Controlling macropore formation in patterned n-type silicon: Existence of a pitch-dependent etching current density lower bound

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ABSTRACT

Experimental results on back-side illumination electrochemical etching of patterned (hole square-lattices with pitch $p$ from 2 to 50 $\mu$m) n-type silicon substrates in HF-based electrolytes are reported. Experiments reveal the existence of a threshold current density $J_{\text{pitch}}$, which is strictly correlated to the pattern pitch, above which pore formation can be finely controlled beyond commonly accepted state-of-the-art rules. For instance, using the same silicon substrate, pore array with density $D$ spanning over two orders of magnitude (from 0.0025 $\mu$m$^{-2}$ up to 0.25 $\mu$m$^{-2}$) can be etched above a minimum porosity $P_{\text{min}}$, and, in turn, a minimum pore diameter $d_{\text{min}}$ which depends on the pattern pitch. Etching current densities below such a critical value give rise to uncontrolled pore growth. The occurrence of the threshold current density $J_{\text{pitch}}$ is interpreted in terms of current burst model.

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1. Introduction

Back-side illumination etching (BSIE) of n-type silicon substrates in HF-based electrolytes has been used for two decades, since 1990, for the fabrication of regular macropore arrays [1–4], and more recently, since 2002, for the fabrication of 2D/3D silicon microstructures [5–8]. Despite the progress in understanding the mechanism of the electrochemical dissolution of silicon in HF-based electrolytes [9,10], it is somewhat hard to predict the result of the etching, but for a strict range of etching parameters and substrate features, even focusing the attention to macropores formed in n-type silicon by BSIE, that is the best-controlled species of pores.

One of main challenges of the BSIE as regards patterned substrates is related to the dependence of feasible pores (in terms of size and pitch) on the doping density of the silicon substrate [11,12]. So far, experiments have been reported showing that the ratio between the density $D$ ($\mu$m$^{-2}$) of stable pores and doping concentration $N_D$ ($\text{cm}^{-3}$) is nearly constant, with a value of $10^{-16}$ (first Lehmann rule: $D = N_D \times 10^{-16}$) [111]. Following this rule of thumb, ordinary substrates with resistivity of a few $\Omega$ cm ($N_D \approx 10^{15}$ cm$^{-3}$) allow pores with density of $10^{-1}$ $\mu$m$^{-2}$ to be etched, which means a pitch of about $3 \mu$m for square-lattice arranged pores. Another empirical formula (second Lehmann rule: $d = P \cdot \sqrt{4 \pi N_D}$) links the diameter $d$ of feasible pores (supposed cylindrical) to the pitch $p$ of square-lattice arranged pores and to the etching current density $J$ via $P = J / J_{\text{ps}}$, where $P$ is the porosity of the etched lattice, $J$ and $J_{\text{ps}}$ are the etching and electropolishing current densities, respectively [11]. The second Lehmann rule allows in principle to etch pores with any diameter by adjusting the value of $J$ with respect to $J_{\text{ps}}$, for a given pitch. Although deviations from these rules have also been reported [10,12], it seems not possible to produce n-macropore arrays by BSIE with $d \gg 1 \mu$m and $P \gg 5 \mu$m using ordinary (resistivity of a few $\Omega$ cm) silicon wafers, according to the state-of-the-art literature.

In this work, experiments on BSIE of patterned (square-lattice arranged holes with different pitch) n-type silicon substrates with fixed resistivity were carried out with the aim of highlighting existing relationship between the pattern characteristics (i.e. pitch) and the etching results, in terms of density, diameter and porosity. Experiments evidenced the occurrence of a threshold current density $J_{\text{pitch}}$ whose value is strictly correlated to the pitch of the predefined pattern, above which pore etching can be finely controlled beyond accepted state-of-the-art rules. The current density $J_{\text{pitch}}$ has been interpreted in terms of current burst model.

2. Experimental

The starting material was a CZ-grown, n-type silicon wafer with resistivity of $3 \div 8 \Omega$cm, 550 $\mu$m thick, (100) oriented, with a silicon dioxide layer (~100 nm thick) on top. Hole lattices with pitch between 2 $\mu$m and 50 $\mu$m were defined on the silicon surface by means of a photolithographic step followed by both a buffered hydrofluoric acid (BHF) and hydroxide potassium (KOH) etch. The KOH etching time was tuned to obtain full pyramidal notches. A further BHF etch was performed to remove the oxide layer from the silicon surface before electrochemical etching. All patterned substrates were electrochemically etched for 1800 s under back-side illumination (250 W halogen
lamp) by using a solution of HF (48%):H₂O (5:37 by volume) with the addition of 1000 ppm of sodium lauryl sulphate as wetting agent. For any pitch, different etching current density values \( J_0 \) were experimented, which corresponded to different pore diameters, and, in turn, porosities, according to the second Lehmann rule. In order to keep the pore diameter constant all over its depth, the (photogenerated) etching current density was linearly decreased with time, with respect its initial value \( J_0 \), by tuning the lamp power [13,14]. A constant etching voltage of 1.2 V was used for all experiments. After the electrochemical etching the samples were rinsed in ethanol and dried in a convection oven at 60 °C for 10 min. All samples were cleaved to allow SEM (scanning electron microscope) observation of the cross-section. For defect-free samples, from now on intended as samples with array of straight pores having an internal pore surface with peak-to-peak ripple lower than 10%, with respect to the pore diameter, and without missing pores and/or branching, a statistical analysis (mean value and standard deviation calculation) of the pore diameter and porosity values has been performed.

3. Results and discussion

An unexpected result comes out from experiments on 3 ÷ 8 Ω cm substrates patterned with hole square-lattices with different pitches: the density of viable pores can be varied up to two orders of magnitude, from 0.25 \( \mu \text{m}^{-2} \) (pitch of 2 \( \mu \text{m} \)) up to of 0.00025 \( \mu \text{m}^{-2} \) (pitch of 20 \( \mu \text{m} \)), if a current density \( J_0 \) greater than (or equal to) a threshold value \( J_{\text{pitch}} \), which depends on the pitch itself, is used. Fig. 1(b–e) shows SEM cross-sections of defect-free pores with pitch of 4, 8, 16, and 20 \( \mu \text{m} \) etched using current density values equal to \( J_{\text{pitch}} \) as reported in Fig. 3(a). The occurrence of such a threshold current density \( J_{\text{pitch}} \) gives rise to both a minimum diameter and porosity, depending on the lattice pitch, above which stable growth of defect-free pores occurs. Current densities below the threshold \( J_{\text{pitch}} \) lead to an unstable growth.

For instance, as shown in Fig. 2(a) defect-free pores with pitch of 16 \( \mu \text{m} \) can be etched with a minimum diameter (average value) of 4.5 \( \mu \text{m} \) (standard deviation 53 nm), and thus with a minimum porosity (average value) of 6.2% (standard deviation 0.15%). By performing the

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**Fig. 1.** Experimental results (SEM cross-sections) on BSIE of patterned (hole lattices with pitch of 2, 4, 8, 16, 20 and 50 \( \mu \text{m} \)) n-type silicon substrates with resistivity of 3 ÷ 8 Ω cm: (a–e) controlled macropore growth obtained using etching current density values greater than \( p = 2 \mu \text{m} \) or equal to \( p = 4, 8, 16, 20 \mu \text{m} \) the threshold value \( J_{\text{pitch}} \); (f) uncontrolled macropore growth resulting from lattices with pitch of 50 \( \mu \text{m} \), which apparently did not show any threshold current density.
etching of the same pattern using a current density value of 2.26 mA/cm$^2$, which is just below the threshold $J_{\text{pitch}} = 0.062/\mu\text{s} = 3.42$ mA/cm$^2$ ($J_{\text{ps}} = 55$ mA/cm$^2$) (all the other parameters were unchanged), an uncontrolled growth of pores occurs (Fig. 2(b)). Similar results were obtained for all the investigated patterns and are quantitatively summarized in Fig. 3, which shows the average minimum values, and standard deviations as error bars, of the threshold current density $J_{\text{pitch}}$, porosity and diameter over which defect-free pores can be etched, as a function of the lattice pitch. The dashed area represents the region where the etching of defect-free pores is not allowed. $J_{\text{pitch}}$ values (Fig. 3(a), right axis) were obtained from experimental minimum porosity values (Fig. 3(a), left axis) according to the relationship $J_{\text{pitch}} = P_{\text{min}}/\text{uni}^2$ $J_{\text{ps}}$, and result in good agreement with experimental current density values used to etch the samples (maximum error lower than 10%).

Fig. 3 quantitatively demonstrates that, for patterned substrates, pore density is not strictly fixed by doping density of the substrate (as postulated by the first Lehmann rule), which still plays a chief role in the etching, but it also depends on both etching parameters and pattern features. Pores with density ranging over two orders of magnitude can be etched on patterned surfaces if etching current densities over $J_{\text{pitch}}$ are employed. On the other hand, even working with a pore density in agreement with the Lehmann first law, which means a pitch of about 3 $\mu$m in this work, defect-free pores can be only etched over a minimum porosity value strictly depending on the lattice pitch. The second Lehmann rule, that is freely changing the porosity for pore densities in agreement to the first law, seems to be not fully accurate, as demonstrated by the occurrence of the diameter/porosity lower bound. Moreover, while on the basis of the Lehmann rules the density and diameter of pores are independent parameters, Fig. 3 provides evidences that a tight correlation between them exists which depends on the etching parameters, for a given substrate doping.

By best fitting experimental data of Fig. 3(b) with a second order polynomial function, which can be considered as a second order approximation (Taylor expansion) of a physical model at this stage not yet defined, the following relationship between the minimum diameter $d_{\text{min}}$ (in $\mu$m) of viable pores and the pitch $p$ (in $\mu$m) is obtained, at least for the range of pitches investigated in this work:

$$d_{\text{min}} = \alpha - p \beta - p^2, \tag{1}$$

where $\alpha = 0.392 \times 10^{-6}$ and $\beta = 0.00683 \times 10^{-6}$ $\mu$m$^{-1}$ are fitting parameters ($R^2 = 0.9999$). Eq. (1) holds for $0 < p < 28.7$ $\mu$m, the upper bound corresponding to the pitch value $p = \alpha/2\beta$ for which $d_{\text{min}}$ reaches its maximum value. From Eq. (1), for square-lattice arranged
pores with circular section, one can obtain the following relationships between either the current density $J_{\text{pitch}}$ or the minimum porosity $P_{\text{min}}$ and the pattern pitch $p$:

$$P_{\text{min}} = \left(\frac{\pi}{4}\right)\left(\frac{d_{\text{min}}}{p}\right)^2 = \left(\frac{\pi}{4}\right)(\alpha - \beta)p^2 \tag{2}$$

$$J_{\text{pitch}} = P_{\text{min}}J_p = P_p\left(\frac{\pi}{4}\right)(\alpha - \beta)p^2. \tag{3}$$

According to Eqs. (1) and (2), arrays of holes with pitch of 2 μm can be finely etched with pore diameters greater than 0.76 μm and porosities higher than 11.3% (i.e., $J_{\text{pitch}} = 0.113J_p$), as experimentally found in this work (Fig. 1(a)) and according to the literature [10]; moreover, experiments on array of holes with pitch of 50 μm, that is greater than the upper bound of Eq. (1), always resulted in secondary pores growing on the side of the main pore (Fig. 1(f)).

The occurrence of the current density $J_{\text{pitch}}$ can be interpreted using the current burst (CB) model [9,10]. According to such a model, electrochemical silicon dissolution involves the following sequence of events, called current burst: i) direct dissolution of silicon; ii) silicon oxidation; iii) oxide dissolution; and iv) hydrogen passivation of silicon. In the CB model, charge transfer, and thus current flow, is intrinsically inhomogeneous in time and space; in particular, there are instants when no charge is transferred in some areas at some time. The lateral extension of a CB is in the nanometer range, but individual CBs may interact in space and time so that areas of the electrode characterized in size by some correlation length $L_{\text{co}}$ are dissolved in a synchronized way. Such an interaction mechanism needs some minimum of oxidation, current densities not too low, so that CBs nucleate in a density high enough to enable next neighbor interaction, and oxide dissolution rates not too large. On the other hand, surface areas where no CBs occurred for some time are more passivated and thus less likely to nucleate a new CB. If strong enough, passivation will tend to cluster CBs in areas where other bursts were prominent, for example because the current was initially confined to same special places by some lithographic defined nucleation areas. Summarizing, macropore formation occurs if a minimum of oxidation allows CB interaction in space together with interaction in time.

In this framework, the threshold current density $J_{\text{pitch}}$ represents the minimum current density required for clustering CBs over an area of correlation length $L_{\text{co}}$, which can be interpreted as the minimum diameter $d_{\text{min}}$ of viable pores, for a given pitch $p$ (Figs. 1 and 2(a)). Current densities lower than $J_{\text{pitch}}$ lead to clustering of CBs over different smaller areas within the same predefined nucleation site, so yielding several pores with smaller diameter (Fig. 2(b)). The correlation length $L_{\text{co}}$ and thus $d_{\text{min}}$ must increase with the lattice pitch (the opposite thus happens for $P_{\text{min}}$ and $J_{\text{pitch}}$) to ensure that most of holes produced by back-side illumination will be utilized at the pore tips so obtaining branching-free pores, in agreement with Fig. 3. In this way, less holes are left available for the etching of pore walls, which become passivated. However, such an increase is expected to be limited to a certain maximum lattice pitch, over which collection of holes at the pore tips for single macropore formation becomes harder (in agreement with Eq. (1)) and the growth of side-pores, which increases the surface-pore ripple, becomes unavoidable (see Fig. 1(f)).

4. Conclusions

BSIE of square-lattice of holes with pitch between 2 and 50 μm has been performed on 3×8 Ω cm n-type silicon substrates. The main result of this study is the existence of a threshold current density $J_{\text{pitch}}$ whose value depends on the pitch pattern, over which macropore formation can be controlled beyond accepted state-of-the-art rules. The existence of such a threshold value gives rise to both a minimum diameter and porosity above which pore lattices with density from 0.25 μm$^{-2}$ up to 0.0025 μm$^{-2}$ can be etched on the same substrate. The threshold current density $J_{\text{pitch}}$ has been interpreted in terms of CB model.

References