#### ECS Transactions, 19 (3) 347-354 (2009) 10.1149/1.3120714 ©The Electrochemical Society

#### Production of High Aspect Ratio Single Holes in Semiconductors

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In many areas of research exists a need for single small holes with diameters from a few nm to several  $\mu$ m and large aspect ratios. Existing technologies for that are complex and rather limited. It is shown by a simple proof of principle that suitable single holes or specific arrays of some single holes can be made by first etching a very large number of small and deep holes or pores into semiconductors like Si or InP by established electrochemical means, followed by masking the desired holes and filling all others with, e.g., a metal in a galvanic process. The potential and limitations of this technique are discussed in some detail.

#### Introduction

In several branches of research, single holes with small diameters in the nm -  $\mu$ m range and large aspect ratios are needed. For example, detailed studies of transport and electrochemical phenomena need holes with nanoscopic dimensions (1 - 4), while applications such as single-pore filtration of cells call for pores or holes with well-defined diameters of a few  $\mu$ m. In ref. (5) "patch clamping" is described, meaning the use of single holes with diameters around 1  $\mu$ m and an aspect ratio of 200 in order to avoid laborious and difficult micromanipulations of a (micro) glass pipette under a microscope. Microfluidic applications (6) would also benefit from single holes or arrays of holes in a defined pattern and that might also be true for some nano-optics and X-ray applications. It goes beyond the scope of this paper (and beyond the experience of the authors) to enumerate all possible uses of small single holes with large aspect ratios or defined arrays of such holes.

While there are many ways of producing such structures, none of the techniques reported is easy to use and mostly very specific to certain materials and dimensions. In references (7 - 10) several methods are reviewed and described in some detail. They include conventional lithography applied, e.g., to thin layers, ion beam and electron beam techniques as well as nuclear track etching.

In this paper we first provide a proof-of-principle for making single holes or defined arrays of holes by first etching a multitude of suitable pores in semiconductors by established electro-chemical processes, followed by complete closing of unwanted pores (all but one in the extreme case). Next the possibilities and limits of the technique proposed will be discussed in some detail.

### **Experimental Techniques and Results**

The electrochemical etching of pores or holes in standard Si substrates of n-type or ptype was established around 1991 (11 - 13) and resulted in three major pore types: Micropores or mesopores with diameters below 2 nm or between 2 nm and 50 nm, respectively, and macropores with diameters > 50 nm. The etching of macropores with diameters between about 0.5  $\mu$ m (14) and up to 10  $\mu$ m or larger (15) in a lithographically defined array and with pore depths of up to 500  $\mu$ m as pioneered by Lehmann and Föll (13) is by now a well established technique and described in two books (16, 17), a number of reviews (18 - 20) and many papers (cf. for example the by now 5 proceedings of the Int. Conf. "Porous Semiconductors Science and Technology ("PSST")). **Fig. 1** gives an impression of what is possible; some ramification of the technique for the purpose of single hole production will be discussed later.

Given a periodic array of pores as shown in **Fig. 1a**), a single hole can in principle be produced if all pores except the one selected are closed and the unetched part of the Si wafer is removed, so that a membrane is formed. It is also clear that closing all pores except the ones selected for a "single hole array" (SHA) can produce any SHA that is commensurate with the basic pore grid geometry. The task at hand is thus to i) produce a suitable hole array, ii) mask selected holes in a way that prevents pore filling; iii) fill the unmasked holes, and iv) produce a "membrane" with just one hole or a SHA by removing the masking and the unetched part of the Si wafer.



**Figure 1:** a) Top view, showing the defined n-Si array of pores as pre-structured by standard lithography used in the experiments. b) Cross-sectional view of a n-type Si macropore array filled with Cu. c) Top view, showing the defined p-type Si array of pores as pre-structured by standard lithography used in the experiments. d) Cross-sectional view of a p-type Si macropore array filled with Cu.

The second task of masking some pores can be done, in principle, by suitable variants of standard lithographical techniques. For the proof of principle reported here it is not important which hole exactly is kept open so a very simple masking technique was chosen. A few holes were kept open by "dusting" some toner from a Laser printer over the surface of a freshly etched pore array. Toner particles have sizes around 5  $\mu$ m and some particles stick to the opening of a pore if they are "fixed", like in the printing process, by heating the specimen to (90 – 95) °C for about 10 min. Fig. 1a) shows three thermally fixed toner particles covering one pore completely and the neighboring pores to some extent.



c)

The third task - filling the unmasked pores - was done by galvanically depositing Cu in all unmasked pores. Filling pores in Si (and in other semiconductors) by some galvanic process with metals or other materials in order to produce a nanocompound has attracted considerable interest in recent years (21 - 24), and there are many open questions with respect to filling pores completely at all and, if possible, within acceptable times. For the teak at hand Cu galvanics proved to be suitable; the experimental conditions were as follows: Electrolyte composition: 300 ml  $H_2O$ , 70 ml  $H_2SO_4$ , 5 g CuSO<sub>4</sub>, 0.1 g DTAC (1dodecyl-trimethylammoniumchloride, 97 %), 0.1 SPS (Bis-3g sodiumsulfopropyldisulfide), 0.1 g PEG (Polyethylenglycol). The Cu deposition was done at constant 20 °C under galvanostatic conditions with a current density linearly ramped from  $-0.2 \text{ mA/cm}^2$  to  $-1.0 \text{ mA/cm}^2$  during the deposition time of about 1.000 min. The potential found changed from about -0.1 V at the beginning of the experiment to about -0.6 V at the end. Complete filling of 77  $\mu$ m deep pores could be achieved in

this (slow) way, cf. **Fig. 1d**); a task not yet possible in much shorter times. **Fig. 1b**) shows pores in a p-type substrate (so-called p-macro(org, litho) pores), cf. (19, 25, 26) obtained with so-called organic electrolytes, demonstrating that the technique can be used with both types of doping. The pores masked with the toner particles did not participate in the filling process as could be expected.

The fourth task of making a membrane is easy after the pores have been filled, since the sample is no longer porous and thus not very brittle. It is possible now to use standard mechanical grinding and polishing.

The single holes obtained in this way are shown in **Fig. 2**. **Figs. 2a,b)** show different pore lattice geometries resulting in single holes with diameters / depths of 1.3  $\mu$ m / 150  $\mu$ m and 1.7  $\mu$ m / 97  $\mu$ m, respectively; the aspect ratios thus were 115 and 57, respectively.

That the holes were open throughout the depth of the sample could be seen with the aid of an optical microscope in transmission. After removing all apertures and using the highest illumination intensities possible, single holes showed up as recognizable bright dots (Fig. 2c)).

We consider the result shown as sufficient proof of principle for making single holes or SHAs. In what follows we discuss the potential and limitation of the method described.

#### **Potential and Limitations**

The following items shall be addressed in the context of selectively filling anodically etched pores in semiconductors: i) Available pores, ii) Details of pore geometry, iii) Masking techniques, iv) Filling techniques, and v) Specialties.

While there is a huge multitude of pores available in several semiconductors (most prominent are Si, Ge (27), III-V compounds like GaAs, InP and GaP (28 - 32), SiC (33), and some II-VI compounds like CdSe (34) and in some anodically formed metal oxides (most prominent are Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and ZrO<sub>2</sub> (35 - 37)), only straight pores arranged in some regular pattern are of conceivable use. This excludes many of the pores produced so far but still leaves the following candidates: 1. Lithographically defined macropores in lightly doped n-type and p-type Si with minimum diameters around 0.5 µm (14) and aspect ratios > 500. 2. Self-organized macropores and possibly mesopores in Si with diameters from about 200 nm to below 50 nm and aspect ratios of > 100. The pictures in (17, 38) may serve as examples. 3. So-called "current line pores" in InP with diameters from about 1 µm to about 50 nm (28, 31, 32) and arranged in a rather well-expressed selforganized single pore crystal under certain circumstances as shown in Fig. 3a) (cf. also (39)). 4. Some pore types in GaAs, GaP or SiC but without offering properties that are not already covered in 1, -3, 5. Pores in the metal oxides mentioned above with diameters typically in the 20 nm - 300 nm range. In summary, the pore diameters in suitable pore arrays span the range from around 20 nm to  $> 10 \,\mu$ m.



**Figure 3:** a) Self-organized hexagonal pore single crystal in n-type InP (40). b) Square pore array obtained from n-type Si macropores after subsequent chemical treatment in KOH (39). c) Pt tubes obtained through the filling on n-type InP pores (23). d) Pb wire array produced by filling Si macropores with liquid Pb (41). For details see the text.

With respect to the detailed single pore geometry, major parameters are straightness, cross-sectional geometry (and its variation with pore depth), and the pore wall roughness. Relative to the large number of geometrically and topologically different pore types alluded to above, only cursory information can be given here. With respect to straightness, a fundamental difference exists between pores that grow strictly in a crystallographic direction (like all n-macro(bsi, aqu) pores and many (but not necessarily all) Si-pmacro(org) pores) and thus are perfectly straight, and so-called current-line pores that grow generally in the direction of current flow and thus might deviate from a straight line. The pores in InP mentioned above belong into this category. At present it is not clear if the smaller kinds of pores can be made with deviations from a straight line much smaller than their diameter. This is not so much a principal problem but rather reflects the fact that neither measurement of this kind have been reported, nor any attempts to optimize this quantity. In our opinion, straight enough pores are possible even for very small diameters for aspect ratios not too large.

The cross-sectional geometry of pores may vary from pore to pore and within a given pore as function of depth. Generally, pore single crystals – produced by defined nucleation (all kinds of lithography) or by self-organization – show rather constant diameters from pore to pore that usually can be experimentally adjusted to a defined value within some bandwidth. More irregular arrays like small macropores or mesopores in highly doped Si tend to show larger variations of the individual diameters. That may have an inherent advantage, since it offers the possibility to select a specific pore with the right dimension for the single hole desired. As far as individual pores are concerned, there is a certain tendency with large macropores that the pore diameter decreases somewhat with depth, but this effect can be kept small, in particular for aspect ratios smaller than 100 - 200. The cross-sectional geometry in defined arrays varies from circular to almost square shaped; in more random arrays it can be multi-facetted with the symmetry of the nearest neighbor surrounding (i.e. typically fourfold - sevenfold). This may be adjusted to some extent by the etching conditions or by some post-etching treatment. Oxidation with subsequent oxide removal may make a pore "rounder" (42), while chemical treatment with highly orientation selective etchants like KOH for Si may produce rather perfect squares as shown in **Fig. 3b**) from the late V. Lehmann.

Not too much is known about the roughness of the surface of pores; for the Si – n-macro(bsi, aqu, litho) case Foca et al. performed a systematic study and showed that the roughness may vary considerably, depending on what kind of "optimizer" had been added to the electrolyte, but can be < 10 nm (43). In contrast, self-arranged arrays of small macropores and mesopores in Si are often very rough or "fuzzy". Not much is known for pores in the other semiconductors except that in typical SEM pictures the pore walls in e.g. InP current line pores appear to be not too rough.

With respect to masking techniques it is generally possible to use a somewhat adjusted standard lithography even on porous substrates as pioneered by Ottow et al. (44). While the technique has not yet been tried for masking single holes, it can be confidentially stated that this should be possible for hole dimensions of 1  $\mu$ m or larger. For much smaller hole dimensions in-situ deposition of e.g. Pt should be possible in e.g. focused ion beam machines (FIB) nowadays available in many laboratories. In addition, electronbeam lithography might be used.

Filling techniques do not need to be restricted to galvanic deposition of metals. While this technique can be used even at small dimensions, cf. **Fig. 3c**), that shows the Pt filling of pores in InP (substrate etched off) from the work of Tiginyanu et al. (23) or refer to (45) where 900 nm  $Al_2O_3$  pores have been filled with Ni, other techniques are available, too. Besides filling pores at some elevate temperatures with liquid polymers (46), liquid metals can be used, too, as demonstrated in (41) and shown in **Fig. 3d**).

Specialties in this context are the coating of "the" pore (or all pores before the filling) with all kinds of layers, e.g. to change the reflectance of the pore surface or intentional modulations of the pore diameter as detailed, e.g. in (47). As far as the passage of light in pore directions is concerned, ref. (48) provides a review of the many effects encountered and the possibilities of pore treatments as outlined above for optimizing optical properties (including far IR and UV). Some of these considerations are also valid for single pores.

Coating the inside of a single hole or of a SHA after it has been made with suitable layers (e.g. by using atomic layer deposition (ALD) (48)), may be used to decrease the pore diameter of more easily made larger single pores to smaller dimensions. The limits of such a technology are not clear at present but diameter reductions of a factor up to 10 (e.g. from 1  $\mu$ m to 100 nm) should not be too difficult. An example is shown in **Fig. 4**.



**Figure 4:** a) Macropore in Si coated with 5 layers of dielectric materials by atomic layer deposition (48). The diameter has been conformally reduced by 60 % and even larger reductions would be possible.

# Acknowledgements

The authors are indebted to Prof. J. Bohr who suggested the topic and was always available for questions and discussions. The help of Prof. Tiginyanu, who supplied one of the pictures, is gratefully acknowledged.

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