

Porous silicon: The material and its applications to SOI technologies

G. Bomchil and A. Halimaoui

Centre National d'Etudes des Télécommunications, BP 98, 38243 Meylan, France

R. Herino

Laboratoire de Spectrométrie Physique, Université Joseph Fourier de Grenoble, 38402 St. Martin d'Hères Cedex, France

Abstract. A general review is presented of the main properties of porous silicon and different structures using this material in silicon-on-insulator technologies. The formation mechanism, morphology of the porous layer, crystallographic structure, oxidation properties, and thermal behaviour are critically reviewed. Applications of the material to SOI technology with its present advantages and limitations are discussed.

Keywords. Porous silicon, electrochemistry, interface properties, silicon-on-insulator technologies.

1. Introduction

Over the past few years various techniques have been developed for the formation of silicon-on-insulator structures [1]. One of these techniques is based on the use of porous silicon [2]. In principle, approaches based on porous silicon offer the potential for achieving an essentially defect-free active silicon layer. The formation of porous silicon requires a very simple electrochemical anodization in a concentrated hydrofluoric acid solution. The process is intrinsically clean. Oxidation of the porous layer leads to standard thermal oxide, using available technological processes.

The porous silicon approach is now ready for industrial evaluation in silicon-on-insulator technologies. Many years of basic research devoted to the material properties have been necessary to reach this point. During these studies new and interesting properties of the material have been discovered. They will certainly deserve further studies in the near future.

In this paper we present a critical review of the current state of the subject,

from the properties of the material to its application in the field of silicon-on-insulator technologies.

2. Formation of porous silicon

Porous silicon is obtained by anodic oxidation of silicon in concentrated hydrofluoric acid. In a conventional electrochemical cell silicon is made the anode, the cathode being in an inert metal-like platinum. The anodization is usually performed at constant current density, but constant voltage anodization can also be used.

The formation of porous silicon critically depends on the doping level of the silicon anode and the electrochemical parameters: HF concentration and current density (or voltage) applied.

If these two parameters are well chosen, it is possible to form porous silicon in both P- and N-type silicon, but the material which is formed presents very different characteristics, according to the doping level of the substrate. In heavily doped silicon of either n-type or p-type, pores are parallel, oriented along the current lines (Fig. 1(a)). There are many small buds on the side of the pores and occasional branches which emerge at wide angles to the main pores. The pore diameters are in the 40–120 Å range, and lead to a material which

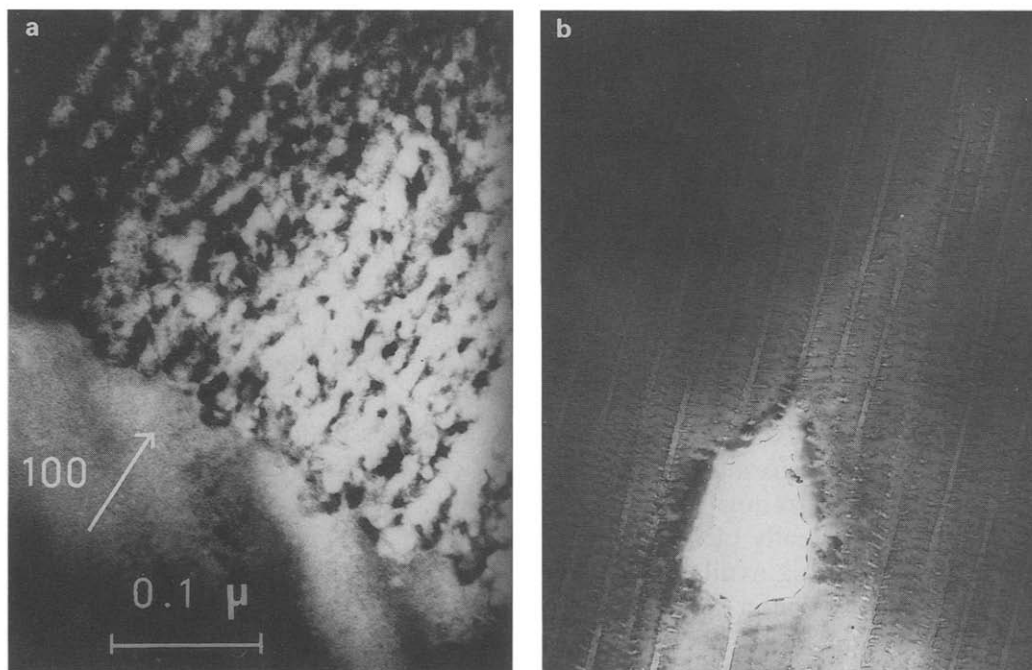


Fig. 1. Cross-sectional transmission electron micrographs of different porous silicon layers formed in: (a) heavily doped (0.01 Ω cm) P-type silicon; (b) lightly doped (1 Ω cm) n-type silicon.

presents a porosity, defined as the percentage of void volume in the film, which can vary between 20 and 80%, depending on the anodization conditions. For lightly doped p-silicon, the porous texture is very different and consists of an apparently random array of very small holes; as for heavily doped materials, pores are highly interconnected with diameters below 30 Å. Another very different texture can be found in lightly doped N-substrates, as illustrated by the TEM photography of Fig. 1(b). The pores look like cylinders parallel to each other, with a small branching density. However, for this material, the obtained porosities remain very small, below 10%.

In conclusion, it clearly appears that the porous texture of the film is first of all determined by the nature and level of the semiconductor doping. However, for each different texture, the porosity and pore diameters can be varied by the anodization conditions.

3. Porosity and pore size

For each type of substrate, similar trends are observed in the dependence of porous film characteristics on the electrolysis conditions.

Figure 2 shows that, for a given HF concentration, the average film porosity increases with the forming current density. For heavily p-doped substrates in 25% HF, the porosity increases regularly from about 20% up to 70% when the current density is raised from 10 mA/cm² to 250 mA/cm². For higher current densities, the porosity becomes very high, and the material loses its mechanical cohesion, and behaves more or less like a powder. If the current density is further increased, then direct electropolishing of the anodized surface takes place, with no film formation. A similar behaviour is observed with heavily doped N substrates: the porosity increases with increasing current

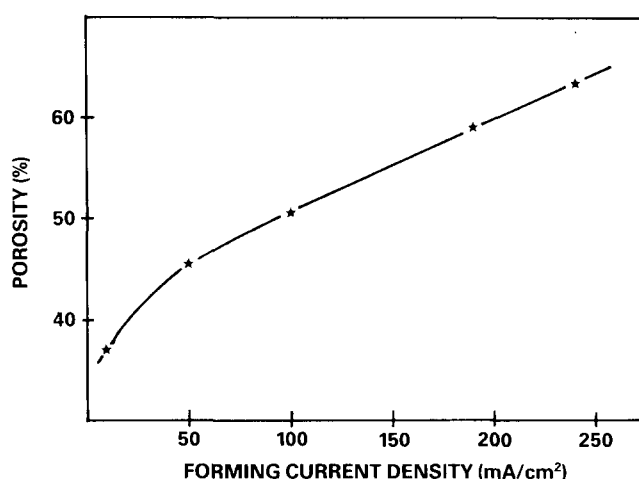


Fig. 2. Gravimetric porosity as a function of forming current density for porous layers prepared on heavily doped P-type silicon (0.01 Ω cm) in 25% HF.

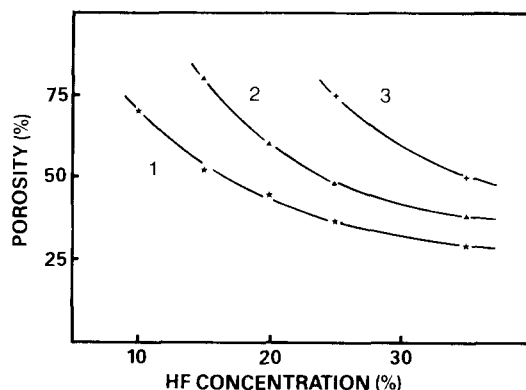


Fig. 3. Gravimetric porosity as a function of the HF concentration for porous layers prepared on heavily P-doped silicon ($0.01 \Omega \text{ cm}$) at 1–20, 2–80, and 3–240 mA/cm^2 .

density. However, at a low current density and for thick porous layers, higher porosities are obtained, which have been related to a chemical dissolution of the porous material taking place simultaneously with the electrochemical reaction [3].

The HF concentration in the electrolyte has also a marked influence on the layer porosity. For all kinds of substrates, an increase in the HF concentration results in a decrease in the porosity, as shown in Fig. 3 for P+ samples. In this case again, when the porosity reaches values above 70%, the layer loses its mechanical properties and behaves like a powder. At a low HF concentration, less than 10%, direct electropolishing of the surface is observed without film formation.

It is interesting to correlate these variations in porosity with the pore size in the material. This parameter is not very easy to obtain: pore dimensions are usually below the resolution limit of scanning electron microscopy and good pictures of pores can only be obtained by using transmission electron microscopy. This technique, although very powerful, requires a careful preparation of samples and is not very suitable for obtaining an overall idea of the whole sample. The other technique which has been extensively used for the characterization of porous films is based on the analysis of gas adsorption isotherms [3].

This technique allows the determination of the specific surface of porous layers; results show that they are in the order of magnitude of those measured for catalysts, and depend mainly on the texture of the porous layer: porous films formed on N+ or P+ substrates exhibit specific surfaces in the range $200\text{--}250 \text{ m}^2/\text{cm}^3$, whereas films formed on lightly doped P substrates have a much higher surface of the order of $600 \text{ m}^2/\text{cm}^3$, attesting to the much finer texture of this substrate. These specific surfaces are not significantly modified by the anodization conditions. From the adsorption isotherm, the pore size distribution in the film can also be calculated, assuming that pores are cylinders open at both ends. Of course, this determination is model dependent, and may

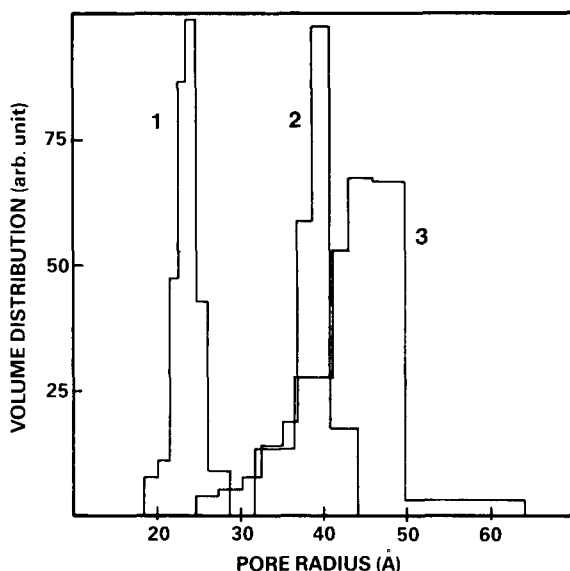


Fig. 4. Pore size distributions for porous layers prepared on heavily P-doped silicon ($0.01 \Omega \text{ cm}$) in 25% HF at 1–10, 2–80, and 3–240 mA/cm^2 .

lead to some uncertainty in the absolute value of pore radii, but in all cases, values obtained by this method allow for comparison between different samples. However, two limitations must be pointed out: the first is that a minimum porous volume is required for an adequate accuracy, the consequence being that only several micron thick layers can be analyzed. The second is that the method is not sensitive to very small pores of radii below 20 \AA , and volumes attributed to 20 \AA pores can correspond to much lower sizes.

Isotherm experiments confirm the results obtained by gravimetry: porosities measured by both methods are in close agreement. Analysis of pore diagrams indicate a close correlation between porosity and pore size. For example, Fig. 4 shows three pore distributions of highly P-doped samples formed at different current densities. The pore distributions are quite sharp, and they broaden with increasing current density. These diagrams also show that the pore size increases with the forming current density just like the porosity.

Similarly, variations in porosity and pore size correlate when the HF concentration in the electrolyte is changed. Figure 5 shows that a P⁺ layer formed at 10 mA/cm^2 in a 25% HF solution presents a pore size of around 25 \AA with a porosity of 37%. It also illustrates that for the same current in a 10% HF solution the porosity has increased by a factor 2, as well as the size of pores. Again, a broadening of the distribution appears for greater porosities.

It is thus possible to form a porous layer which presents the same porosity by choosing different anodization conditions. For example, a 48% porosity layer can be found either at 80 mA/cm^2 in 12 M/l HF solution, or at 240 mA/cm^2 in 17 M/l HF solution. In both cases, the pore sizes are similar.

The situation is completely different if the silicon doping is changed.

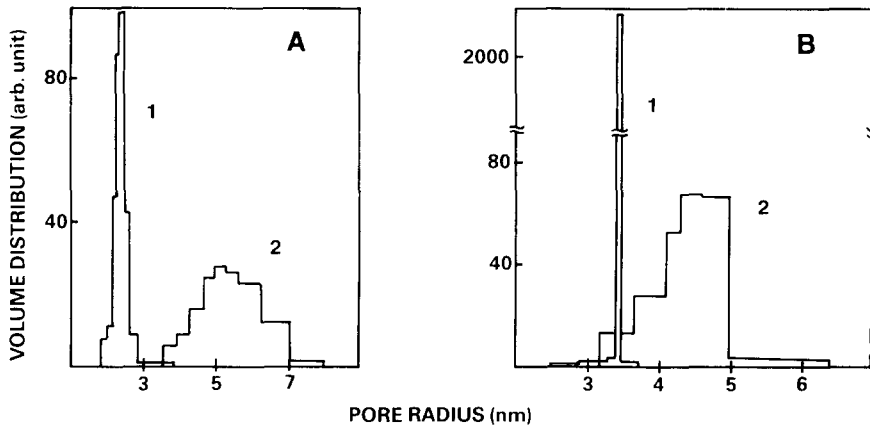


Fig. 5. Influence of the HF concentration on pore size distribution of porous layers prepared on heavily doped silicon ($0.01 \Omega \text{ cm}$) at constant current density: (a) 10 mA/cm^2 , (1) 25% HF, (2) 10% HF; (b) 240 mA/cm^2 , (1) 35% HF, (2) 25% HF.

Although, by varying the anodization conditions, similar porosities can be obtained for different levels of silicon doping, the pore sizes are not equivalent. Figure 6 shows the analysis of 50% porosity layers formed in P+ silicon and in $1 \Omega \text{ cm}$ silicon. In the latter case, the pore sizes are below 20 \AA . Unfortunately, because the resolution limit of the method is 20 \AA , it is not possible, with this type of sample, to study the size distribution and its variation.

For N+ samples, the same trends are obtained: porosities and pore sizes correlate.

In conclusion, the porous texture of the different porous layers which can be formed by anodization of silicon is well characterized and appears to be determined mainly by the type and level of silicon doping. The porosity and pore size are found to be closely related for a given porous texture, and are easily modified by the anodization conditions. However, there is still a lack of

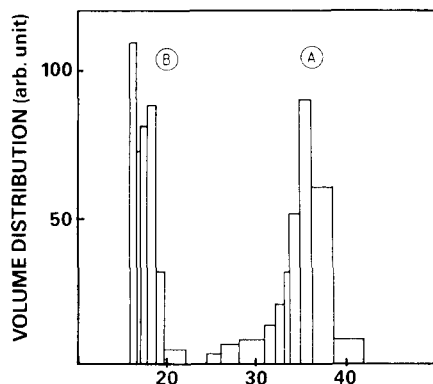


Fig. 6. Comparison of pore size distributions of porous layers of equivalent porosity (50%) formed on (a) heavily ($0.01 \Omega \text{ cm}$) and (b) lightly ($1 \Omega \text{ cm}$) P-doped silicon substrates.

detailed information concerning the lightly P-doped material, for which the isotherm method cannot be used, and the lightly N-doped silicon still remains unstudied.

4. Structural properties

Double crystal X-ray diffractometry was employed to measure the lattice parameter of the porous silicon and the silicon substrate for several different lattice planes [4, 5].

First, two distinct peaks occur for any studied X-ray reflection, one from the substrate, the other only at slightly smaller Bragg angles, from the porous silicon layer (Fig. 7). The full width at half maximum of these peaks provides information on the crystal perfection. The experimentally measured widths are always very small, typically 7", very similar to the value measured for the reference substrate peak and in agreement with the value predicted by the dynamical diffraction theory for the diffraction of perfect crystals. Most of the above work was performed on highly doped p-type substrates. Electron diffraction patterns indicate that similar results would be obtained with highly doped n-silicon [6].

It is important to note that the crystalline quality of porous silicon depends on the porosity. For porous silicon porosities lower than 35% the crystalline quality of the material is very good and similar to that of the silicon substrate. When the porosity increases the crystalline quality deteriorates.

The lattice parameter of porous silicon differs slightly from the lattice parameter of an equally doped silicon substrate. In the as prepared material the ratio is $\Delta a/a \approx 10^{-4}$, the exact value being dependent on the porosity of the material. It appears that this lattice expansion is a genuine effect and not an artifact resulting from stress provoked by the lattice misfit between the porous silicon layer and the silicon substrate. Lattice expansion has also been measured in self-supported porous silicon layers. There is still no clear explanation for this effect.

It was first suggested that lattice expansion results from a surface effect. This explanation is not consistent with the fact that samples of nearly equal surface areas but different pore sizes show different lattice parameter values. Another explanation assumes the formation of a layer of native oxide all along the pore walls. Due to the volume expansion associated with silicon oxidation, the oxide is under compressive stress. The porous silicon layer remains in compression at the interface plane with the silicon substrate and expands in a direction normal to the interface. This explanation cannot be invoked, however, to explain the lattice expansion in self supported porous silicon films [7].

A third possibility is that lattice expansion results from an intrinsic effect of a small particle size silicon network. Porous silicon in fact is a monocrystalline material formed by an assembly of very small particles. Small-angle scattering

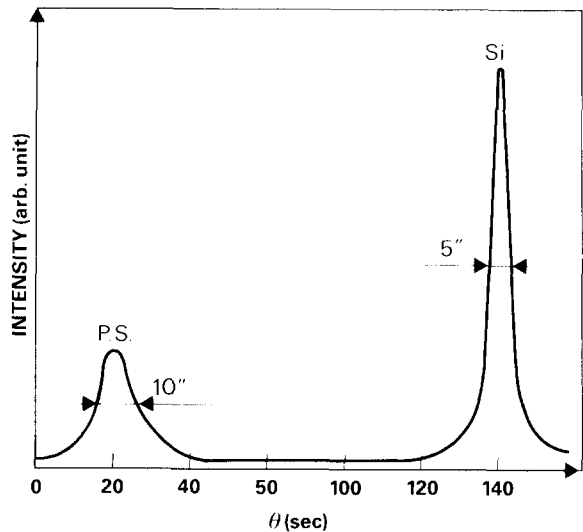


Fig. 7. Double crystal rocking curve of porous silicon layer on a silicon substrate. 400 reflection—porosity $\approx 34\%$.

X-ray techniques (also neutrons) are an appropriate tool for the study of such systems. Compared to the bulk material the small-angle scattering contribution of porous silicon is very high. Plots of $\log I(q)$ versus q^2 , where $I(Q)$ is the intensity scattered at $q = 4 \sin \theta / \lambda$, do not hold as it should for a classical two-density material (voids crystal). On the other hand, the experimental results can be well fitted as shown in Fig. 8 by an expression of the type

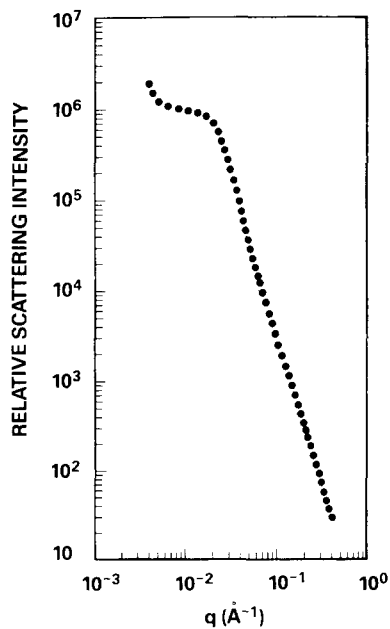


Fig. 8. Relative scattered intensity at low angles as a function of the scattering vector q by a porous layer formed in heavily P-doped silicon ($0.01 \Omega \text{ cm}$).

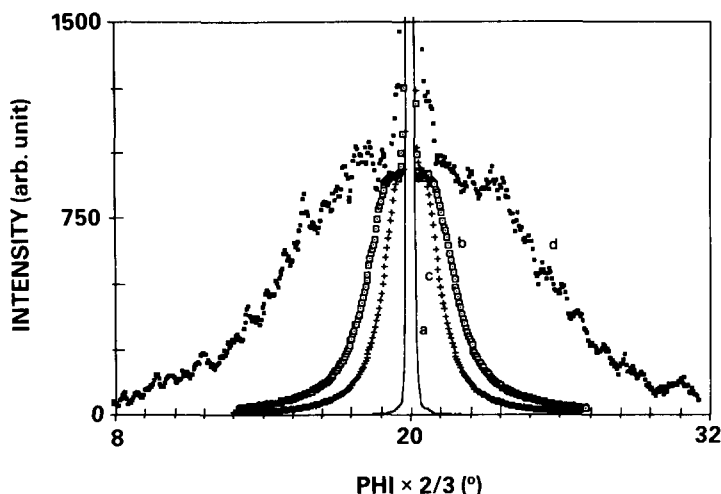


Fig. 9. Bragg diffraction peaks obtained for different porous silicon layers: (a) bulk material; (b) heavily P-doped silicon formed at 10 mA/cm² in 25% HF; (c) heavily N-doped silicon formed at 130 mA/cm² in 25% HF; (d) lightly P-doped silicon formed at 10 mA/cm².

$I(q) \cdot q(6-D)$ -constant for $D=3.5$, thus resulting in a slope 2.5. This behaviour is characteristic of fractal surfaces. We believe that this result opens up a very interesting field of study for porous silicon material [8].

X-ray reflection from a porous silicon surface near critical angle incidence is also an appropriate technique for the study of the near surface porous silicon porosity. The technique can be used in three different set ups: reflection, Bragg diffraction, and fluorescence measurements as a function of the incident angle, thus enabling the porosity of the material to be calculated. Results are in agreement with those obtained by gravimetric measurements. Figure 8 shows the characteristic shape of Bragg diffraction peaks for a near critical incident angle. The presence of pores provokes a broadening of the peak which in fact is the Fourier transform of the pore structure [9]. The dimension of the pores calculated from this broadening is of the order of 100 Å. Agreement with values obtained by the adsorption isotherm technique is not always perfect, an interesting point worthy of further studies.

5. Optical properties

At the porous silicon/silicon interface there is a discontinuity of the refractive index. Interference fringes with well-defined peak values are always observed. The refractive index of the porous material falls monotonically from the value of monocrystalline silicon (3.47 for $\lambda = 1 \mu\text{m}$) as the porosity of the material increases. For the highly doped samples very good agreement is obtained between the optical density and gravimetric, using a model that requires only crystalline silicon and voids. However, for porous silicon samples prepared in high-resistivity P-substrates (very small pore size, large surface area) it is necessary to consider a third phase—silicon dioxide—to fit both

densities. In addition, photoluminescence results indicate that the heavily doped samples maintain the monocrystalline properties of the substrate whereas the lightly doped display amorphous phase features in agreement with TEM and X-ray measurements [10].

6. Impurities

Due to its high internal surface area porous silicon was suspected of containing large amounts of impurities; several studies have shown that this is not the case.

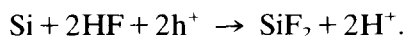
Nuclear analyses have shown, however, that porous silicon contains large amounts of hydrogen. This is probably the reason why the internal porous silicon surface can be kept clean. Occasionally oxygen, carbon, and fluorine have also been found [11]. It is likely that the presence of H, O, C could explain the decrease in random yield found in RBS experiments which otherwise should be comparable to bulk silicon as the technique is not sensitive to material porosity. More studies are required, however, to exclude the hypothesis of a pseudocanalization effect in the pore network.

7. Porous silicon formation mechanisms

When discussing the formation mechanisms of porous silicon, it seems necessary to divide the subject into two separate problems:

- (1) What is the anodic process responsible for anodic dissolution of silicon in hydrofluoric acid?
- (2) Why, under certain conditions, is the anodic dissolution of silicon localized, leading to the formation of a porous material?

Neither of these two basic questions has been clearly answered. Concerning the problem of anodic dissolution of silicon, it is well agreed that silicon goes into solution through a hole transfer of two charges per silicon atom, according to the overall equation



In fact, this mechanism was proposed more than 20 years ago by Memming and Schwandt [12], and assumes the following sequence.

Initially, the silicon surface is supposed to be completely covered with fluorine. A first step, supposed to be rate determining, would correspond to the breaking of a silicon-silicon bond, leading to an unpaired electron in the surface state. The following two steps correspond to the nucleophilic attack of the surface by F^- ions, and results in the formation of a difluorinated silicon. Divalent compounds of silicon are known to be unstable, and several chemical reactions may take place, leading to the stable SiF_6^{2-} ion. No particular chemical step has been experimentally demonstrated, the only clear fact being

that all mechanisms require hydrogen evolution, which is effectively observed even after the end of the electrolysis. It can be argued, however, that the silicon surface is not fully fluorinated. Analysis by infra-red spectroscopy of the as formed porous silicon surface shows that the silicon surface is largely hydrogenated: several Si.H bands have already been identified [13].

Concerning the localized anodic dissolution, which leads to the formation of pores, several hypotheses have been put forward in the literature. Some are based on the assumption that there is local passivation on the silicon surface [14], which could result from deposition of a chemical species, or from the presence of hydrogen bubbles on the silicon surface. However, such a phenomenon can hardly explain the differences in microstructure observed when silicon doping is changed.

Another approach is to consider that the basic formation mechanism can be analyzed in terms of current flow at the semiconductor-electrolyte interface. There is a large number of experimental facts indicating that at equilibrium the silicon surface in contact with HF solutions is depleted: thus a Schottky barrier exists at the interface, giving rise to rectifying characteristics [15]. For a P-type silicon, the current will be proportional to the hole concentration at the surface which is determined by the surface potential [16]. At the beginning of the reaction, the surface potential is modulated by ionic absorption at the silicon surface, and this can induce large differences in the current flow at the interface. In regions of locally high current density, preferential attack will occur, resulting in the formation of small depressions at the surface. In these depressions, the interface can no longer be considered as planar, but more or less spherical. In such a case, the surface potential, which is inversely proportional to the radius of curvature, would be higher at these depressions. Therefore, the current density and dissolution rate will be locally enhanced, enlarging these depressions and leading to the formation of pores. In the hypothesis where the current is only determined by the Schottky barrier, it is likely that the texture of the pore network depends on the two factors which modulate the surface potential: ionic adsorption and local radius of curvature. Under these conditions, the formation of a random pore structure can be understood, and such a model can be applied to lightly P-doped silicon. In the case of heavily doped silicon, the barrier thickness becomes sufficiently narrow (less than 80 Å) for tunnelling to occur, and it has been proposed [15] that in this case the major part of the current through the interface will occur by tunnelling. Here again, geometrical considerations show that the depletion layer width for a spherical interface decreases with decreasing radius; consequently, there will be an enhancement of current in the depression regions and as in the previous case, a locally higher dissolution rate. However, at adjacent pores, there is overlapping of the depleted region, and consequently, tunnelling can only occur at the pore tips, thus leading to the anisotropic texture observed in TEM.

Finally, for lightly doped n silicon anodic polarized, the Schottky barrier is reverse biased, and the current remains very low. Higher potentials are

required to provoke the breakdown of the junction. The onset of breakdown will greatly depend on the microscopic defects present on the surface, and will occur at random. At these points, anodic dissolution will take place resulting in the formation of depressions. Due to the curvature of the interface in these regions, the breakdown voltage of the junction will be largely decreased, and the reaction will thus proceed at the tip of the pores, leading to the very anisotropic texture observed in TEM photographs.

Another approach could be based on the fact that porous silicon can be considered a fractal material. Fractal models of kinetic growth [17] applied to porous silicon would give new insight in to the understanding of such a complex material. Theoretical work on this subject still remains to be done.

Technology has not been waiting for answers to these questions, and applications of porous silicon in the field of integrated circuits have already reached a mature level. The development of these applications has for a long time been hindered by the difficulties encountered in the oxidation of porous silicon.

8. Thermal treatment and oxidation

The aim is to transform a porous silicon layer into a homogeneous SiO_2 film, presenting the same properties of thermal oxide grown on crystalline silicon. At first sight, oxidation of porous silicon may appear to be an easy technological step. The material is expected to oxidize throughout the whole volume due to its open porosity, and in a relatively short time, because the silicon thickness to oxidize does not exceed the pore wall thickness (about a hundred angströms). In fact, many different oxidation procedures have been used leading to a more or less good oxide quality.

We believe that the origins of the difficulties in oxidizing porous silicon are related to the instability of the material upon thermal treatment. For temperatures higher than 400°C , under vacuum, coarsening of the porous texture occurs, and drastically increases with temperature [18]. After heating at 900°C , large voids of about $1\text{ }\mu\text{m}$ can be formed in the material, surrounded by thick silicon walls and the specific surface is dramatically decreased by more than a factor of 10. It is clear that the complete oxidation of such a coarsened structure will become very difficult, if not impossible. This coarsening of texture obtained by progressive collapsing of pores is attributed to surface diffusion of silicon atoms along the pore walls, which tends to minimize the high surface energy. Why does this restructuring appear only for temperatures above 400°C ? The answer can probably be found in experiments which show the hydrogen desorption from a porous silicon film as a function of heating temperature under vacuum [13, 19]. The as formed porous surface is largely covered with hydrogen atoms, and this covering seems to be stable up to 200°C . For higher temperatures, the partial hydrogen pressure increases rapidly, reaching a maximum at around 400°C and total hydrogen desorption is

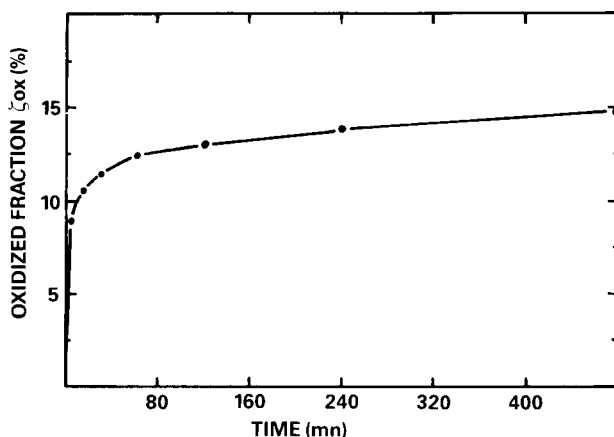


Fig. 10. Oxidation kinetics at 300°C in dry oxygen for a heavily P-doped porous silicon (0.01 Ω cm, 51% porosity).

complete at 500°C. Silicon-hydrogen bonds appear, therefore, as a stabilizing factor for the structure at temperatures below 300°C.

The problem is to know if the structure can be stabilized for higher temperatures. If we follow the weight increase of a sample heated at 300°C under dry oxygen (Fig. 10), we can see that in two hours 12% of silicon atoms in the layer has been oxidized. This corresponds roughly to the growth of one oxide monolayer over the whole surface of the sample: the oxidized amount for longer periods of time saturates because the temperature is not high enough to allow diffusion of the oxidant through this surface layer.

This oxide monolayer has the advantage of stabilizing the texture against heat treatment at higher temperatures. As long as no reducing atmosphere is used, heating of the layer can be performed for hours up to 900°C, without any major changes in the porous texture [18]. This is clearly demonstrated when comparing the pore size distribution of the as formed layer to that obtained for the same sample, oxidized for two hours at 300°C, and heated at 800°C under vacuum for one hour (Fig. 11). Consequently, when such a low-temperature oxidation is performed ('preoxidation'), the porous texture is stabilized and oxidation can be studied under reproducible conditions (20).

From oxidation kinetic result (Fig. 12) it clearly appears that complete oxidation of the layer is achieved only if the temperature is above 750°C. Although oxidation always occurs throughout the whole porous volume, the temperature has to be high enough to allow complete oxidation of the pore walls. However, even under these conditions of complete oxidation, TEM observation and dissolution rates in buffered HF solutions indicate that the oxide maintains some porous character.

Obtaining a dense oxide, with characteristics similar to standard thermal SiO_2 , requires a densification step. This densification is obtained by viscous flow of silica, and requires temperatures higher than 1000°C, to obtain a sufficiently low silica viscosity. The minimum time required for complete

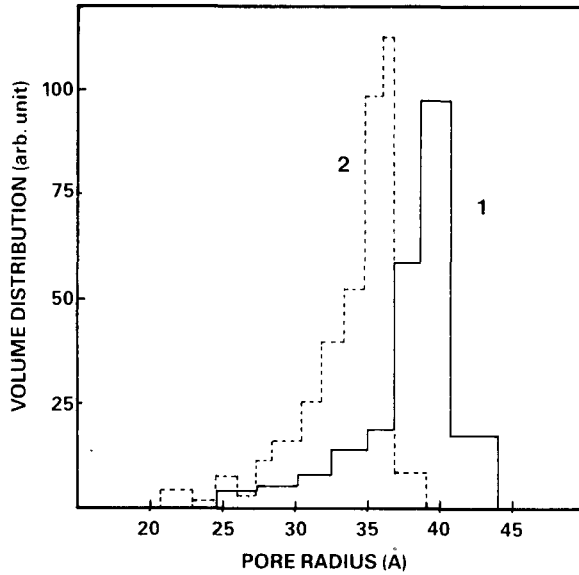


Fig. 11. Pore size distributions of porous silicon films: (1) as prepared sample and (2) preoxidized at 300°C and annealed at 800°C in vacuum for 1 hour.

densification appears to vary exponentially with the inverse of the absolute temperature [20]. The activation energy of the process is found to be very close to the activation energy of silica viscosity. Large differences are observed in the densification times of different porous microstructures. The very fine structure of lightly P-doped layers is densified in time an order of magnitude shorter than for P+ layers, although the initial porosity is the same.

In conclusion, a well-controlled oxidation procedure is now established to obtain good silica layers from porous silicon. It consists of successive steps which are well understood: (i) preoxidation to stabilize the texture; (ii) oxida-

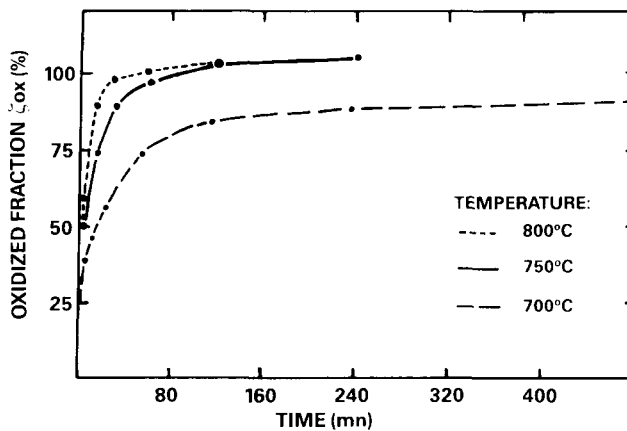


Fig. 12. Oxidation kinetics in steam for heavily P-doped (0.01 Ω cm) porous silicon samples (51% porosity) at 700, 750, and 800°C.

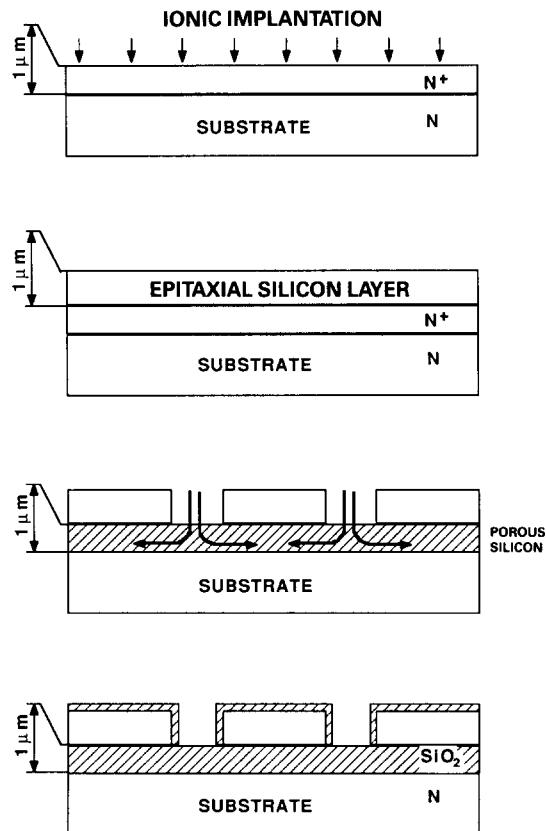


Fig. 13. Successive technological steps leading to SOI structure by oxidation of a buried porous silicon layer.

tion at low temperature, about 750°C but below 1000°C to prevent blocking of pores; (iii) densification at temperatures higher than 1000°C in wet oxygen, with a duration adapted to the microstructure of the layer.

9. Applications to SOI technologies

Different approaches have been used for applications of porous silicon to SOI technologies.

The first was based on the selectivity of the electrochemical reaction between n- and p-type silicon [21]. Using an implanted n-type layer on a p-type substrate porous silicon was formed all around the n island and good SOI structures were obtained after oxidation of the porous layers. In fact this was the first structure used to fabricate complete SOI circuits with very good characteristics and speed gains of 30% compared to equivalent bulk technologies. This approach, however, was not followed up by further developments because it was limited to small-size silicon islands, the maximum width

of the silicon island being limited to 10 μm to avoid stress provoked by thick oxide layers.

The most promising approaches are those based on structures such as p/p+/p or n/n+/n [23, 24], where porous silicon is only formed in a thin (1–3 μm) heavily doped buried layer accessible through upper layer (Fig. 13). The latter structure is being studied in several laboratories. In a lightly doped n-type silicon substrate a heavily doped (antimony) n layer is created by ionic implantation followed by the epitaxial growth of a lightly doped n layer. The implantation dose and energy are chosen to give, after redistribution, an n^+ layer with a doping concentration in the range 10^{18} – 10^{19} at/cm^3 . The optimum concentration results from a compromise: heavily doped layers (10^{19}) lead to homogeneous porous layer that subsequent oxidation transforms into an oxide equivalent to silicon dioxide throughout the whole thickness of the porous layer. It has been argued that during the oxidation step some antimony could diffuse to the upper layer and increase the background doping level of the active layer. It is also possible to decrease the dopant concentration in the buried layer to about 10^{18} at/cm^3 , but the quality of the oxide deteriorates from the epi silicon/oxide interface down to the substrate. Work is in progress to optimize the best structure and porous silicon preparation conditions. Using this structure, SOI circuits with very good characteristics have already been fabricated [25, 26]. More recently, it has been shown that the thickness of the epitaxial layer can be reduced to very small values—about 1500 Å. Circuits have been fabricated for fully depleted silicon layers and the possibility of using these porous silicon structures in submicron technologies is now open [27].

From an industrial viewpoint one disadvantage often mentioned by circuit designers is related to the geometry necessary for access to the buried layer and formation of porous silicon. Although this geometry can be arbitrary, for example that of the first mask level of the circuit, the approach remains an 'in-line process'.

Another different approach to obtaining SOI structures using porous silicon is based on the fact that porous silicon prepared under certain conditions maintains the monocrystalline characteristics of the silicon substrate. Using molecular beam epitaxy (MBE) it has been shown that it is possible to obtain good epitaxial layers of silicon on porous silicon [28, 29].

Epitaxial growth is performed at relatively low temperatures to avoid porous silicon restructuring. For near future applications in VLSI circuits the MBE technique has certain limitations. Recently, equivalent results have been obtained at laboratory level using LPCVD epitaxial growth at low temperatures (800°C) of silicon on porous silicon. For this purpose porous silicon was first preoxidized and once in the epi reactor 'in situ' cleaned before the epitaxial step. Good silicon layers with low defect density at the interface were obtained. There was only a little porous silicon restructuring and good oxides were obtained after patterning the epitaxial layer with a standard LOCOS mask. Work is in progress to evaluate this technique for industrial applications.

10. Conclusion

Silicon-on-insulator structures based on the use of porous silicon are now ready for further evaluation in near-future industrial applications. Silicon epitaxy on porous silicon appears to be a very promising technique. This technique is currently well known in heavily doped substrates, and these studies will hopefully be extended to the case of lightly doped substrates. In addition, the basic aspects of the material properties are very attractive to scientists. For example, the recent results which show that porous silicon is a fractal surface will undoubtedly lead to an increase in interest in the material as a model for more studies in this frontier field.

References

- [1] D. Bensahel, Heterostructures on silicon, in: Y. Nissim, E. Rosencher, K. Ploog, eds., *Proceedings NATO Summerschool*, Cargese, France, May 1988.
- [2] S. S. Tsao, Porous silicon techniques for SOI structures, *IEEE Circuits and Devices Mag.* **3** (1987) 3–7.
- [3] R. Herino, G. Bomchil, K. Barla, C. Bertrand and J. L. Ginoux, Porosity and pore size distributions of porous silicon layers, *J. Electrochem. Soc.* **134** (1987) 1994–2000.
- [4] K. Barla, G. Bomchil, R. Herino, J. C. Pfister and J. Baruchel, X-ray topographic characterization of porous silicon layers, *J. Crystal Growth* **68** (1984) 721–726.
- [5] K. Barla, R. Herino, G. Bomchil, J. C. Pfister and A. Freund, Determination of lattice parameter and elastic properties of porous silicon by X-ray diffraction, *J. Cryst. Growth* **69** (1984) 726–732.
- [6] V. A. Labunov, V. P. Bondarenko, L. Glinenko and I. N. Basmanov, Epitaxial growth of silicon on porous silicon, *Mikroelektronika* **12** (1983) 11–16 (in Russian).
- [7] I. M. Young, M. I. J. Beale and J. D. Benjamin, X ray double crystal diffraction study of porous silicon, *Appl. Phys. Lett.* **46** (1985) 1133–1135.
- [8] A. Goudeau, A. Naudon, G. Bomchil and R. Herino, X-ray small-angle scattering analysis of porous silicon layers, *Appl. Phys. Lett.* (to appear).
- [9] A. Bensaid, M. Brunel, F. De Bergervin, G. Patrat, G. Bomchil and R. Herino, Etude du silicium poreux par rayons X rasants, *Réunion Annuelle de La Société Française de Cristallographie*, Lyon, 88.
- [10] C. Pickering, M. I. J. Beale, D. J. Robbins, P. J. Pearson and R. Greef, Optical studies of the structure of porous silicon films formed in p-type degenerate and non-degenerate silicon, *J. Phys. C: Solid State Phys.* **17** (1984) 6535–6552.
- [11] L. G. Earwaker, J. P. G. Farr, P. E. Grzeszczyk, I. Sturland and J. M. Keen, Analysis of porous silicon, *Nucl. Instr. Meths. Phys. Res.* **B9** (1985) 317–320.
- [12] R. Memming and G. Schwandt, Anodic dissolution of silicon in hydrofluoric acid solutions, *Surface Science* **4** (1965) 109–124.
- [13] Y. Kato, T. Ito and A. Hiraki, Configuration of hydrogen atoms chemisorbed in porous silicon film during anodisation process, *1988 European Silicon On Insulator Workshop*, Meylan, France, 1988.
- [14] T. Unagami, Formation mechanism of porous silicon by anodisation in HF solution, *J. Electrochem. Soc.* **127** (1980) 476–483.
- [15] M. I. J. Beale, N. G. Chew, M. J. Uren, A. G. Cullis and J. D. Benjamin, Microstructure and formation mechanism of porous silicon, *Appl. Phys. Lett.* **46** (1985) 86–88.

- [16] F. Gaspard, A. Bsiessy, M. Ligeon, F. Muller and R. Herino, Charge exchange mechanism responsible for P-type silicon dissolution during porous silicon formation, *J. Electrochem. Soc.* (to appear).
- [17] D. W. Schaefer, Fractals models and the structure of materials, *MRS Bull.* **13** (1988) 22–27.
- [18] R. Herino, A. Perio, K. Barla and G. Bomchil, Microstructure of porous silicon and its evolution with temperature, *Materials Lett.* **2** (1984) 519–523.
- [19] P. Gupta, V. L. Colvin and S. M. George, Hydrogen desorption kinetics from monohydride and dihydride species on silicon surfaces, *Phys. Rev. B* **37** (1988) 8234–8243.
- [20] J. J. Yon, K. Barla, R. Herino and G. Bomchil, The kinetics and mechanism of oxide layer formation from porous silicon formed on p-Si substrates, *J. Appl. Phys.* **62** (1987) 1042–1048.
- [21] K. Imai and H. Unno, FIPOS Technology and its application to LSI's, *IEEE Trans. Electron. Dev.* **ED31** (1984) 297–302.
- [22] T. Mano, T. Baba, H. Sawada and K. Imai, FIPOS CMOS 16 K static RAM, *1982 Symposium on VLSI Technology*, Oiso, Japan, 1982.
- [23] S. S. Tsao, D. R. Myers, T. R. Guilinger, M. J. Kelly and A. K. Datye, Selective porous silicon formation in buried p+ layers, *J. Appl. Phys.* **62** (1987) 4182–4186.
- [24] R. P. Holmstrom and J. Y. Chi, Complete dielectric isolation by highly selective and self-stopping formation of oxidized porous silicon, *Appl. Phys. Lett.* **42** (1983) 386–388.
- [25] K. Barla, G. Bomchil, R. Herino, A. Monroy and Y. Gris, Characteristics of SOI CMOS circuits made in N/N+/N oxidized porous silicon structures, *Electron. Lett.* **22** (1986) 1291–1292.
- [26] E. G. Zorinsky, D. B. Spratt and R. L. Virkus, The "ISLANDS" method: a VLSI compatible SOI technology, *IEEE SOS-SOI Workshop*, Captiva Island, U.S.A., 1986.
- [27] N. J. Thomas, J. R. Davis, J. Keen, J. Castledine, D. Brumhead, M. Goulding, J. P. G. Farr, L. G. Earwaker, J. l'Ecuyer, I. M. Sturland and J. M. Cole, Fully depleted thin-film CMOS transistors in porous anodised silicon, *1st European SOI Workshop*, Meylan, France, 1988.
- [28] F. Arnaud D'Avitaya, K. Barla, R. Herino and G. Bomchil, Improvement of Silicon epitaxy on porous silicon substrates, *1st International Symposium MBE*, Toronto, Canada, 1985.
- [29] M. I. J. Beale, G. Chew, A. G. Cullis, D. B. Gasson, R. W. Hardeman, D. J. Robbins and I. M. Young, A Study of silicon MBE on porous silicon substrates, *J. Vac. Sci. Technol.* **B3** (1985) 732–735.
- [30] L. Vescan, G. Bomchil, A. Halimaoui, R. Herino and A. Perio, Low temperature low pressure silicon epitaxy on porous silicon, *Materials Lett.* (to appear).