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Institute for Materials Science, Christian-Albrechts-University of Kiel, Kaiserstr. 2, 24143 Kiel, Germany

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* Corresponding author: e-mail hf@tf.uni-kiel.de

In many areas of research a need for single small holes with diameters from a few nm to several µm and large aspect ratios exists that is hard to meet with existing technologies. In a proof of principle it is shown 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 is briefly discussed.

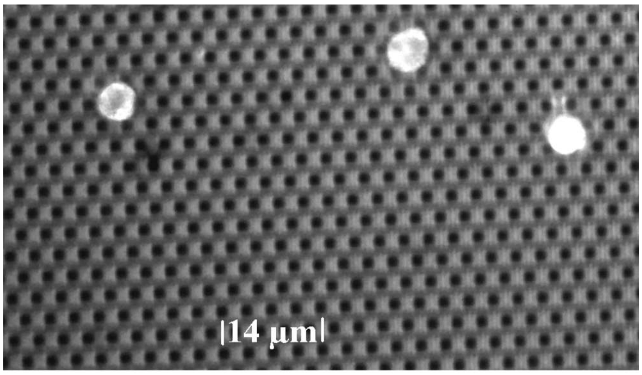
1 Introduction In several branches of research, single holes with small diameters in the nm–µm range and large aspect ratios are needed. Detailed studies of transport and electrochemical phenomena need holes with nanoscopic dimensions [1–4], while applications such as single-pore filtration of cells call for pores or holes with well-defined diameters of a few µm. “Patch clamping” as described in [5] uses single holes with a diameter around 1 µm and an aspect ratio of 200 in order to avoid laborious and difficult micromanipulations of a (micro) glass pipette under a microscope. Microfluidic applications, as described in [6], would also benefit from single holes or arrays of holes in a defined pattern. In the field of X-ray and electron beam imaging, defined single holes or hole arrays could also be beneficial [7] but it goes beyond the scope of this letter to enumerate all possible uses.

While there are many ways of producing such structures, none of the techniques reported is easy to use and mostly they are very specific to certain materials and dimensions. In Refs. [8–11] 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.

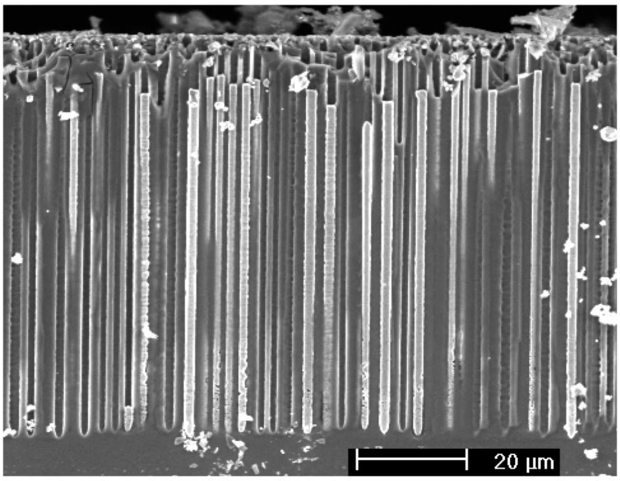
Here we provide a proof-of-principle for making single holes or defined arrays of holes with diameters in the 1 µm region and aspect rations of >120 by first etching a multitude of suitable pores in silicon by established electrochemical processes, followed by complete closing of unwanted pores (all but one in the extreme case). The possibilities and limits of this technique will be discussed.

2 Experimental techniques and results The electrochemical etching of pores in standard Si substrates of n-type or p-type was established around 1990 [12] and resulted in two major variants: (i) micropores and mesopores with diameters >2 nm or 2–50 nm, respectively, and (ii) macropores with diameters >50 nm. Only macropores are of interest because they can be produced absolutely straight. The etching of macropores with diameters between 0.5–10 µm or larger in a lithographically defined array and with pore depths of up to 500 µm, as pioneered by Lehmann and Föll [12], is by now a well established technique and is described in two books [13, 14] and a number of reviews [15–17]. Moreover, suitable pores with diameters down to 10 nm can also be produced in other semiconductors, most notably in InP, and in metal oxides, cf. [18, 19]. Figure 1 gives an impression of what is possible with Si macropores. Note that it is not possible to electrochemically etch single holes (or only a few holes) directly, since single pores immediately form side branches in contrast to pores in an ordered array [20].

Given a periodic array of pores = holes as shown in Fig. 1(a), a single hole can be produced if all pores except for a few selected ones or just one are closed and the unetched part of the sample is removed, so that a membrane is formed. It is also clear that closing all pores except



a)



b)

Figure 1 a) Si sample; top view, showing one of the pore arrays used in the experiments. b) Cross-sectional view of a Si macropore array filled with Cu.

the ones selected for a "single hole array" (SHA) can produce any SHA that is commensurate with the basic pore grid geometry. Within existing pore etching technologies, hole and grid geometries between 50 nm and 10 µm are easily possible. 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 an SHA by removing the masking and the unetched part of the Si wafer.

For the first task lithographically pre-structured 1 cm^2 Si samples obtained from a standard 150 mm wafer (n-type, {100} orientation, 5 Ω cm; p-type 20 Ω cm) were etched in an apparatus described in detail in [21]. The electrolyte was based on 5 wt% aqueous HF. Galvanostatic etching under intense back side illumination (bsi) for 80 min produced typical "n-Si-macro(aqu, bsi, litho)" pores (cf. [16] for this self-explaining short-hand) to a depth of 97 µm. In the case of p-Si-macro(org, litho) pores, the "organic" electrolyte was based on 7 wt% HF diluted in DMF (dimethylformamide). The current density was 10 mA/cm^2, producing the 77 µm deep pores as shown in Fig. 1(b).

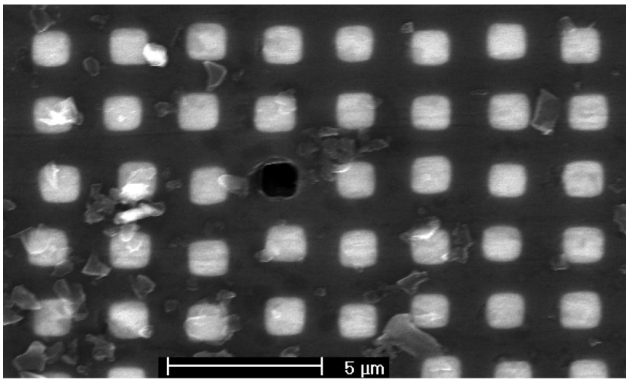
For the proof of principle reported here, the second task of masking some pores was done by manually depositing some toner from a laser printer with a "femtopipette" on the surface of a freshly etched pore array. Toner particles have sizes around 5 µm and some particles stick to the opening of a pore if they are "fixed" by heating the specimen to 90–95 °C for about 10 min. Figure 1(a) shows three toner particles covering one pore completely and the neighboring pores to some extent. Of course this is not a well reproducible and controllable process, but it still allows for a proof of principle. There is, however, no principal problem (except time and cost) of using lithographical techniques (cf. [22, 23]), in-situ deposition techniques, e.g. with focussed ion beam techniques (even down to nanometer dimensions) [22], or possibly ink-jet technology [24], for masking single pores selected at will.

The third task – filling the unmasked pores – was done by galvanically depositing Cu in all unmasked pores. While filling pores in Si (and in other semiconductors) galvanically with metals or other materials has attracted considerable interest in recent years [25–28], there are still many open questions. There are, however, many other ways of filling techniques available; cf. [29] for a particularly simple one. For the task at hand Cu galvanics proved to be suitable; the experimental conditions were as follows. Basic electrolyte composition: 300 ml H_2O, 70 ml H_2SO_4, 5 g $CuSO_4$ plus a few minor additions. The Cu deposition was done at 20 °C under galvanostatic conditions (in the case of n-type Si) with a current density linearly ramped from –0.2 mA/cm^2 to –1.0 mA/cm^2 during the deposition time of about 1000 min, following a constant current density of –1 mA/cm^2 for 2 min in the beginning of the experiment. The necessary potential changed from about –0.1 V at the beginning of the experiment to about –0.6 V at the end. In the case of p-type Si complete filling of 77 µm deep pores could be achieved under potentiostatic conditions at 0.5 V in 2400 min, Fig. 1(b) shows the result. Both n-Si-macro(bsi, aqu) and p-Si-macro(org) pores have thus been used, demonstrating that the technique is applicable to both types of doping. The pores masked with the toner particles did not participate in the filling process as was expected.

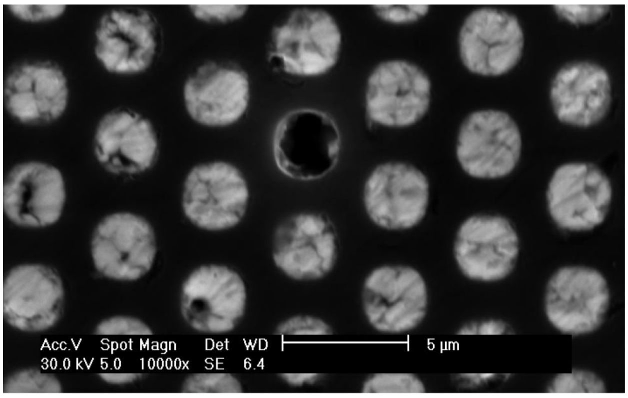
The fourth task of making a membrane is easy after the pores have been filled, since the sample is no longer porous and thus no longer brittle. It is possible now to use standard mechanical grinding and polishing.

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

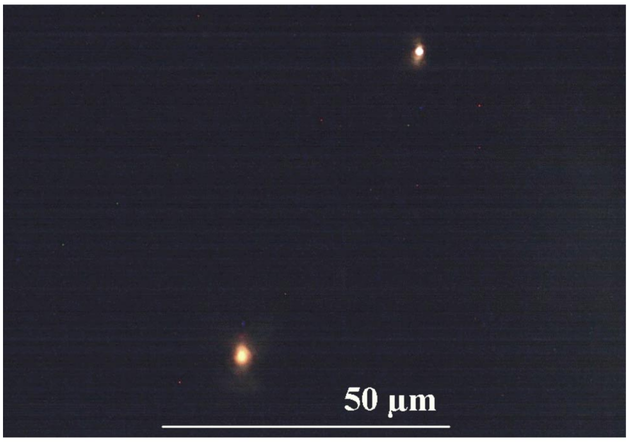
That the holes were open throughout the depth of the sample could be seen with the aid of an optical microscope in transmission. After removing all apertures and using the highest illumination intensities possible, single holes showed up as recognizable bright dots (Fig. 2c).



a)



b)



c)

Figure 2 (online colour at: www.pss-rapid.com) Single holes in a Si/Cu membrane. a) Almost square shaped holes with 1 µm diameter. b) Round holes with 1.7 µm diameter. c) Optical transmission through two single holes.

We consider the results shown as a sufficient proof of principle for making single holes or SHAs. It is clear that with a somewhat more involved technology the approach will allow to make single holes or SHAs with diameters from a few 100 nm to 10 µm and very large aspect ratios. It is likely that much smaller holes are also possible after optimizing the necessary processing steps.

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