Controlling the Electrochemical Etching of Pores with High Aspect Ratio at the Submicrometer Scale in Silicon

G. Polito, C. Cozzi, G. Barillaro

Dipartimento di Ingegneria dell’Informazione, Università di Pisa, via G. Caruso 16, 56122 Pisa, Italy

The controlled electrochemical etching at high anodic voltage (up to 35 V) of two-dimensional arrays of ordered pores with sub-micrometric diameter (down to 800 nm) at high depths (up to 40 µm) and high density (spacing 1.8 µm), yielding a maximum aspect ratio of 50, using low-doped (resistivity 3-8 Ωcm) n-type silicon is hereby for the first time demonstrated and discussed.

Introduction

Since porous silicon formation was first reported in 1950s (1, 2), much of effort has been given to understand and control the formation mechanism of porous silicon, aimed at continuously extending potential applications. The extensive study carried out over several decades revealed the formation process to be strongly affected by numerous parameters such as both type and concentration of silicon doping, electrolyte composition, etching voltage and current density, temperature, and many more (3-5). Nowadays, despite such a wide range of parameters, features like pore morphology and size can be effectively tuned during the etching process, thus addressing porous silicon as a highly versatile material. In recent years, ordered and random forms of porous silicon (6, 7), from both p-type and n-type silicon, have been prepared by anodic dissolution of silicon in aqueous solutions containing hydrofluoric acid (HF), finding application in fields ranging from biosensing and healthcare (8, 9), to photonics (10), heat dissipation (11), and energy storage (12, 13). In particular, high-density random meso and nanoporous silicon has been commonly prepared from p-type silicon electrochemically etched in dark conditions at high HF concentrations (7), while ordered macropores and complex microstructures (6, 4) have been fabricated by back-side illumination electrochemical etching (BIEE) of n-type silicon at low HF concentrations (14). Notwithstanding such a thorough investigation, the controlled etching at high anodic voltage of two-dimensional (2D) arrays of high-depth sub-micrometric ordered pores by BIEE of low-doped n-type silicon using low-HF-concentration electrolytes has not yet been reported.

Materials and Methods

Materials and Chemicals

The starting material was a (100)-oriented CZ-grown n-type silicon wafer with resistivity of 3-8 Ωcm covered by a 298-nm-thick pre-patterned silicon dioxide layer, provided by STMicroelectronics (Milan, Italy). The pattern on the silicon dioxide layer consisted of multiple repetitions of 1 × 1 cm² 2D lattices of square holes with side of 1
µm and spacing of 1.8 µm. HF 48 wt%, pentane 99 wt%, acetone 99 wt% and 2-Propanol 99.8 wt% were purchased from Sigma-Aldrich. Sodium lauryl sulphate (SLS) powder was purchased from Carlo Erba Reagents. Potassium hydroxide (KOH), pure powder at 85%, and ethanol 99.8 wt% were purchased from Fluka Analytical.

Fabrication of ordered pore arrays

Ordered pore arrays were fabricated by means of back-side illumination electrochemical etching (BIEE) (15) under potentiostatic anodic regime using slabs with size of 2 × 2 cm² cut from the pre-patterned silicon wafer and featuring a single 2D lattice of square holes. The pre-patterned silicon dioxide layer was used as a mask to replicate the array layout into the silicon surface by KOH etching so as to create an array of inverted pyramid-shaped defects acting as seed-points for pore growth during the following BIEE. KOH etching was performed for 750 s at 50 °C in a 20 wt% solution of KOH in deionized water, saturated with 2-Propanol to improve the solution wetting capability and, in turn, to increase the etching uniformity. The silicon dioxide layer was dissolved using a solution of HF:ethanol (1:1 by vol.) for 60 s at room temperature right before loading the sample in a three-electrode etch-cell to proceed with the electrochemical etching. The etching area was ~0.64 cm² with circular shape (r=0.45cm) for all samples and the composition of the etchant was 5 vol% HF:95 vol% deionized water with 1000 ppm of SLS acting as a wetting agent. The etching time was 2000 s for all samples. The photogenerated etching current density ($J_{etch}$) was set to a given initial value $J_{etch0}$ and linearly decreased with time to keep the pore diameter constant, thus achieving an anisotropic etching in the out-of-plane direction. Two different $J_{etch0}$ values were tested, namely 13.4 and 20.2 mA cm⁻², which were linearly reduced over time with a rate of -0.938 and -1.453 µA s⁻¹ cm⁻², respectively, by reducing the lamp power over time. The BIEE of all samples was performed under a potentiostatic anodic regime and, for each $J_{etch0}$ value investigated, three different etching experiments were performed, setting the etching voltage ($V_{etch}$) to the value of 1.2, 20, and 35 V respectively, and keeping it constant during the etching. For each given $J_{etch0}$-$V_{etch}$ pair, etching experiments were replicated at least 3 times. Eventually, any residuals of SLS from the etched samples were removed through an overnight static bath in a solution of HF:ethanol (1:4 by vol.), followed by 300 s static rinses in ethanol and pentane, respectively, and hot-plate bake drying at 100 °C. All samples were diced in two pieces along the (100) direction to allow morphological investigation of cross-sections.

Characterization of ordered pore arrays

Ordered pore array characterization was performed using a JEOL JSM-6390 scanning electron microscope (SEM). Cross-section micrographs were acquired at an acceleration voltage of 3kV and pore depth and diameter measurements were performed using the dedicated feature of the SEM operating software.
Results and Discussion

Experimental results

SEM micrographs reported in Figure 2a,b show a typical cross-section and top-view, respectively, of pores resulting from BIEE of n-type silicon pre-patterned with hole lattice with size of 1 µm and spacing of 1.8 µm at \( V_{etch} = 1.2 \) V and \( J_{etch0} = 13.4 \) mAcm\(^{-2}\).

Figure 1. Influence of the etching voltage \( V_{etch} \) and the etching current density \( J_{etch} \) value on the controlled etching of pores with sub-micrometric diameter and spacing below 2µm. (a) Cross-section and (b) top-view SEM micrographs showing the result of uncontrolled etching on silicon samples etched by BIEE with \( V_{etch} = 1.2 \) V, \( J_{etch0} = 13.4 \) mAcm\(^{-2}\) and P \~{} 20%; (c) pore formation occurring in all available defect sites with only a limited
number of pores featuring a shorter depth resulting from the beneficial effect of the etching voltage on the controlled etching of silicon samples etched by BIEE with $V_{etch}=20$ V, $J_{etch0}=13.4$ mAcm$^{-2}$ and $P \approx 20\%$; (d) SEM cross-section of a silicon sample etched by BIEE with $V_{etch}=20$ V, $J_{etch0}=20.2$ mAcm$^{-2}$ and $P \approx 30\%$ showing a uniform array of ordered pores featuring same diameter and depth successfully obtained increasing the $J_{etch}$ value with respect to the sample shown in (c); (e) Cross-section and (f) top-view SEM micrographs showing a uniform array of sub-micrometric ordered pores featuring same diameter and depth successfully obtained increasing the $V_{etch}$ value with respect to the sample shown in (c).

This $J_{etch0}$ value corresponds to an average porosity (i.e. dissolved silicon to total silicon volumetric ratio, $P$) of $\approx 20\%$. It can be noticed that silicon dissolution occurring at pre-patterned defects is uncontrolled, thus leading to pore formation only in few of the available defect sites. Increasing the $V_{etch}$ value to 20 V, though maintaining the same current density value $J_{etch0}=13.4$ mAcm$^{-2}$, turned out to have beneficial effects on the controlled electrochemical etching of pores. As appreciable in the SEM cross-section shown in Figure 2c, at $V_{etch}=20$ V pore formation occurs in all available defect sites though for a limited number of pores the growth still stops at a certain depth. Increasing the $J_{etch0}$ value to 20.2 mAcm$^{-2}$, which corresponds to an average porosity of $\approx 30\%$, a fully uniform array of pores with no missing pores is achieved, as shown in the SEM cross-section of Figure 2d. The same result can be also achieved through an increase of the $V_{etch}$ value to 35 V at lower $J_{etch0}=13.4$ mAcm$^{-2}$ (i.e. porosity of $\approx 20\%$), as shown in the SEM cross-section and top-view of Figure 2e,f, respectively. Remarkably, by increasing the anodic voltage for a given $J_{etch0}$ value, the controlled etching leads to uniform arrays of pores featuring sub-micrometric diameter of $\approx 800$ nm (Figure 2e,f), which is $\approx 3$ time smaller than the diameter of pores etched at low anodic voltage (i.e. 1.2 V). Similarly, controlling the etching by increasing the $J_{etch0}$ value for a given high anodic voltage, uniform arrays of pores are still obtained, though featuring both higher diameter ($\approx 1000$ nm) and depth ($\approx 40$ µm) (Figure 2d).

According to the literature (16), our experimental results show that a $J_{etch0}$ threshold value exists setting the minimum porosity value (e.g. $P_{min}$ about 30% at 20V) versus pore density over which stable growth of pores can be achieved at high anodic voltages.

**Controlled etching of submicrometric pores with high aspect ratio**

The electrochemical dissolution of silicon in HF-based aqueous solutions is enabled under anodic bias by the presence of electron vacancies (holes) in the silicon crystal. For $n$-type silicon, holes represent minority charge carriers and can be generated through illumination of the sample (6). Under back-side illumination, straight pore formation is promoted thanks to both the higher electric field established during the anodization process in correspondence of either native or pre-patterned surface defects and to the pore wall passivation that arises upon silicon hole depletion at the silicon/electrolyte interface thus preventing pore wall dissolution (17). Controlling the balance between the number of holes in the silicon and the number of fluoride ions available at the pore tip is critical for the formation of straight pores with high aspect ratio (i.e. depth to width ratio), constant diameter and same depth (18). During the nucleation phase (Figure 1a), holes generated at the back-side surface by illumination diffuse through bulk silicon and are collected at the silicon/electrolyte interface in correspondence of pre-patterned surface defects, these latter acting as seed-points for pore growth and, in turn, localizing the
etching at the pore tip. At low $V_{etch}$ values (<3 V) the hole-focusing effect has been proven to be highly effective when diameter and spacing of defects/pores are greater than a few microns (>2 µm) (19). Lehmann and Föll demonstrated already in the early 1990s the controlled etching of uniform arrays of ordered pores with period of 4 µm and high-aspect-ratio (>100) by BIEE of pre-patterned n-type silicon in HF-based aqueous solutions (15). On the contrary, when patterned features are reduced below 2 µm, as for the patterned silicon of this work with 2D lattices of 1-µm-side holes with spacing of 1.8 µm, the electrochemical etching at low anodic voltages under back-side illumination does not allow the fabrication of uniform arrays of pores with constant diameter and same depth, in agreement to both literature data and experimental data of this work. In fact, when diameter and spacing of defects/pores are below 2 µm, low $V_{etch}$ values (<3 V) lead to an unstable and non-uniform pore growth, where some of the pores stop growing and other pores continue their growth though uncontrolled both in depth and diameter. The phenomenology of pore formation in n-type silicon with pre-patterned features below 2 µm is sketched in Figure 1. After the nucleation phase (Figure 1a), an unstable growth phase starts at low anodic voltage as sketched in Figure 1b, which leads to the uncontrolled etching of pores. We argue that such an uncontrolled etching is due to the defocusing of electric field lines resulting from partial overlapping of the depletion regions between adjacent pores occurring at low $V_{etch}$ values. In fact, by increasing the $V_{etch}$ value (from 20 up to 35 V, the higher electric field at the defects/pores allows restoring independent hole focusing and collection paths at each defect/pore site, thus allowing to control the etching at scales smaller than 2 µm and achieve, in turn, stable and uniform growth of arrays of submicrometric pores (Figure 1c).

Figure 2. Phenomenology of pore formation by BIEE in n-type silicon with pre-patterned features smaller than 2 µm: (a) pre-patterned surface defects act as seed-points for pore growth by collecting holes photogenerated on the backside and diffusing through bulk silicon, (b) at low $V_{etch}$ values (<3V) and for small defect/pore size (<2 µm), defocusing of electric field lines arising from partial overlapping of the depletion regions between adjacent pores leads to uncontrolled pore etching, (c) at high $V_{etch}$ values (from 20 up to 35 V) and for small defect/pore size (<2 µm) hole focusing and collection at the pore tips is restored as a consequence of the higher electric field, thus enabling the control of the etching of submicrometric pores with high aspect ratio.
Conclusions

In conclusion, the controlled etching of 2D arrays of ordered sub-micrometric (down to 800 nm) high-depth (up to 40 µm) and high density (spacing below 2µm) pores with high aspect ratio (~50) is successfully achieved by BIEE of low-doped (resistivity 3-8 Ω•cm) n-type silicon at high anodic voltage (up to 35 V) using low-HF-concentration electrolytes (5% by vol. in deionized water). These results can promisingly lead to the controlled electrochemical etching of ordered meso and nanopores and structures in low-doped n-type silicon. If successful, this would result to have significant impact and remarkable implications in the silicon micro and nanofabrication arena, with applications (though not limited) to nanomedicine, nanoelectromechanical systems (NEMS), and nanoelectronics.

Acknowledgments

G. B. thanks ECSEL Joint Undertaking through the R2POWER300 project (Grant no. 653933) for funding.

References