A Study on Porous and Nanoporous Semiconductors and its Emerging Applications

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Abstract

Pores in single-crystalline semiconductors, including a nanometer regime, can be generated in a broad variety of geometries and morphologies. Porous semiconductors can have entirely different properties than bulk and met materials with, for example, non-natural optical properties are developing. A variety of innovative sensors, but even more “exotic" applications such as high explosives or electrodes for micro fuel cells, may be used for porous semiconductors. The paper discusses pores (including more applied dimensions of wide-ranging etching), the features of porous half-conductors and evolving applications.

1. Introduction

The prevalent component of silicone in the microelectronics along with the detection of light-emitting Si [1, 2] has already before 1991 been the focus of electrochemical research on this semiconductor (for a recent review see [3]). While porous silicon were already discovered by Uhlir [4] in 1957 (but not recognized by what they were), it was important to find conditions for pore production in Ge [5-7] until 2000. Latest investigations have also taken place on porous III–V semiconductors (mainly GaP, GaAs, InP); see[8]. Pores were also documented in GaN[9], SiC[10, 11] and ZnSe[12] in the meantime, and the exploration of the space available for the parameter is continuous in several laboratories [13].

2. POROSIFICATION OF SEMICONDUCTORS

It is helpful to describe a few terms first to identify the vast variety of pores (cf. Figure 1). Pore geometry implies (average) pore diameters and the pores distance, i.e. the pores measurements, whereas pore morphology covers the pores (e.g., cylindrical, branched, facetted, fractal,).

Micro-, meso- or macro-pore, according to IUPAC specifications, corresponds to pores with common measurements of < 2 nm, 2 nm–50 nm or > 50 nm. Therefore, the word "nanoporos" may be interpreted; here we use it slightly loosely for pores below 1 μm.

In general, purification can be accomplished under appropriate conditions by anodizing the semiconductor into a suitable electrolyte. A chemical reaction is typically needed on a semiconductor-electrolyte interface: a mixture of direct dissolution, oxide forming and oxide dissolution with information that are subject to several parameters, such as electrolyte chemistry, the potential or current density applied, temperature, electrolyte flow conditions, semiconductor light state and the sort and degree of doping (polished, rough, masked). The ultimate reaction will occur continuously as electropolishing (often seen at large current densities) on the surface, uniformly but everywhere, or strongly placed, including any autonomous organisation - that is the pores.

A few generic comments can also be made here, vague. During the forming of pore, direct semiconductor dissolution nearly often competes with oxidation plus eventual oxide dissolution. Therefore, the electrolyte must dissolve the oxide. Therefore, fluoride containing electrolytes are needed for silicon whereas the option is relaxed for other semiconductors (GeO2, e.g., even dissolves in water). An electronic hole is the second requirement for the dissolution reaction and pores' creation in a semiconductor. In general, a hole is necessary to start the reaction chain at the interface, which eventually contributes to the "loss" of an atom (or molecule in the case of compound semiconductors). One of the key "tricks" for adequate cleaning trials is the nearby availability of hole. This trick only works in n-doped stuff, in which minority carriers are holes. Holes will then be supplied by illumination [14], by electric tunnel collapse or by landslide, owing to the high degree of field intensity as in the case of pores in III–V compounds [8]. Although no pores in most p-doped semiconductors are yet to be obtained, the exceptions are Si, SiC [15] and recently Ge [7, 16].

In the case of p-type products, the device must be driven in a condition in which holes can be consumed in certain locations only. In general, one works either by low current density (p-type macro-pores in aqueous electrolytes [17]) or by utilising electrolytes containing worse and fewer oxide [3] inherently, in a system of inadequate oxidation. Alternatively, the use of a highly doped semiconductive, which reduces the majority of the voltage on the junction's electrolyte side, leads to 'quick' chemistry which promotes direct dissolution compared to anodic oxidation (p-type mesopores), which increases the passivation relative to oxidation during dissolution. Micropores in p-type Si are just another case; quantical-wire effects are at least a part of their formation [2]. Although a "quantum-wire model" can count for micropores in Si, it is not unique to Si and thus does not account for the absence of micropores in most others. Former semiconductor training is a strongly interdisciplinary business. There is also cause to believe that a stochastic portion, like self-organization in time and space, championed in the "current explosion" model can only be adequately represented by calling upon all of the above elements in addition to anything mentioned.[18]

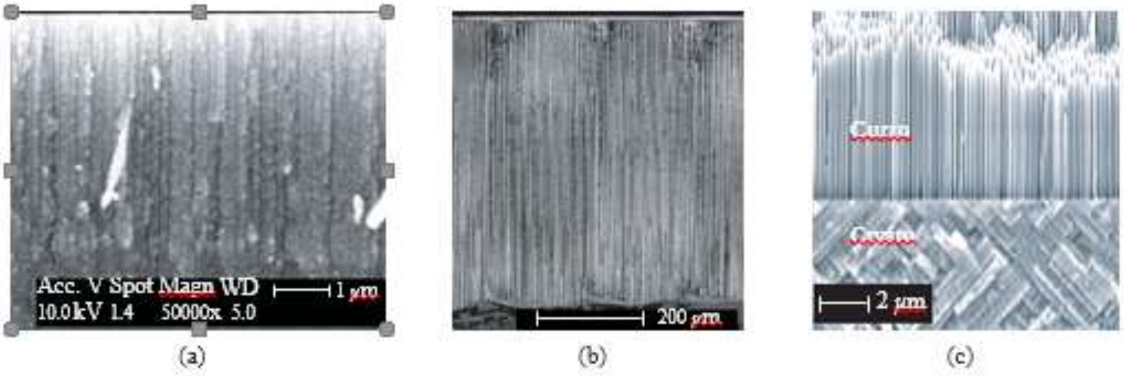

Figure 1: Variety of pores in semiconductors: (a) mesopores in Si, (b) macropores in Si with lithographic prestructuring, (c) “Curro”-“Crys- to” transition in InP.

3. ETCHING AND ETCHING EQUIPMENT

In order to get reproducible performance, a potential stat or a galvanostat with one or two reference electrodes is almost unavoidable rather than a basic power supply. Although early lighting studies use halogen lamps (with cold filters), high-energy IR-LED arrays have more stability and intensity for these experiments (for detailed information on all used hardware, see [19]). Both chemical processes are highly affected by temperature, rendering it inevitable in the range of 0.1 to C to use computer-controlled heating/cooling systems with temperature stabilization. A quick movement of the electrolyte is often unavoidable to maintain continuous electrolyte conditions at the device. Easy magnetic agitators (or no agitations at all) easily contribute to a lack of uniformity in space and time. As certain electrolytes are extremely hazardous and/or corrosive, even for tiny samples with areas in the 1cm2 area, these conditions are challenging, although standardized etching of entire wafers has become very scientific.

A few settings have been suggested to create homogenous porous layers over entire wafers [3, 20], which, however, just cope with a portion of the space parameter. Our group has built and marketed a robust etcher that meets all needs [19]. (Including safety issues). The wafer is vacuumed and hung head-on in the electrolyte. The electrolyte convection is assured through a rocking table, where the whole setup is installed. Since the wafer and the etching cell shape an almost smooth surface, the rocking action is adequate to maintain an even electrolyte flow on average. This prevents unsafe pumping equipment and makes an all-teflon design that can handle even ultra-aggressive electrolytes such as HF/organic solvent mixtures, which remove almost everything other than Teflon. Wafers with a diameter of up to 200 mm have been treated with exceptional accuracy (figure 2) and can scale up to 300 mm.

Figure 2: First, electrochemically etched 200 mm p-type wafers (in-set: macropores in the organic electrolyte; the most demanding etching process).

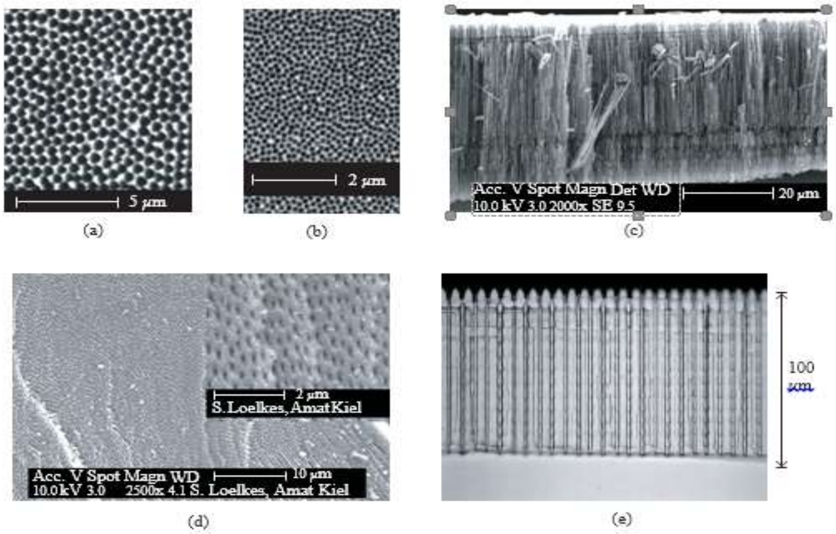

Figure 3: Fast pore etching in Si. (a) Plain view of pores on a (111) surface with hexagonal self-ordering. (b) On (100), a geometrically frustrated ordering of pores is evident. (c) Cross-section ((111) sample). (d) The homogeneous pore distribution of 100 nm pores in the cross-section of (111)-Si. (e) “Pulsed” fast macrospore growth to a depth of 100 µm.

4. MACRO-, MESO-, AND MICROPORES IN SILICON

Macrospores in Si were first observed in 1990 [14]; cylindrical pores with diameters of between 350 and 10 µm usually expand slowly (1 µm/min) in 100 and 113 directions [3]. For other methods, it is almost difficult to achieve certain drastic aspect ratios. An intrinsic drawback of the typical macro-foam method is the sluggish growth rate along with the necessarily low HF concentrations in this mode which is a severe problem for any mass production. However, our community has recently advanced towards growing the etching pace in two ways:

I mixing large HF concentrations with pulsed etch voltage while also using backlight; (ii) Usage of a less oxidising organic electrolyte at large HF concentrations without illumination in the breakdown mode [21]. In the first example, the regular backlight setup is used where an HF concentration greater than 6 wt. percent will usually result in undesirable poor pores morphologies (heavy branching, rough walls, etc.). This influence may be deleted if the etching distortion is pulsed constantly. Although the pore diameter somewhat reacts to the pulsing, the formation of side pores is effectively suppressed by dramatically raising the rate of etching (up to 4 µm/min, cf Figure 3(e)).

In the second case, it was attempted to mimic pores as seen in InP, where beautiful pore arrays [22] with high etching rats can be produced. In this situation, whole production is limited to electrical breakdowns, as compared to the normal macropore etching setup, where disintegration is prevented so tiny side pores will drill through the entire pores (cf. .Figures 3, 5, and 6). The second ingredient expected in the InP pores study was to remove the oxide formation with the use instead of water of an organic solvent (acetonitrile (MeCN) or dimethyl formamide (DMF)) complemented by sufficient salts since the conductivity of the organic solvent were poor. In this case the speed of development is closely coupled with the pace of oxide dissolution, which is by far the slowest process [18]. The HF concentration was then pushed to 15-20 wt percent, under conditions that regular macropore development no longer continues properly. The first observations were promising. Any illustrations are seen in Figure 3. As in InP, some self-organization was observed: a high degree of hexagonal self-ordering was discovered on (111) surfaces, where near wedging caused pores to be sorted and normal threefold crystallographic symmetry harmonized, al-beit not as prominent as in the InP situation. While on (100) inP, pores still constitute hexagonal arrays [22]; on (100) A new function in self-organization was found: the formation of a so-called frustrated crystal. As the four-fold symmetry of the crystal competes with a closing hexagonal symmetry, a geometrically frustrated pores distribution results with no angular correlation of the closest neighbor pos This is a rather desirable design for basic optical and magnetic research since it has a sufficiently specified form, but without translational symmetry, which, for example, may induce Moire's unwanted patterns. It should be noted that these macrospores are not subject to the normal macrospore restrictions (i.e. growth rates of 1 µm/min and diameter of > 200 nm) as seen in Figure 3, where many exampres with 100 nm pores may be seen; hence the mesoporous system is within control (following the strict IUPAC Convention).

Normal mesoporos in Si are often cultivated on strongly doped samples and at reasonably high levels of HF, needing just a few volts to drive large graft currents. The growth rates will approach many 10 µm/min, suggesting that the key process is the direct dissolution of silicon. The resulting morphology is a network of pores like needles and strongly ramified (see Figure 1(a)). Figure 4 indicates the reliance on the fluoride concentration for type Si of pore diameter and pore depth (cf. also [23] for a detailed analysis of parameters and resulting morphology).

In order to achieve a narrow distribution of the pores, uniform nucleation is required and a branch-ing is suppressed. This involves either prepatterning with lithographs of < 100 nm, or a certain degree of self-organisation, as seen in Figure 3 for the (macro) pores.

This takes us to micropores, the smallest pores (following IUPAC). Micropores typically develop on low-doped p-type material with ca. 1 µm/min; crack-free development above certain µm thickness can be troublesome. The resulting morphology is a disorderly network of Si-branches of up to 80 percent (that virtually every atom on the left is a surface atom), however we miss further information of this much-examined pore form and refer to two recent books[24, 25].

Although the enormous research devoted to light-emitting Si, microporous Si, actual devices are most possibly focused on quantum structures built using various technologies. However, microporous layers continue to provide sufficient ground for testing and can be viewed as test vehicles for structures created utilising more sophisticated technologies that are unavailable in most laboratories. As a very unwanted aspect it is important to add that previous attempts to manufacture microspores in semiconductors other than Si have struggled with anodic etching, rather than 6H SiC [11]. This is not only disappointing, but shocking as the widely agreed micropores forming process (which is highly based on quantum wire effects) is not Si-specific, but can occur in any semiconductive environment.

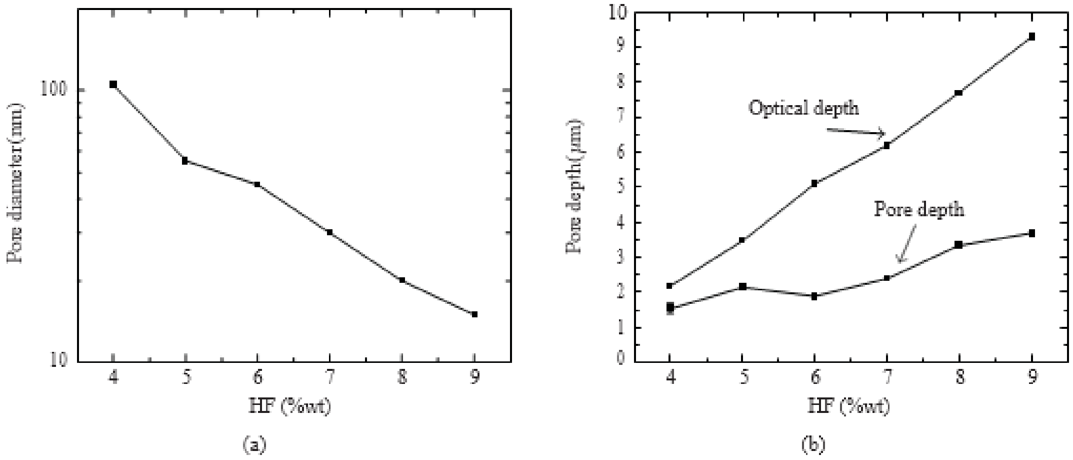

Figure 4: (a) Diameter and (b) depth of mesopores on n-Si (100, ρ = 5–20 Ωcm), j = 30 mA/cm2, tetch = 100 seconds. The “optical thickness” (ellipsometer) differs form the geometric thickness, because the pore density decreases, while the refractive index increases with increasing HF concentration.

5. Some applications of semiconductors

The number of applications that take advantage of the above-mentioned special properties is extensive; it is divided into many subgroups. One or two examples shown in bold letters are explored more thoroughly from each subject. I Photonic crystals[34], optical short-pass filters[25, 30], and Bragg and Rugate mirrors obtained through modulation porosity with depth are the latest optical components with validated capabilities [35].

(ii) Nonlinear objects (e.g. pore frequency doubles in GaP[26] and Si[36]) are still partly proven to be new applications like phase balancing, engineered waveguides[37] and innovative anisotropic (e.g. birefringent) materials [29].

Structures that can be used as integrated waveguides in InP are able to move from crysto to curro pores abruptly; Figure 7 shows an illustration. The quickly caused porosity shifts are combined with a change in the waveguiding refractive index. In comparison to traditional techniques, these frameworks are simple to build if all their properties (including damping) are ideal for optoelectronic applications, but their utility in the sensing of gas optics is evident. Optical gas and fluid sensing are expected to send light through a gas or fluid-filled space and detect spectrum shifts at

(iv) Porous layers are, for instance, GaN on SiC as buffer layers for daunting epitaxial processes [44].

(v) Porous layers are used as models for several forms of nanorod or nanotube [45].

(vi) Microporous Si is a main explosive ingredient [31].

If the microporous Si pores are filled with an oxidizer because of the large surface region, the effects are powerful. This (accidentally discovered) property is currently being investigated for applications including an airbag firing system. Exotic as it is, this application may be nearer to a product than several sensor inventions. One big challenge is to confine the illumination to a limited cross-section in order to examine small concentrations of compounds. The signal to noise even improves as the light is concentrated. The standard light waveguides are solid, i.e. cannot penetrate the examined material. A porous waveguide prevents this issue without leaving the properties of the waveguide.

A cubic crystal with pores in many crystallographic corresponding directions has no further cubic symmetry from the point of view of light with wavelengths greater than the pores' geometry. Indeed, (110) directed Si displays a marked birefringence, with two sets of mesopores spreading in 100 directions [28] that can be considerably stronger than in the natural crystals. This impact has recently been recalculated with significant precision; additionally, the principle has been generalised to include other pore geometries. For certain polar geometries, entirely new anisotropic action has been predicted that could be generated in GaAs or InP [29]. (cf. Figure 8). The pores are to be packed with metal with heavy plasmonic resonances (e.g., for Ag) and these optical anisotropies are to be further reinforced [38].

Mechanics

(i) Porous layers are typically useful as sacrificial layers and as dielectric layers or as a thermal insulator for MEMS applications. Macroporous Si electrodes and microporous Si electrodes are used for micro-fuel cells [39–41].

(ii) Ultrasonic generation has been subject to exceptionally poor thermal conductivity [42].

(iii) In one of the very few applications to date, canon utilises pore layers as a kind of "zipper" while producing insulator silicon [43].

Sensing chemistry

In general, some specific effects for the chemical sensing of pore surfaces I are solely susceptible to certain materials and specifically observable properties such as photo-light, (spectra-)reflectivity, or conductivity/impedance connect the analytes. (ii) Unique optical elements made of porous materials, in particular reflectors and resonators from Bragg, conveniently calculate their main characteristics (e.g., wave-length reflections/diffraction at a certain angle). (iii) For example, very limited effective light transmission speed may be used to miniaturise traditional optical gas spectrometers for photonic crystals made of porous materials [46].

The Bragg reflector concept is smart dust from San Diego [47] car party in San Diego [47]. For various protein classes (i.e., one mirror colour is the same protein), multiple sets of mesoporous silicon rugate filters are functionalized and may then be ground to ashes, blown into the atmosphere or houses. Once introduced to the test material or gas, the particles of dust bind the protein to be detected and then alter its reflection to something potentially observable by LASER.

Uses in Biotech

(i) Protein and other particulate filters. Because of their limited pore size dispersions, electrochemically etched meso- and macroporous substances are optimal candidates for filtering high-size selectivity applications for the ex- sufficient protein blends filtering. The mixture of large macropores and smaller meso-pores, as described in the 'Membrane processing' portion of this article, give a rare combination of mechanical flexibility, development ease and filtering capability.

(ii) Very standard macropore arrays in Si are already being implemented to biochip applications (DNA); and if appropriate, technol- ogy is quickly scaled to far smaller sizes [25].

(iii) For example, Bio MEMS applications use porous structures as models for living cells on porous substrates [48].

(iv) Reactor and nano reactor. Although some work has been done in this regard [49], it remains a vision rather than a reality. With certain techniques straight pores may be linked when manipulating the pore geometry; Figure 9 shows examples. Figure 9(a) indicates that the pores are 111 but turn back and forth to 113 (in three similar directions) as the voltages are cycled in the right way. The "fast etching" methods for Si (see Figure 3) and InP (see Figure 1(c)) have identical morphologies overlaying crystalline and currose pores. Reveals mesopore-linked macropores (usu- ally considered a nuisance). These systems are all like tissues which are biologically optimised to absorb complex liquids and are tempted to wonder regarding the above-mentioned applications.

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