Commercial applications of porous Si: optical filters and components

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It is shown that porous Silicon in various geometries and morphologies can be used for novel optical elements by combining theoretical insights with suitable porous structures and some pre- and post-processing of the Silicon. The paper restricts itself to light propagation in the pore direction. Theoretical and experimental results will be presented for the following novel optical elements: environmentally stable optical components from mesoporous Silicon, long wave pass filters, macroporous Silicon UV Filters, and polarization components for the UV range. Either new components are presented, mostly with first experimental results, or the state-of-the art for previously discussed elements is considerably improved upon.

1 Introduction

Initially the interest in porous Si (PS) was due to strong luminescence observed in microporous Si [1, 2]. However, exploiting this property for devices proved difficult if not impossible up to now. While meso- and macroporous Si (MPSi) do not show luminescence, the large set of different porous Si structures does contain many elements with peculiar if not unique optical properties, and this paper attempts to describe a subset with the common denominator that wave propagation in pore direction will be considered.

If the size scale of the pores (average diameter, distances, etc.) is sufficiently small in relation to the wavelength considered, the porosity changes the effective index of refraction of the material. Since porosities and pore geometries can be adjusted in a wide range [3], many applications based on adjustable refractive index have been suggested and are investigated. Most prominent are variants of so-called Bragg mirrors, i.e. structures with alternating layers of different porosity, which allow to design spectral transmission and reflection properties almost arbitrarily [4]. However, a number of problems have been encountered with such devices, in particular environmental instability and poor IR transparency. Some solutions of these problems will be reviewed here.

If the porous semiconductor can no longer be treated as optically homogeneous, the interaction of light and the porous structure can take many forms. If some periodicity in the pore structure is produced, either by “seeding” pores with appropriate structuring techniques or by exploiting self-organization features, photonic crystals result [5]. In two-dimensional photonic pore crystals usually only the propagation of light perpendicular to the pores is of interest. Comparatively little work has been done concerning the propagation of light in pore direction, in particular for geometrically well-defined arrays of straight pores with large aspect ratios. In [6] it was shown that uniform and ordered arrays of straight macropores with
diameters in the 1 \( \mu \text{m} \) region and lengths of several 100 \( \mu \text{m} \) act as efficient short pass filters in the blue to UV region. Here we will present and summarize new results on wave propagation along pores in a variety of structures. Some necessary background issues are briefly reviewed, and theoretical and experimental results are given relative to possible applications. More complicated structures than just plain porous membranes (e.g. coated and filled pores) are introduced and discussed. It will be shown that porous semiconductors employed in this way show great promise for a multitude of novel optical components; in fact, first products are already on the market.

## 2 Mesoporous silicon filters

Reflective type optical filters or mirrors based on mesoporous silicon superlattices were proposed over a decade ago [7]. Mesoporous silicon superlattices were etched on p- or n-doped (100) oriented (5-15) m\( \Omega \text{cm} \) wafers, while the porosity modulations were formed by modulating the applied current density during the electrochemical etching. Since then a large number of papers was published with respect to (meso)porous silicon filters and mirrors. A detailed review of these activities can be found in [8]. Recently [9, 10] it was suggested that mesoporous silicon filters also offer advantages for mid and far IR filter applications that require cooling the filter to cryogenic temperatures (e.g. for most of astronomical applications). SEM of mesoporous silicon far IR filter is provided in Fig. 1a.

**Fig. 1** a) SEM image of the mesoporous silicon far IR filter; b) SEM image of the silicon-sealed mesoporous silicon filter surface; c) SEM image of the cross-section of the mesoporous silicon filter close to the bonding interface, and d) Transmission spectrum taken through a mesoporous silicon filter etched on a bonded wafer at angle of incidence ~ 14° from normal at room temperature.
The benefit of mesoporous silicon filters in such applications is the absence of thermal or mechanical stresses between the individual layers. Since the layers are “all-silicon”, they are mechanically and thermally perfectly matched. In contrast, common interference filters are always composed of layers with dissimilar mechanical properties and thermal expansion coefficients, causing considerable problems when cooled.

Several problems with mesoporous silicon filter technology were found, though, with the main problems being the environmental instability of mesoporous silicon layers (see, e.g. [11]) and the absorption in the highly doped silicon substrate usually used for mesoporous silicon filter fabrication. During the last decade several approaches were suggested for solving the environmental instability problem. This includes the pre-oxidation of mesoporous silicon sample either chemically (by boiling in HNO₃) or thermally (see, e.g. [12]), coating the mesoporous silicon surface with layers of SiO₂ by Plasma Enhanced Chemical Vapor Deposition (PECVD) or by Low Pressure Chemical Vapor Deposition (LPCVD) [13]. However, most of these techniques were found to be inapplicable for far-IR filters intended for use at cryogenic temperatures.

In [10] it was proposed to use a magnetron-sputtered silicon layer on the mesoporous silicon surface as a method of improving the environmental stability of the far IR filters. The advantage of such an approach is based on the fact that the thermal expansion coefficient of a sputtered silicon layer will be the same or close to that of the mesoporous silicon multilayer and silicon substrate. In other words, the filter structure remains all-silicon in composition. This method was proven to be successful in solving the environmental instability problem. An SEM image of such a filter structure is given in Fig. 1b.

Another problem with mesoporous silicon IR filters in the transmission mode comes from free carrier absorption (also known as multiphoton absorption) in the silicon substrate remaining beneath the mesoporous layer. Highly doped silicon wafers with resistivities in the range of 1 mΩcm to 20 mΩcm are totally opaque in most of the mid IR and far IR spectral range at room temperature. The only solution offered so far has been the removal of the mesoporous silicon multilayer from the etched silicon substrate by means of a current spike at the end of the etching process, which “lifts off” the mesoporous silicon filter structure [14], i.e. produces a free-standing mesoporous silicon membrane. However, while some mesoporous silicon membranes are relatively robust and flexible (if sufficiently thick, as for far IR filters), many membranes would not survive this rather violent process. In particular, thinness or high porosity renders free standing membranes unacceptably brittle for practical applications.

In [10], a new approach was suggested. Instead of a homogeneously doped silicon wafer, a “two layer” silicon wafer composed of a highly doped Si layer with the proper thickness for the intended mesoporous layer bonded to low-doping density “handle” wafer is used. This provides the high carrier concentration necessary for mesoporous multilayer formation on silicon that is highly transparent throughout the far IR range. The key point in choosing a wafer bonding technique suitable for these purposes is a uniform and generally high conductivity across the bonding interface. A fusion bonding technique is capable of meeting this requirement. Experiments proved the feasibility of such an approach. A SEM image of a portion of the mesoporous silicon filter around the bonding interface is given in Fig. 1c. In order to prove the transparency of the mesoporous silicon multilayer with a handle wafer, one of the etched wafers was examined in an FTIR at room temperature. The transmission spectrum is shown in Fig. 1d. One can see that the structure is indeed transparent in the far IR range.

Further optimization and refinement of the mesoporous silicon fabrication procedures is currently under way.

3 Long wave pass filters

Random arrays of macropores in Si scatter the light at wavelengths below the average pore-to-pore distance. Recently [10] it was proposed to use this property to make an infrared long-wave pass filter (LWPF) that would scatter the light with wavelengths below an edge wavelength that is defined by the porous layer morphology, but transmit the light effectively and uniformly for wavelengths above this
edge. Infrared LWPFs have a number of important applications. They are used both in combination with
narrowband pass filters (in order to achieve a narrow pass band with wide and deep rejection bands) and
by themselves in applications where the radiation from shorter wavelengths should be suppressed in
order to improve the signal-to-noise performance of detectors (as in astronomy, Fourier transform spec-
troscopy, etc.).

For the far IR range a scattering-type filter was already proposed in [15], utilizing a layer of diamond
particles (or other transparent materials) of suitable sizes, which are spread on a surface of a sheet or
substrate of a material that is transparent in the desired IR region (e.g. polyethylene, quartz or sapphire).
Light with wavelengths around or below the size of the particles in the "active" layer is blocked by
means of scattering, while the light with wavelengths above the size of the particles is transmitted. Such
filters are truly long wave pass filters, i.e. the transmission above the rejection edge is uniform over the
wavelengths where substrate and particles are transparent. Such filters can be used both in room tempera-
ture and cryogenic applications. However, the mechanical stability of such filters is usually poor, since
the active layer can be easily peel or flake off. Moreover, the versions made with thin polymer films
cannot withstand large pressure differentials very well, thus requiring slow pumping time.

From the MPSi point of view, silicon has a sufficiently high refractive index in the IR spectral range
(around 3.5), thus permitting efficient scattering of light. Pores, if etched on a flat, unstructured surface,
form a random array with a relatively narrow distribution of pore sizes that can be easily fine-tuned in a
wide range by choosing suitable substrate and etching parameters [3]. Hence, one can expect that such a
material will exhibit long wave pass behaviour similar to diamond particle filters.

Fig. 2 a) SEM cross-sectional views of a MPSi layer
formed on p-doped (111)-oriented silicon wafers; b)
log-log plot of the transmission through the MPSi
LWPF etched on (111)-oriented substrate, and c)
normal incidence transmission spectra through a
number of far IR LWPFs made from MPSi layer
etched on (100) oriented silicon wafers.

Experimental results confirmed such predictions. An SEM image of a random MPSi array etched on
(111)-oriented p-doped substrate is presented in Fig. 2a. An optical evaluation (see Fig. 2b) confirmed
that indeed random MPSi arrays exhibit well-pronounced long wave pass behavior. It was found that by
changing the silicon doping, electrolyte concentration, current density and temperature during the electrochemical etching process, it is possible to fabricate good-quality (optically and mechanically) long wave pass filters with edge positions anywhere from ~3 μm to 35 μm (as illustrated in Fig. 2c). The sharpness of the rejection edge could also be controlled within wide limits by adjusting the total thickness of the MPSi layer and by optimizing (usually lowering) the temperature during electrochemical etching. Temperature control also allows to some extent to influence the spread of the average pore distance distribution in the array.

The pass band of MPSi LWPF filters was found to be flat up to a wavelength of 200 μm at room temperature. The reason for this is that the silicon wafers used for fabrication of LWPF are typically low doped, thus the free-carrier absorption is relatively low. Thermal and mechanical stability of MPSi LWPF filters was also found to be superior. The technology is already sufficiently developed and the filters were introduced to the market in 2005 by Lake Shore. This is, to best of the author’s knowledge, the first commercially marketed optical product based on porous Si.

4 Macroporous silicon UV filters

Most of currently available UV (pass) filters are based on interference in multilayer stacks and have to be used with well-collimated beams and carefully aligned angles of incidence. Such filters show strong drawbacks in the deep UV spectral range due to the limited number of materials sufficiently transparent, environmentally stable and with enough refractive index contrast to provide sufficient rejection while maintaining adequate transmission. Dye-doped polymer filters offer wide and deep rejection, but thermal and environmental stability is a big concern, and the control of the position and shape of the pass band is also not straightforward. Ultraviolet filters based on MPSi were proposed recently [6, 16, 17] as an attractive alternative to the existed technology. Such filters utilize the leaky waveguide transmission through the pores in MPSi material.

Initially the UV pass band in MPSi membranes was demonstrated on the pure silicon MPSi layers [6], but later it was shown [16, 17] that the optical characteristics of the filter can be significantly improved by coating the pore walls with a multilayer dielectric structure. Figure 3a shows a diagram of the MPSi UV filter. The schematic drawing of the filter structure is given in a center of the figure, the overview SEM image of the cross-section is given in the top right corner, the magnified cross-sectional SEM image (showing dielectric multilayer structure) is given in the bottom left corner, while the coarse and magnified SEM images of the top surface of the filter are given in a top left and bottom right corners respectively.

As an example, Fig. 3b gives the simulated plot of transmission through the eight-layer (SiO$_2$/HfO$_2$) coating on the pore walls of MPSi membrane with 350 μm deep pores. One can see that the numerical calculations predict an extremely deep and wide rejection band, a steep rejection edge, and sufficiently good transmittance within the solar-blind region of spectrum, thus making MPSi filters very good candidates for a number of solar-blind applications such as electrical spark imaging and Non Line Of Sight (NLOS) UV optical communications.

In addition to wide and strong rejection, MPSi filters offer a number of other unique properties, such as the independence of the shape and position of the spectral features, or omnidirectionality [16], and the capability of achieving a virtually unlimited rejection band on the longer wavelength side. The MPSi layer itself (uncoated or coated with dielectric multilayers), in addition to the pass band in the UV, also shows a pass band throughout the near IR and IR, which is due to the transparency of Si in the IR [18]. It was demonstrated, however, that it is possible to completely suppress the transmission through “in-Si” waveguide modes by covering the first, second or both surfaces of the MPSi structure by a thin (100-200 nm) metal film to prevent the light from either coupling into or out of the Si waveguides [18]. Such a property was experimentally verified (see Fig. 3d). The omnidirectionality property originates from the independence of the filtering of, and light coupling to, leaky waveguide processes. It was also experimentally demonstrated [18]; cf. Fig. 3c.
Formation of MPSi membranes, suitable for UV filter applications can be done by following “standard” process [6], consisting of photolithography, anisotropic wet chemical etching, electrochemical etching and membrane opening by either alkaline etching or reactive ion etching. The key process in fabrication of functional MPSi UV filters is the pore wall coating. The simplest process for obtaining a single-layer pore wall coating is thermal oxidation of the MPSi membrane [16, 17]. However, in order to obtain multilayers of different dielectric materials on the pore walls, a different technique has to be used. In [18] it was shown that a Low Pressure Chemical Vapor Deposition (LPCVD) process can be used for these purposes. However, using LPCVD techniques, it may be difficult to obtain the necessary uniformity of the individual layer thicknesses along the pore length. In addition, stresses in the films may be quite large, causing various problems. In [19] an Atomic Layer Deposition (ALD) technique was suggested as a better process for pore wall coating. A number of pore wall coatings (SiO2, HfO2, alumina titanate) were already experimentally demonstrated so as the multilayers with up to 50 layers of individual materials [19]. Currently the development of such filters is in the pore wall coating optimization stage.

Fig. 3  a) Diagram demonstrating the structure of the MPSi UV filters; b) Simulated transmission plot through the “solar-blind” MPSi filter structure; c) experimental transmission spectra through the MPSi membrane with multilayer pore wall coating taken at different angles of incidence, and d) experimental transmission plot through the short-pass MPSi UV filter with the enlarged blocking range.

5 Macroporous silicon polarizers

Optical polarization components are used in numerous applications that include photography, liquid crystal displays, polarimetry, astronomy, defence, sensing, and photolithography, to name just a few.
Polarizers based on metal wires, birefringence in crystals, and on specially designed dielectric multilayers are among the widest spread types. While polarizers oriented for the visible and near IR wavelengths ranges perform well, that is not the situation in the UV, especially for deep and far UV where the choice is much narrower and the performance of available polarizers is worse.

An entirely new concept for a UV optical polarizing material that promises solutions to the problems described above was proposed recently [20]. These new polarizers consist of ordered, macroporous silicon with the pore walls covered by dielectric multilayers, similar to the MPSi-based UV filters considered in Section 4. The polarizing behavior in this case originates from the elongated shape of the pores, which provides selection of one preferential linear polarization in transmitted light (see Fig. 4a). This behavior originates from the higher propagation losses of the leaky waveguide modes for electric field vectors directed along to the shorter pore axes compared to those of leaky waveguide modes with their electric field vectors directed along the longer pore axis. Fig. 4b gives a calculated plot of the transmission spectral dependences through a 200 μm thick MPSi layer, with the pores of 1.3 x 0.7 μm cross-sections and a 5-layer SiO₂/Si₃N₄ coating on the walls.

![Schematic drawing of an MPSi-based UV polarizer](image)

Fig. 4 a) Schematic drawing of an MPSi-based UV polarizer; b) simulated spectral dependences of the transmission of light with two orthogonal polarizations through an MPSi structure similar to that in a). 1st polarization corresponds to the electric field vector aligned along the longer pore axis, while the 2nd is along the shorter pore axis. c) SEM image of the top surface of the fabricated MPSi polarizing component, and d) Experimental extinction spectrum of an oxidized MPSi sample shown in c).

Although classical macropores have a circular or quadratic shape, it is possible to generate rectangular slit shapes by a number of techniques [21]. For optical demonstration of the polarization behavior, an
MPSi membrane with elongated pores was made. The SEM image of the top surface of MPSi layer used for optical testing is given in Fig. 4c. The design goal (see Fig. 4a) was not met yet and more optimization of the electrochemical etching process is required. However, the feasibility of the approach was demonstrated: Fig. 4d shows the spectral dependence of the extinction through the fabricated MPSi membrane after forming the thin thermally grown SiO₂ layer on the pore walls. The oxide on the pore walls manifests itself as a strong peak of the extinction centred at ~350 nm.

The experimentally achieved values of extinction for the MPSi-based polarization component were far less spectacular than those predicted by theory. This is well understandable, however, since the quality of the tested MPSi layer was quite far from the design goals. Deep UV and far UV polarizing properties of the material weren’t tested yet since the used commercial polarizer (analyzer) used showed a transmission cut-off at about the 260 nm wavelength. However, experimental results confirmed the main predictions of the theory [20].

6 Conclusions

The unique control of the optical properties available with porous silicon technology resulted in a number of designs and realizations of different optical components with advantageous properties. Some of them are already introduced to the commercial market, while others are expected to follow in the near future, offering an attractive commercial opportunity at present.

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