

Controlled nonuniformity in macroporous silicon pore growth

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Photoelectrochemical etching of uniform prestructured silicon wafers in hydrofluoric acid containing solutions yields periodic structures that can be applied to two- and three-dimensional photonic crystals or microfluidics. Here we demonstrate experimentally macroporous silicon etching initiated by a nonuniform predefined lattice. For conveniently chosen parameters we observe a stable growth of pores whose geometrical appearance depends strongly on the spatially different nucleation conditions. Moreover, we show preliminary results on three-dimensionally shaped pores. This material can be used to realize hybrid photonic crystal structures and incorporate waveguides in three-dimensional photonic crystals. © 2005 American Institute of Physics.

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Porous silicon,^{1,2} and in particular, macroporous silicon,^{3,4} has attracted a lot of attention as a unique possibility to structure silicon.⁵ This material system has been applied to optical shortpass filters⁶ as well as to two-dimensional (2D) and three-dimensional (3D) photonic crystals.^{7,8} All these applications depend on the uniformity of the porous material. This property results from the perfect, lithographically arranged, uniform inverted pyramids acting as nuclei for the pore growth and the self-stabilized photoelectrochemical etching process used. The so-manufactured 3D photonic crystals show complete band gaps of about 5%. Recently, we proposed large 3D photonic band gaps in diamondlike structures, which may be fabricated using complex structured silicon wafers.⁹

Here we present a detailed investigation focused on spatially different nucleation conditions. A simple quadratic lattice with a basis of two nonequally sized inverted pyramids is defined. We will demonstrate under which experimental conditions a stable pore growth is observed. Moreover, the nonequally sized nuclei result in a significant initial offset in height between adjacent pores. We will answer the question of how this considerable difference is affected by the self-stabilized interaction between the pores. This approach is well suited to incorporate air defects in photonic band-gap materials in two and three dimensions acting as resonators or waveguides. In particular, this is a step towards the experimental realization of the predicted 2D photonic crystal hybrid structures suggested by Trifonov *et al.*¹⁰

Typically macroporous silicon is grown in a photoelectrochemical etching process.⁵ An arbitrary 2D lattice is defined lithographically on the (100)-oriented *n*-type silicon wafer. A subsequent anisotropic etching in potassium hydroxide (KOH) forms inverted pyramids acting as nuclei for the pore growth. This structured frontside is exposed to hydrofluoric acid (HF). Illuminating the backside of the silicon wafer generates electron-hole pairs. The electrons are extracted by the applied anodic bias whereas the electronic holes—the minority charge carriers—diffuse through the whole wafer to the silicon electrolyte interface. Due to the depletion layer at this interface an extended space-charge

region (SCR) builds up and accelerates the electronic holes and concentrates them mainly to the pore tip promoting the silicon dissolution there. The SCR passivates the pore walls against dissolution. The mentioned self-stabilizing effect is composed of the homogeneous carrier supply, the SCR, and the growth velocity, which depend on the concentration and the temperature of the HF. The diffusion-limited transfer of dissociated HF molecules involves a declining HF concentration with pore depth and hence a reduced growth velocity. Assuming that a single pore is a little bit deeper than the surrounding ones, it will consume more charge carriers due to the SCR effect. Therefore, the HF concentration will drop in this pore leading to a slower pore growth, less charge carriers can then be consumed, and hence they are shared over the adjacent pores. This stabilization levels any inhomogeneities in depth and guarantees the uniform appearance of macroporous silicon.

Assuming a planar one-dimensional 1D Schottky contact, present at the silicon electrolyte interface, relates the width W_{SCR} of the SCR to the doping level N_D and the acting voltage V as the difference of the applied voltage and the built-in voltage $V = V_{\text{appl}} - V_{\text{in}}$, where ϵ_{Si} is the dielectric constant of silicon, ϵ_0 is the dielectric constant of the vacuum, and e is the elementary charge:

$$W_{\text{SCR}} = \sqrt{\frac{2\epsilon_0\epsilon_{\text{Si}}V}{eN_D}}. \quad (1)$$

The spacing between the pores can be chosen from 10 μm down to 0.5 μm if the width of the SCR is adjusted. Figures 1(a)–1(c) show three unit cells having the same overall porosity (the ratio of air volume fraction to the volume of the unit cell), but different numbers of pores indicated by the black squares in the gray silicon matrix. Although the porosity is equal for all these lattices quadrupling the number of pores, as shown in Fig. 1(b) requires a higher doping level, to etch the pores in a stable fashion.

In the experiments described below we defined the lattice depicted in Fig. 1(c) onto the silicon wafer surface realizing different initial conditions depending on the size of the inverted pyramid [Figs. 1(d) and 1(e)]. The lattice constant is 6 μm , whereas the side length of the big inverted pyramid is 3 μm . The side lengths of the small inverted pyramids are either 0.76 μm in lattice *A* or 0.56 μm in lattice *B* at the

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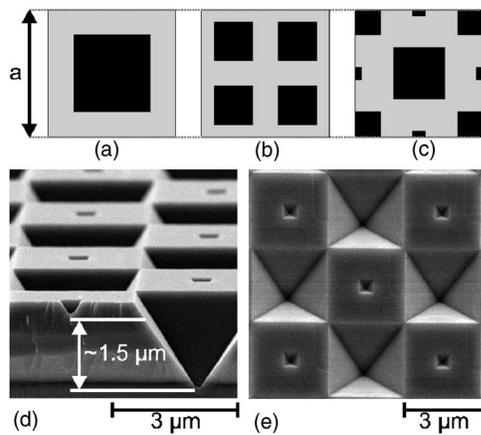


FIG. 1. (a)–(c) Schematic depiction of unit cells of pores (black) in a silicon matrix (gray) having all the same porosity of 0.36. (d), (e) Scanning electron micrographs (SEM) of the initial hierarchically structured silicon surface. The lithographically realized offset between the tips of the inverted pyramids (pits) is about $1.5 \mu\text{m}$.

same wafer. This significant difference in the lateral dimensions between the big and small inverted pyramids creates an initial vertical offset of about $1.5 \mu\text{m}$ between the tips [Fig. 1(d)].

All experiments were performed in HF of $c_{\text{HF}}=5 \text{ wt } \%$ at a temperature $T=8^\circ\text{C}$ on silicon wafers with a specific resistivity of $\rho_1=5 \Omega \text{ cm}$ and $\rho_2=1 \Omega \text{ cm}$, respectively. Although lattice constants of $3 \mu\text{m}$ up to $6 \mu\text{m}$ grow in a stable fashion on silicon wafers with a specific resistivity of $\rho_1=5 \Omega \text{ cm}$, we observed no pores initialized by the small inverted pyramids. This is due to the extension of the SCR, which is 2.6 times wider [after Eq. (1)] than for substrates with a doping level of $1 \Omega \text{ cm}$. Hence, the big pyramids determine the SCR and consume all of the generated minority charge carriers.

In contrast, we observe stable growth of $100\text{-}\mu\text{m}$ deep pores for all sizes of inverted pyramids using substrates with the higher doping level corresponding to $1 \Omega \text{ cm}$ shown in Fig. 2(a). Instead of the expected equal diameters of all pores, their resulting distribution reflects the ratio of the side lengths of the two kinds of inverted pyramids, which is about 4 (5) for lattice A (B). The diameter of the thin pores initialized by the small inverted pyramids of field a is $0.68 \mu\text{m}$ and the diameter of the big ones is $2.5 \mu\text{m}$ [Fig. 2(b)]. A spacing of $3 \mu\text{m}$ between the pores is the upper limit for a stable etching process. In particular, the thick pores show a tendency to branch.

Moreover, this experiment demonstrates that there is still a certain offset in the depth of these pores. This offset is caused by the different initial conditions. In contrast to small deviations in homogeneous samples, the self-stabilization does not level the initial offset. We investigated this unexpected behavior by measuring the height of the offset depending on several experimental parameters, including the size of the small inverted pyramids, the applied constant anodic bias, and the depth of the pores.

Figure 3 shows the corresponding values obtained from scanning electron micrographs. The initial offset of about $1.5 \mu\text{m}$ decreases with pore depth for all parameters during a transition period, in which cylindrical pores evolve from the sharp inverted pyramids. After this transition of approximately $30 \mu\text{m}$ a stable and constant offset of about $0.7 \mu\text{m}$

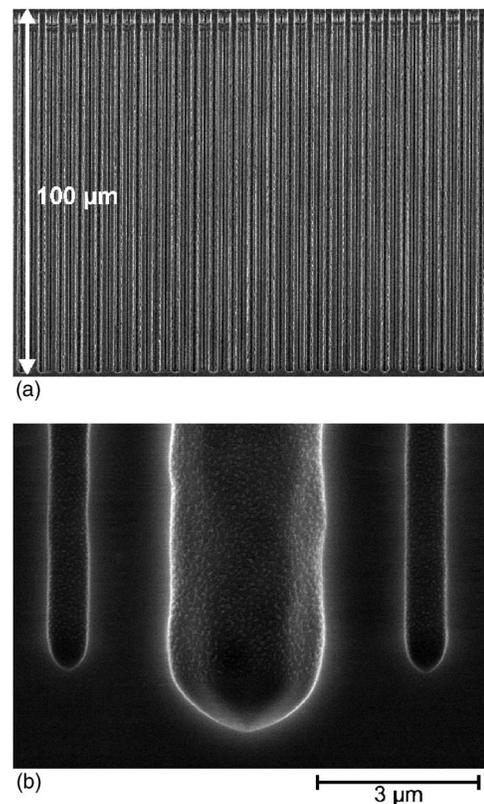


FIG. 2. SEM images of etched and cleaved silicon wafers. (a) The pores grow in a stable fashion up to $100 \mu\text{m}$ in depth with a stable offset. (b) The bottom of the pores in a depth of $10 \mu\text{m}$.

results if a bias of 2.5 V is applied. This confirms that all pores have the same growth velocity for these specific parameters.

The transition period is shortened when applying a voltage of 3.5 V . However, the resulting offset reduces more and more over depth. In this case, the pores with small diameter grow faster than the others. Recently, we have shown that for such experimental conditions a substantial amount of charge carriers is generated by the high voltage itself¹¹ enabling electric breakdown. This is more pronounced for the thin pores due to the smaller radius of the curvature at the pore tip.¹² This behavior is observed for both sizes of the small inverted pyramids for lattices A and B. However, the offset is larger for a pit size of $0.56 \mu\text{m}$ than for $0.76 \mu\text{m}$, which confirms that it is indeed determined by the initial conditions of the structured silicon surface.

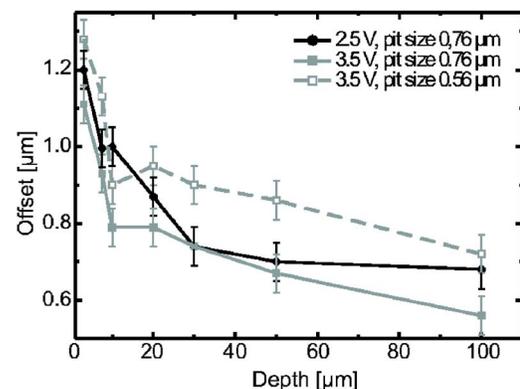


FIG. 3. Measured offset depending on depth, applied voltage, and initial pit size.

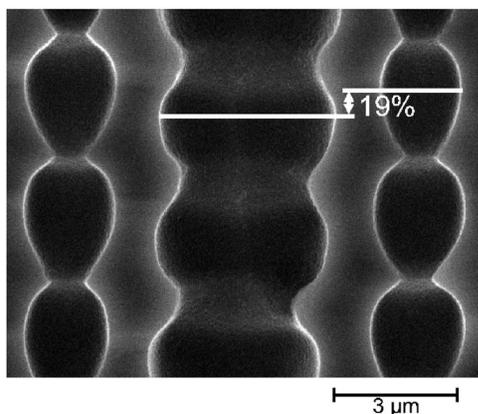


FIG. 4. SEM image of a modulated etched macroporous silicon sample. The maximum diameter of the thin pore occurs at a different depth than the maximum diameter of the thick one.

Moreover, we investigated the dependence on porosity and etched several samples at a constant voltage of 2.5 V realizing a stable offset in a depth of 30 μm , but we incremented the overall porosity for each sample and hence the diameter is increased for the thin and the thick pores. The created offset is constant and independent of the porosity as long as the diameter of the thin pore is smaller than the side length of its initial inverted pyramid.

As mentioned above, the electrochemical dissolution of silicon requires electronic holes—the minority charge carriers—which are generated by light absorption. Thus it is possible to vary the amount of consumed holes by changing the intensity of the backside illumination. Applying an etching-current-voltage profile we manufactured a periodic diameter variation in both kinds of pores as shown in Fig. 4. Due to the stable offset the maximum diameter in the thin pores occurs at a different depth than the maximum of the thick pores. This phase shift is estimated to be 19%, but it depends on the period of the modulation.

The diameters of the pores cannot be chosen independently from each other, because the porosity of the unit cell is given by the supply of charge carriers. The distribution of charge carriers is ruled by the SCR, which in turn depends on the geometrical situation on one hand and the applied voltage and the doping level [see Eq. (1)] on the other hand. Thus the ratio of the diameters is given by the ratio of the lateral dimensions of the initial inverted pyramids. Due to their lithography based production it is possible to manufacture every side length allowing for a very sensitive control. A mod-

erate difference in size of the inverted pyramids may result in a less critical etching process but may keep the effect of different pore diameters, allowing designed waveguide structures.

In conclusion, this investigation shows that complex structured silicon wafers can be converted into a porous material. For conveniently chosen parameters a stable pore growth is observed. Due to the complex initial conditions the stability involves an offset whose height depends on the initial dimensions of the lithographically predefined inverted pyramids. The well-known self-stabilizing effect operating during usual macroporous silicon etching starting from a planar surface with nucleation at the pits of equal depth does not level these differences. Moreover, the lateral dimensions of these pyramids determine the diameter of the manufactured pores. This property can be applied for the fabrication of air defects and waveguides in photonic crystals. In particular, this difference in combination with 3D macroporous silicon etching permits to sculpture silicon three dimensionally realizing reliably different shapes in the same depth resulting in complex 3D structures for photonic crystal or microfluidic applications.

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