Electrochemical Preparation of In-Silicon Hierarchical Networks of Regular Out-Of-Plane Macropores Interconnected by Secondary In-Plane Pores Through Controlled Inhibition of Breakdown Effects

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In-silicon hierarchical networks of ordered out-of-plane macropores interconnected by high-density secondary in-plane pores are prepared by controlled electrochemical etching of n-type silicon in HF:H2O2 electrolyte through the synergistic use of back-side illumination, avalanche breakdown anodization voltage, and high-oxidizing-power chemical. Preparation of the hierarchical networks of pores is enabled by controlled inhibition of breakdown effects at high anodization voltages (in the breakdown region) through back-side illumination of the silicon electrode. Inhibition of breakdown effects in pre-patterned silicon electrodes etched under galvanostatic condition at high anodization voltages is used to simultaneously control formation of out-of-plane macropores by regulating the photogenerated etching current density flowing at the pore tips and enable in-plane branching of out-of-plane pores by increasing leakage current at the lateral pore surface through high voltage effects. Further, high-oxidizing-power chemical, namely H2O2, is used to increase density, length, and diameter of branching and, in turn, enable interconnection of out-of-plane macropores with in-plane secondary pores.

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1. INTRODUCTION

In recent years electrochemical dissolution processes, both anodic and electroleas etchings, have been attracting increasing attention for micro and nanostructuring of materials, e.g. silicon [1–3], aluminum [4], silicon carbide [5], etc., thanks to their unique features of low cost and high versatility.

Anodic dissolution of silicon in HF (hydrofluoric acid)-based electrolyte has been largely used for the preparation of both random and ordered forms of porous silicon [6,7]. Porous silicon is today acknowledged as a highly versatile material with a plethora of applications that is addresed by tuning pore morphology and size to a large extent. Morphology of pores is tuned from cylinder-like to trench-like, thus enabling high flexibility in micro and nanofabrication [8]. Size of pores is controlled over four order of magnitudes, from a few nanometers to tens of micrometers [9]. A number of parameters do influence the etching outcomes, such as doping, both type and concentration, of silicon, HF concentration and composition of electrolyte, etching voltage and current density, illumination and temperature, etc. [6,7]. The effect of the above-mentioned parameters on the etching result has been thoroughly investigated though not always fully understood, except for some specific and simple cases, thus stimulating continuous research on electrochemical dissolution of silicon since half a century.

A fascinating challenge about electrochemical dissolution of silicon concerns the controlled etching and synergistic integration of both out-of-plane and in-plane pores with different length-scales in the same structure at the same time, aimed at the formation of hierarchical networks of pores. This would pave the way towards novel applications that have not been fully addressed yet with the existing porous silicon technology level. Random nanopores and mesopores [7] with high density have been commonly prepared by electrochemical etching in dark condition of p-type silicon at high HF concentration, and employed for environmental [10], biomedical [11] and healthcare [12] applications. Ordered macropores [6] and complex microstructures [1,8] with smooth surfaces have been fabricated by back-side illumination electrochemical etching of n-type silicon at low HF concentration and employed for energy storage [13,14] and (bio) sensing [15,16] applications. Nonetheless, as we are aware of, preparation of hierarchical networks of ordered out-of-plane macropores interconnected by high-density secondary in-plane pores by electrochemical dissolution of silicon has not been reported.

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Hierarchical structures with multiscale morphological features are at the forefront of material research. They have been fabricated through different top-down and bottom-up approaches [17–22], with application to, among others, superhydrophobic and superhydrophilic materials [17,18], supercapacitors and batteries [19,20], chromatography and synthesis of fine chemicals [21,22].

In this work in-silicon hierarchical networks of ordered out-of-plane macropores, with diameter up to the micrometer range, interconnected by high density in-plane secondary pores, with diameter of hundreds of nanometers, are prepared by controlled electrochemical etching of n-type silicon in HF:H2O electrolyte through the synergistic use of high anodic voltage, back-side illumination, and high-oxidizing-power chemical.

Electrochemical characterization of n-type silicon in HF:H2O electrolyte carried out under different back-side illumination intensities both at low (throughout the open-circuit potential -OCP- region) and high (in the breakdown region) anodic voltages using linear voltammetry allows demonstrating, for the first time, controlled inhibition of breakdown effects (at high anodic voltages) through back-side illumination of the silicon electrode. By building on this result, preparation of hierarchical networks of macropores is successfully achieved by galvanostatic etching of pre-patterned n-type silicon electrodes in HF:H2O electrolyte, at high anodic voltage and under back-side illumination. Back-side illumination is used to inhibit breakdown effects at the pore tips and set the photosynthesized etching current density value and, in turn, the diameter of the out-of-plane macropores in the network. High anodic voltage (in the breakdown region) is used to increase leakage current through the lateral surface of pores and enable in-plane branching of out-of-plane macropores and, in turn, formation of secondary smaller pores in the network. High-oxidizing-power chemical, namely H2O2, is used to enhance branching effect and increase density, length, and diameter of secondary in-plane pores and, in turn, obtain fully interconnected hierarchical networks.

2. MATERIALS AND METHODS

2.1. Materials and Chemicals

CZ-growth n-type silicon, resistivity 3-8 Ω cm, (100) oriented, with a 298-nm-thick silicon-dioxide layer on top is provided by ST microelectronics.

Hydrofluoric acid (HF) 48 wt%, Perdrogen™ H2O2 30 wt%, pentane (CH3(CH2)3CH3) 99 wt% and 2-Propanol (CH3CHOH) 99.8 wt% are purchased from Sigma-Aldrich. Potassium hydroxide (KOH), pure powder at 85%, and ethanol (CH3CH2OH) 99.8 wt% are purchased from Fluka Analytical. Ammonium fluoride solution (NH4F) 40 wt% is purchased from Riedel-De Haën (Aldrich).

2.2. Electrochemical characterization of n-type silicon electrode in HF-based electrolyte by linear voltammetry at low and high voltages

The electrochemical characterization of n-type silicon electrode is carried out in the presence of two different electrolytes, namely (48%HF:H2O (1:1 by vol) and (48%HF:H2O: (30%H2O2 (1:1 by vol), with same HF concentration except the latter containing H2O2 as oxidizing agent, by linear sweep voltammetry both at low (around the open-circuit potential) and high (around the breakdown potential) voltages, under back-side illumination of the silicon material at different intensity values (between 0 and 100% of the lamp power). The silicon-dioxide layer on top of silicon is removed using a solution of (99.8%ethanol (1:1 by vol) before the silicon sample is loaded in a three-electrodes electrochemical cell. A linear voltage variable between both +25 and -1 V and +17 and +13 V with sweep rate of -0.1 V/s is applied between silicon material (used as the anode) and pseudo-reference electrode (Pt wire), and the current flowing through silicon material and counter electrode (Pt disk) is monitored, so as to record the current density-voltage (I-V) curve of the electrochemical system under investigation. A set of ten measurements is carried out for each parameter configuration, at least. Details of the electrochemical etching setup are provided in Appendix A (Supplementary data).

2.3. Electrochemical preparation of in-silicon hierarchical networks of macropores by galvanostatic etching at high anodization voltages

The electrochemical preparation of hierarchical networks of ordered out-of-plane macropores interconnected by high density secondary in-plane pores in n-type silicon electrodes is investigated for both the HF-based electrolytes above reported, i.e. with and without H2O2, by galvanostatic etching of the silicon electrode under constant anodic biasing in the breakdown region and back-side illumination. A square hole array oriented along (110) direction with side-to-side pitch of 3.5 µm is patterned on the silicon-dioxide layer by standard optical lithography and subsequent buffered hydrofluoric acid (BHF) etching. The BHF etching is performed at room temperature with a solution consisting of (48%) HF:(40%)NH4F (4.25 by vol). The pattern is transferred into the silicon surface by potassium hydroxide (KOH) etching using the silicon-dioxide layer as mask, so as to create an array of inverted pyramid-shaped defects acting as dissolution sites during the electrochemical etching. The KOH etching is performed at 50 °C in a 20 wt% KOH solution, saturated with 2-Propanol to improve silicon wettability and, in turn, to increase etching uniformity. The silicon-dioxide layer on top of silicon is then removed using a solution of (48%)HF:(99.8%)ethanol (1:1 by vol). Pre-patterned silicon samples are loaded in a three-electrodes electrochemical cell and etched either in (48%)HF:H2O2 (1:1 by vol) or in (48%)HF:30%H2O2 (1:1 by vol) for 300 s under back-side illumination, keeping both etching voltage (VETCH) and current density (JETCH) constant throughout each experiment. A VETCH value of 15 V is applied for all experiments, whereas JETCH value is varied within different sets of experiments. More specifically, JETCH is set by tuning the back-side illumination intensity (lamp to 12, 15, and 20% of full power) at three different values, namely 15.72, 25.15, and 50.30 mA/cm² so as to investigate possible effects on out-of-plane/in-plane pore morphology. After electrochemical etching the samples are rinsed in deionized water, ethanol and pentane, respectively, then dried on hotplate at 100 °C and diced in two pieces along the (100) direction. Details of the electrochemical etching setup are provided in Appendix A (Supplementary data).

2.4. Morphological characterization by scanning electron microscopy

A scanning electron microscope (SEM) JEOL JSM-6390 at an acceleration voltage of 3 kV is used to investigate the cross-section of electrochemically-etched samples in order to infer on diameter and length (average value and standard deviation -sd-) of both ordered out-of-plane macropores and interconnected in-plane pores as a function of JETCH values.

2.5. Preparation of silicon-dioxide replicas of the hierarchical networks by thermal oxidation

Electrochemically-etched (pre-patterned) silicon samples are thermally oxidized at 1050 °C for 22 min in the presence of water (relative humidity 100%) so as to obtain a 250-nm-thick silicon-dioxide negative replica of the hierarchical network of out-of-plane/in-plane pores. KOH etching of silicon is performed on oxidized samples at 50 °C in a 20% KOH solution so as to free the silicon-dioxide replica up to a depth of 5 µm and allow SEM
observation of secondary in-plane pores interconnecting adjacent out-of-plane macropores in the network. After KOH etching, the samples as rinsed in water, ethanol, and pentane, then dried at 100 °C on hotplate.

3. RESULTS AND DISCUSSION

3.1. Inhibition of breakdown effects on electrochemical etching of silicon at high anodization voltages through back-side illumination

Although J-V behavior of n-type silicon electrodes in the presence of aqueous HF-based electrolytes at low anodic voltages and under back-side illumination has been thoroughly explored [1], investigation at high anodic voltages in the breakdown region, also for HF-based electrolyte containing H2O2, has been somehow overlooked.

Fig. 1 shows typical experimental J-V curves (average value and standard deviation) of n-type silicon electrodes in the presence of the two electrolytes under investigation, namely (48%)HF:(30%) H2O2 (1:1 by vol) (Fig. 1a,b) and (48%)HF:H2O (1:1 by vol) (Fig. 1c, d), both throughout the OCP region between −1 and +2.5 V and around the breakdown region between +13 and +17 V, at different illumination intensity values obtained by tuning the lamp power from 0 to 15, 25, 50, 75 and 100%. The J-V curves mostly refer to the anodic region of the silicon/electrolyte system, being silicon dissolution in HF-based electrolytes only occurring under anodic biasing. The HF:H2O electrolyte (without H2O2) is used as control solution being it a well-known mixture commonly employed for the electrochemical dissolution of both p- and n-type silicon at low anodic voltage, both in dark and under illumination, aimed at the formation of porous silicon [1].

J-V curves of the two silicon/electrolyte systems clearly show how the electrochemical dissolution (etching current density) of n-type silicon in HF-based electrolytes is finely controlled both at the lower, throughout the OCP region (Fig. 1a,c), and higher, in the breakdown region (Fig. 1b,d), anodization voltages through the use of back-side illumination of the silicon electrode, regardless of the presence of H2O2. Current density values recorded in the presence of both the electrolytes under different illumination intensities of the silicon electrode are almost constant at anodic voltages above 2 V (up to 17 V), thus suggesting that electrical current flowing through the silicon/electrolyte junction is largely due to photo-generated charge carriers (holes) both at low and high anodization voltages. This result clearly demonstrates, for the first time, inhibition of breakdown effects at anodization voltages in the breakdown region through illumination of the silicon electrode, thus allowing decoupling high anodic voltage and etching current density effects on the morphological outcomes of the etching.

More in detail, the silicon/electrolyte system is reverse-biased under anodic biasing of the silicon electrode, for both the two electrolytes under investigation.

At low anodic voltages (up to 2.5 V) only a small current flows through silicon/electrolyte junction in dark condition (red curves in Fig. 1a, c). In this region, current density in dark has an average value of 0.1 and 0.01 mA/cm² in the presence of the two electrolytes under investigation, with and without H2O2,

Fig. 1. Controlled inhibition of breakdown effects in n-type silicon anodized at high voltages: experimental J-V curves (average value and standard deviation) of n-type silicon electrode in the presence of two different electrolytes, namely (48%)HF:(30%)H2O2 (1:1 by vol) and (48%)HF:H2O (1:1 by vol), both throughout the OCP region between −1 and +2.5 V (a, c) and around the breakdown region between +13 and +17 V (b, d), respectively, at different illumination intensity values obtained by tuning a 250W halogen lamp power from 0% to 15, 25, 50, 75 and 100%.
respectively. The OCP value in dark is -1 and -0.8 V for the two electrolytes, with and without H₂O₂, respectively. The increased current density and cathodic OCP shift in dark condition for the electrolyte containing H₂O₂ can be ascribed to H₂O₂ reduction, which is known to inject holes in silicon [2,23]. Under illumination of the silicon electrode, electrical current flowing through the silicon/electrolyte junction significantly increases thanks to contribution of holes photogenerated at the back-side silicon surface and collected at the silicon/electrolyte interface after diffusing through bulk silicon (Fig. 1a,c). The OCP value anodically shifts under illumination to -0.6 and -0.2 V for the two electrolytes under investigation, with and without H₂O₂, respectively, in agreement with the literature [24]. Typical electropolishing current density peak Iₚₑₚ≈120-140 mA/cm² occurs at anodic voltage Vₑₚ≈0.8-0.9 V under high illumination intensity, regardless of the presence of H₂O₂. At anodic voltages beyond Vₑₚ, current density increases and tends to saturate at the edge of this region, between 2 and 2.5 V. Current density saturation values are almost unchanged for the two electrolytes and mostly depend on illumination intensity. The relationship between photogenerated current density and lamp power in this region is sigmoidal (R²>0.99) with a linear region from 15 to 75% (Fig. S1a).

At high anodic voltages (from 13 to 17 V) a significantly higher electrical current flows through the silicon/electrolyte junction in dark condition for both the electrolytes under investigation, with and without H₂O₂, due to electron-hole pairs generated through breakdown effects sustained by high electric field at the silicon/electrolyte junction (red curves in Fig. 1b,d). In this region, current density in dark oscillates between 20 and 50 mA/cm². This behavior is well-known in the literature and is ascribed to continuous formation and removal of silicon oxide at the silicon/electrolyte interface [6]. Interestingly, under back-side illumination of the silicon electrode, current density flowing through the silicon/electrolyte interface is stable and finely controlled by tuning the illumination intensity (Fig. 1b,d). Current density value under illumination is quite independent of the anodization voltage and mainly depends on illumination intensity. For a given illumination intensity, the current density value in the high voltage region well complies with the saturation value recorded in the low voltage region (at anodic voltage >2 V). The relationship between photogenerated current density and lamp power in the high voltage region is sigmoidal (R²>0.97) with a linear region from 15 to 75%, as for the low voltage region (Figure S1b). We argue that back-side illumination of the silicon electrode allows inhibiting breakdown effects occurring at the silicon/electrolyte interface in dark at the higher anodization voltages. This enables to control etching current density flowing through the silicon/electrolyte interface with high accuracy by modulating the illumination intensity at the higher anodic voltages. In fact, comparable current density values are recorded under back-side illumination both at low and high anodization voltages (compare Fig. 1a and 1b, as well as 1c and 1d), thus suggesting that main component of the electrical current flowing through the silicon/electrolyte junction under backside illumination is due to photogenerated carriers and that breakdown current is, in turn, significantly reduced. Interestingly, by properly reducing illumination intensity of the silicon electrode (i.e. lamp power to 15%), photogenerated current density value can be even reduced below the breakdown current density value in dark (compare cyan and red curves in Fig. 1b, d). This further corroborates inhibition of breakdown effects at the silicon/electrolyte junction under illumination at the higher anodization voltages.

### 3.2. Electrochemical preparation of in-silicon hierarchical networks of regular out-of-plane macropores interconnected by secondary in-plane pores through the synergistic use of breakdown voltage, back-side illumination, and high-oxidizing chemical

Preparation of hierarchical networks of regular out-of-plane macropores interconnected by secondary in-plane pores is carried out by electrochemical etching under back-side illumination at anodic voltage in the breakdown region of n-type silicon substrates containing a regular square array of pyramid-shaped defects with side-to-side pitch of 3.5 μm (Fig. S2). In dark condition, high anodic

Fig. 2. Phenomenology of electrochemical preparation of in-silicon hierarchical networks of regular out-of-plane macropores interconnected by secondary in-plane pores in pre-patterned n-type silicon: (a) uncontrolled etching of regular out-of-plane macropores in (48%HF:H₂O₂ (1:1 by vol) at avalanche breakdown voltage (V_BD) in dark; (b) controlled etching of regular out-of-plane macropores with secondary in-plane pores in (48%HF:H₂O₂ (1:1 by vol) under breakdown inhibition through back-side illumination; (c) enhanced branching of regular out-of-plane macropores and formation of interconnecting secondary in-plane pores in (48%HF:30%H₂O₂ (1:1 by vol) under breakdown inhibition through back-side illumination.
voltages in the breakdown region make electron-hole pairs generated by high-electric-field avalanche process available for silicon dissolution at the tip of surface defects. Defect sites act as dissolution points through which most of the breakdown current flows. Nevertheless, breakdown current (value) is hardly controlled over space and time in dark condition. In particular, synchronization in space and time of silicon dissolution steps occurring at the different active domains, both within each and among diverse defect sites, due to breakdown current is intrinsically poor. As a result, the etching is not controlled and clusters of out-of-plane pores, consisting of a main pore surrounded by a multitude of secondary pores running both along in-plane and out-of-plane directions, form at each defect site, as sketched in Fig. 2a. Further, pores at each defect site result to be different in density, diameter, length, and position.

Under back-side illumination, both at low and high anodization voltages, holes photogenerated at the back-side silicon surface are mostly focused at the tip of surface defects where electric field is higher. Again, surface defects act as silicon dissolution points through which photogenerated current largely flows giving rise to out-of-plane pore formation. Inhibition of breakdown effects at the defect/pore tips due to back-side illumination of the silicon electrode allows synchronization in space and time of silicon dissolution steps at the defect/pore tips to be greatly improved (with respect to dark condition), thanks to negative feedback mechanism well-known for regulating macropore formation in n-type silicon under back-side illumination [6,8]. This significantly improves the etching control, thus enabling the formation of a single out-of-plane pore to be obtained per each defect site, with no secondary pores in the out-of-plane direction, as sketched in Fig. 2b. Diameter of out-of-plane pores is set by tuning the photogenerated current (value), and it is smaller at the higher anodization voltages than at the lower ones due to voltage-enhanced etching rate. As to formation of secondary in-plane pores, at low anodization voltages silicon between adjacent pores is (quite) depleted of holes, thus preventing significant silicon etching of the pore lateral surface and, in turn, pore branching. Conversely, at anodization voltages in the breakdown region, current flowing in silicon between adjacent pores (through the pore lateral surface) is enhanced by high electric-field-induced phenomena, thus enabling branching of out-of-plane pores and, in turn, formation of secondary in-plane pores (Fig. 2b,c).

Fig. 3a,b reports typical SEM cross-section images (at two different magnifications) of an array of ordered out-of-plane macropores with pitch of 3.5 μm and depth of about 41 μm interconnected along 〈011〉 directions by secondary in-plane pores with length of about 3 μm. The sample is obtained by back-side illumination electrochemical etching in HF:H2O2 electrolyte for 300 s at 15 V and 15.72 mA/cm². Out-of-plane macropores in Fig. 3a feature a fairly regular diameter of 0.47 μm (average value) over the whole depth, though a lack of regularity also associated with a slight diameter increase is observed after a depth of 20 μm. Secondary in-plane pores interconnecting adjacent out-of-plane macropores along the 〈011〉 directions feature a diameter of 265 nm (average value) (Fig. 3b), which is maintained roughly constant over the whole etching depth. We argue that both lack of regularity and increase in the diameter of out-of-plane macropores with etching depth can be ascribed to decrease of HF concentration within pores as the etching progresses, a phenomenon that is known to occur for back-side illuminated electrochemical etching of pores, although at significantly higher depth (>50 μm) [1]. In fact, silicon volume dissolved per unit time/depth under back-side-illumination electrochemical etching is proportional to the ratio between etching current density and electropolishing current.

![Fig. 3](image_url)

Fig. 3. Experimental results on in-silicon hierarchical networks of regular out-of-plane macropores interconnected by secondary in-plane pores prepared in HF:H2O2 electrolyte: (a) SEM cross-section of ordered silicon out-of-plane macropores interconnected by secondary in-plane pores etched under back-side illumination in (48%HF: (30%H2O2 solution 1:1 by vol) at etching voltage of 15 V and etching current density of 15.72 mA/cm²; (b) magnification of (a) highlighting out-of-plane macropores and secondary in-plane pores; (c) SEM bird-eye view of a negative silicon-dioxide replica of out-of-plane macropores interconnected by secondary in-plane pores obtained by thermal oxidation and KOH etching of the sample in (a); (d) magnification of (c) highlighting the hierarchical network of pores.
density, this latter dependent on HF concentration. As HF concentration decreases with etching depth, the electropolishing current density value at pore tip also decreases. This leads to an increased silicon volume etched per unit depth and, in turn, to an augmented pore diameter with depth, for samples etched at constant current density [25]. Such a decrease in HF concentration with depth is expected to be significantly higher for highly branched macropores, which is the case of this work, than for smooth (i.e. non-branched) macropores commonly etched by back-side illumination, because of the additional consumption of HF for pore branching in the former.

The hierarchical network of interconnected out-of-plane/in-plane pores is better visible in Fig. 3c,d, which shows typical SEM bird-eye view images (at two different magnifications) of a negative silicon-dioxide replica of the sample in Fig. 3a. The replica process allows to better point out the high regularity of pore interconnections in the network (Fig. 3c,d), as well as the high density of secondary in-plane interconnections among adjacent out-of-plane macropores and along the out-of-plane macropore depth. Note that, the replica process is intrinsically prone to two main artifacts affecting the real morphology of the network, namely increased thickness of silicon-dioxide interconnections with respect to original pores due to volume expansion during thermal oxidation step [26], and collapse of narrower silicon-dioxide interconnections due to both KOH etching and drying steps. Nonetheless, it allows immediately and effectively demonstrating the formation of such a hierarchical network of out-of-plane/in-plane pores.

A thorough investigation of main features, namely diameter and length, of both out-of-plane and in-plane pores in the network as a function of photogenerated etching current density values is further carried out. Fig. 4 reports average values and standard deviations (error bars) of the diameter of both regular out-of-plane macropores and interconnected in-plane pores versus etching current density values used in this work. A linear trend predicting an increase of the diameter of out-of-plane macropores in the range 0.47-0.85 μm as etching current density is varied in the range 15.72-50.30 mA/cm² is noticeable in Fig. 4a. Specifically, out-of-plane macropores with average diameter of 0.47 μm (sd=81 nm), 0.56 μm (sd=165 nm), and 0.85 μm (sd=203 nm) are obtained using etching current density values of 15.72, 25.15, and 50.30 mA/cm², respectively. Conversely, independently of etching current density value, depth of out-of-plane macropores is constant, about 40 μm in value corresponding to an etching rate of 8 μm/min. No significant dependence of diameter of interconnecting pores on etching current density value is appreciable, as shown in Fig. 4b, at least within the investigated range. Specifically, average diameters of secondary in-plane pores obtained by using etching current density values of 15.72, 25.15, and 50.30 mA/cm² are 265 nm (sd=115 nm), 295 nm (sd=81 nm), and 207 nm (sd=63 nm), respectively. Slight differences in diameter average values of secondary in-plane pores at the different etching current densities fall within uncertainty of the experimental measurement method (SEM analysis). Length of interconnecting in-plane pores ranges from 2.5 to 3 μm, reducing as the diameter of out-of-plane macropores increases, but always allowing to fully interconnect adjacent out-of-plane macropores regardless of etching current density value.

On the basis of experimental results, we claim that by inhibiting breakdown effects at the pore tips through back-side illumination, for a given etching voltage and time, etching current density value and HF concentration independently set diameter and etching rate of regular out-of-plane macropores, respectively, whereas voltage value and H₂O₂ mainly affect diameter, length, and density of interconnecting in-plane pores.

We argue that the presence of H₂O₂, which injects additional holes (h⁺) in silicon according to H₂O₂ reduction reaction in Eq. (1):

\[ \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O} + 2\text{h}^+ , \]  

(1)

contributes to enhance the electrochemical etching of silicon (with respect to HF:H₂O electrolyte without H₂O₂) at the pore tips (active sites of dissolution), both for out-of-plane and in-plane pores, according to Eq. (2) and (3):

\[ \text{Si} + 4\text{HF}_2^- + \text{h}^+ \rightarrow \text{SiF}_6^{2-} + 2\text{HF} + \text{H}_2 + \text{e}^- \]  

(2)

\[ \text{SiO}_2 + 2\text{HF}_2^- + 2\text{HF} \rightarrow \text{SiF}_6^{2-} + 2\text{H}_2\text{O} , \]  

(3)

where Eq. (2) and (3) concern direct (divalent) and indirect (tetravalent silicon-oxidation mediated) dissolution of silicon, respectively.

Being HF concentration in the electrolyte fairly high, about 25%, it is reasonable that both the dissolution reactions could play a role in the hierarchical network formation. Nonetheless, due to the high voltage value (15 V) used to carry out the electrochemical etching experiments, indirect dissolution via silicon oxidation and subsequent silicon-dioxide removal (Eq. (3)) might be favored. In this case, due to the high HF concentration the limiting step of silicon dissolution is the silicon-dioxide formation step, in agreement to the current-burst-model [27]. Under this assumption, an increase
of silicon-dioxide formation rate through the use of H$_2$O$_2$ is compatible with an augmented proliferation of the branching phenomenon, both in terms of etching rate and size/density of branched pores [28–30]. On the other hand, higher consumption of HF per unit depth due to increased branching leads to an augmented reduction of HF concentration with depth, with respect to standard HF:H$_2$O electrolyte without H$_2$O$_2$, and, in turn, to a decrease of etching rate for out-of-plane macropores. This is indirectly corroborated by the augmented lack of regularity of out-of-plane pores at etching depth from 20 to 40 $\mu$m (Fig. 3a).

To better highlight the effect of H$_2$O$_2$ on interconnecting in-plane pores, electrochemical etching experiments in HF:H$_2$O electrolyte with same HF concentration but without addition of H$_2$O$_2$ are performed as control. Fig. 5a,b shows typical SEM cross-section images, at two different magnifications, of a sample electrochemically etched in HF:H$_2$O electrolyte for 300 s at 15 V and 15.72 mA/cm$^2$ (same etching parameters of sample in Fig. 1). Out-of-plane macropores in control samples have average diameter of 0.38 $\mu$m (sd=143 nm) and depth of about 45 $\mu$m (Fig. 5a), which are slightly smaller and deeper, respectively, than those of pores etched in electrolyte containing H$_2$O$_2$ with same etching parameters. As regards in-plane pores between adjacent out-of-plane macropores (Fig. 5b), a maximum average diameter of 100 nm (sd=28 nm) is measured, which is less than a half of average diameter of interconnecting pores etched in the presence of H$_2$O$_2$ under same etching conditions. Fig. 5c,d shows bird-view SEM images, at two different magnifications, of a negative silicon-dioxide replica of the sample in Fig. 5a,b, which points out as the hierarchical network of out-of-plane/in-plane pores is not fully interconnected, and features finer and tapered secondary in-plane pores not long enough to interconnect adjacent out-of-plane macropores. Also, density of in-plane pores is reduced in control samples with respect to those etched in the presence of H$_2$O$_2$ with same etching parameters. The increased depth (etching rate augmented to 9 $\mu$m/min) of out-of-plane macropores in control samples is in agreement with such a reduced branching phenomenon. Therefore, experimental results on control samples are compatible with the hypothesis that H$_2$O$_2$ acts in increasing diameter, density, and length of secondary in-plane pores, thus positively affecting the formation of hierarchical networks of pores under inhibition of breakdown effects.

4. CONCLUSIONS

Inhibition of breakdown effects through back-side illumination of anodically-etched n-type silicon electrodes in contact with HF-based electrolytes is demonstrated, thus allowing decoupling effects of high anodization voltage and etching current density on the outcomes of electrochemical etching. This result is successfully exploited for the electrochemical preparation of in-silicon hierarchical networks of ordered out-of-plane macropores, with diameter tunable in the range 0.47 – 0.85 $\mu$m, interconnected by high density secondary in-plane pores, with diameter of about 250 nm, through the synergistic use of back-side illumination, breakdown voltage, and high-oxidizing-power chemical. Back-side illumination mainly sets the etching current density and, in turn, out-of-plane pore diameters; breakdown voltage enables out-of-plane pore branching and, in turn, the formation of secondary in-plane pores; high-oxidizing-power chemical, namely H$_2$O$_2$, positively contributes to increase length, size and density of in-plane pores and, in turn, to yield the net of out-of-plane macropores fully interconnected. Negative silicon-dioxide replicas of the network allow hierarchy level and high density of interconnections among different pores to be clearly appreciated.
Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2015.11.006.

References