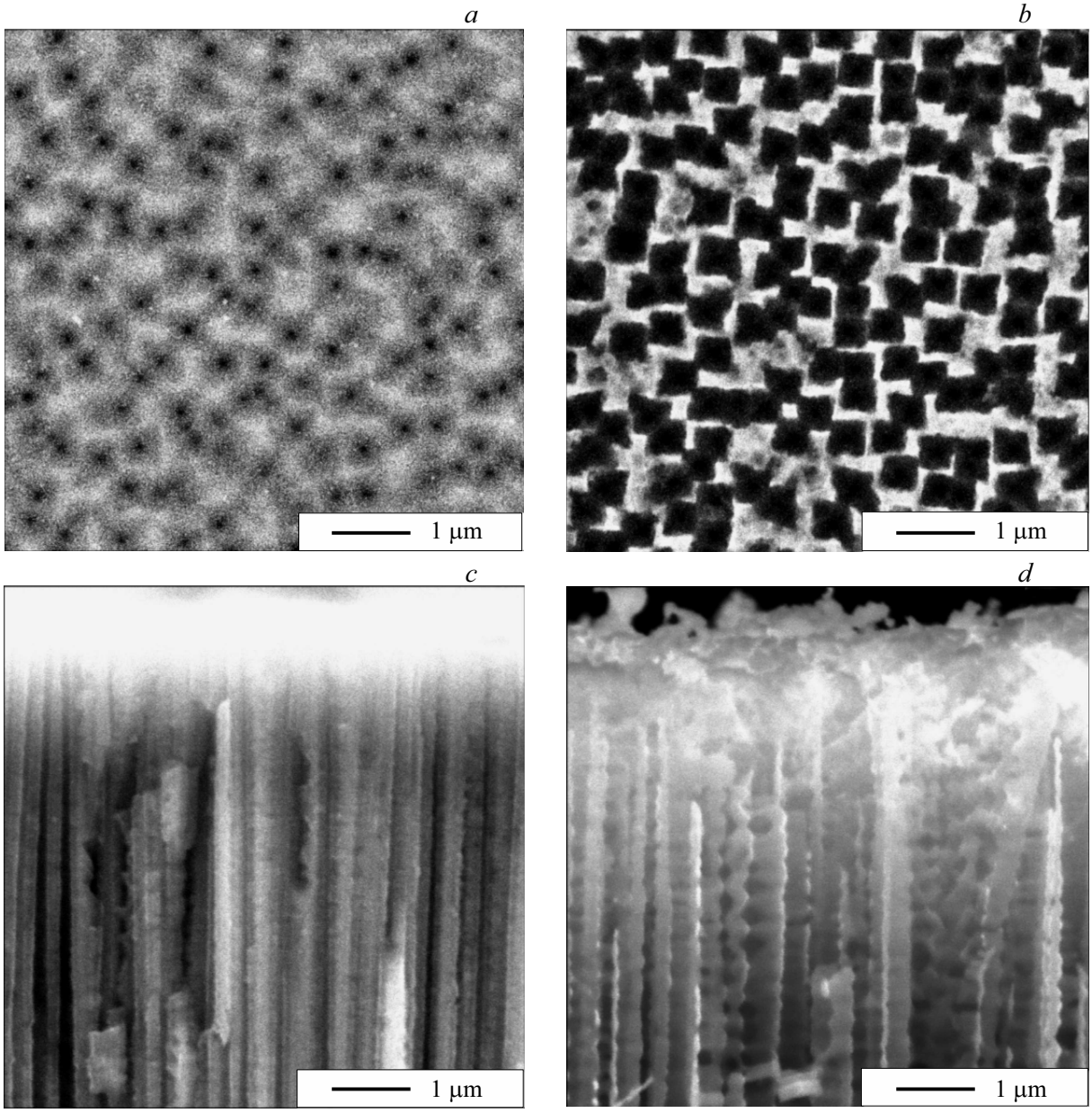

Figure 1. SEM-images of porous silicon obtained with illumination with an incandescent lamp from a distance of 40 cm at a voltage of 140 V; *a, c* — before exposure to NaOH, *b, d* — after; *a, b* — top view, *c, d* — transverse section.

pore walls are clear, the pore diameter at the surface increases significantly (Figure 1, *b, d*), the cross section of the pores is approximately square. Pyramidal holes appear on the walls of the pores (Figure 1, *d*). As is known, during electrochemical etching of silicon under certain lighting conditions, macropores are formed, covered with a layer of microporous silicon [11]. The surface roughness and dark halos around macropores (Figure 1, *a*) are explained by the greater porosity of microporous silicon on the walls of macropores compared to the near-surface layer. Microporous silicon easily dissolves in alkali solutions. Moreover, if the NaOH concentration is low enough, the walls of macroporous silicon do not dissolve. An increase in pore diameter indicates the dissolution of microporous silicon.

Figure 2 shows a graph of the dependence of the macropore diameter on the layer depth at various voltages applied to an incandescent lamp in the process of producing porous silicon. It follows from this that the thickness of microporous silicon on the walls of macropores decreases with depth, probably due to the absorption of light during the formation of the porous layer. Without illumination, microporous silicon is also formed on the walls of macropores to a depth of $\sim 20\,\mu$m. Based on the data on the change in the diameter of macropores with depth, taking into account the quasi-square cross section of the pores and

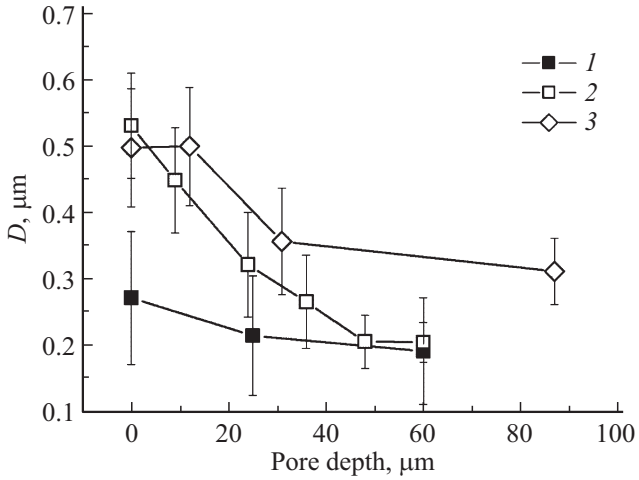

Figure 2. Change in pore diameter after exposure to a NaOH solution with layer depth depending on the illumination mode: *1* — without illumination, *2* — 140 V, *3* — 180 V, distance to the lamp 40 cm.

the constancy of the pore density with depth, it is possible to estimate the porosity p of the macroporous layer using the formula [9]

$$p = \frac{n}{H}\int_0^H (\overline{D}^2 + \sigma^2)dh, \qquad (1)$$

where p — porosity, n — pore density, $\overline{D(h)}$ — average pore diameter at depth$h$, σ — standard deviation of the transverse pore size, H — thickness of the macroporous layer.

Table 1 shows the values of porosity, density and pore diameter at various voltages applied to the lamp during the anodizing process. The increase in pore density with light flux density is explained by an increase in the concentration of photoinduced minority charge carriers (holes) necessary for the dissolution of silicon. The diameters of the pores at a low luminous flux density increase, but when the distance between the pores decreases, they stop increasing due to the „repulsion“ between them. This occurs when the concentration of holes in the pore walls becomes critically low [12,13].

As can be seen from Table 2, the silicon etching rate decreases with increasing distance to the lamp, and therefore with decreasing luminous flux density. As the light flux density increases, the thickness of the microporous silicon layer increases [11]. Meanwhile, a redistribution of the current passing through the walls and bottoms of macropores occurs, which leads to a decrease in the rate of etching of the silicon wafer deep into the substrate.

Membranes with through channels were formed on the basis of the described porous silicon. To do this, a spherical hole was mechanically polished on the back side of a porous silicon sample before opening the porous

Table 1. Dependence of the diameter (D) and pore density (n) on the voltage supplied to the lamp (U), distance to the lamp 40 cm

U, V	0	100	140	160	180
D, μm	0.4	0.42	0.53	0.52	0.49
$n, 10^8$ cm^{-2}	0.98	1.09	1.28	1.39	1.67
p, %	5.6	12	17	27.5	31.2

Table 2. Dependence of speed (v), pore density (n) and thickness of the microporous layer (w) on the distance to the lamp (d) with a voltage of 220 V applied to it

d, cm	v, μm/min	$n, 10^8$ cm^{-2}
25	6.9	1.4
40	11.5	1.88
Without illumination	12.8	0.98

layer. At the final stage, the well was subjected to ion beam milling with Ar^+ ions with an energy of 5 keV to remove finely dispersed silicon remaining after mechanical treatment. Figure 3 shows SEM images of the -membrane. The thickness of the membrane is $\sim 60\,\mu$m, the diameter of the channels on the upper surface of the membrane is $0.57 \pm 0.08\,\mu$m, on the well side — $0.25 \pm 0.08\,\mu$m.

The features of the formation of porous silicon layers under illumination conditions are reviewed. The formation of macropores along the crystallographic direction ⟨100⟩ and a layer of microporous silicon on the walls of macropores was discovered during electrochemical etching of silicon n-conductivity of type under illumination from the front side. The density of macropores and the thickness of microporous silicon depend on the light flux density. By removing

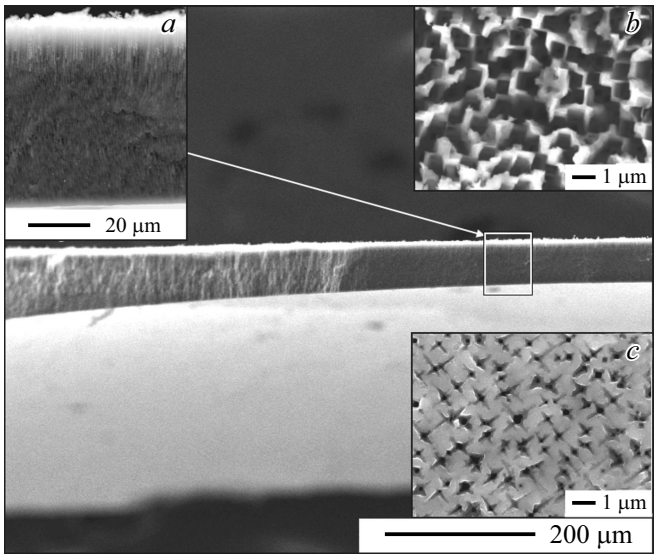

Figure 3. SEM-images of a membrane cleavage with through channels: *a* — enlarged image of the cleavage, *b* — top view, *c* — bottom view.

microporous silicon in an alkaline solution, macroporous layers with pore diameters from 300 to 550 nm, channel density from $1 \cdot 10^8$ to $2 \cdot 10^8$ cm^{-2} were obtained. Thus, the proposed method makes it possible to form porous silicon containing macroporous channels coated with a layer of microporous silicon. By changing illumination modes, it is possible to vary the thickness of microporous silicon, and therefore the diameter of the channels formed after exposure to alkali. Porous layers with these characteristics can be used to create gas-permeable filter layers.

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Conflict of interest

The authors declare that they have no conflict of interest.

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