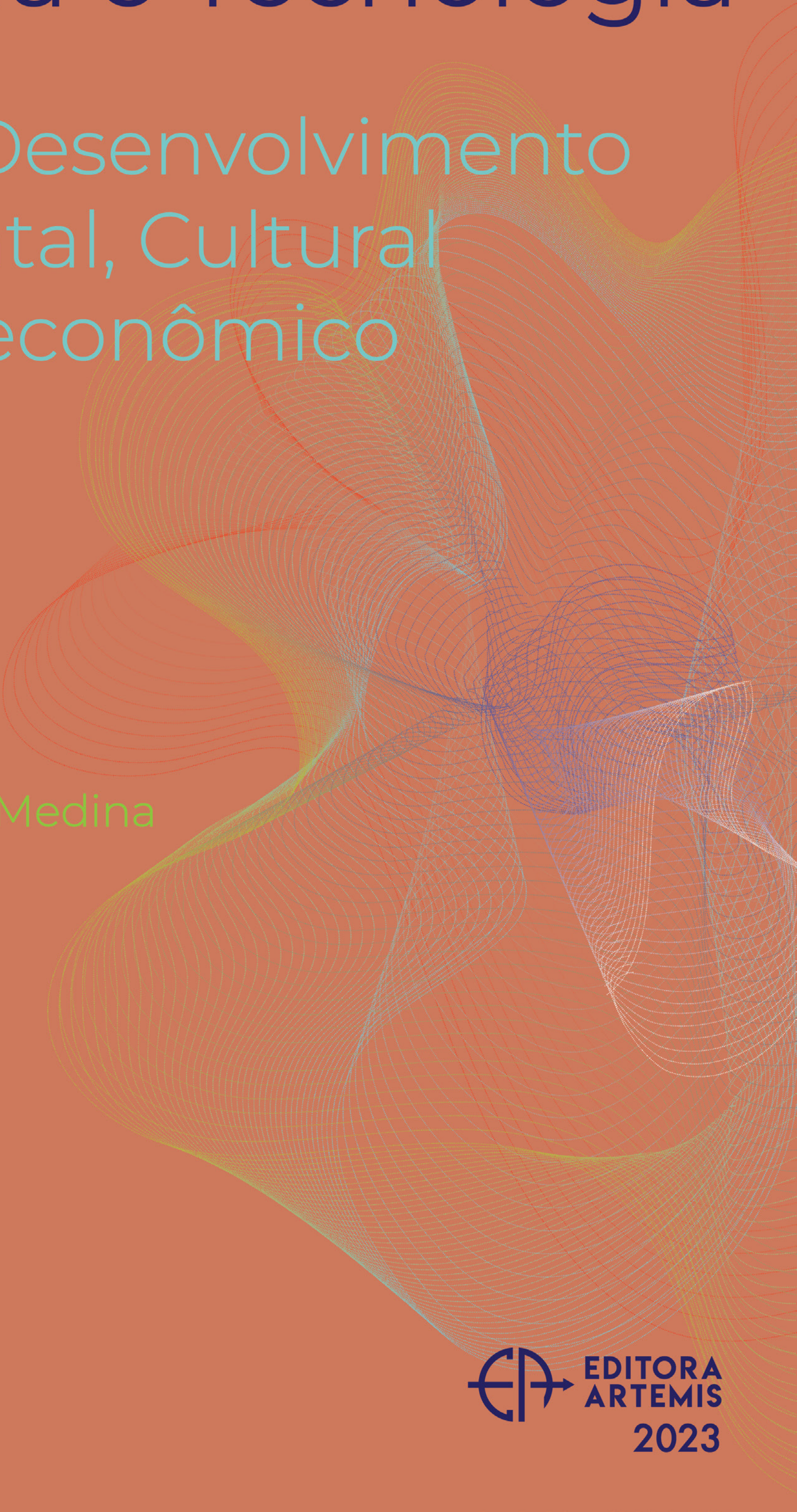
Ciência e Tecnologia

Para o Desenvolvimento Ambiental, Cultural e Socioeconômico



Xosé Somoza Medina
(organizador)

EDITORA ARTEMIS
2023

VOL II

Ciência e Tecnologia

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C569 Ciência e tecnologia para o desenvolvimento ambiental, cultural e socioeconômico II [livro eletrônico] / Organizador Xosé Somoza Medina. – Curitiba, PR: Artemis, 2023.

Formato: PDF
Requisitos de sistema: Adobe Acrobat Reader
Modo de acesso: World Wide Web
Inclui bibliografia
Edição bilíngue
ISBN 978-65-87396-76-7
DOI 10.37572/EdArt_270223767

1. Desenvolvimento sustentável. 2. Tecnologia – Aspectos ambientais. I. Somoza Medina, Xosé.

CDD 363.7

Elaborado por Maurício Amormino Júnior – CRB6/2422

EDITORA
ARTEMIS
2023

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PRÓLOGO

Este libro presenta una colección de artículos de investigación que bajo distintos ámbitos de conocimiento realizan avances de interés en la ciencia y la tecnología. La sociedad del siglo XXI se distingue de la de épocas pretéritas por su capacidad analítica. A diferencia de lo que ocurría en otras épocas, en nuestro mundo contemporáneo tenemos demasiada información y avanzar en el conocimiento significa realizar una investigación original sobre otros antecedentes previos y analizar una gran cantidad de datos para poder extraer conclusiones que signifiquen un desarrollo, un avance entre la situación anterior y la posterior, aunque sea a pequeña escala en un contexto local y en un ámbito científico muy concreto. La suma de miles de esos pequeños avances y la interconexión mundial sostienen a la ciencia y la tecnología del siglo XXI.

Este es el objetivo de este libro, realizar avances en la ciencia y la tecnología para el desarrollo ambiental, cultural y socioeconómico, desde un posicionamiento académico, comprometido con el rigor científico y el desarrollo del ser humano.

Para ello se han compendiado veinticuatro artículos de investigación en dos apartados, ciencia y tecnología. En el primer conjunto nos encontramos con artículos que desde las ciencias ambientales o las ciencias sociales realizan propuestas de mejora de aspectos concretos sobre hidrología, regeneración de suelo agrícola, cuidado ambiental, recursos humanos, ciudades igualitarias o paisajes culturales.

En el segundo bloque, se agrupan trabajos de ingeniería química, ingeniería industrial o ingeniería forestal que relatan avances en distintas tecnologías, relacionadas con el biogás de los vertederos de residuos, los usos de nuevos materiales sintéticos, la química de determinados productos y su toxicidad, o las características bioestructurales de la madera de roble.

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CAPÍTULO 16

MACROPOROUS SILICON STRUCTURES IN 700 NM AND 500 NM[1]

Data de submissão: 21/12/2022
Data de aceite: 10/01/2023

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ABSTRACT: Macroporous Silicon is a structured material with which innovative optical and electrical characteristics can be obtained. It consists in a crystalline silicon slab where tubular perforations are made. Several fabrication methods exist, electrochemical etching being one of the most versatile. With it, the diameter of the pores can be modulated in depth, resulting in 3D structures. Also, structures with very large aspect ratio (depth / diameter) can be achieved. One particular field of use of macroporous silicon is in photonics. Such applications generally require the fabrication of ordered structures whose dimensions are directly correlated with the optical response of the fabricated devices. In particular pore diameter and lattice pitch define the working wavelengths of the devices. Common uses of optical technology in areas such as communications or gas sensing require working with wavelengths in the Near Infrared (NIR) and the Medium Infrared (MIR) regions. That is, for wavelengths ranging from 1 μm to 20 μm. Devices able to work in the shorter wavelengths thus call for photonic structures of smaller dimensions. To enable such devices, the macroporous silicon fabrication technology has been developed and improved to allow the fabrication of structures with 700 nm and 500 nm lattice pitch.

KEYWORDS: Macroporous silicon. Electrochemical etching. Gas sensors. Mid Infrared.

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[1] ACKNOWLEDGEMENT: This work has been funded by the Spanish Ministerio de Ciencia e Innovación with grant PID2021-124572OB-C31. The authors declare no conflict of interest.

1 INTRODUCTION

Macroporous silicon (MpS) is a versatile material which has found uses in many fields. For example, one field in which macroporous silicon has awaken great interest is in optical and photonic applications. In particular, the creation of periodic structures confers the ability to alter the passage of electromagnetic waves through the material, thus creating the so-called photonic crystals (PhCs), resulting in photonic devices with dimensions comparable to the wavelength, and whose spectral characteristics can be designed to meet some specifications.

Several techniques exist for the fabrication of MpS. One of the most practical and flexible is the electrochemical etching (EE) of silicon. This technique is simple to use and allows changing the shape of the structure during the processing with little effort. Obtained structures can have very high aspect ratios, and the pores may have modulated profiles. Three-dimensional photonic crystals can therefore be easily fabricated that work in the three spatial axes.

The range of possible applications for macroporous silicon is really wide. For optical applications, EE offers advantages over more traditional, microelectronics-centric, techniques. Some devices based on PhCs are modulators, sources, or receivers. Other applications include filters and optical resonators for chemical/gas sensors. Macroporous silicon has also been proposed as a photonic crystal for the creation of omnidirectional selective optical filters. Some of the possible applications for devices of this nature are gas detection or thermo-photovoltaic applications. Further applications include anti-reflective layers and selective thermal emitters. Non optical applications of MpS include electronic devices (high capacity capacitors), energy storage (batteries), micro-fluidic applications (drug delivery, Brownian filters), chemical applications (reactors, catalysts), etc. In these cases, the use of macroporous silicon is highly novel and few groups are investigating these applications.

A common trait of photonic structures is that the photonic response is directly dependent on geometric aspects of the photonics crystals. Of these geometrical parameters, the most relevant are the pore diameter, the pore lattice, and the lattice pitch (in general photonic crystals require that the features – pores – are arranged in an ordered – periodical – fashion). Many interesting optical applications work in the infrared wavelength range, especially for gas sensing, where many gases have fingerprint responses in the $1 \mu m$ to $4 \mu m$. Optical communications also has important uses in this range of wavelength.

2 FABRICATION OF MACROPOROUS SILICON

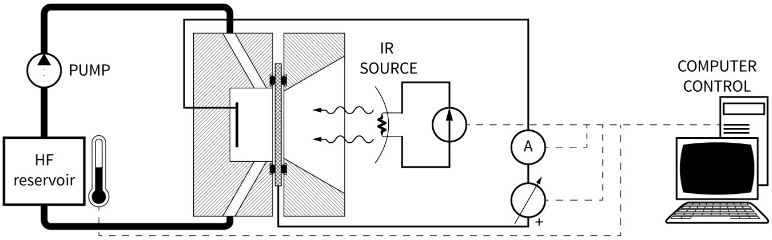
Porous silicon (PS) is commonly made by electrochemical anodizing of silicon (Si) wafers in solutions containing hydrofluoric acid (HF). Silicon can be selectively dissolved when immersed in hydrofluoric acid solutions and an electric current is passed through it. The anodic dissolution of silicon in an aqueous HF medium takes place only at the HF/Si interface where the charge carriers meet the F^- anions. For the silicon etch to occur, positive electrical carriers (holes) are required for the electrochemical reactions to take place in the vicinity of the are to dissolve. Both *n*- and *p*-type silicon can be dissolved by this technique (Lehmann, 1993; Lehmann & Föll, 1990). The chemical dissolution occurs on certain specific regions of the surface giving rise to small etch pits. Afterwards, electrical currents are preferentially focused to the tips of these pits, resulting in the enlargement of the pits in the following the current lines therefore giving rise to the tubular growth characteristic of electrochemically etched MpS.

Aside from the applied current, the physical characteristics of the silicon substrate and other parameters are also key in the obtained results. In particular, HF concentration, illumination, temperature, crystallinity and wafer resistivity are some of the parameters that one needs to take into account for the EE of Si. For example, the size of the pores is closely related to the type and level of substrate doping (Lehmann, 1996).

For *n*-type silicon substrates, since the material is not capable of supplying holes, an external way must be provided. One of the most widespread methods is to produce them by photogeneration, as proposed by Lehmann [2], illuminating the working silicon with a suitable light (IR with $\lambda \approx 1\,\mu$m). Generally, the sample is illuminated from the opposite side to the one exposed to HF. The generated, holes then diffuse to the face that is being attacked making possible to control the reaction. This method is known as *photo-assisted EE*. An schematic diagram of the etching cell and control system used by our group is shown in Figure 1.

Current density and electrode potential determine the amount of silicon etched per unit time. Interestingly, the rate at which silicon is dissolved is fairly constant in the “vertical” direction, so any change in photocurrent results in a net change of the pore diameter.

Figure 1. Diagram of the system used in our lab for the manufacture of macroporous silicon.



2.1 ORDERED GROWTH OF PORES

Unless the pores' position is predefined prior to EE, pores grow randomly throughout the substrate surface, resulting in a structure with a non-uniform pore spatial placement and size. In general, this is not desirable if the MpS structures are to be used as PhCs; such structures are called *random macroporous silicon*. The opposite is *ordered macroporous silicon* and to fabricate these structures the places where pores are desired must be prepared before etching. The method used here is through lithography (by any suitable method like UV or NIL). This step uses a mask to define the pore pattern on the silicon substrate. This allows very flexible designs, for example it is possible to define areas with a regular pattern, while other areas may define trenches.

2.2 MODULATION OF THE DIAMETER OF THE PORES

As previously stated, dissolved silicon is proportional to the current flow through the electrochemical cell, however, the pore front advances at an almost constant speed. This implies that, assuming stable growth regime, the current will etch a larger or smaller diameter pore in a given time. This can be approximated with a cylinder of fixed height and changing radius. This property can therefore be used to create pores with *changing profile in depth*, i.e. modulated pores.

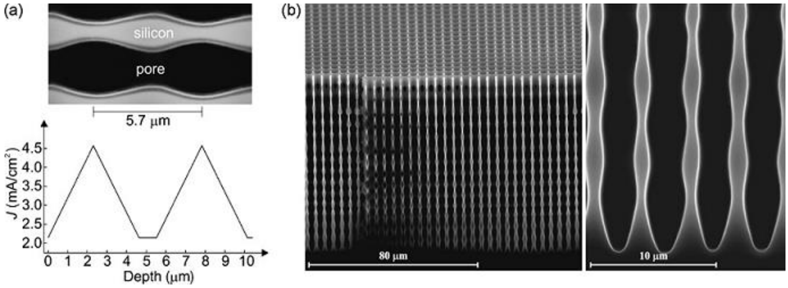
In particular, for ordered MpS, the current density at the pore front (the pore tips) has been found to be $j_{\mathrm{tip}} = J_{\mathrm{PS}}$, where J_{PS} is a characteristic current density value that depends on the substrate and cell electrical properties and other parameters. Now it is possible to define the *porosity* of the etched sample as the ratio of "air volume" to total volume $P = V_{\mathrm{etched}} / V_{\mathrm{Si}}$. At a given time, this can be approximated as the 2-D cross-section area ratio of air over silicon at depth $z(t)$. A further simplification can be done for ordered patterns of pores, as in this case the porosity ratio of the repeating unitary cell is the same as the whole sample porosity, thus $p = A_{\mathrm{pore}} / A_{\mathrm{unit\ cell}}$. If we now apply that the pore area is proportional to the passing current and that the pores can be approximated by a cylinder, we obtain that.

$$p = \frac{A_{\mathrm{pore}}}{A_{\mathrm{unit\ cell}}} = \frac{\pi}{4}\left(\frac{d}{a}\right)^2 = \frac{J}{J_{\mathrm{PS}}}$$

where d is the pore diameter, a is the lattice pitch, and J is the steady state current density applied to the electrochemical cell. From this result, it can be seen that the *pore diameter is proportional to the current*. An example of a PS layer with modulated porosity is shown in Figure 2.

Although there are limits to the achievable shapes, imposed by the electrochemical porosification system, it is possible to create very complex structures such as sinusoidal modulations [14], embedded defects [15], etc. MPS pores can have diameters as small as 100 nm [16], The smallest reported 3-d MPS is approximately 500 “nm” in periodicity.

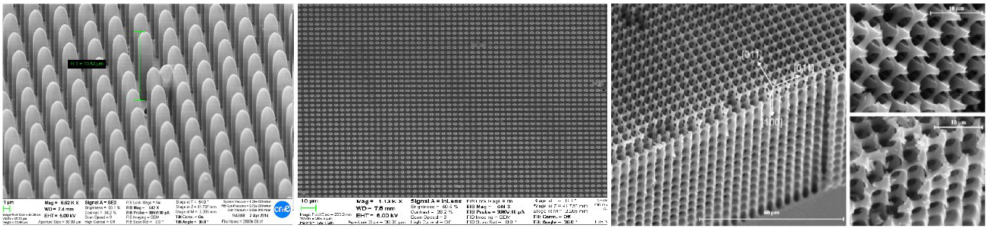
Figure 2. (a) triangular etching current profile and SEM micrograph of the resulting modulated pore. (b) SEM image of 14-period modulated pores arranged in a square lattice with a pitch of 4 μm . (Trifonov et al., 2008)



2.3 POST-PROCESSING

Macroporous silicon technology has very interesting properties (Levy-Clement et al., 1992) that allow the manufacture of devices in many application areas (Cullis et al., 1997; Lehmann & Rönnebeck, 2002; Rodríguez et al., 2005). However, to widen the range of possible uses of MpS, post-processing of the as etched samples is a necessary step. Some notable examples of the attainable applications now are the micromanipulation of particles, catalysts and biosensors, gas sensors (López et al., 2010; Vega et al., 2014) or microfluidics devices etc. Some common post-processes are the oxidation of the fabricated structures, the creation of suspended membranes with an alkaline etch of the back face of the MpS sample, or the change of the surface characteristics by layer deposition. Examples of post-processed samples are shown in Figure 3.

Figure 3: SEM micrographs of the fabricated macroporous membrane with straight pores. Left: Bird’s eye view of the silicon dioxide microfilms on the back of the sample. Center: top view of silicon dioxide micropillars. Right: bird’s-eye view SEM photograph of the 3D structure produced by symmetrically modulated pore etching and subsequent pore enlargement, with successive oxidation and oxide removal steps. The structure is a fully 3D network of interconnected holes in silicon.



3 SUB-MICRON PORE NETWORKS

Macroporous silicon samples with interpore separation of several microns are routinely manufactured by different research groups using photo-assisted EE. In the following sections, the fabrication process of ordered arrays of pores with dimensions and periodicities bellow 1 μm is described.

3.1 SUB-MICRON PORE NETWORKS. STATE OF THE ART

Optical filters in the mid infrared band require a reduction of the periodicity. Unlike the technology for the manufacture of periodicity samples of 2 μm or greater, there is not much experience published in literature in the manufacture of modulated SMP samples for periodicities lower than 1 μm. It has been therefore necessary to develop the technology, advance in the knowledge of the material and to characterize the structures. Such technology is optimal applied to gas sensing by spectral and non-dispersive infrared techniques.

In our group, technology for manufacturing macroporous silicon matrices with 0.7 and 0.5 micron periodicities has been developed and improvements have been obtained with respect to those published in the literature. In comparison to other groups, we have been able to obtain the smallest 3D MpS that has been published has a periodicity of approximately 500 nm (Bru et al., 2017).

3.2 SUBMICRON MANUFACTURING TECHNOLOGY

Fabrication of submicron structures required the correct adaptation of the etching parameters to have stable growth conditions. The process steps are similar to those described for the fabrication of larger structures. The first difference is the lithography method used for the pore etch pit formation. In this case, Nano Printing Lithography (NIL) has been used. In contrast to the more common UV lithography, the mask is transferred to de substrate by mechanical means, by pressing a master mould onto the sample. This mould can be fabricated by techniques such as e-beam lithography, laser interfermometry, or other methods.

In the work presented here, patterns with square networks of wells have been designed. The dimensions are just right to create MpS with periodicities of 700 nm and 500 nm.

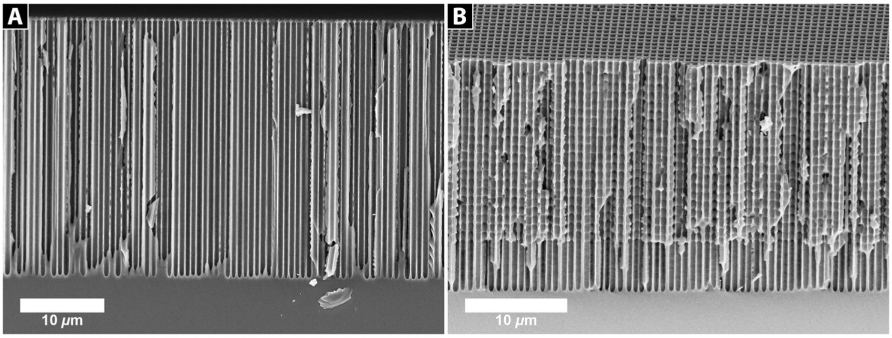
4 700 NM PITCH PORE ARRAYS

In our group we have been able to advance the EE method to allow us the routine fabrication of MpS samples with modulation, geared at gas sensing.

4.1 SAMPLE PREPARATION

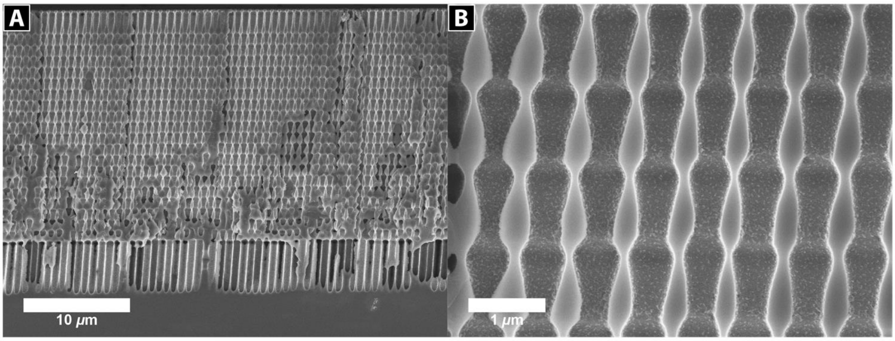
Samples were processed as described in the previous points to obtain a suitable substrate for anodic porosification. The mask was created using NIL and the pore etch pits later defined by a short anisotropic silicon etch. The pattern used is a square lattice of pores with 700 nm periodicity.

Figure 4. SMP samples of 700 nm periodicity, straight (A) and modulated (B), after optimization of the attack parameters. You can see the uniform growth of the pores and the absence of defects or dead pores.



After preparation, EE was performed, obtaining up to 40 μm deep pores, resulting in an aspect ratio better than 40:1, both straight and with noticeable modulations (see Figure 4.) Good optical response requires high refractive index contrast (i.e. porosity change). This has been achieved, as seen in Figure 5. Later, optimized samples, have achieved modulation indexes M better than 41%, with pore diameters in the range $d_{\mathrm{pore}} = 250\ \mathrm{nm}...690\ \mathrm{nm}$.

Figure 5. Optimized profile to achieve a “strong” modulation for photonic SMP crystals capable of working in NIR. General view of the section (A) and detail (B). In this case, a modulation index of approximately 41% has been achieved.

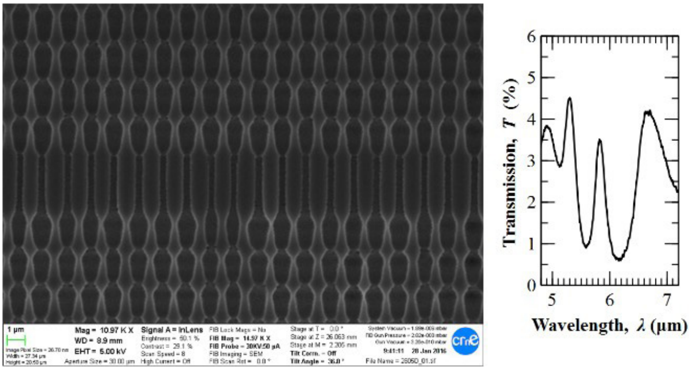


4.2 COMPLEX STRUCTURES IN 700NM PITCH MACROPOROUS SILICON

As EE allows freely changing the pore profile, advandec structures can be fabricated by using complex modulations schemes. For example, it is possible to create resonant cavities inside the MpS samples by changing one or several cycles of the profile at a certain depth. In this way, single and multiple resonators have been designed by tailoring the modulations of the pores (Cardador et al., 2017b). These cavities create reflection and transmission peaks in the spectral response of the samples. The use of multiple resonating cavities allows to either enhance a single resonance peak, or creating several, close, peaks at wavelengths of interest.

The primary application has been gas detection by NDIR technique (Hodgkinson & Tatam, 2013). For this, single peaks with high quality factor Q are better. Initially obtained results are shown in Figure 6, with a single cavity resonance, but not good enough for gas sensing. Later introducing more cavities, the peak Q increases as well as the bandgap is enlarged, achieving a better optical response, bringing a step forward for a suitable gas sensing device.

Figure 6. Sample of a MpS PhC with an embedded resonator and its effect in the transmission spectrum: a resonance peak that can be tuned to the absorption line of the target gas.



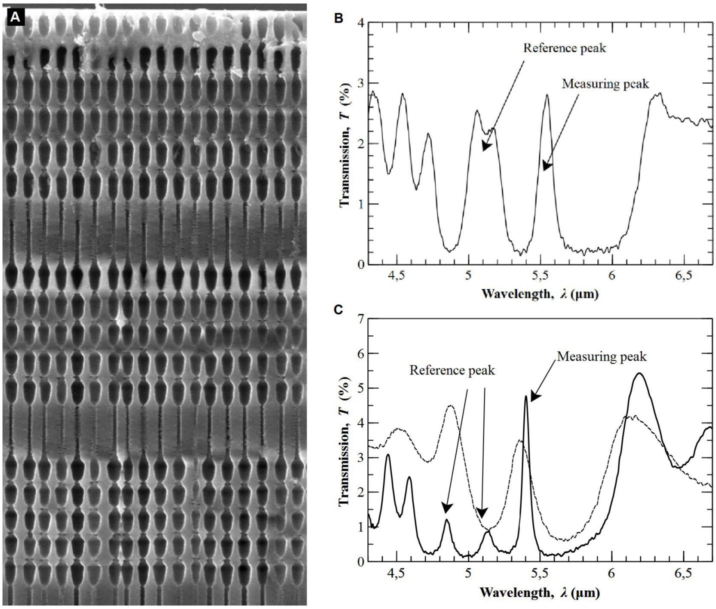
4.3 FROM SINGLE CAVITY TO MULTIPLE RESONANT CAVITIES

Single resonant cavity 700 nm structures have noticeable resonance peaks in the optical transmission at wavelengths in the margin of 5 to 7 microns, however of low Q -factor (around 25) with a transmission floor of about 1% inside the bandgap. To improve these results, sets of multiple coupling cavities have been studied by simulation. The added cavities resulted in the splitting of the resonance peak and a widening of the bandgap as evidenced in Figure 7. These structures where later fabricated and spectrally measured Furthermore, adjusting the number of modulation period between cavity defects, it is possible to help isolate the resonance peaks or enlarge the bandgap (Cardador et al., 2017a).

The obtained results show good correlation between simulation and measurement, revealing that the we have been able to optimize the 700 nm EE fabrication. As seen in the results of Figure 7(b), the two cavity system is able to increase Q to about 75, while the 3 cavity structure (Figure 7(c)) achieves up to 175 Q-factor. Jointly with a bandgap enlargement from 1.25 μm (2 cavities) to 1.75 μm (3 cavities), the MpS structures are now suitable for gas sensing use.

Furthermore, EE technology allows for more advanced structures, such as chirped modulated pore profile. These can offer improved peak isolation resulting in better sensing of the target gas.

Figure 7. SEM image for a two cavities photonic crystal (A). Transmission spectra, measured and simulated, for two (B) and three (C) cavities. (Cardador et al., 2017b)



5 500 NM PROCESS

In the case of the lower periodicity structures that we have fabricated, the pores are also arranged in a square lattice, but of 500 nm periodicity, and the pore diameter range from around 200 nm to 350 nm. The results show straight pores with good uniformity and controlled dimensions.

Though the EE fabrication process is a very flexible method of silicon micromachining (Trifonov et al., 2008), achieving the required process control for the fabrication of ordered pore arrays whose sizes are between 200 nm and 350 nm, and with a separation of 500 nm is relatively complex (Laffite et al., 2011).

5.1 INITIAL PREPARATIONS. DIFFERENCES WITH OTHER PROCESSES

Before preparing samples it is necessary to determine the adequate substrate that result in stable pore growth. In particular, a more closely spaced pore network, whose diameters are expected to be of the order of 350 nm, leaves an inter-pore space of 150 nm. This makes necessary find the ideal resistivity of the substrate. It was decided that the same substrates as those used for the 700 nm MpS would continue to be used.

A second point to consider is an electrolyte with a different HF concentration. In order to be able to create modulations in a controlled manner, useful for PhCs, the etch speed is of great importance. Initially, a 2% HF solution was tested, with the idea of having a lower J_{PS} and a lower forward speed. In the end, due to stability issues, a 5% concentration was used.

5.2 SAMPLE PREPARATION

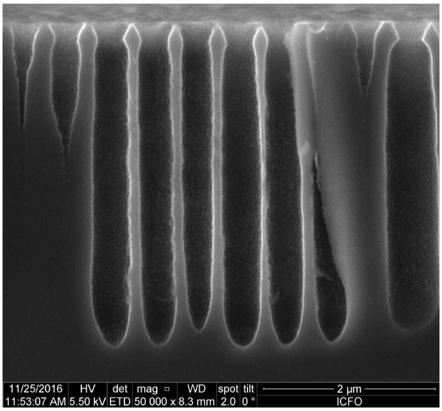
Samples for the 500 nm process were prepared following the same basic procedure as before: define the pattern of nucleation points using NIL lithography, transfer the pattern to the substrate, and creating said points later using an anisotropic attack of silicon (TMAH.)

Though the EE parameters need to be optimized for each case, samples of good quality were already obtained by using wafers of the same type and resistivity as for the 0.7 micron process: HF concentration 5% wt., *n*-type substrate with (100) orientation, and suitable resistivity.

5.3 STRAIGHT PORES OF 500NM PITCH

Initially, pores up to approximately 5 μm in depth were fabricated. The etch time was approximately 7 minutes, giving an etch speed of approximately 0.7 μm/min. Under low current conditions, pore death (premature pore termination) was high, as seen in Figure 8. Currents, as well as voltages, were tuned and optimized to obtain stable pore growth, which resulted in samples with little, but still some, pore death. No branching was observed using the selected etching conditions, suggesting that the voltage range used was adequate for the silicon substrates used. Evolution of microporous silicon is observed in the pore walls.

Figure 8. Straight pores in a 500 nm MpS structure. Etch conditions (low current) are the cause of the premature death of a significant number of pores.



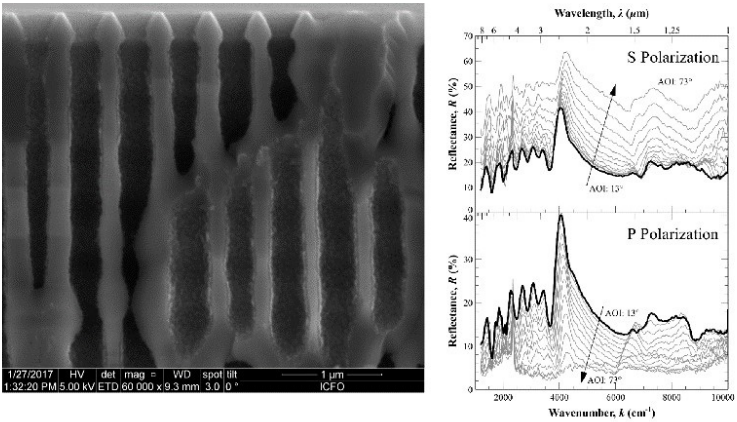
5.4 MODULATED PORES (500NM PITCH)

MpS crystals with modulated pore profiles were obtained once the etching parameters were adjusted. Several profiles where testes, changing both the amplitude, period, and duty cycle. As a starting point, a square wave with rise and fall time approximately 1/6 of the period was used. The maximum porosity was 32.2%, while the minimum porosity was 24.6%. Given the substrate and electrolyte used, it was observed that pore growth control was limited, but enough to obtain a noticeable modulated structure.

An example of a fabricated sample is shown in Figure 9. It can be seen that stable pore growth, with modulation, has been achieved. As control of the pore growth is narrow, the current ratio from the “small” to “large” diameter regions is necessarily small, which results in a structure with a “smooth” modulation. The results obtained show that modulated pores with a diameter of less than 300 nm can be successfully achieved.

As the pore modulation amplitude is small, there is enough dielectric contrast to result in a characteristic optical behaviour that already approximates the desired responses in NIR, but with relatively poor definition (see Figure 9). In particular, the response obtained needs further improvement by achieving a higher modulation amplitude of the pores.

Figure 9. Sample of MpS modulated with the highest modulation amplitude at the time. The variation of the recorded profile is less than what the model predicted.



6 CONCLUSION

In this work, we describe the fabrication steps to achieve modulated MpS with *modulated pores* whose *diameters are less than 300 nm*, and we show the main characteristics of the obtained samples. As it is shown, stable pore growth with modulation is possible; however, work is still underway to tune the model to obtain strong modulation profiles. These results open up new possibilities for the creation of devices capable of operating in the range of optical communications, and for sensors(Shankar & Lončar, 2014; Wehrspohn et al., 2013), employing this technology. Furthermore, these structures may be used in other non-optical fields of application.

REFERENCES

Bru, D. V., Maza, D. C., & Martinez, A. R. (2017). Electrochemical Etching of silicon with sub-500 nm feature size. *2017 Spanish Conference on Electron Devices (CDE)*, 1–4. https://doi.org/10.1109/CDE.2017.7905245

Cardador, D., Vega, D., Segura, D., & Rodríguez, A. (2017a). Macroporous silicon structures in 700 nm and 500 nm. *NanoSpain Conf 2017*. https://www.nanospainconf.org/2017/Abstracts/Nanospain2017_Rodriguez_Angel_147.pdf

Cardador, D., Vega, D., Segura, D., & Rodríguez, A. (2017b). Study of resonant modes in a 700nm pitch macroporous silicon photonic crystal. *Infrared Physics & Technology*, *80*, 6–10. https://doi.org/10.1016/j.infrared.2016.11.004

Cullis, A. G., Canham, L. T., & Calcott, P. D. J. (1997). The structural and luminescence properties of porous silicon. *Journal of Applied Physics*, *82*(3), 909. https://doi.org/10.1063/1.366536

Hodgkinson, J., & Tatam, R. P. (2013). Optical gas sensing: a review. *Measurement Science and Technology*, *24*(1), 012004. https://doi.org/10.1088/0957-0233/24/1/012004

Laffite, G., Roumanie, M., Gourgon, C., Perret, C., Boussey, J., & Kleimann, P. (2011). Formation of Submicrometer Pore Arrays by Electrochemical Etching of Silicon and Nanoimprint Lithography. *Journal of The Electrochemical Society*, *158*(1), D10–D14. https://doi.org/10.1149/1.3514584

Lehmann, V. (1993). The Physics of Macropore Formation in Low Doped n-Type Silicon. *Journal of The Electrochemical Society*, *140*, 2836. https://doi.org/10.1149/1.2220919

Lehmann, V. (1996). Porous silicon-a new material for MEMS. *Proceedings of Ninth International Workshop on Micro Electromechanical Systems*. https://doi.org/10.1109/MEMSYS.1996.493820

Lehmann, V., & Föll, H. (1990). Formation Mechanism and Properties of Electrochemically Etched Trenches in n-Type Silicon. *Journal of The Electrochemical Society*, *137*(2), 653–659. https://doi.org/10.1149/1.2086525

Lehmann, V., & Rönnebeck, S. (2002). MEMS techniques applied to the fabrication of anti-scatter grids for X-ray imaging. *Sensors and Actuators A: Physical*, *95*(2–3), 202–207. https://doi.org/10.1016/S0924-4247(01)00737-3

Levy-Clement, C., Lagoubi, A., Tenne, R., & Neumann-Spallart, M. (1992). Photoelectrochemical etching of silicon. *Electrochimica Acta*, *37*(5), 877–888. https://doi.org/10.1016/0013-4686(92)85039-N

López, E., Irigoyen, A., Trifonov, T., Rodríguez, A., & Llorca, J. (2010). A million-channel reformer on a fingertip: Moving down the scale in hydrogen production. *International Journal of Hydrogen Energy*, *35*(8), 3472–3479. https://doi.org/10.1016/j.ijhydene.2010.01.146

Rodríguez, A., Molinero, D., Valera, E., Trifonov, T., Marsal, L. F., Pallarès, J., & Alcubilla, R. (2005). Fabrication of silicon oxide microneedles from macroporous silicon. *Sensors and Actuators, B: Chemical*, *109*(1), 135–140. https://doi.org/10.1016/j.snb.2005.03.015

Shankar, R., & Lončar, M. (2014). Silicon photonic devices for mid-infrared applications. *Nanophotonics*, *3*(4–5), 329–341. https://doi.org/10.1515/nanoph-2013-0027

Trifonov, T., Rodríguez, A., Marsal, L. F., Pallarès, J., & Alcubilla, R. (2008). Macroporous silicon: A versatile material for 3D structure fabrication. *Sensors and Actuators A: Physical*, *141*(2), 662–669. https://doi.org/10.1016/j.sna.2007.09.001

Vega, D., Marti, F., Rodriguez, A., & Trifonov, T. (2014). Macroporous silicon for spectroscopic CO_2 detection. *IEEE SENSORS 2014 Proceedings*, 1061–1064. https://doi.org/10.1109/ICSENS.2014.6985187

Wehrspohn, R. B., Schweizer, S. L., Gesemann, B., Pergande, D., Geppert, T. M., Moretton, S., & Lambrecht, A. (2013). Macroporous silicon and its application in sensing. *Comptes Rendus Chimie*, *16*, 51–58. https://doi.org/10.1016/j.crci.2012.05.011

SOBRE O ORGANIZADOR

Xosé Somoza Medina (1969, Ourense, España) Licenciado con Grado y premio extraordinario en Geografía e Historia por la Universidad de Santiago de Compostela (1994). Doctor en Geografía e Historia por la misma universidad (2001) y premio extraordinario de doctorado por su Tesis "Desarrollo urbano en Ourense 1895-2000". Profesor Titular en la Universidad de León, donde imparte clases desde 1997. En la Universidad de León fue Director del Departamento de Geografía entre 2004 y 2008 y Director Académico de la Escuela de Turismo entre 2005 y 2008. Entre 2008 y 2009 ejerció como Director del Centro de Innovación y Servicios de la Xunta de Galicia en Ferrol. Entre 2007 y 2009 fue vocal del comité "Monitoring cities of tomorrow" de la Unión Geográfica Internacional. En 2012 fue Director General de Rehabilitación Urbana del Ayuntamiento de Ourense y ha sido vocal del Consejo Rector del Instituto Ourensano de Desarrollo Local entre 2011 y 2015. Ha participado en diversos proyectos y contratos de investigación, en algunos de ellos como investigador principal, con temática relacionada con la planificación urbana, la ordenación del territorio, las nuevas tecnologías de la información geográfica, el turismo o las cuestiones demográficas. Autor de más de 100 publicaciones relacionadas con sus líneas de investigación preferentes: urbanismo, turismo, gobernanza, desarrollo, demografía, globalización y ordenación del territorio. Sus contribuciones científicas más importantes se refieren a la geografía urbana de las ciudades medias, la crisis del medio rural y sus posibilidades de desarrollo, la evolución del turismo cultural como generador de transformaciones territoriales y más recientemente las posibilidades de reindustrialización de Europa ante una nueva etapa posglobalización. Ha participado como docente en masters y cursos de especialización universitaria en Brasil, Bolivia, Colombia, Paraguay y Venezuela y como docente invitado en la convocatoria Erasmus en universidades de Bulgaria (Sofia), Rumanía (Bucarest) y Portugal (Porto, Guimarães, Coimbra, Aveiro y Lisboa). Ha sido evaluador de proyectos de investigación en la Agencia Estatal de Investigación de España y en la Organización de Estados Iberoamericanos (OEI). Como experto europeo en Geografía ha participado en reuniones de la Comisión Europea en Italia y Bélgica. Impulsor y primer coordinador del proyecto europeo URBACT, "come Ourense", dentro del Programa de la Unión Europea "Sostenibilidad alimentaria en comunidades urbanas" (2012-2014). Dentro de la experiencia en organización de actividades de I+D+i se pueden destacar la organización de diferentes reuniones científicas desarrolladas dentro de la Asociación de Geógrafos Españoles (en 2002, 2004, 2012 y 2018).

ÍNDICE REMISSIVO