

# Chapter 1

## Electrochemical Etching Methods for Producing Porous Silicon

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**Abstract** Porous silicon produced by electrochemical etching of silicon has become one of the most popular materials used in many scientific disciplines as a result of its outstanding and unique set of chemical and physical properties and cost-competitive fabrication processes. To understand the electrochemical mechanisms taking place in the course of the etching of silicon is a key factor to control and modify the structure of this versatile porous material. This makes it possible to produce a broad range of structures, which can range from a porous matrix to arrays of nanowires. These structures are unique and bring new opportunities for multiple research fields and applications such as biotechnology, medicine, optoelectronics, chemistry and so forth. This chapter is aimed at compiling and summarising the fundamental aspects behind the production of porous silicon structures by electrochemical and metal-assisted etching of silicon wafers. Our objective is to provide a simple but detailed overview about the fabrication process of porous silicon, with special emphasis on the different fabrication conditions and geometric and morphological features of the resulting silicon nanostructures.

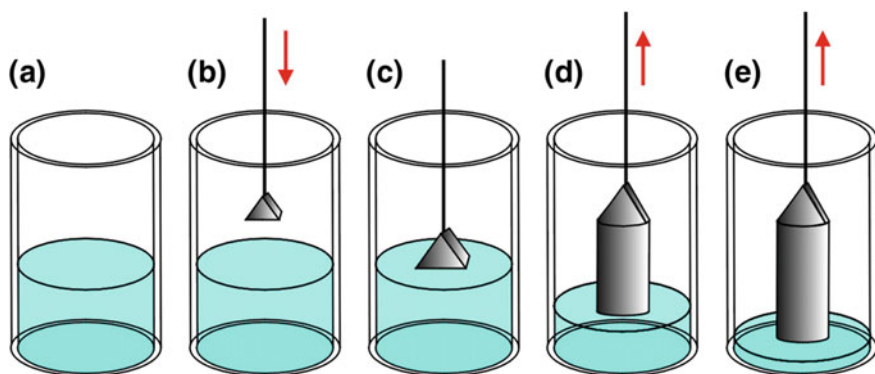
### 1.1 Introduction

Regardless of the emergence of other materials with supreme electronic properties such as graphene, gallium nitride (GaN) or gallium arsenide (GaAs), silicon is and will most probably continue to be the material of choice in semiconductor technology for developing integrated circuits and other microdevices during the next decades. Silicon is the second most abundant element on earth and it is most widely distributed in dusts and sands as various forms of silica (silicon dioxide) or silicates. Typically, electronic grade silicon wafers (high purity silicon 99.999999 %—9 N)

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**Fig. 1.1** Schematic diagram illustrating the Czochralski growth method for producing silicon wafers at industrial scale [1]. **a** Melting of polysilicon from raw silicon sources. **b** Introduction of the seed crystal. **c** Beginning of the silicon crystal growth. **d** Silicon crystal pulling (withdraw mode). **e** Resulting silicon crystal with residue of melted polysilicon

are produced by Czochralski growth method. In this process, a cylindrical ingot of high purity monocrystalline silicon is formed by pulling a seed crystal from a bath composed of polysilicon (Fig. 1.1) [1]. Silicon can be doped in the course of this process with donor impurity atoms (e.g. boron or phosphorus) by adding precisely controlled amounts of these elements to the batch. This process makes it possible to produce n-type (P doping) or p-type (B doping) silicon wafers with controlled doping and thus with different electronic properties. To avoid undesired contaminations, this process is normally performed under inert atmosphere (e.g. argon gas) in an inert crucible made of quartz. The width of the resulting cylindrical ingot is accurately controlled by the temperature and the speeds of rotation and withdrawn. After that, the crystal ingot, which can be up to 2 m in length, is sliced to produce silicon wafers. Note that commercial silicon wafers are available as single-crystalline wafers featuring diameters of 100, 125, 150, 200 and 300 mm, the thickness of which is usually within the range of 0.4–0.7 mm. Moreover, these wafers can be produced with different crystal orientations, which typically are (100), (111) and (110). These silicon wafers became the base of the silicon age, which started with the invention of the integrated circuitry by Jack Kilby and Robert Noyce [2].

Silicon wafers can be electrochemically etched through different approaches to produce a broad range of porous silicon (pSi) structures. The first report on pSi dates back to 1956, when the Uhlirs discovered coloured deposits on electrochemically etched silicon when they were working on electrochemical methods to machine silicon wafers for microelectronic applications at the Bell Laboratories. However, the obtained results differed from the expected polish finishing and the potential applications of the resulting material were almost ignored [3]. This work was followed by a flood of studies focused on different chemical/electrochemical approaches aimed to etch silicon wafers under different conditions [4–10]. The first

study on the porous nature of pSi was reported by Watanabe and Sakai in 1971 [11]. Throughout the following decades, many studies on pSi and its properties were published. In particular, interest in pSi nanostructures exploded when Ulrich Gösele identified quantum confinement effects in the absorption spectrum of pSi and Leigh Canham observed efficient, bright red-orange photoluminescence from pSi nanostructures [12, 13]. These studies were the origin of a series of works aimed at understanding the pore formation mechanism and controlling the properties of pSi such as surface chemistry and pore geometry. The objectives of these studies were to expand and explore the use of pSi in different applications such as optoelectronic devices and sensors. Several theories about the formation mechanisms of pSi were postulated, including crystallographic face selectivity, enhanced electric field, tunnelling, quantum confinement and space-charge limited [14–30].

This chapter is aimed at describing the fundamental aspects of electrochemical and metal-assisted etching methods used to produce porous silicon structures. First, the fundamental and basic concepts related with the production and fabrication of pSi will be summarised and described. Then, we will introduce the main aspects involved in the fabrication of pSi by electrochemical etching method. Subsequently, we will provide a detailed description of metal-assisted etching of silicon, which is considered as an outstanding alternative or complementary method to traditional electrochemical etching of silicon. Finally, we will conclude this chapter with a general overview and a prospective outlook on the future trends in this field.

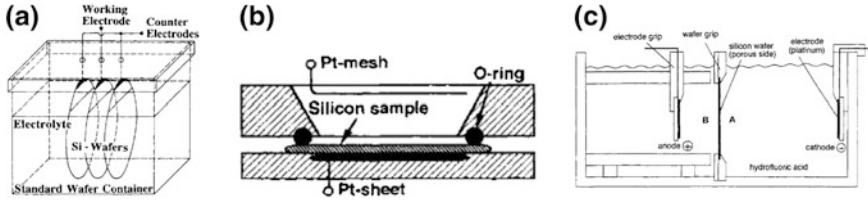
## 1.2 Basic Concepts

Typically, porous silicon structures are produced by electrochemical etching of silicon wafers in organic solutions of acetonitrile ( $\text{CH}_3\text{CN}$ ) or dimethylformamide ( $\text{C}_3\text{H}_7\text{NO}$ ) containing hydrofluoric acid (HF) [31, 32]. Nevertheless, other approaches such as chemical etching in mixtures of HF and nitric acid ( $\text{HNO}_3$ ) and metal-assisted etching have been intensively used to produce a variety of pSi structures. It is worth stressing that HF is highly corrosive towards living tissues and its inhalation, ingestion or skin contact are all extremely hazardous and can be lethal. Therefore, in addition to the standard laboratory protection, it is mandatory to first consider all the safety aspects related to HF handling. In general, during production of porous silicon by chemical or electrochemical etching methods, HF should be handled under a hood with proper ventilation, wearing personal HF gas monitor with audible alarm, safety sensor for liquids and proper personal protective equipment such as safety goggles, face shield, chemically resistant butyl rubber gloves and apron [31]. Note that prior to etching, the native oxide layer formed on commercial silicon wafers under ambient atmospheric conditions must be removed. There are several procedures to remove that oxide layer although the most widespread method is the so-called RCA cleaning process [33]. This process is divided into three steps: namely; (i) removal of organic contaminants, (ii) removal of the native oxide layer and (iii) removal of ionic contaminations. The first step is

performed in a mixture of deionised water, ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) at 80 °C for 10 min. This step removes organic residues and also particles from the surface of the silicon wafer. Furthermore, this treatment results in the formation of a layer of silicon dioxide with controlled thickness (i.e. 10 Å). The second step consists of a short immersion in a mixture of HF and water at 25 °C for about 15 s in order to remove the native oxide layer and some fraction of ionic contaminants. Finally, the third step is typically performed in order to effectively remove the remaining traces of metallic contaminants and create a thin passivating layer on the wafer surface. This step is carried out by dipping the silicon wafer in a mixture of water, hydrochloric acid (HCl) and  $\text{H}_2\text{O}_2$  at 80 °C for 10 min. Finally, after these pre-treatments, silicon wafers are ready to be electrochemically or chemically etched to produce pSi structures.

Another important aspect to have into account in the fabrication of pSi structures is the design of the electrochemical cell. This is extremely important as an inappropriate design of the cell can lead to broken samples, leaky set-ups and corroded contacts. Note that aspects such as materials, contacts and sealants are critical in the design of the electrochemical cell used to produce pSi by electrochemical or chemical etching approaches. Traditionally, since most common acid electrolytes used to prepare pSi are HF-based solutions, the materials of choice used to fabricate the body of the etching cells are resistant to HF. The most representative examples of these are polyvinyl chloride (PVC) and polytetrafluoroethylene (PTFE). However, other alternatives such as polyvinylidene fluoride (PVDF) can be used as well. As far as the sealant is concerned, standard black O-rings made of acrylonitrile-butadiene copolymer (Perbunan) or vinylidene fluoride-hexafluoropropylene (Viton) are preferred as they are stable in HF at concentrations up to 50 %. Furthermore, a good ohmic contact must be implemented in these cells used to produce pSi by electrochemical etching. In that respect, it is critical to consider the resistance of the metal used as a contact towards corrosion since a continuous exposure to the etching electrolyte can degrade its integrity with use and thus its performance. Typically, noble metals such as platinum or gold are the best choice as they are inert. Other materials such as stainless steel, brass, tungsten or aluminium can be used if the electrochemical cell is designed to prevent the electrical contact from exposure to the etching electrolyte (i.e. etchant). Therefore, an optimal design of the electrochemical cell becomes essential in order to produce pSi structures with controlled features under optimised conditions. It is worth stressing that, in addition to the aforementioned fundamental aspects, etching cells can feature multiple characteristics such as circulation of etching electrolyte, temperature controller and cooling system, automated stirring for bubble removal and enhanced reaction rate, illumination and so forth. The most representative examples of etching cells are the immersion cell, the O-ring cell and the double cell. Figure 1.2 shows illustrations of these etching cells used in pSi technology.

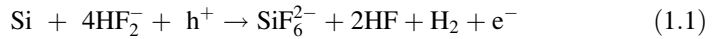
As discussed above, after the cleaning step and immersion in HF solutions, the silicon wafer surface is terminated with hydrogen atoms (Si-H). Hydrogen-terminated silicon surfaces are hydrophobic, showing a large contact angle for a drop of water [34, 35]. Silicon surfaces dipped in HF or in ammonium fluoride ( $\text{NH}_4\text{F}$ ) show equivalent hydrophobic character. However, the roughness of these



**Fig. 1.2** Schemes depicting basic designs of electrochemical cells typically used to produce porous silicon by electrochemical etching (adapted from [31]). **a** Immersion cell. **b** O-ring cell. **c** Double cell

surfaces is highly dependent on the chemical treatment and type of etchant. While  $\text{NH}_4\text{F}$  provides atomically flat surfaces for (111) and (100) oriented silicon surfaces, a treatment with HF creates surfaces with nanometric roughness [36, 37].

As far as the chemical dissolution of hydrogen-terminated silicon is concerned, this process requires the replacement of superficial H atoms by fluoride ions ( $\text{F}^-$ ), which are incorporated from the etching electrolyte solution. Under open circuit conditions, the silicon surface remains passivated. Therefore, an electronic hole ( $\text{h}^+$ ) must be generated to create a neutralized Si-F bound. The Si-F bound can be created under certain anodic bias by the polarisation effect induced by the F atom over the Si atom. Following this mechanism, a new  $\text{F}^-$  atom bounds the Si atom at a different position and a gas hydrogen molecule ( $\text{H}_2$ ) is generated. The progressive repetition of this process weakens the Si-Si bonds by the strong electronegativity of F atoms through nucleophilic attack (1.1).



Finally, Si atoms are etched away from the Si surface by reaction with HF and thus pores are generated into the Si wafer progressively [38, 39]. For this reason, the fabrication process of pSi is considered a top-bottom approach. So far, many different mechanisms have been proposed to explain the pore formation in pSi. Most of the theories deal only with certain aspects of the pore formation mechanism. Nonetheless, it is generally accepted that pore formation in pSi is a result of different mechanisms [32]. Therefore a complete model explaining the formation mechanism of pSi is yet to come.

Another important aspect in the fabrication of pSi structures is the use of wet chemical etching with alkaline etchants, which are mainly used for chemical polishing or anisotropic etching of silicon. These pre- and post-treatments make it possible to design and engineer a broad range of pSi structures. The most widespread alkaline etchants used to etch silicon are potassium hydroxide (KOH) and tetramethyl ammonium hydroxide (TMAH), although other inorganic and organic compounds such as lithium hydroxide (LiOH), sodium hydroxide (NaOH), rubidium hydroxide (RbOH), caesium hydroxide (CsOH), ammonium hydroxide ( $\text{NH}_4\text{OH}$ ), cholin and ethylenediamine have been used as well [33, 40–53]. It is worthwhile mentioning that the etching rate of silicon in these etchants is highly dependent on

the crystal planes, the doping level of the silicon crystal and the etchant concentration and its temperature.

Porous silicon structures featuring a broad range of pore geometries, sizes and morphologies can be produced by electrochemical etching of silicon wafers. The resulting pore features of pSi rely not only on the etching conditions but also on such parameters as the doping level of the Si wafer, its crystallographic structure, pre- or post-treatments and so on [30, 54]. Following the International Union of Pure and Applied Chemistry (IUPAC) nomenclature used to classify porous materials as a function of their pore size ( $d_p$ ), pSi structures can be divided into three categories: (i) microporous silicon ( $\mu$ pSi) with  $d_p < 2$  nm, mesoporous silicon (mpSi) with  $2 \text{ nm} < d_p < 50$  nm and macroporous silicon (MpSi) with  $d_p > 50$  nm. Although pSi can present a variety of morphological details, these can be divided into two main categories: (i) sponge-like pSi, which features densely and randomly distributed branched pores and (ii) pSi featuring cylindrical pores, which can have rough or smooth walls. While  $\mu$ pSi and mpSi structures feature sponge-like morphology, MpSi structures have cylindrical pores.

As far as the spatial distribution of pores, MpSi structures present a random distribution. However, these structures can be produced featuring a perfectly ordered spatial distribution of pores. To this end, the surface of the silicon wafer must be patterned by lithographic techniques before the electrochemical etching process is carried out. In contrast, the sponge-like morphology of  $\mu$ pSi and mpSi cannot be defined by a concrete spatial distribution because of the complex structure of their porous network.

As mentioned above, the resulting pore structure in pSi is intrinsically dependent on the doping level of the Si wafer. For example, MpSi is produced by electrochemical etching of n-type wafers. The etching of p- and n-type Si wafers with a high or moderate level of doping yields mpSi structures and  $\mu$ pSi structures. The reason why the pore characteristics of the resulting pSi structures depend upon the doping type and its level of the silicon wafer is that the pore formation mechanisms relies on these parameters. For instance, different formation mechanisms are involved in the formation of MpSi structures by electrochemical etching of n-type Si wafers (i.e. crystallographic face selectivity, enhanced electric field, tunnelling and quantum confinement). The enhanced electric field and tunnelling mechanisms are associated with the formation of mpSi structures when highly or moderately doped Si wafers are electrochemically etched in HF solutions. Finally, the space-charge limited mechanism is associated with the pore formation in  $\mu$ pSi structures, which results when n-type silicon wafers are electrochemically etched in HF solutions.

### 1.3 Electrochemical Etching of Silicon

The fabrication process of pSi structures by electrochemical etching is a cost-competitive and versatile method, by means of which a variety of porous structures with outstanding physical and chemical properties can be produced. This

**Table 1.1** Summary of the most representative electrochemical etching conditions used to produce porous silicon structures and their geometric features (adapted from [31])

| Type | J (mA cm <sup>-2</sup> ) |                              | Doping Density (cm <sup>-3</sup> )             |                                                 |                                                |
|------|--------------------------|------------------------------|------------------------------------------------|-------------------------------------------------|------------------------------------------------|
|      |                          |                              | 1 × 10 <sup>17</sup>                           | 1 × 10 <sup>18</sup>                            | 1 × 10 <sup>19</sup>                           |
| p    | 300                      | Pore morphology and porosity | Sponge-like 80 %                               | Narrow long pores with dendritic branches 75 %  | Wide long pores with high wall roughness 80 %  |
|      | 30                       |                              | Sponge-like 70 %                               | Sponge-Like 60 %                                | Medium long pores with dendritic branches 50 % |
|      | 3                        |                              | Sponge-like 60 %                               | Sponge-Like 40 %                                | Narrow long pores with dendritic branches 40 % |
| n    | 300                      | Pore morphology and porosity | Wide long pores with low wall roughness 35 %   | Wide long pores with medium wall roughness 40 % | Narrow long pores with dendritic branches 45 % |
|      | 30                       |                              | Medium long pores with dendritic branches 10 % | Narrow long pores with dendritic branches 15 %  | Narrow long pores with dendritic branches 20 % |
|      | 3                        |                              | Sponge-like 10 %                               | Sponge-like 20 %                                | Sponge-like 30 %                               |

has turned pSi into one of the most widespread materials, which is currently present in many research fields with multiple applications. This section deals with the different aspects involved in the production of MpSi, mpSi and  $\mu$ pSi structures by electrochemical etching of silicon wafers. Table 1.1 summarises the most representative etching conditions and geometric features of pSi structures produced by electrochemical etching of silicon wafers.

### 1.3.1 Macroporous Silicon

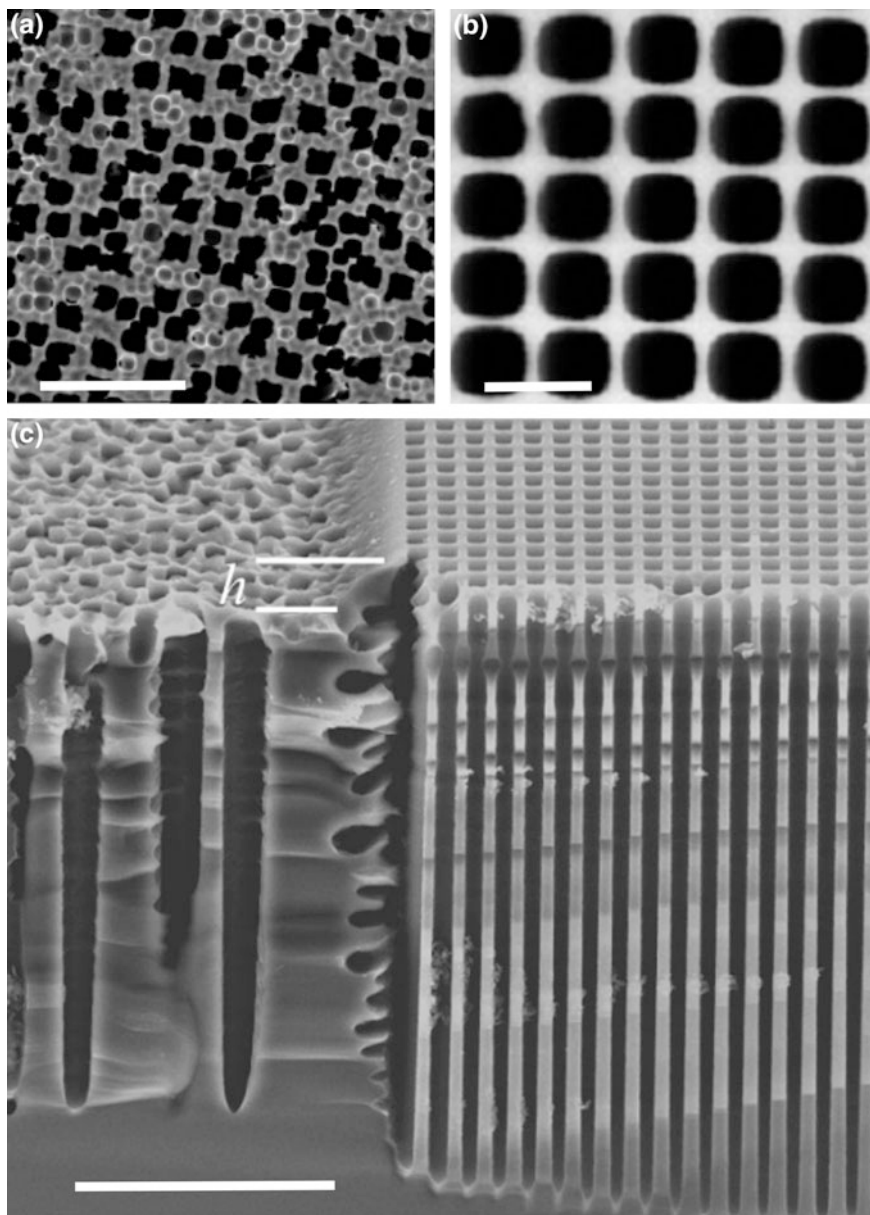
Macroporous silicon is typically produced by electrochemical etching of n-type silicon wafers. The porous structure of MpSi is very versatile and can be broadly modified by different electrochemical approaches. As far as the pore formation mechanism of MpSi is concerned, electronic holes initiate the dissolution process of silicon and these are minority charge carriers in n-type silicon. Therefore, the concentration of electronic holes in n-type silicon under equilibrium conditions is very low. However, electronic holes can be generated by illuminating the backside

of the silicon wafer. Under such circumstances, three types of charges are present in the bulk silicon: namely, electronic holes, electrons and ionized donors. The system is at neutral state when the concentration of electrons is equal to the concentration of electronic holes and ionized donors together. Therefore, for a given level of doping, the growth of MpSi in n-type silicon substrates can be led by the current density and the illumination applied in the course of the etching process. As-produced MpSi has a random pore distribution since pores nucleate uniformly on the Si wafer surface (Fig. 1.3a, c). Nonetheless, a pre-treatment by a lithographic patterning stage enables the production of MpSi structures with perfectly ordered pores featuring square or triangular arrangement (Fig. 1.3b, c).

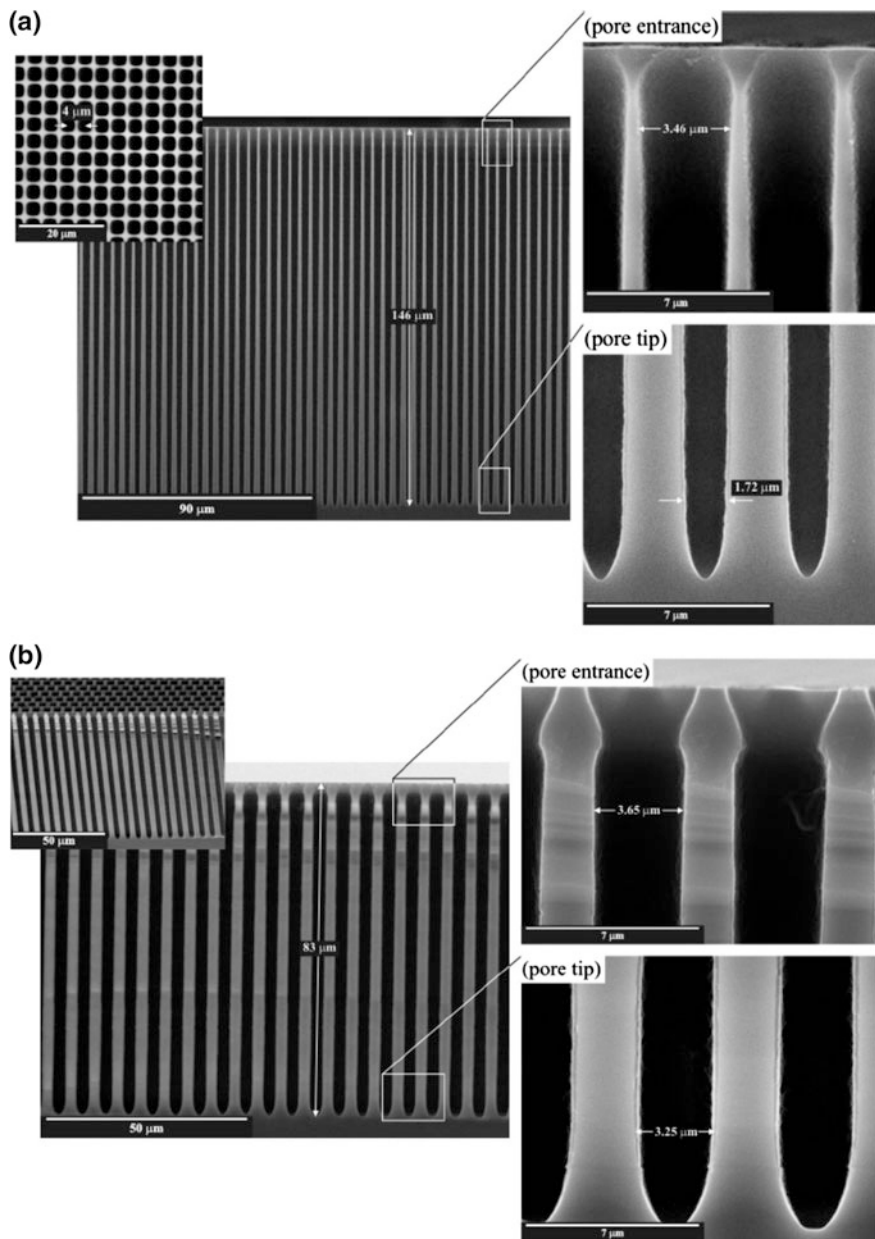
The growth of well-defined cylindrical macropores from top to bottom in MpSi can be precisely controlled through the etching parameters (e.g. etching current density, HF concentration and its temperature, wafer doping, illumination intensity, etc.). In particular, among these parameters, the etching current density ( $J$ ) is a critical factor to lead a homogeneous pore growth as the longer the pore the more effective the collection of photo-generated holes. Therefore, the etching current density must be increased as macropores grow in order to obtain straight and well-defined cylindrical pores from top to bottom. This can be achieved by adjusting the illumination intensity at the backside of the Si wafer during the etching process. Otherwise, according to the Lehmann's law, the increasing collection of photo-generated holes results in a progressive reduction of the pore diameter with depth, yielding cone-like pores with decreasing diameter from top to bottom [31].

This effect is shown in Fig. 1.4, which depicts the difference between macroporous silicon structures formed under constant (Fig. 1.4a) and progressively modified (Fig. 1.4b) illumination intensity. However, far from being a disadvantage, this approach can be readily used to develop some optical structures such as photonic crystals and optical waveguides in the visible and NIR range as the refractive index of MpSi can be engineered in depth along the pore yielding a waveguide structure embedded in the array of macropores [55, 56]. Furthermore, this technique can be combined with lithographic patterning to produce 2D infrared photonic crystals featuring perfectly ordered and straight macropores [57–64]. In this process, arrays of macropores are coated by a lithographic mask after electrochemical etching. Next, MpSi is selectively removed from the unmasked areas by a wet chemical etching. This results in a set of deep bars of macropore rows with well-defined pore geometry [61–63, 65].

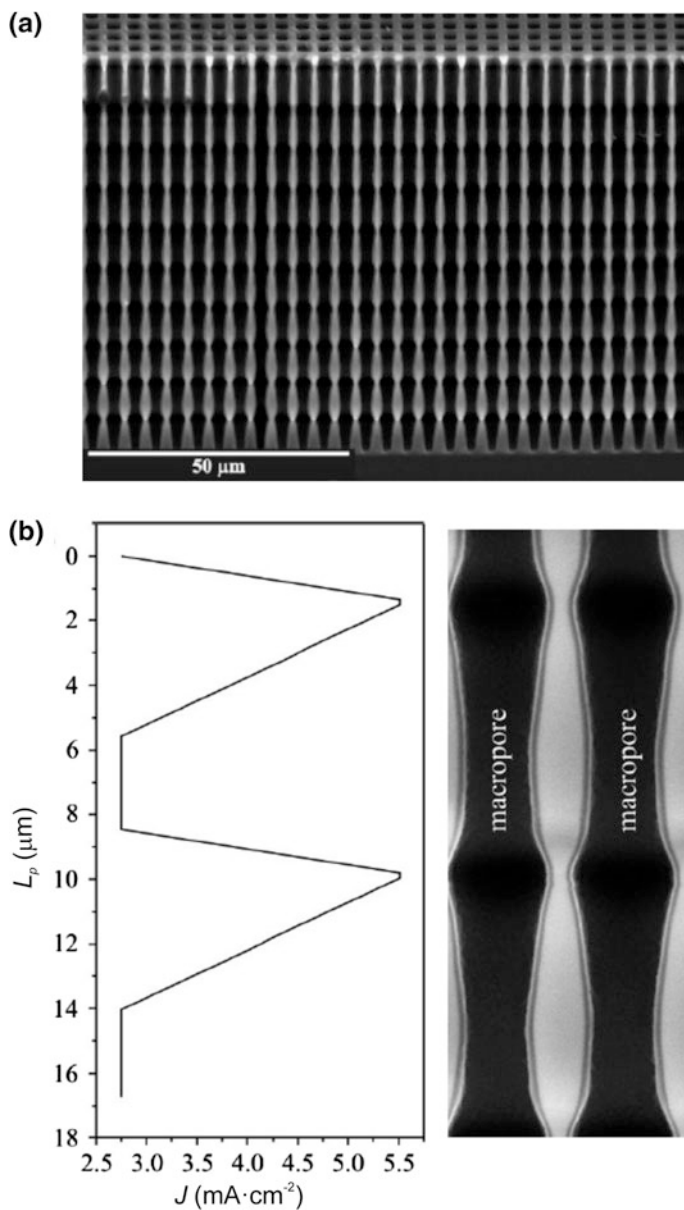
Following a similar approach based on the Lehmann's model, the pore diameter in macroporous silicon can be periodically modulated (Fig. 1.5). This approach takes advantage from the fact that the porosity of the resulting MpSi structure is established by the ratio between the total current density and the critical current density (i.e.  $J_{PS}$ —current density limit between the formation of pSi and electro-polishing of silicon). According to the Lehmann's model for the formation of MpSi, the current density at the pore bottom tips is equal to the critical current density.



**Fig. 1.3** Scanning electron microscopy images of macroporous silicon structures produced in n-type silicon substrates (adapted from [54]). **a** *Top-view* of as-produced MpSi (scale bar = 40  $\mu\text{m}$ ). **b** *Top-view* of MpSi patterned by photolithography (scale bar = 5  $\mu\text{m}$ ). **c** *Cross-section* depicting details of pores shown in structures (a) and (b) (scale bar = 40  $\mu\text{m}$ )



**Fig. 1.4** Scanning electron microscopy images of macroporous silicon structures produced in n-type silicon substrates under **a** constant and **b** progressively adjusted illumination intensity (adapted from [54])

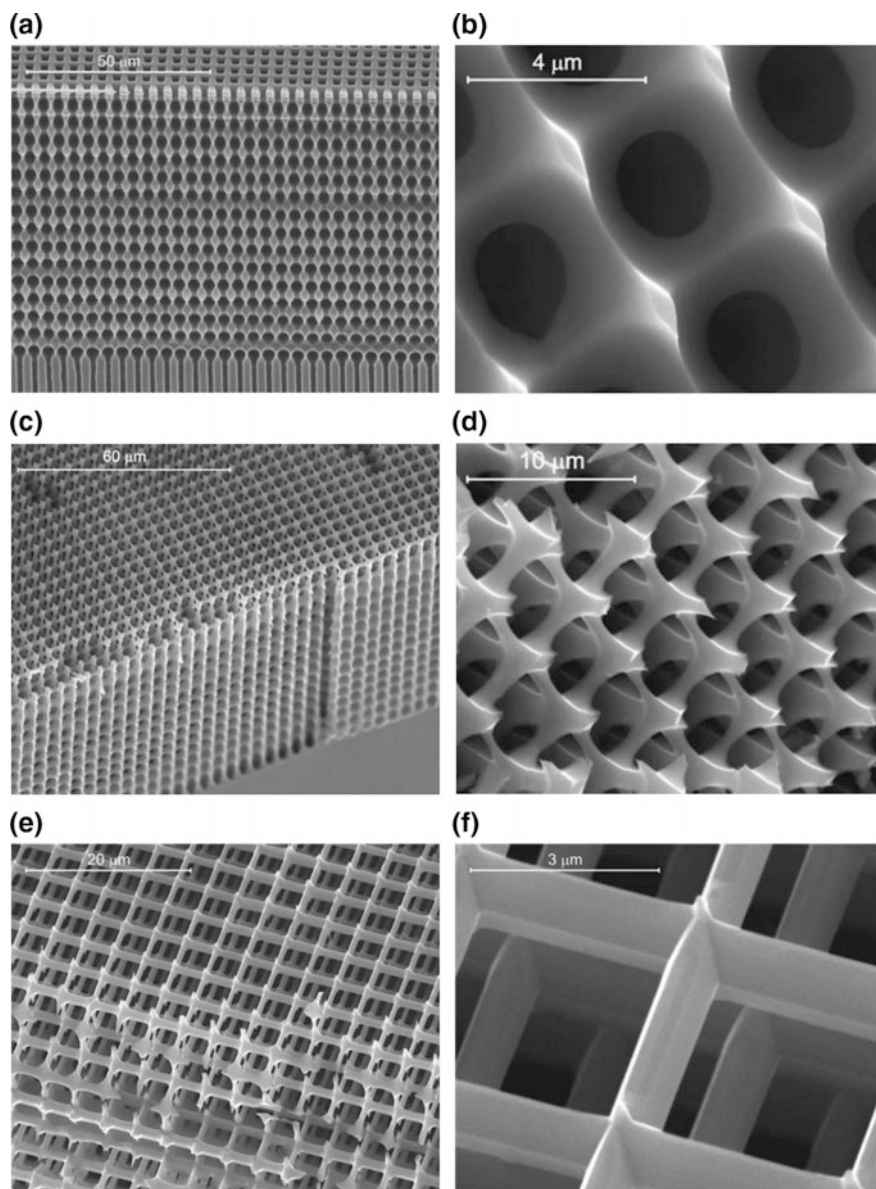


**Fig. 1.5** Scanning electron microscopy images of macroporous silicon structures featuring pore diameter modulations with depth (adapted from [54]). **a** Slanted cross-section view of MpSi with pore diameter modulations. **b** Relationship between current density profile and pore length and magnified view of macropores featuring diameter modulations

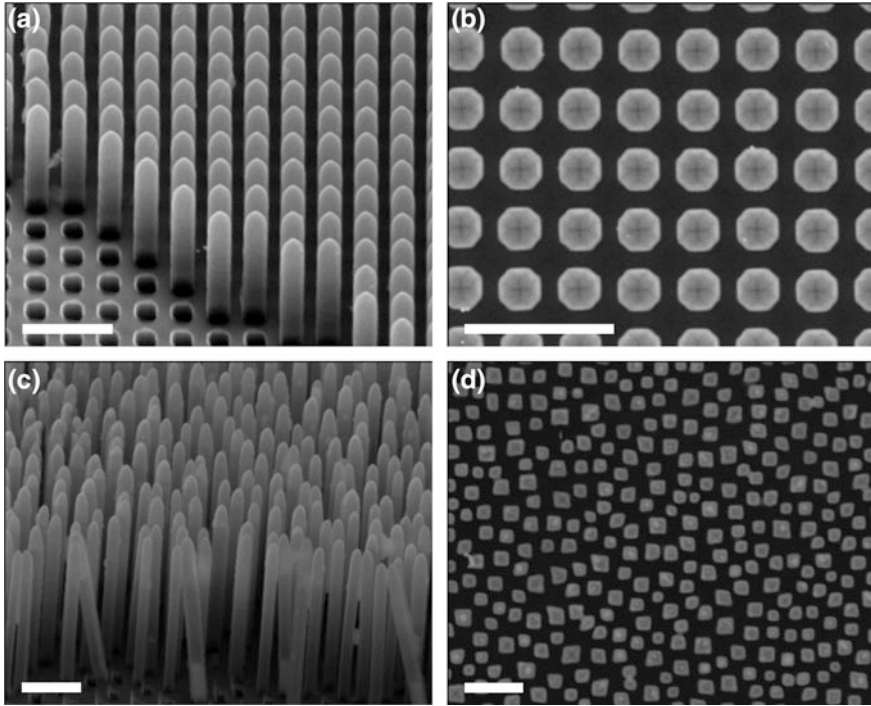
Therefore, an increment of the illumination intensity at the backside of the silicon wafer during etching leads to the generation of electronic holes, which directly contribute to the total current density. Note that the critical current density is constant at the pore bottom tips and thus the increment of the total current density produced by the generation of electronic holes widens the pore diameter. Following this procedure, the pore structure of MpSi can be modulated to produce periodic ratchet-type (i.e. asymmetric) or circular (i.e. symmetric) pore modulations.

In summary, pore diameter in MpSi can be periodically modulated by a periodical change of the illumination intensity at the backside of the Si wafer during the etching process since the current density profile is translated into the pore structure [66]. It is worth stressing that, if the etching conditions are not controlled, the period length, which is defined as the distance between two consecutive pore modulations, decreases with the pore depth due to diffusion limitations (i.e. lower concentration of HF at the pore bottom tips). As a result, the critical current density decreases and the pore growth rate becomes slower. Finally, pore diameter modulations in MpSi can yield a 3D network of interconnected macropores, which can be achieved by a suitable post-treatment (Fig. 1.6).

Other interesting structures that can be obtained from MpSi are silicon dioxide micropillars, the geometry of which is directly related to the pore geometry of the macroporous silicon structure (Fig. 1.7). To this end, a post-treatment is required after the fabrication of MpSi. This post-treatment starts with a thermal treatment of the MpSi structure at 1100 °C for 100 min under oxygen atmosphere. This generates a silicon dioxide layer of 200 nm along the inner surface of the pores of MpSi. Note that the structure of MpSi can result broken by oxide-induced stress in the course of this stage. Thinner MpSi layers minimise this problem since the bending curvature of silicon wafers relies linearly on the specific area of the MpSi structure [67]. Next, the silicon oxide layer is selectively removed from the backside of the silicon wafer by a wet chemical etching in a buffer HF solution (BHF). Finally, the remaining silicon is etched away by a wet chemical etching in a solution of TMAH 25 % wt at 85 °C. After that, a new structure based on silicon dioxide micropillars rises from the backside of the wafer as the silicon dioxide layer covering the pore walls is not etched by TMAH. The length of the resulting silicon dioxide pillars can be established by the etching time and by the pore length in the MpSi structure [68]. Additionally, free-standing silicon dioxide pillars (i.e. micropods) can be obtained if the TMAH etching step is extended until the whole Si wafer is removed. Furthermore, the backside of the silicon wafer can be patterned by lithographic methods after the oxidation stage, enabling a selective etching on the wafer backside by TMAH. Given that the etching process in TMAH is selectively performed over these areas without protective mask in an anisotropic manner, this approach makes it possible to produce arrays of silicon dioxide pillars inside truncated pyramids. The features of these 3D structures can be precisely controlled by the etching parameters and the features of the lithographic patterning. Furthermore, arrays of cone-like silicon dioxide pillars can be produced when conical MpSi is used as the starting material.



**Fig. 1.6** Examples of 3D networks produced from MpSi structures with modulated pores in depth (adapted from [54])



**Fig. 1.7** Scanning electron microscopy images of silicon dioxide micropillars produced from macroporous silicon structures (scale bars = 10  $\mu\text{m}$ ) (adapted from [54]). **a, b** Slanted cross-section and *top views* of silicon dioxide micropillars produced from MpSi featuring perfectly organised pore arrays, respectively. **c, d** Slanted cross-section and *top views* of silicon dioxide micropillars produced from MpSi featuring randomly distributed pore arrays, respectively

### 1.3.2 Mesoporous and Microporous Silicon

As discussed above, pore formation in pSi takes place under anodic conditions in HF electrolytes for current densities lower than  $J_{PS}$ . When the doping density in the silicon wafer is increased, the electric field strength increases, decreasing the width of the depletion region and enabling charge carriers to pass through the space charge region (SCR) by tunnelling. Therefore, at high doping densities (i.e.  $\geq 10^{18} \text{ cm}^{-3}$ ) tunneling mechanism dominates the charge transfer while avalanche breakdown is the dominant mechanism at low doping densities. Note that the electric field relies also on the pore geometry [20]. The electric field strength increases around the depressions and pits present on the silicon wafer surface. This results in a local reduction of the depletion region width, which increases the tunneling probability of charge carriers, incrementing the local current density. This effect becomes more significant when the size of the depression or pit is smaller than the SCR width [69]. In the course of the first seconds of the electrochemical

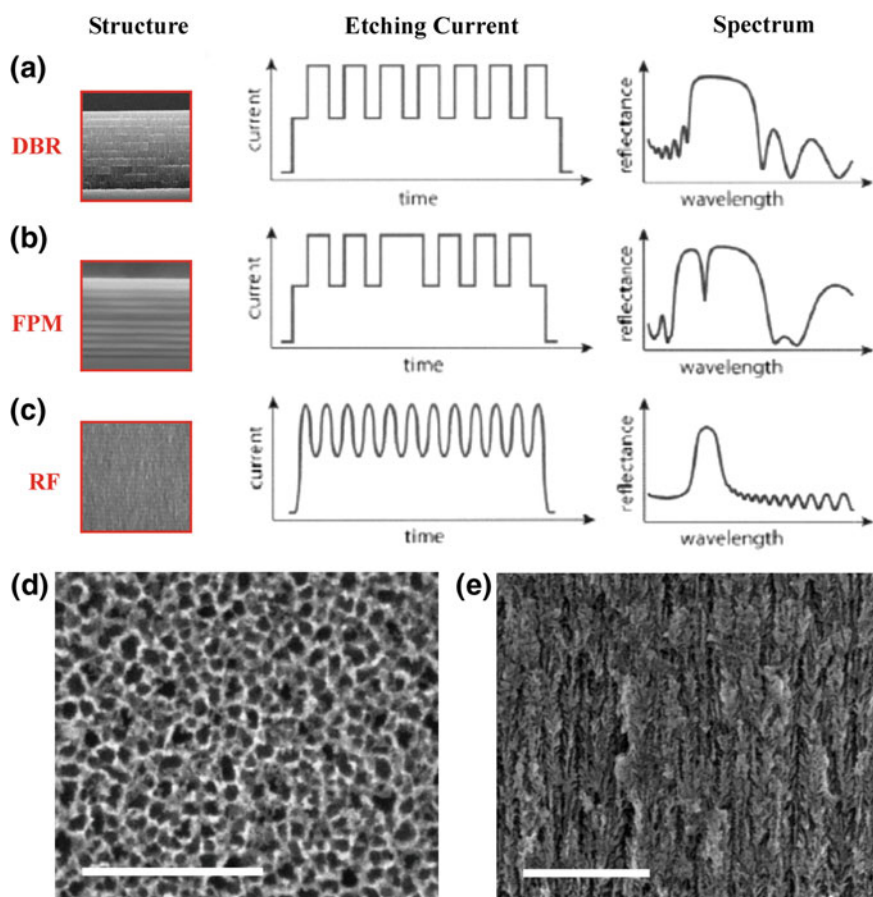
etching, some of these pits present on the surface of the silicon wafer develop into mesopores, the density of which across the surface is established by the doping level and the etching conditions. These mesopores are randomly distributed across the surface without organisation. Therefore, mpSi structures feature a sponge-like morphology with a distribution of pore diameters.

Microporous silicon structures can be obtained by electrochemical etching of p-type silicon wafers. Pore formation in  $\mu$ pSi is a complex phenomenon involving different mechanisms (i.e. quantum confinement, crystallographic face selectivity, tunnelling and enhanced electric field) [40].  $\mu$ pSi structures have high porosity and feature a porous structure with silicon walls of a few nanometres thick separating adjacent micropores. The formation of  $\mu$ pSi structures can be explained by the quantum confinement model, in which the energy bandgap in the wall region increases as a result of quantum confinement effect, generating an energy barrier for electronic holes. If that energy barrier is bigger than that of the bias-dependent energy of electronic holes, the porous structure is depleted of holes and thus passivated from dissolution during the etching process. Under these conditions, electronic holes enter the electrolyte preferentially at the pore bottom tips rather than across the pore walls, yielding the formation of micropores in the silicon structure from top to bottom [13]. Note that other models considering tunnelling effect and crystallographic face selectivity have been proposed to explain the formation of  $\mu$ pSi [70]. Nevertheless, a complete model explaining all the aspects involved in the formation of  $\mu$ pSi structures is yet to come.

In contrast to MpSi, the geometric dimensions of mpSi and  $\mu$ pSi are too small to scatter light in the visible range. So, the interaction of light with mpSi and  $\mu$ pSi structures is explained by the effective medium concept, where the optical properties of the material are established by its bandgap. Therefore, the interaction between light and matter in these porous structures can be designed by engineering their effective refractive index [71]. In that respect, it is worth noting that the refractive index of mpSi and  $\mu$ pSi structures presents certain anisotropy along the specific crystallographic axes. This anisotropy, which can range from 1 to 10 %, is associated with the elongated pore shape along the growth direction [72]. Furthermore, the effective refractive index of mpSi and  $\mu$ pSi structures is inversely proportional to their porosity [73]. The porosity of mpSi and  $\mu$ pSi relies mainly on the current density applied during the etching process. For this reason, multilayered mpSi and  $\mu$ pSi structures, which consist of stacks of porous silicon layers featuring different levels of porosity, can be produced from top to bottom by modifying the current density in the course of the etching process [74]. As a result of their geometric and optoelectronic properties, these structures have been extensively used to produce a variety of optical structures such as microcavities, distributed Bragg reflectors, waveguides, omnidirectional mirrors and rugate filters. The effective refractive index of each layer is directly related with the porosity level. So, the effective refractive index of pSi can be engineered in depth by alternating the current density during the etching process. In addition, the thickness of each layer can be precisely controlled by the etching time as the former is directly proportional to the latter. Therefore, the interaction between incident light and matter in mpSi

and  $\mu\text{pSi}$  structures can be engineered to produce optical nanostructures for a broad range of applications.

For instance, multilayered  $\text{mpSi}$  and  $\mu\text{pSi}$  structures can be used to develop distributed Bragg reflectors (DBR). Basically, a  $\text{pSi}$ -based DBR structure consists of multiple layers of  $\text{pSi}$  with different porosity levels and thicknesses (Fig. 1.8a) [75]. The interfaces between two consecutive layers of dielectric material reflect incident light due to the effective refractive index contrast. Therefore, constructive light interference can be engineered by designing the structure of the  $\text{mpSi}$ - or  $\mu\text{pSi}$ -based DBR (i.e. by designing the porosity and thickness of each layer). These



**Fig. 1.8** Schematic diagram showing the most representative optical structures based on meso and microporous silicon, their fabrication conditions (i.e. etching current) and their optical spectra. **a** Distributed Bragg reflector (DBR). **b** Fabry-Pérot microcavity (FPM). **c** Rugate filter (RF). **d** Scanning electron microscopy *top view* image of microporous silicon (scale bar = 200 nm) (adapted from [75]). **e** Scanning electron microscopy *cross-section view* image of microporous silicon (scale bar = 500 nm) (adapted from [83])

structures have been extensively used to develop optical filters and sensors [74, 76–82]. Furthermore, DBR structures based on mpSi and  $\mu$ pSi can be implemented into Fabry–Pérot filters, also called optical microcavities, which are composed of two parallel DBRs with a space layer of different effective refractive index in between (Fig. 1.8b). Note that the effective optical thickness of the space layer (i.e. product between the physical thickness and the effective refractive index of the layer) is typically engineered as the wavelength of the incident light or half of it [83]. The reflectivity spectrum of microcavities based on mpSi and  $\mu$ pSi shows a narrow pass-band centred at the wavelength where the light is reflected with the highest intensity. Therefore, the structural design of microcavities based on mpSi and  $\mu$ pSi makes it possible to develop optical pass-band filters and sensors [84, 85]. If the current density profile is modified in a sinusoidal manner in the course of the electrochemical etching, the effective refractive index of mpSi and  $\mu$ pSi can be modulated to produce rugate filters, which are another type of optical structure used in optoelectronic and sensing applications (Fig. 1.8c) [86, 87].

Another important optical property of mpSi and  $\mu$ pSi structure is their photoluminescence (PL), which has been extensively studied during the last decades [88]. Bulk crystalline silicon presents a very weak PL peak at 1100 nm. This limits the use of silicon to develop optoelectronic devices, which are aimed at converting light into electricity (e.g. photodetectors, solar cells, etc.). However, the discovery of bright red-orange photoluminescence and the identification of confinement effects in the absorption spectrum of pSi by Canham and Gösele in 1990, respectively, were the starting point of a flood of studies focused on the development of optoelectronic devices based on mpSi and  $\mu$ pSi structures such as switches, displays and lasers [12, 13]. PL properties of mpSi and  $\mu$ pSi structures depend on the etching conditions. The different PL bands in pSi can be tuned from blue-green, red-orange to IR by adjusting the etching conditions. For instance, an increment of the current density, a decrease in the concentration of HF or an increase of the illumination intensity lead to blue shifts in the PL peak of mpSi and  $\mu$ pSi. In addition, it is worth stressing that PL in pSi is dependent on the porosity level as well as the doping density [89].

## 1.4 Metal-Assisted Etching of Silicon

Metal-assisted chemical etching of silicon is considered a simple and cost-competitive alternative to conventional electrochemical methods. This approach has been used to produce pSi structures with precisely defined geometric features and characteristics not achievable by other fabrication approaches [90, 91]. As discussed above, electrochemical etching of silicon occurs anisotropically along (100) directions. In contrast, the etching direction in metal-assisted etching can be controlled on (100) and non-(100) directions to produce pSi structures with slanted growth directions [92, 93]. Furthermore, metal-assisted etching enables the fabrication of pSi structures with high surface-to-volume ratio, high crystalline quality

and low level of defects [94–96]. In addition, metal-assisted etching makes it possible to produce pSi structures within a broad range of feature sizes, which can range from 5 nm to >1  $\mu\text{m}$  [97, 98]. For these reasons, metal-assisted etching of silicon has become an alternative approach to conventional electrochemical etching methods. Porous silicon structures produced by this approach have demonstrated their applicability in a broad range of fields such as sensing, energy storage and conversion and so on [99–110]. Metal-assisted etching of silicon was pioneered by Dimova et al. in 1997 when they etched a silicon substrate covered by a thin film of aluminium in a solution composed of HF,  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$  [111]. After this, Li and Bohn found that thin films of noble metals such as gold (Au) and platinum (Pt) sputtered on the surface of silicon catalysed the formation of pSi in an ethanoic electrolyte composed of HF and  $\text{H}_2\text{O}_2$  [112]. The resulting pSi structures featured wires and straight pores. These studies revealed that when a silicon substrate is partly covered by a noble metal and it is immersed in an etchant solution composed of an oxidative agent (e.g. hydrogen peroxide) and HF, the silicon beneath the noble metal is etched at a faster rate than that of the uncovered silicon. As a result, the noble metal sinks into the silicon substrate, producing pores or pillars depending on the etching conditions and the metal features. Basically, the geometric features of the resulting pSi structures are established by the noble metal mask. Furthermore, under some conditions and likewise in electrochemical etching, microporous silicon structures can be generated in the off-metal regions of the silicon wafer (i.e. areas without noble metal cover) as a result of chemical etching [112, 113].

#### ***1.4.1 Pore Formation Mechanism in Metal-Assisted Etching of Porous Silicon***

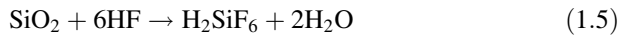
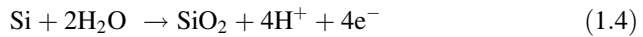
As far as the mechanisms and reactions involved in the formation of pSi structures produced by metal-assisted etching is concerned, it is well-known that chemical and electrochemical reactions occur near the interface between the noble metal and the silicon substrate when the system is immersed in an etchant composed of HF and  $\text{H}_2\text{O}_2$  [114–120]. So far, several reaction models have been proposed to describe the electrochemical reactions taking place during the formation of porous silicon by metal-assisted etching [112, 121]. In this system, the noble metal works as a cathode, where hydrogen peroxide is reduced at the metal surface following these electrochemical reactions (1.2 and 1.3) while the silicon works as the anode:



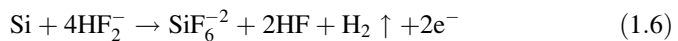
It is worth stressing that, although these electrochemical reactions are well-accepted, other studies have attributed the evolution of gas during the etching process to anodic reactions [118, 122]. As far the anode, the silicon substrate is

progressively oxidised and dissolved in the course of the metal-assisted etching. Several electrochemical models explaining the anodic reactions taking place in this process have been proposed. These can be divided into three groups:

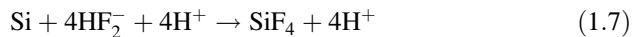
*Model I:* In this model, silicon is first oxidised (1.4), yielding silicon dioxide, which is subsequently dissolved by HF (1.5) [118, 119, 123–127].



*Model II:* Silicon is directly dissolved in divalent state (1.6) [115, 118].



*Model III:* Silicon is directly dissolved in tetravalent state (1.7 and 1.8) [112, 114, 116, 117, 121, 128–130].



Although these models explain partially the formation process of porous silicon by metal-assisted etching, a complete model explaining this electrochemical phenomenon as a whole is yet to come [90]. In analogy with chemical etching of silicon, it is accepted that charge transfer between noble metal and silicon occurs for the oxidation and dissolution of the latter by hole injection mechanism [112, 128, 131–135]. In that system, the noble metal plays the role of cathode, where the reduction of the oxidant takes place. Holes generated in the noble metal are then injected into the silicon substrate, oxidising silicon atoms, which subsequently are dissolved by reacting with HF. Note that electronic hole injection is verified by the dependence of the etching morphologies on the level of doping and the etchant solution. In summary, metal-assisted etching of porous silicon can be divided into five stages (Fig. 1.9):

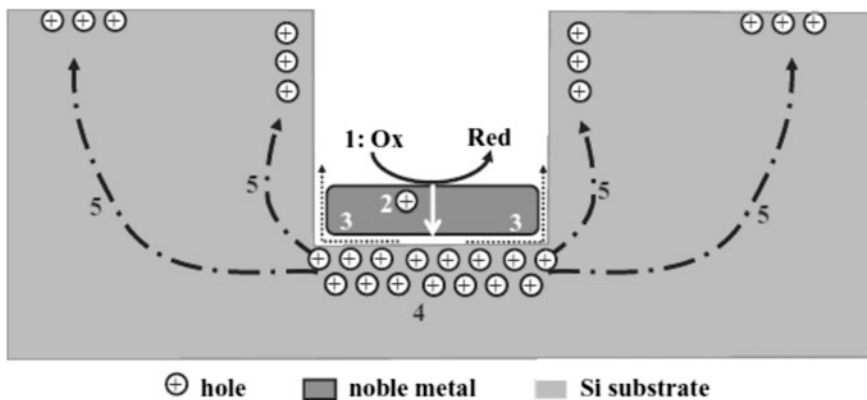
*Stage 1:* The oxidant is reduced at the noble metal surface due to its catalytic activity.

*Stage 2:* The reduction of the oxidant generates electronic holes, which are subsequently injected into the silicon substrate through the noble metal interface.

*Stage 3:* Electronic holes oxidise silicon atoms at the interface noble metal-silicon, which are then etched away by HF molecules.

*Stage 4:* The concentration of electronic holes is maximum at the interface noble metal-silicon and thus its dissolution rate is much faster there.

*Stage 5:* The remaining electronic holes (i.e. those not consumed during the dissolution of silicon) diffuse from the interface noble metal-silicon to the bulk silicon.



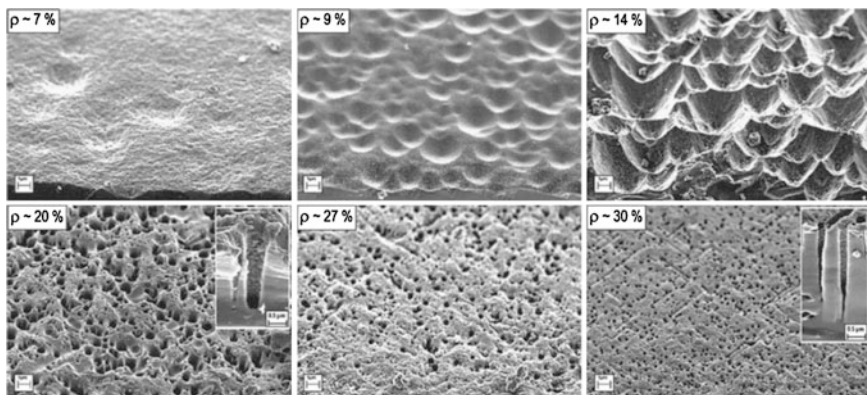
**Fig. 1.9** Schematic diagram illustrating the formation mechanism of porous silicon by metal-assisted etching of silicon (adapted from [90]). Note that numbers 1, 2, 3, 4 and 5 denote the different stages involved in this electrochemical process

### 1.4.2 Influence of Fabrication Parameters in Metal-Assisted Etching of Porous Silicon

The resulting structural features of pSi produced by metal-assisted approach rely on different parameters such as the etchant composition and its temperature, the nature of the noble metal, the illumination and the intrinsic properties of the silicon substrate (e.g. doping type and level, crystallographic orientation, etc.). In this section, we will provide a brief but comprehensive description of the main parameters playing a role in the fabrication process of pSi by metal-assisted etching of silicon.

Regarding the type of oxidant, hydrogen peroxide is the most commonly used although other oxidants such as oxygen bubbles, oxygen dissolved in water, silver nitrate ( $\text{AgNO}_3$ ), chloroauric acid ( $\text{HAuCl}_4$ ), potassium gold(III) chloride ( $\text{KAuCl}_4$ ), chloroplatinic acid ( $\text{H}_2\text{PtCl}_6$ ), potassium hexachloroplatinate ( $\text{K}_2\text{PtCl}_6$ ), iron nitrate ( $\text{Fe}(\text{NO}_3)_3$ ), nickel nitrate ( $\text{Ni}(\text{NO}_3)_2$ ), magnesium nitrate ( $\text{Mg}(\text{NO}_3)_2$ ), potassium permanganate ( $\text{KMnO}_4$ ), sodium persulphate ( $\text{Na}_2\text{S}_2\text{O}_8$ ) and potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) have been explored as well [93, 112, 115, 125, 129, 136–142]. Note that the resulting morphologies and structural features of metal-assisted etched pSi differ from one oxidant to another as they can change the morphology of the metal or produce different precipitates in the course of the etching process [90].

Another important parameter that directly affects the geometric features of the resulting pSi produced by metal-assisted etching is the concentration and composition of the etchant electrolyte. For instance, etching of silicon wafers coated with platinum particles in an etchant with low concentration of HF ( $\text{HF}(50\%): \text{H}_2\text{O}_2(30\%): \text{H}_2\text{O} = 2:1:8$ ; v:v:v) yields pores with cone-like morphology from top to bottom. Nevertheless, this effect can be notoriously reduced by increasing the



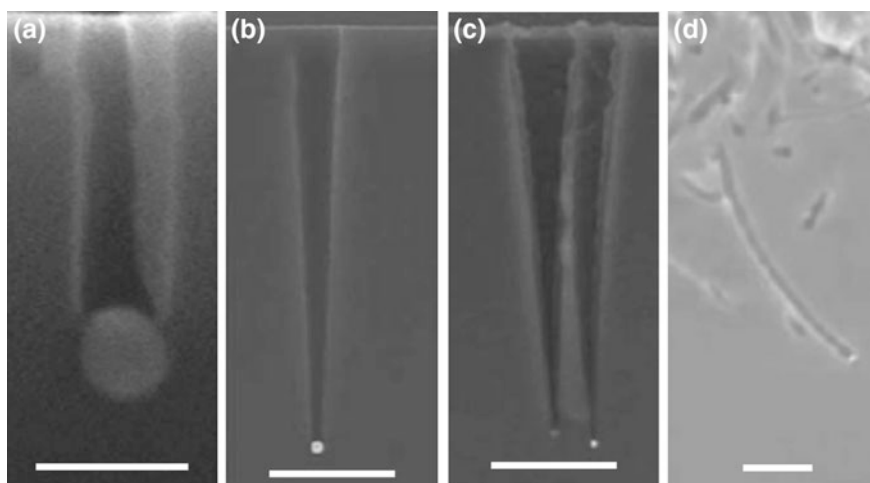
**Fig. 1.10** Scanning electron microscopy images showing morphological details of porous silicon structures produced by metal-assisted etching of silicon with different ratio acid/etchant ( $\rho = [\text{HF}]/([\text{HF}] + [\text{H}_2\text{O}_2])$ ) (adapted from [118])

concentration of HF fourfold ( $\text{HF}(50\%):\text{H}_2\text{O}_2(30\%) = 10:1$ ; v:v) [113]. In that respect, Chartier et al. studied the effect of the ratio  $\text{HF}/\text{H}_2\text{O}_2$  on the resulting morphology of pSi in a systematic manner (Fig. 1.10) [118]. In their study, p-type (100) silicon wafers were first coated with silver particles by electroless deposition. The obtained results revealed that for  $100\% > [\text{HF}]/([\text{HF}] + [\text{H}_2\text{O}_2]) > 70\%$ , the resulting pores featured cylindrical and straight geometry, which almost matched the diameter of the silver nanoparticles at the bottom of the pores. Nevertheless, cone-line pores were obtained for  $70\% > [\text{HF}]/([\text{HF}] + [\text{H}_2\text{O}_2]) > 20\%$ , with decreasing pore diameter from top to bottom. For  $20\% > [\text{HF}]/([\text{HF}] + [\text{H}_2\text{O}_2]) > 9\%$ , crater-like pSi structures featuring micrometric opening diameters were obtained. Finally, a nanometric pitted surface was obtained when the silicon wafers were etched in an etchant with  $9\% > [\text{HF}]/([\text{HF}] + [\text{H}_2\text{O}_2]) > 0\%$ . This change of pore morphology and geometric features with the ratio acid/oxidant was explained by the fact that at high concentrations of HF (i.e.  $100\% > [\text{HF}]/([\text{HF}] + [\text{H}_2\text{O}_2]) > 70\%$ ), the etching rate is determined by the oxidant concentration and the electronic holes generated at the interface noble metal-silicon are rapidly consumed as a result of the excess of HF available to dissolve silicon. However, when the ratio acid/oxidant is lower than  $70\%$ , the etching rate starts to be determined by the HF concentration. In such a scenario, the generation of electronic holes is higher than their consumption rate and thus the excess of electronic holes diffuse away to the pore walls, where  $\mu\text{pSi}$  structures are generated. At high concentrations of oxidant (i.e.  $20\% > [\text{HF}]/([\text{HF}] + [\text{H}_2\text{O}_2]) > 9\%$ ) electronic holes diffuse massively towards the surface of silicon in contact with HF, resulting in an isotropic etching independent on the silver particles present on the wafer surface.

Apart from the ratio between acid and oxidant, the etching rate is also affected by other factors such as the etchant temperature and the diffusion of by-products (e.g.  $\text{SiF}_6^{2-}$ ) and etchant through the pores [117]. In that respect, some studies have

demonstrated that bigger pores enable faster etching rates as a result of a more efficient diffusion of etchant and by-products through the pores and the interface noble metal-silicon. Furthermore, more efficient diffusion rates can be achieved by stirring the etchant during the etching process. Another important factor directly related with the etching rate is the temperature of the etchant. Cheng et al. demonstrated that the etching rate of silicon nanowires produced by metal-assisted etching of silicon in  $\text{HF}/\text{H}_2\text{O}_2$  and  $\text{HF}/\text{AgNO}_3$  increases with the temperature from 0 to 50 °C [143]. Moreover, it was established a linear relationship between the silicon nanowires length and the etching time within the aforementioned range of temperature.

As far as the different aspects associated with the noble metal is concerned, the most typical metals used to etch silicon by metal-assisted approach are silver, gold, platinum and palladium. These metals can be deposited by thermal evaporation, electroless deposition, electrodeposition, sputtering, electron beam evaporation, focused ion beam deposition, spin-coating and self-assembly of particles [93, 112, 121, 122, 124–127, 142, 144–146]. Furthermore, some of these deposition methods can be combined with lithography masks generated by micro and nanofabrication techniques. This enables the production of metal-assisted pSi structures with highly ordered geometric features. When isolated particles are used to produce metal-assisted pSi, the structure, geometric features and morphology of the resulting pSi are dependent on the noble metal. For instance, while Ag or Au particles yield pSi featuring straight pores (Fig. 1.11a, b), the pore geometry in pSi produced by etching through Pt particles can vary from well-defined straight pores,



**Fig. 1.11** Scanning electron microscopy images showing morphological details of pores produced by different noble metal nanoparticles through metal-assisted etching of silicon. **a** Silver nanoparticles (scale bar = 75 nm) (adapted from [130]). **b** Gold nanoparticles (scale bar = 10  $\mu\text{m}$ ) (adapted from [117]). **c** Platinum nanoparticles (scale bar = 15  $\mu\text{m}$ ) (adapted from [117]). **d** Platinum nanoparticles (scale bar = 1  $\mu\text{m}$ ) (adapted from [125])

helical-like pores or curvy-like pores (Fig. 1.11c). Under some conditions, Pt particles move randomly in the course of the etching process, producing complex pSi structures (Fig. 1.11d) [117, 130, 134, 135]. In addition, the etching rate varies from one noble metal to another. As an example, the etching rate achieved during the etching through Au particles is much slower than that obtained when Pt particles are used [112]. Another interesting phenomenon dependent on the noble metal is the formation of  $\mu$ pSi structures on the side walls of pores or wires during the etching process [113, 117, 135]. A detailed explanation of the origin of these effects is yet to come although some authors have pointed out towards the role of the noble metal type in the catalytic activity for the reduction of the oxidant. In that respect, Huang and Meyer et al. indicated that the more the injected electronic holes the faster the etching rate, resulting in a more efficient diffusion of electronic holes towards the side walls during the etching process and enabling the formation of  $\mu$ pSi structures on the side walls of pores or wires [147]. Apart from these effects, the geometric features and morphology of the resulting pSi structures are mainly established by the shape of the noble metal deposited on the surface of the silicon wafer as a result of its catalytic effect, which results in a much faster etching rate at the interface noble metal-silicon. Usually, well-defined and separated pores are produced from single particles distributed across the silicon surface. In contrast, when the distance between adjacent particles is reduced, wire-like or wall-like pSi structures are produced [148].

Typically, pores produced by metal assisted etching feature a cone-like structure with pore diameter decreasing with depth. This conical effect can be more or less pronounced, depending on the etching conditions, and the pore diameter at the pore mouth can be bigger or smaller than that of the initial noble metal particle [117]. This effect can be associated with the diffusion of electronic holes injected from the noble metal-silicon interface to the side walls, the partial dissolution of silicon by the etchant and the progressive dissolution and re-deposition of noble metal in the course of the etching process [31, 93, 113, 118, 120, 137]. In addition, silicon wires with well-defined geometry and shape are obtained when a homogeneous noble metal film featuring holes is deposited on the surface of a silicon substrate and subsequently etched in a suitable etchant solution. Note that the resulting silicon wires can be produced with highly ordered distribution and precisely controlled geometry if the surface of the silicon is patterned by lithographic approaches prior to the deposition of the noble metal film. Note that the thickness of the noble metal film has a direct effect on the morphology of the resulting pSi structures as well. For instance, 3 and 5 nm thick films of gold lead to pores or wires, respectively [134]. In the case of silver films, 5 nm thick films yield pores while films of 20–50 nm thickness result in silicon wires [144]. Furthermore, it is important to bear in mind that the morphology of the resulting noble metal films can vary with the deposition technique and the nature of the noble metal [93, 145].

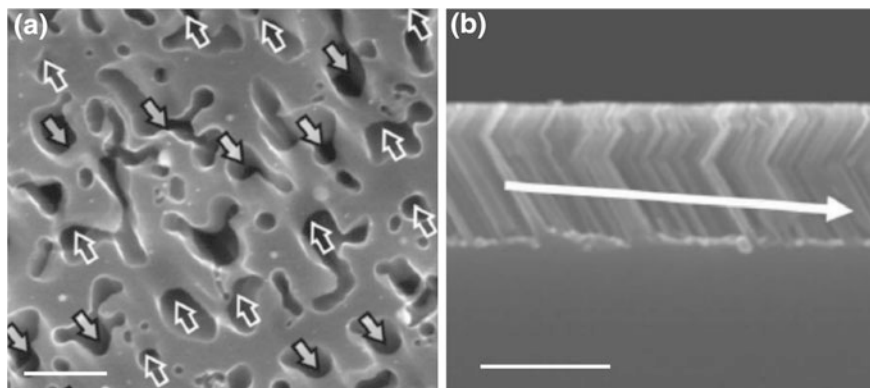
Regarding the stability of the noble metal in the etchant, this is highly dependent on its nature and some noble metals can be oxidised and dissolved in the course of the etching process according to the existing relationship between the electrochemical potentials of the noble metal and the oxidant. Typically, Au and Pt

particles are stable at high concentrations of oxidants, maintaining their shapes during the etching. However, as mentioned above, Ag particles dissolve and re-deposit during the etching process as a result of the relatively low electrochemical potential of silver. Therefore, Ag particles can change their shape and morphology during this process, leading to pores or wires with heterogeneous geometric features and morphologies with depth [117, 135]. Usually, Au particles and films are preferably used to produce pSi structures with well-defined and precisely controlled geometric features and morphologies due to its stability in the etchant. For instance, Au meshes have been used to fabricate silicon wires of high aspect ratio (i.e.  $>200$ ) [145].

As far as the effect of light illumination in metal-assisted etching of silicon, this has a direct effect on the etching rate. It has been reported that the etching rates for p-type and n-type (100) silicon substrates of resistivity 1–10  $\Omega$  cm differ whether the etching process is conducted with or without illumination. For instance, the etching rate of p- and n-type silicon wafers under room light illumination is about 0.05 times faster than under dark conditions. This difference becomes even higher (i.e. 150 times faster) when 20 W illumination is used. This effect can be explained by the fact that under illumination the number of photoexcited electronic holes can be higher than the number of electronic holes injected from the oxidant agent, thus enabling faster etching rates.

Another important parameter affecting the resulting pSi structures produced by metal-assisted etching are the different intrinsic properties of the silicon substrate, which have a direct effect on the geometric features and characteristics of the resulting pSi structures. Actually, metal assisted etching of silicon is anisotropic and dependent on the crystallographic orientation of silicon. As an example, slanted porous silicon structures can be produced by etching (111) and (110) silicon wafers (Fig. 1.12a, b) [104, 116, 117, 119, 149, 150]. In analogy with anisotropic electrochemical etching of silicon in HF and chemical etching in alkaline solutions, this phenomenon has been related to the back-bond breaking theory [97, 119, 151, 152]. In this theory, the number of the back-bonds of a silicon atom on the surface of the substrate is established by the crystallographic orientation of the substrate. The back-bonds of the silicon atoms located on the surface of the substrate must be broken during the oxidation and dissolution of silicon. Therefore, the etching of silicon atoms becomes more difficult for stronger back-bonds. In that respect, it is worth noting that silicon atoms have one, two and three back-bonds in (100), (110) and (111) substrates [153].

Regardless of this hypothesis, which explains some aspects of the dependence of the metal-assisted etching of silicon with the crystallographic orientation, a definitive and complete model entirely explaining this phenomenon is yet to come [90]. Furthermore, other aspects such as the influence of the doping type and its level on the etching rate of silicon by metal-assisted approach remain unclear [112, 134]. As far as the doping type is concerned, Zhan et al. reported that the etching rate in n-type silicon is faster than that of p-type silicon for (100) and (111) crystallographic orientations with the same resistivity (i.e. 7–13  $\Omega$  cm) [120]. Nevertheless, the etching rate is not the only parameter affected by the type of doping. It has been



**Fig. 1.12** Scanning electron microscopy images showing the effect of the crystallographic orientation of the silicon substrate on the resulting pores produced by metal-assisted etching of silicon. **a, b** Top and cross-section images of a (110) silicon substrate etched by silver nanoparticles (scale bars = 200 and 800 nm, respectively) (adapted from [93]). Note that the *white arrow* in **(b)** denotes the propagation direction of silver nanoparticles in the course of the etching process

reported that the morphology of silicon nanowires produced by metal-assisted etching of silicon changes with the doping level of the wafer as well and they can present rough surface or contain mpSi or  $\mu$ pSi structures on the side walls with increasing doping level [109, 120, 154, 155]. This result could be ascribed to the fact that in highly doped silicon wafers the diffusion of electronic holes occurs from the interface noble metal-silicon to the bulk silicon substrate, which would result in the etching of the side walls, producing mpSi or  $\mu$ pSi structures.

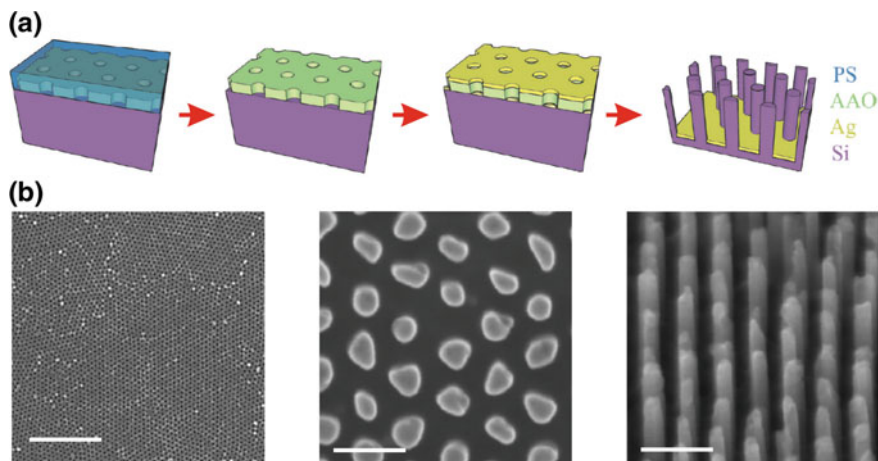
### 1.4.3 Metal-Assisted Etching of Porous Silicon Combined with Lithographic Methods

As mentioned above, pSi structures with precisely controlled and exquisitely defined morphology and geometric features can be produced when the surface of the silicon wafer is patterned by lithographic techniques prior to the etching step. In particular, some lithographic methods have demonstrated outstanding results when combined with metal-assisted etching. The most representative ones are interference lithography, nanoporous anodic alumina masks and nanospheres lithography.

Interference lithography (IL) is a top-down nanofabrication technique with high throughput and scalability for large surface areas used in the production of nanostructures. IL provides excellent definition of features at nanometric scale. Usually, an IL pattern is generated by two coherent laser beams and subsequently transferred to a film of photoresist covering the substrate [156]. Then, the resist film is developed and an array of parallel and orthogonal lines of photoresist is generated

on the silicon substrate surface. IL can be combined with metal-assisted etching to produce silicon nanowires. For instance, Choi et al. used this approach to produce silicon nanowires by metal-assisted etching [94]. In this study, first, silicon substrates were coated by a layer of photoresist, which was cured and exposed to IL. Unexposed photoresist areas were removed after immersion in the developer, revealing free areas for etching. Then, the size of the photoresist features was enlarged by oxygen plasma etching. After that, the patterned silicon substrate was coated with a layer of gold and metal-assisted etching was carried out. This process resulted in perfectly ordered arrays of silicon nanowires. Note that the geometric features and arrangement of these arrays of silicon wires can be accurately designed by modifying the IL patterns and the feature size and its shape [95]. Therefore, silicon wires with square, rectangular and circular cross-sections can be produced by this approach.

Another approach used to etch the surface of silicon wafers at specific positions by metal-assisted etching is the use of nanoporous anodic alumina (NAA) masks. Self-ordered NAA is basically a nanoporous matrix based on alumina (aluminium oxide— $\text{Al}_2\text{O}_3$ ) that features close-packed arrays of hexagonally arranged cells, at the centre of which a cylindrical nanopore grows perpendicularly to the underlying aluminium substrate [157–161]. NAA is produced by electrochemical anodization of aluminium, which is typically performed in acid electrolytes based on aqueous solutions of sulphuric ( $\text{H}_2\text{SO}_4$ ), oxalic ( $\text{H}_2\text{C}_2\text{O}_4$ ) or phosphoric acids ( $\text{H}_3\text{PO}_4$ ). In this system and similar to electrochemical etching of silicon, the anode (i.e. aluminium foil) and cathode (e.g. platinum wire) are immersed in the acid electrolyte and the growth of nanopores is produced by the application of current or voltage. Note that the geometric features of pores in NAA can be precisely controlled by the anodization parameters. Typically, pore sizes in NAA can range from 20 to 400 nm, with a pore density from  $5 \times 10^8$  to  $3 \times 10^{10}$  pores per  $\text{cm}^2$  [161–163]. Huang et al. used ultrathin masks of NAA in order to deposit noble metal films on the surface of silicon wafers [137]. The noble metal films were patterned with holes, the size, geometry and arrangement of which were determined by the NAA mask. In this approach, a NAA mask 300 nm thick with pores of 20 nm of diameter was placed on the surface of a silicon substrate by solution-based transfer process. Then, RIE etching was carried out in order to transfer the NAA pattern on the silicon surface with high accuracy and fidelity. Subsequently, the NAA mask was dissolved by wet chemical etching and a thin layer of Au or Ag was deposited on the surface of the patterned silicon substrate. Next, the system was etched in a solution composed of HF and  $\text{H}_2\text{O}_2$  in order to generate silicon nanowires. This lithographic approach makes it possible to produce silicon wires with controlled geometry, morphology and size with high crystalline quality and smooth surface. Furthermore, the geometric and morphological features of the resulting silicon nanowires are dependent on the thickness of the noble metal film. Nonetheless, the pores produced by RIE etching can have a thin defective region, which can prevent or hinder the metal-assisted etching process. To overcome this drawback, the same authors used a slight modification of the aforementioned approach in order to avoid the use of RIE (Fig. 1.13a, b) [93]. In this new approach, a film of Ag was deposited on the

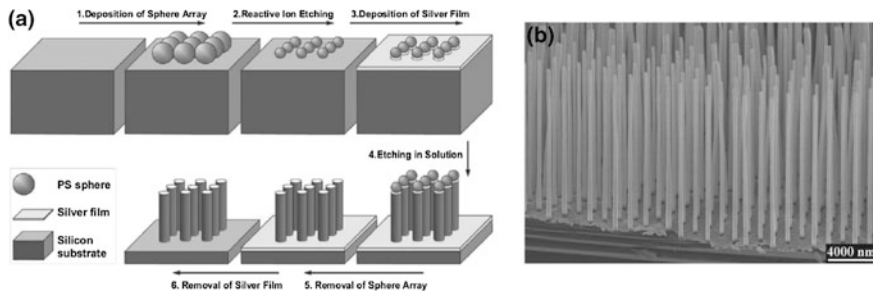


**Fig. 1.13** Approach developed by Huang et al. to use nanoporous anodic alumina mask to produce porous silicon nanowires by metal-assisted etching of silicon (adapted from [93]). **a** Schematic diagram illustrating the fabrication process. **b** Top view of Ag-coated NAA mask, cross-section and slanted cross-section images of the resulting silicon nanowires (scale bars = 100 nm)

NAA mask and the whole system etched in the aforementioned etchant solution. In this way, the Ag film with holes was transferred from the top of the NAA mask to the surface of the silicon substrate as a result of the dissolution of the NAA mask. Then, the etching occurred on the surface of the silicon by metal-assisted etching catalysed by the Ag film.

The main advantage of the use of NAA masks to produce pSi structures by metal-assisted etching is that it can be carried out in a simple wet chemistry laboratory without expensive facilities. However, self-ordered NAA structures present defects and domains, which are inevitably transferred to the patterned structure on the silicon substrate and thus to the resulting arrays of silicon nanowires. This can be overcome by producing NAA mask with perfect pore organisation, which can be achieved by nanoimprint lithography [164, 165]. Another limitation of this approach is that only silicon nanowires featuring circular section can be obtained.

Nanosphere lithography method is another lithographic approach extensively used to produce pSi structures by metal-assisted etching. Huang et al. developed an approach where a monolayer of self-assembled polystyrene (PS) nanospheres was first deposited on the surface of a silicon substrate (Fig. 1.14a, b) [136]. After this, the size and distance between adjacent nanospheres were increased by RIE etching and a noble metal film was deposited on the silicon surface by thermal evaporation. Note that the feature size and geometric and morphological characteristics of the noble metal film were determined by the mask created by the nanospheres. Therefore, a noble metal film with ordered arrays of pores resulted after metal deposition. The resulting system was etched in a mixture of HF and H<sub>2</sub>O<sub>2</sub> and silicon nanowires with well-defined morphology and geometry were produced by



**Fig. 1.14** Nanospheres lithography used to produce porous silicon by metal-assisted etching of silicon (adapted from [136]). **a** Schematic diagram depicting the fabrication process. **b** Cross-section scanning electron microscopy image of the resulting silicon nanowires

this approach. Silicon nanowires matched with high degree of fidelity the pattern determined by the nanospheres mask. This approach can be extended over large areas with a broad range of geometries given that these features are established by the size of the spheres, which can be produced with controlled geometry. Furthermore, a broad range of nanospheres composed of different materials can be used for this purpose [149]. Finally, it is worthwhile mentioning that silicon nanowires of high aspect ratio tend to form bundles or collapse as a result of surface tension forces during the drying process [166]. This drawback can be overcome by supercritical drying approach [145, 162].

## 1.5 Conclusions

Micro and nanostructures based on porous silicon have been used in research fields, which range from optoelectronics, sensing, energy generation and storage, medicine, chemistry and so forth. Traditionally, electrochemical and chemical etching methods have been used to produce a variety of porous silicon structures featuring multiple geometric and morphological details. These methods have become more and more popular in the last years, making porous silicon one of the most extensively used materials in science. In that respect, a good understanding of the different physical and chemical phenomena taking place during chemical and electrochemical etching of silicon is a key factor in the development of this technology. A better understanding of the different formation mechanisms playing a role in the formation of porous silicon has enabled the implementation of multiple strategies and approaches aimed at engineering the structure of this porous material. Note that this is a critical factor given that the physical and chemical properties of the resulting porous silicon are directly related to its porous structure. Particularly, in the recent years, special attention has been devoted to the development of optical sensing systems and drug delivery nanocarriers based on porous silicon. While its outstanding optical properties make porous silicon a unique material to develop

optical structures suitable for optical sensing, its biocompatibility and degradability properties have enabled the use of porous silicon structures as micro and nano-carriers for drug delivery.

In this chapter, we have compiled and described the fundamental and basic aspects of the fabrication of porous silicon by electrochemical and metal-assisted etching methods. While conventional electrochemical etching is the most widespread approach used to produce macro, meso and microporous silicon, metal-assisted etching has become a popular method to produce other type of structures based on porous silicon such as silicon nanowires. The different mechanisms involved in these processes have been properly described, although completed models explaining all the physical and chemical phenomena taking place during the formation of porous silicon are yet to come.

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