

Chapter 2

Fundamentals of porous silicon and applications

In this chapter, the porous silicon formation process is explained. This process consists of the electrochemical etching of silicon wafers in solutions based on hydrofluoric acid. Firstly, the electrochemical etching process is described and the different stages of the porous silicon formation are explained. The anodization parameters that influence on the final characteristics of the fabricated layers are also discussed and the porous silicon photoluminescence is briefly explained, as the discovery in the 90s of this property generated the scientific interest on this material. Finally different applications of porous silicon are presented. Although porous silicon has many potential applications in many areas we especially focus on the optical applications, that are the ones studied during this work.

2.1. History of Porous silicon

Porous silicon was discovered in 1956 by Uhlir [1] while performing electropolishing experiments on silicon wafers using an electrolyte containing hydrofluoric acid (HF). He found that under the appropriate conditions of applied current and solution composition, the silicon did not dissolve uniformly but instead fine holes were produced, which propagated primarily in the $\langle 100 \rangle$ direction in the wafer. Therefore, porous silicon formation was obtained by electrochemical dissolution of silicon wafers in aqueous or ethanoic HF solutions.

In the 1970s and 1980s the interest on porous silicon increased because the high surface area of porous silicon was found to be useful as a model of the crystalline silicon surface in spectroscopic studies [11,12], as a precursor to generate thick oxide layers on silicon, and as a dielectric layer in capacitance-based chemical sensors [13].

In the 1990s Leigh Canham published his results on red-luminescence [14,15] from porous silicon, that was explained in terms of quantum confinement of carriers in nano-crystals of silicon which are present in the pore walls. Since that time, the interest of researchers and technologists to this material (and other porous semiconductors as well) is constantly growing and the number of publications dedicated to this class of materials increases every year. With the discovery of efficient visible light emission from porous silicon came an explosion of work focused on creating silicon-based optoelectronic switches, displays, and lasers. During the last twenty years, the optical properties of porous silicon have become a very intense area of research [16].

Porous silicon is a very promising material due to its excellent mechanical and thermal properties, its obvious compatibility with silicon-based microelectronics [17] and its low cost. Its large surface area within a small volume, its controllable pore sizes, its convenient surface chemistry, and the ability to modulate its refractive index as a function of depth [18] makes porous silicon a suitable dielectric material for the formation of multilayers [19].

All these features also leads, on one hand, to interesting optical properties by mixing silicon with air in the effective medium approximation. On the other

hand the pores allow the penetration of chemical and biological substances, liquids, cells, molecules to change i.e. the optical behavior of the original system. These effects inspired research into different applications like optical sensing applications [20,21] and biomedical applications [22,23].

2.2. Basics of the porous silicon formation process

2.2.1. Electrochemical etching of porous silicon

One of the most important advantages of porous silicon is its simple and easy preparation [24]. Since the first studies of Uhlir [1] and Turner [25], and lately Cahnam [2], porous silicon has been mainly obtained by electrochemical dissolution of silicon wafers in solutions based on hydrofluoric acid (HF) [26].

A schematic of the porous silicon formation process can be seen in Fig. 2.1. The surface of a silicon wafer, contacted on the back, is in contact with a solution containing hydrofluoric acid (HF). After applying a voltage (in the right direction) between the wafer backside contact and an electrode in the HF solution, a pore growth by silicon dissolution starts, provided certain key parameters are set correctly.

In the past, many studies of porous silicon formation have been limited exclusively to an electrochemical characterization of its current-voltage (i - V) relationships with the Schottky diode model of the semiconductor/electrolyte interface playing a predominant role. Although additional analysis techniques have been recently used to study porous silicon, the understanding of porous silicon formation still comes from the i - V relationships, and a basic knowledge of silicon electrochemistry is essential to understand the fundamentals of pore formation [27-32]. An overview of semiconductor electrochemistry can be found in Fig. 2.2.

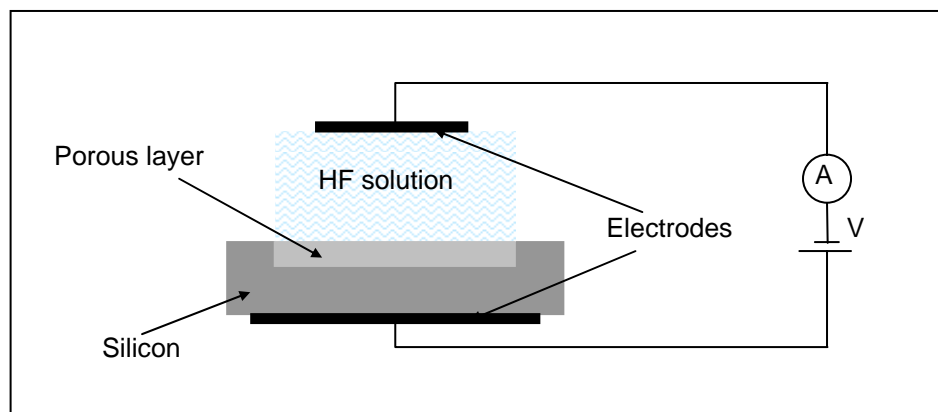


Fig. 2.1. Schematic diagram of the porous silicon anodization circuit.

In this section we outline only the more basic electrochemical features of the i - V relationships. Fig. 2.2 shows the typical i - V curves for n- and p-type silicon in aqueous HF. The i - V curves show some basic similarities to the normal Schottky diode behavior expected from a semiconductor/electrolyte interface, including photogenerated currents at reverse bias. But there also exist some differences [27-30,33]. The first of all is that even though the type of majority carriers changes between n- and p-type, the chemical reactions at the interface remain the same. Second the reverse-bias dark currents have been reported at least three orders of magnitude higher than those normally expected for Schottky diodes.

Both n- and p-type silicon are stable under cathodic polarization. The only important cathodic reaction is the reduction of water at the silicon/HF interface, with the simultaneous formation of gaseous hydrogen. This reaction occurs only at high cathodic overpotentials or, using Schottky-diode terminology, at reverse biased breakdown.

Dissolution of silicon occurs only under anodic polarization. At high anodic overpotentials the silicon surface goes under electropolishing. On the contrary, at low anodic overpotentials the surface morphology is dominated by a dense array of channels penetrating deeply into the bulk of the silicon [34].

The pore formation occurs only during the initial rising part of the i - V curve, for a potential value below the potential of the first sharp peak. The current at this peak is named as the electropolishing current (J_{PS}). The zone of the i - V curve at which the pore formation occurs is gray colored in Fig. 2.2.

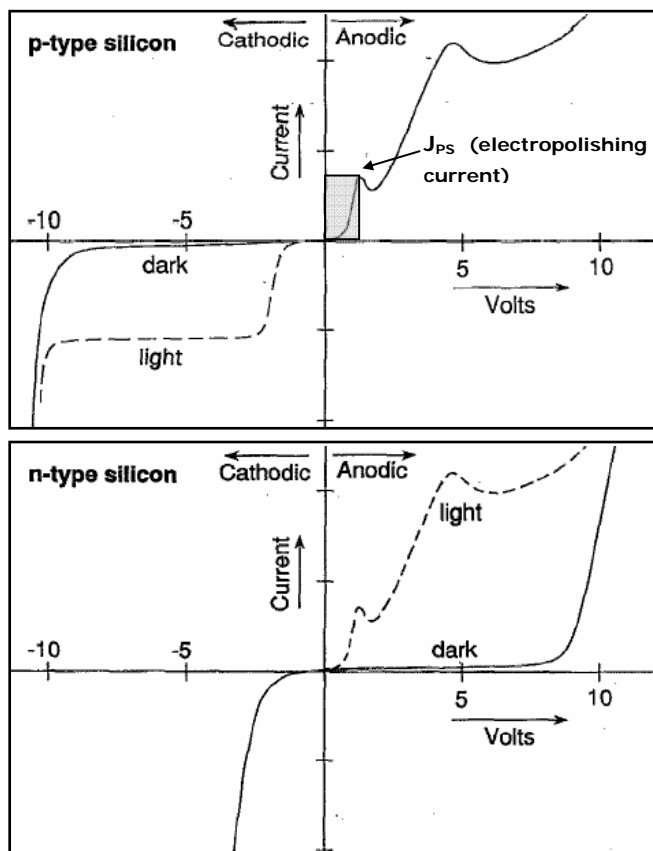


Fig. 2.2. Characteristic i - V curves for n- and p-type doped silicon in aqueous HF. The solid line indicates the dark response and the dashed line shows a response under illumination. The first (lower) current peak J_{PS} corresponds to the formation of a surface anodic oxide formed during, and required for, electropolishing. The second (higher) current peak marks the beginning of stable current (potential) oscillations with the possible formation of a second type of anodic oxide. The gray area indicates the useful regime for the formation of porous silicon [Adapted from 26].

The quantitative values of the i - V curves, as well as the values corresponding to the electropolishing peak, depend on the etching parameters and wafer doping. For n-type substrates, this typical i - V behavior is observed only under illumination because hole supply is needed. More details about the characteristics of the curves i - V are extensively explained in [26,33,35].

It is worth to underline that the parameter that has physical meaning in the anodization process is the current density J (at the silicon/electrolyte interface), rather than the absolute current i . J and i scale with a fixed constant for a given cell, provided that the area of the silicon sample exposed to the electrolyte is well defined and fixed.

2.2.2. Porous silicon formation chemistry

To form porous silicon the current at the silicon side of the silicon/electrolyte interface must be carried by holes, injected from the bulk towards the interface. The current must be kept between zero and the electropolishing threshold, as has already been shown in Fig. 2.2. In order to achieve significant hole current in n-type silicon, external illumination of the sample is required, depending on the doping level. If the current exceeds the electropolishing threshold, the anodization results in a progressive, complete removal of silicon. The wafer has then a mirror-like appearance.

Up to now, several different mechanisms regarding the dissolution chemistry of silicon have been proposed but it is generally accepted that holes are required for both electropolishing and pores formation.

The global anodic semi-reaction can be written during pore formation as



The final and stable product for silicon in HF is H_2SiF_6 , or some of its ionized forms; it follows that during the pore formation only two of the four available silicon electrons participate in an interface charge transfer while the remaining two undergo a corrosive hydrogen formation.

Amongst the various models proposed for the silicon dissolution reaction, the mechanism presented by Lehmann and Gösele [4] is the most accepted in the porous silicon community.

Similarly to most semiconductor junctions, at the silicon/electrolyte interface a depletion zone is formed (see Fig. 2.3). The width of this depletion zone depends on the doping and may explain the different pore sizes found in p- and p+ type doped silicon. In addition, the depletion layer width depends on the surface curvature: the anodization preferentially occurs at the pore tips where the curvature is largest. Moreover, when the depletion zones of adjacent pores meet each other, the current flow is suddenly pinched off. Further silicon etching is blocked, and pore collapsing is prevented. For this reason the reaction is self limited in the colored anodization regimes of and leads to a porous structure rather than to electropolishing. As further practical consequence, in stationary conditions, the porosity remains approximately constant, whereas the overall thickness of the porous silicon layer grows essentially linearly in time.

Further dissolution occurs only at the pore tips, where enough holes are available, as is schematically represented in Fig. 2.3. In this way the etching of porous silicon proceeds in depth with an overall directionality which follows the anodic current paths inside silicon. Once a porous silicon layer is formed no more electrochemical etching occurs but a slow chemical one starts, due to the permanence in HF.

For the case of n-type silicon, the application of back-side illumination in potentiostatic regime allows further control on the hole injection, both in terms of carrier flux (which is proportional to illumination intensity) and of localization of the injection, which is concentrated in the region of the pore tips, acting as hole collectors. The etching process leads to a very regular pore growth, which is most effectively exploited to fabricate macroporous photonic crystal devices, as the one presented in Fig. 2.4.

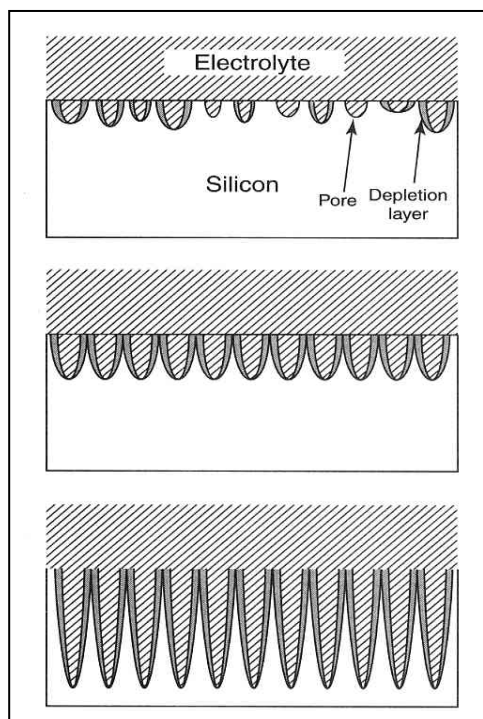


Fig. 2.3. Pore formation in porous silicon. The upper figure shows the initial stage, where the pores develop randomly on the silicon surface. In the middle, the self-regulating process is shown. When the depletion zones around each pore overlap, the pore growth changes from an isotropic growth to a highly directional growth. The bottom figure shows how the dissolution advances only at the pore tips. [After 36].

Up to this point, we can say that the main requirements for porous silicon formation are:

1. The silicon wafer must be anodically biased. This corresponds to forward biasing for p-type doped silicon, and reverse biasing for n-type doped silicon.
2. For n-type doped and semi-insulating p-type doped silicon, light must be supplied.
3. Current densities below the critical value, J_{PS} , must be used.

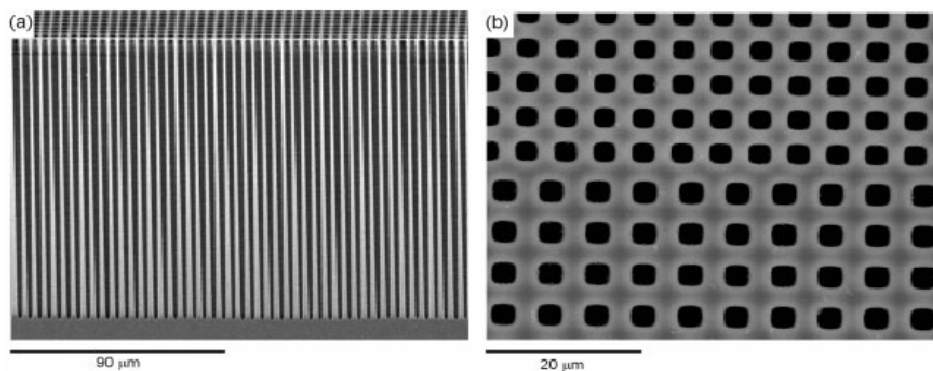


Fig. 2.4. Example of a two-dimensional photonic crystal. a) Cross section and b) top-view images of the same sample. It was realized with ordered macroporous porous silicon in a n-type doped silicon substrate [After 37].

The first two conditions are due to the fact that holes are consumed during the silicon etching. When the third condition is not fulfilled, the reaction is limited by mass transfer to the solution: holes pile up at the silicon-HF interface and electropolishing occurs.

For all the three conditions mentioned above the holes play an important role: in fact, porous silicon formation is a self-regulated mechanism, with hole depletion as the limiting agent. The dissolution reaction begins at defects on the silicon wafer surface, the pores are formed and their walls are eroded until they are emptied of the holes. This formation process passivates them from further attack, and the reaction proceeds at the pore end, as is represented in Fig. 2.3.

The overall etching process is self-adjusting and the average pore size is given by the electrochemical parameters only.

2.2.3. Pore size and morphology

The existing nomenclature, adopted by the International Union of Pure and Applied Chemistry (IUPAC), distinguishes three categories with regard to the pore dimensions [38]: micropores, mesopores and macropores with average pore diameters of < 2 nm, 2-50 nm and > 50 nm, respectively.

This categorization is related only to the pore diameter, but does not contain much information about the pore morphology. The term pore morphology is used for properties like shape (smooth, branched, faceted, etc.), orientation, interconnection of pores, etc. The morphology is the least quantifiable aspect of porous silicon. It is very difficult to systematically characterize the morphology of porous silicon, which has extremely rich details with respect to variations in pore size, shape and spatial distribution. In terms of the pore morphology, it can be summarized that microporous and mesoporous silicon exhibit typically a sponge-like structure with densely and randomly branched pores, which do not show a clear orientation. The tendency to branch increases with decreasing pore diameter. In contrast, macroporous silicon can have discrete pores with smooth walls, with short branches or with dendritic branches.

The pores grow preferentially along $\langle 100 \rangle$ directions and towards the source of positive carriers (holes), which are involved in the electrochemical dissolution reaction. Pores with smooth walls tend to be aligned to the source of holes, while dendritic pores are aligned in the $\langle 100 \rangle$ direction. In this thesis we study microporous silicon and the pore size and shape are not considered but for the reason that their variation and presence determine the refractive index of the porous silicon layer.

The formation of porous silicon is selective with respect to the doping of the substrate. Some general trends on the layer morphology can be derived for different types of starting silicon substrates. Fig. 2.5 shows four cross-sectional TEM images of porous silicon samples with different starting substrates [24]. The difference in morphology is evident. For p-type doped silicon both size and interpore spacing are very small (Fig. 2.5a), typically between 1 and 5 nm, and the pore network looks very homogeneous and interconnected. As the dopant concentration increases, pore sizes and interpore spacing increases, while the specific surface area decreases. The structure becomes anisotropic, with long voids running perpendicular to the surface, very evident in highly p-type doped silicon (p^+), as shown in Fig. 2.5c.

For n-type doped silicon the situation is more complicated. Generally, pores in n-type doped silicon are much larger than in p-type doped silicon, and pore size and interpore spacing decreases with increasing dopant concentrations. Lightly doped n-type substrates anodized in the dark have low porosity (1-10 %), with pores in the micrometer range. Under illumination higher values of porosity can be achieved, and mesopores are formed together with macropores. The final structure depends strongly on anodization conditions, especially on light intensity and current density. While highly n- and p-type doped silicon show similar structures (compare Fig. 2.5c and d), in n-type doped silicon the pores tend to form a randomly directed filamentary structure and tend to pipe forming large straight channels approaching the electropolishing regime (see Fig. 2.5b).

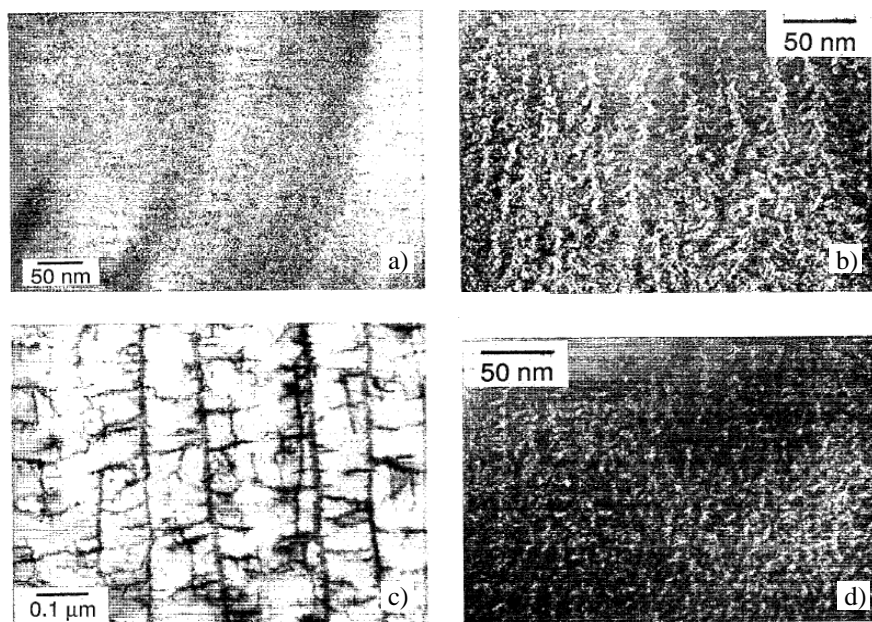


Fig. 2.5. Cross-sectional TEM images showing the basic differences in morphology among different types of samples. (a) p-type silicon; (b) n-type silicon; (c) p⁺-type silicon; (d) n⁺-type silicon. [After 26].

2.2.4. Anodization parameters

The porous silicon formation process with electrochemical anodization has been widely developed by many authors. [39-44]. The parameters that influence on this formation process are:

- The substrate doping.
- The current density.
- The HF concentration: the higher the concentration, the lower the pore size and the porosity. HF concentration determines J_{PS} , that is the upper limit to current density values. With a fixed and low HF concentration the range over which the current density can be varied is short, and it becomes wider by increasing the HF concentration.
- The solvent where the HF is diluted: since porous silicon is organophilic and hydrophobic, the use of ethanol guarantees a higher homogeneity, due to a better wettability of the surface than deionized water.
- The etching time: longer etching times lead to thicker layers, but for long times an anisotropy in depth in the layer due to the chemical action of the electrolyte is introduced.
- The illumination during the etch, essential for n-type substrates [40].

The porosity, thickness, pore diameter and microstructure of porous silicon depend on the anodization conditions, as is briefly explained in Table 2.I. These conditions include HF concentration, current density, wafer type and resistivity, anodization time, illumination (required for n-type silicon and semi-insulating p-type silicon), temperature, ambient humidity and drying conditions.

For a fixed current density, the porosity decreases when HF concentration increases [45,46]). Fixing the HF concentration and the current density, the porosity increases with the thickness. This happens because of the extra chemical dissolution of the porous silicon layer in HF.

| | Porosity | Etch rate | Critical current |
|-----------------------|------------------|------------------------|------------------|
| HF concentration | <i>decreases</i> | <i>decreases</i> | <i>increases</i> |
| Current density | <i>increases</i> | <i>increases</i> | - |
| Anodization time | <i>increases</i> | <i>almost constant</i> | - |
| Temperature | - | - | <i>increases</i> |
| Wafer doping (p-type) | <i>decreases</i> | <i>increases</i> | <i>increases</i> |
| Wafer doping (n-type) | <i>increases</i> | <i>increases</i> | - |

Table 2.I. Effect of anodization parameters on porous silicon formation. An increase of the parameters of the first column leads to a variation of the elements in the rest of columns. Adapted from [47].

The thickness of a porous silicon layer is determined by the time that the current density is applied, that is the anodization time. To have a thicker layer, a longer anodization time is required. For this reason, the periodic variation of the current density during the etching process allows the production of multilayers formed by layers with different optical thicknesses.

Another advantage of the formation process of porous silicon is that once a porous layer has been formed, no more electrochemical etching occurs for it during the following current density variations. Hence, the porosity can be modulated in depth [48]. This fact allows the fabrication of any refractive index profile.

A longer permanence time of silicon in HF solution results in a higher mass of chemically dissolved silicon. This effect is more important for lightly doped silicon, while it is almost negligible for heavily doped silicon. This is due to the lower specific surface area.

All these characteristics contribute to the easy formation of porous silicon one-dimensional photonic structures, with no need to use excessively expensive equipment [49].

2.2.5. Photoluminescence of porous silicon

The discovery by Canham [2] in 1990 of strong visible luminescence from anodically etched p-doped silicon generated much interest within the scientific community because porous silicon became an attractive material in the field of electronics and optoelectronics [50-53].

Porous silicon offers a considerable technological interest because it may allow the convenient incorporation of optical elements into silicon integrated circuits. The incorporation of a stable and efficient luminescent porous silicon element into a microelectronic circuit encourages the possibility of commercial applications significantly.

Porous silicon based structures have been reported to luminescence efficiently across the whole range from the near infrared ($\sim 1.5 \mu\text{m}$), through the visible region, and into the near UV. Emission over such a broad spectral range arises from a small number of clearly distinct luminescence bands of different origin, which are listed in Table 2.II.

| Spectral range | Peak wavelength (nm) | Luminescence band label | PL | EL |
|----------------|----------------------|-------------------------|------------|------------|
| UV | ~ 350 | <i>UV band</i> | <i>Yes</i> | <i>No</i> |
| Blue-green | ~ 470 | <i>F band</i> | <i>Yes</i> | <i>No</i> |
| Blue-red | <i>400-800</i> | <i>S band</i> | <i>Yes</i> | <i>Yes</i> |
| Near IR | <i>1100-1500</i> | <i>IR band</i> | <i>Yes</i> | <i>No</i> |

Table 2.II. Porous silicon luminescence bands [After 54]

The general properties of each luminescence band and the conditions under which they are observed have been briefly reviewed quite recently [55]. The so-called ‘‘S-band’’ luminescence has received by far the most attention to date [56-59], and has the most technological significance, since it can be efficiently electrically excited. This band has been tuned across the entire visible range from deep red to blue [60]. However, it is worth briefly mentioning the most likely origin of the other luminescence bands. The blue-

green photoluminescence (PL) emission (the so-called “F-band” due to its fast nanosecond decay time) was first reported by Harvey *et al.* [61] in 1992. Following the demonstration by Kovalev *et al.* [62] of quite strong PL output of this type from oxidized porous silicon produced by RTO treatment, the F-band has been the subject of several recent studies [55,63-66]. It is, however, only observed in oxidized structures and is very likely to originate from contaminated [67] or defective silicon oxide [63].

Infrared emission at room temperature was first achieved by Fauchet *et al.* [68] for material annealed under ultrahigh vacuum (UHV). As discussed in [69] the origin of this radiation could be dangling bond related [70], although no direct correlation has yet been demonstrated.

Ultraviolet emission was first reported by Jiang *et al.* [171] in 1993 from oxidized material under soft x-ray excitation. Stronger room temperature output has been subsequently reported [72-76]. As with the blue-green F-band, the UV bands are only observed from oxidized layers and are likely also to arise from the defective oxide phase [73].

2.3. Applications of porous silicon

Porous silicon is a dielectric material with many different applications. The potential application areas of porous silicon are summarized in Table 2.III, where the property of porous silicon used for each application is shown.

In this work, porous silicon has been used for the fabrication of multilayers for optical applications, using the photonic bandgap characteristic of these multilayers for the formation of filters, microcavities, omnidirectional mirrors and waveguides. These applications are explained in detail in the next subsections together with some other porous silicon applications widely reported.

| Application area | Role of porous silicon | Key property |
|--------------------------|---|--|
| Optoelectronics | LED Waveguide Field emitter Optical memory | Efficient electroluminescence Tunability of refractive index Hot carrier emission Non-linear properties |
| Micro-optics | Fabry-Pérot Filters Photonic bandgap structures All optical switching | Refractive index modulation Regular macropore array Highly non-linear properties |
| Energy conversion | Antireflection coatings Photo-electrochemical cells | Low refractive index Photocorrosion cells |
| Environmental monitoring | Gas sensing | Ambient sensitive properties |
| Microelectronics | Micro-capacitor Insulator layer Low-k material | High specific surface area High resistance Electrical properties |
| Wafer technology | Buffer layer in heteroepitaxy SOI wafers | Variable lattice parameter High etching selectivity |
| Micromachining | Thick sacrificial layer | Highly controllable etching |
| Biotechnology | Tissue bonding Biosensor | Tunable chemical reactivity Enzyme immobilization |

Table 2.III. Potential application areas of porous silicon [Adapted from 77].

2.3.1. Distributed Bragg Reflectors

Distributed Bragg reflectors are dielectric multilayers based on the effect of multiple interferences that occurs when a light beam is reflected by various dielectric interfaces. A simple scheme of multiple interferences is shown in Fig. 2.6 [78], where a single film is compared with a stack of thin films (multilayer). At each interface between the two materials with different refractive index, a reflection occurs. In the case of a single layer film the reflected beam is the result of the interference of the two beams reflected at the air-film and film-

substrate interfaces. Instead in the case of the multilayer film, the reflected beam is the result of the interference of the multiple beams reflected at each of the different interfaces. By choosing, in an appropriate way, the thicknesses and the values of the refractive indices of the various layers, it is possible to generate different reflectivity spectra. The final result is the possibility to realize constructive and destructive interferences at different wavelengths.

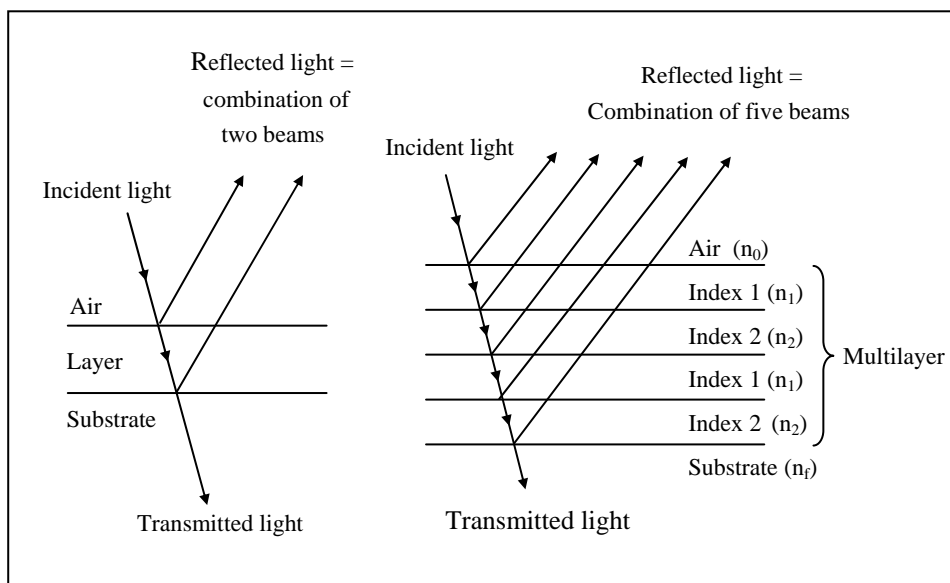


Fig. 2.6. On the left part of the figure it is shown the reflection and transmission of light by a single thin film. On the right the case of a multilayer is shown. After [78].

Distributed Bragg Reflectors (DBR) are multilayer structures formed by the periodic repetition of two layers with different refractive index (n_H and n_L) and thicknesses (h_H and h_L , respectively). The reflectivity spectrum of a DBR presents a high reflectivity for a given spectral region, centered at wavelength λ . The reason of this is due to the fact that for the wavelengths close to this λ all the beams, which are reflected by the multiple interfaces, have the same phase when they reach the top interface. Thus they interfere constructively. For other

wavelengths the interference is no longer constructive and the reflectivity consequently drops. The range of wavelengths that are reflected is called the photonic stopband. Within this range of wavelengths, light is "forbidden" to propagate in the structure.

The most commonly used structure of DBR is the so called quarter wave DBR, where the optical thickness of the layers is $n_H h_H = n_L h_L = \lambda/4$ and the period of the structure is $\Lambda = h_H + h_L$ [40]. The schematic structure of a DBR can be observed in Fig. 2.7.

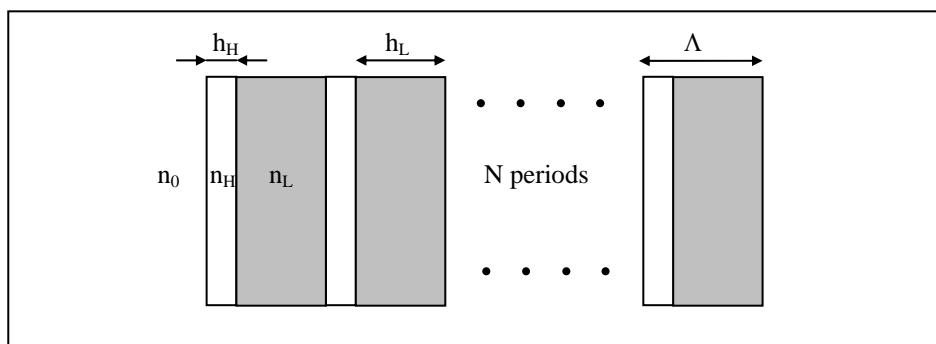


Fig. 2.7. Schematic cross-section of a periodic DBR. n_i and h_i are the refractive index and thickness of layer i , respectively. N is the number of periods.

In the explanation of the porous silicon formation process, we have observed that it is a very suitable material for the fabrication of multilayers because the refractive index and thickness of the layers can be selected by changing the formation parameters during the fabrication process [19].

Porous silicon DBRs have been fabricated by many different groups [79-84,]. The reflectivity of these structures has been widely studied [19,80,85], but also their photo-emission [85] and the roughness between their layers [86]. The most common application of these DBRs is filtering [81,87], but they have

also been used as sensors of the light polarization [88] and part of lasers [89] and waveguides [90].

2.3.2. Microcavities

The structure of microcavities, also called Fabry-Pérot filters, consists of two parallel DBR separated by a spacer layer, whose refractive index can be the same or different to the ones used for the DBRs. The optical thickness of the spacer layer can be λ or $\lambda/2$ [91]. Fig. 2.8 shows the schematic structure of a microcavity. The reflectivity spectrum of this structure is characterized by a very narrow pass-band centered in a high reflectivity wavelength range.

Microcavities can be used as band-pass filters with a tuned position of the peak [19,92], tunable mirrors [93] and detectors of substances like ethanol, methanol, acetone, chlorobenzene and nitrogen dioxide, among others [94-97]. They also improve the light emitting capacity of porous silicon. Microcavity structures can also be advantageous for photoluminescence and electroluminescence in order to reduce the full width at half maximum (FWHM) [91,98-101].

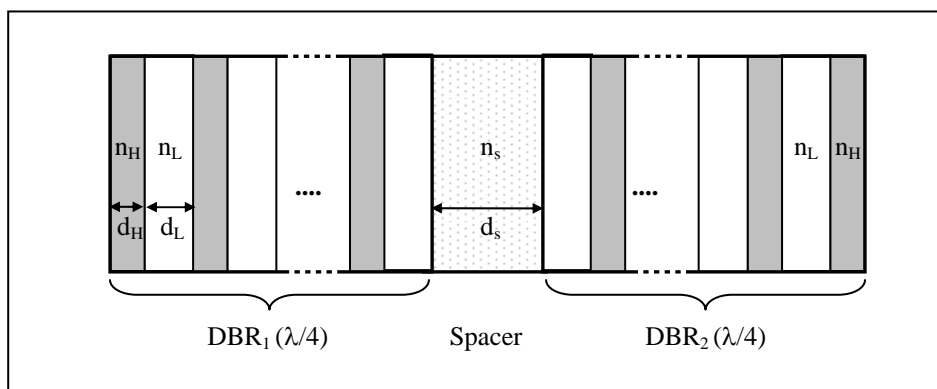


Fig. 2.8. Schematic cross-section of a microcavity. The spacer layer refractive index is n_s and its thickness is d_s . It is inserted in between two symmetric DBR with refractive indices n_H and n_L and thicknesses d_H and d_L .

2.3.3. Rugate filters

These filters are characterized by a continuous, mostly sinusoidal change of the refractive index with depth [102]. These structures have been investigated for 20 years, because a smooth index profile can improve many features of optical devices with respect to dielectric multilayers [103]. The main difficulty is the experimental realization, which requires gradual mixing of different materials; this is the reason for the low number of works in this area. Rugate filters have been reported in the past by evaporation [104-105], reactive sputtering [106], plasma-enhanced chemical vapor deposition [107] and glancing angle deposition [108].

Porous silicon is an excellent material for the fabrications of rugate filters because the anodization current can be gradually modulated obtaining soft index profiles [48]. In the last years, some groups have reported the first porous silicon-based rugate filters [102,109]. Some of the main advantages of these structures are that they do not show higher harmonics and that the typical DBR sidelobes of the reflection bands are reduced or even suppressed [103].

2.3.4. Omnidirectional mirrors

Omnidirectional mirrors are multilayers that reflect light for any incidence angle and for any polarization in a wavelength range [110]. This characteristic is due to the existence of a bandgap that exists for any incidence angle and for both polarizations TE and TM.

The most widely used structure of one-dimensional mirrors is the one consisting of the periodic repetition of two dielectric layers with different refractive index [111,112], although other structures have been reported. [39,113,114]. Dielectric mirrors have many advantages over metallic mirrors, like low optical loss, no light absorption, high mechanical strength, and high reflectivity within a wide range of wavelengths [115,116].

Although different groups have reported dielectric omnidirectional mirrors, porous silicon omnidirectional mirrors have been only analyzed and fabricated by the group of G. Léron del [39].

2.3.5. Waveguides

Since the first report on the use of porous silicon as an optical waveguide medium in the 90s, significant development has been made towards the understanding and applicability of such material. Different groups have studied the fabrication of porous silicon waveguides and their basic properties (modes, losses) [117-121].

The infiltration of liquids in the pores resulting in an induced phase shift and/or variation in the guided light intensity allows the use of porous silicon waveguide as sensors. For example, the introduction of solvents (acetone, methanol, and propan-2-ol) into the pores is shown to dramatically reduce the loss of the waveguides in a reversible manner [122,123].

Waveguides based on porous silicon multilayers allow the micromachining of photonic integrated circuits as it can be used to confine, manipulate, and guide the photons [124-127].

Waveguides based on multilayers have attracted a great interest because their guiding mechanism is completely different to the conventional waveguides based on total internal reflection [125,128] but these waveguides made of porous silicon have not been widely reported [129].

2.3.6. Sensors

Porous silicon multilayers have been used for sensing different substances. In particular microcavity structures have been used for hydrocarbon sensors [42,130] or biosensors [131,132], where changes of the optical properties of the porous silicon microcavity are analyzed. On the other hand, porous silicon monolayers have been used in humidity sensors, designed to detect humidity through changes of its electrical properties [133-134]. Despite optical measurements may be more robust for some applications, only a few authors proposed the analysis of the optical properties of porous silicon microcavities for the detection of humidity changes [135].

2.3.7. Other applications

The possibility of electroluminescent devices fabricated with porous silicon was realised soon after the demonstration of photoluminescence from porous silicon. Electroluminescent devices like light emitting diodes (LEDs) or injection lasers [136-140] made of porous silicon have been reported. To complement light emission from the material a variety of photodetectors made of porous silicon have also been reported [141,142]. Porous silicon multilayers have also been used for the realization of integrated optoelectronic devices, consisting of a LED connected to a photodetector with a waveguide [124,143]. This material has also been investigated as a possible anti-reflecting coating in solar cells [144]. Porous silicon dissolves quickly in alkaline solutions, which has led to numerous applications for porous silicon as sacrificial layer in micromachining [145-148].