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Vertical nanopatterning of 6H-SiC(0001) surfaces using gold-metal nanotube membrane lithography

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ABSTRACT Large-area membranes consisting of arrays of gold metal nanotubes were used as shadow masks to generate vertical nanopatterned 6H-SiC(0001) substrates. The gold membranes are formed by a replication technique based on electrochemical deposition of anodic aluminium oxide membranes or silicon substrates containing lithographically generated etch pits. Using the gold metal membranes as masks in reactive ion etching, spatially well-resolved protrusions in the SiC substrate were etched, arranged in periodic and non-periodic two-dimensional arrays. Final vertical morphological reorganizations were obtained in a hot-wall reactor under hydrogen flow. The obtained large-area networks of nano-objects have many potential applications in magnetism, electronics and biology.

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1 Introduction

The introduction of material porosity to standard semiconductor materials has proven a promising approach to obtain new physical properties for future applications of semiconductors. The preparation of nanometer-sized pipes has been reported for materials like silicon, gallium phosphide, alumina and silicon carbide [1–4]. Potential applications concerning photonic crystals, sieves and membranes have been discussed. SiC is recognized as an interesting semiconductor material exhibiting important electrical, optical and mechanical properties. SiC is biocompatible and nanoporous SiC membranes can be used for biomedical applications [5], for photonic crystals for visible light [6, 7] and for vertical electronic devices. Concerning SiC, most studies related to patterning concentrate on the fabrication of porous material. The obtained cavities are arranged in branched networks of nanotubes and nanopores. The influence of hydrogen etching on their morphology has been discussed by Sagar et al. [8]. Pores have been created in the SiC surface by anodization and grow vertically in a highly branched structure. A branched structure after electrochemical treatment has also been reported by Shishkin et al. [9]. Only very few results are reported so far on regular nanotube networks in SiC [10, 11]. In silicon [12–14] and alumina [15] these networks are routinely obtained by now.

The present paper is the continuation of our previous work on the fabrication of regular nanometer-sized pores in 6H-SiC(0001) using a combination of focused ion beam (FIB) and subsequent hydrogen etching [10, 11]. The morphology of the obtained pores was extremely homogeneous, exhibiting flat and steep side walls. All pores were oriented perpendicular to the 6H-SiC(0001) surface and arranged in a regular network. Important potential applications are expected for networks of nanopores. In the latter work, related to the FIB etching used, the patterned area was limited to several hundred square microns and the patterning was performed sequentially. The use of large-area metal nanotube membranes as shadow masks for subsequent reactive ion etching (RIE) enables the parallel preparation of arrays of nanopores covering areas of up to square centimeters.

2 Experimental results

The samples were cut from an on-axis, nitrogen-doped, n-type (resistivity 0.03–0.12 $\Omega\,m^{-1}$) silicon- terminated 6H-SiC(0001) wafer [16]. Gold-nanotube membranes used as shadow masks in the present work were prepared by replicating a master pattern structure of a nanoporous anodic aluminum oxide (AAO) membrane according to the method reported previously [17], which can be readily extended to fabricate various metal nanotube membranes from a wide range of different metals (e.g. Ag, Pt, Pd, Ni) that can be electrochemically deposited from aqueous solutions. In brief, a thin metallic gold film was first sputtered onto the surface of a long-range-ordered AAO membrane [18]. This process resulted in a thin conducting metal layer on the top part of the inner nanochannel surface as well as on the top surface of the AAO membrane. Subsequent electrochemical deposition of Au homogeneously thickens the metal layer, resulting in a tubular metallic nanostructure of 800 nm inside the alumina nanochannels. After removal of the alumina template in 30 wt % H_3PO_4 (60 °C), the resulting gold membrane was floating on the surface of the etching solution. After a cleaning procedure the Au-nanotube membrane was transferred onto SiC substrates from the solution (see Fig. 1a). As a next step,

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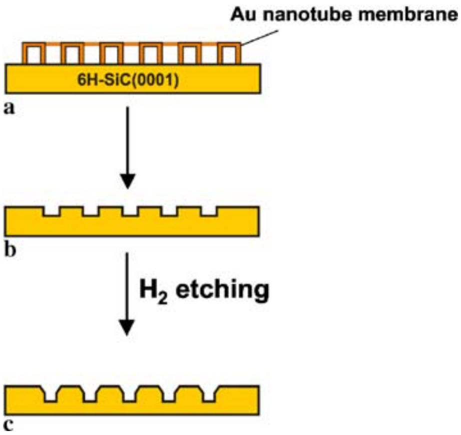

FIGURE 1 Schematic view of the use of an Au-nanotube membrane for preparation of holes in SiC

reactive ion etching of SiC covered with the Au membrane was performed. The etching was performed using a mixture of SF_6 and Ar (2 : 1) at 10 mbar and 200-V DC bias for 60 s. After the etching, the Au membrane was removed (see Fig. 1b) and the SiC samples were investigated with scanning electron microscopy (SEM).

Figure 2 reproduces a SEM image of the obtained pores in the SiC surface in a first set of experiments for the case of a self-ordered AAO membrane which shows only short-range but no long-range ordering. The inset in Fig. 2 shows a fraction of the membrane used that had remained on the sample surface. The membrane effectively protected the SiC surface from erosion except for the holes of the membrane. Thus, the reactive ion etching transferred the hole pattern of the membrane to a pore pattern in SiC. As the holes in the Au membrane were irregular in shape and position, the resulting pores in SiC show the same characteristics.

The holes patterned in the SiC surface were subsequently etched in hydrogen in a horizontal graphite hot wall reactor [19]. Prior to hydrogen etching the samples were cleaned in methanol in an ultrasonic bath. Hydrogen etching was performed at a pressure of 13 mbar, with no other gas added. The samples were heated to 1800 °C at a hydrogen flow of 6 l/min, which was also applied during heating and cooling. The exposure to hydrogen at 1800 °C lasted for 20 min. Hydrogen etching resulted in typical morphological reorganizations [10, 11, 20]. The irregularly shaped holes transform into hexagonally shaped troughs (see Fig. 3 and the schematic drawing in Fig. 1c). Six facets with sides running along $\langle 11\bar{2}0\rangle$ directions are arranged around a flat (0001)-oriented basal plane. The morphological shape reorganization is independent of the initial hole size and shape and only varies in diameter. Steps and step bunches visible between different holes are due to the pinning of individual steps at the holes during the surface erosion process [20, 21]. Thus, the hydrogen etching transformed the irregular pores into well-defined pores. The irregular arrangement of the pores was, however, not changed during the etching process.

In a second set of experiments, membranes with periodic arrays of monosize Au nanotubes were used as masks. These membranes are typically several square centimeters in size. The SEM image reproduced in Fig. 4 shows a patterned SiC

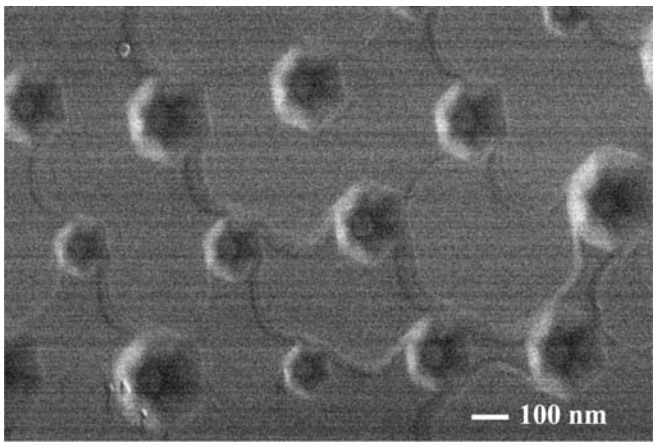

FIGURE 3 Scanning electron microscopy image of a non-periodic hole network in SiC after hydrogen etching. See text for comments

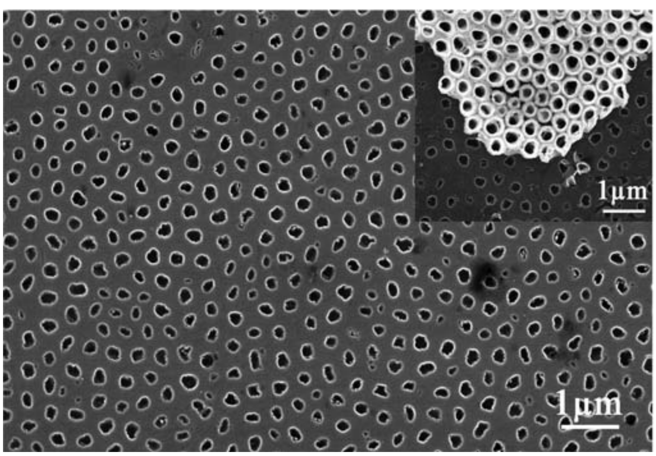

FIGURE 2 Scanning electron microscopy image of a non-periodic hole network in SiC after RIE and before hydrogen etching. The *inset* reproduces an image with a fraction of the mask. See text for more details

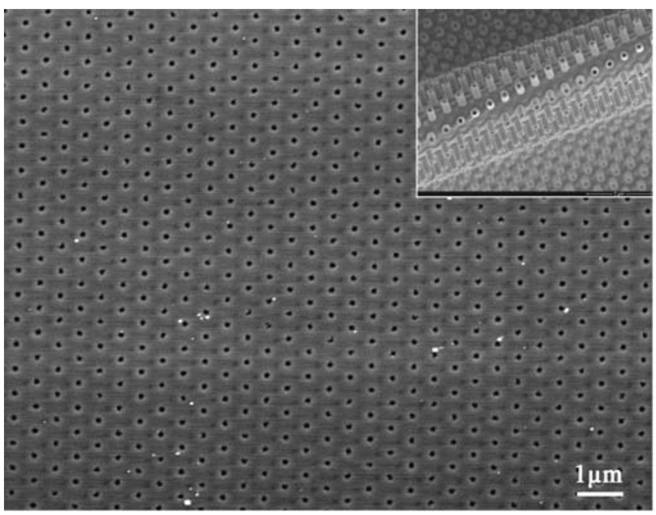

FIGURE 4 Scanning electron microscopy image of a periodic hole network in SiC after RIE and before hydrogen etching. The *inset* reproduces part of the ordered membrane used from the rear side. See text for more details

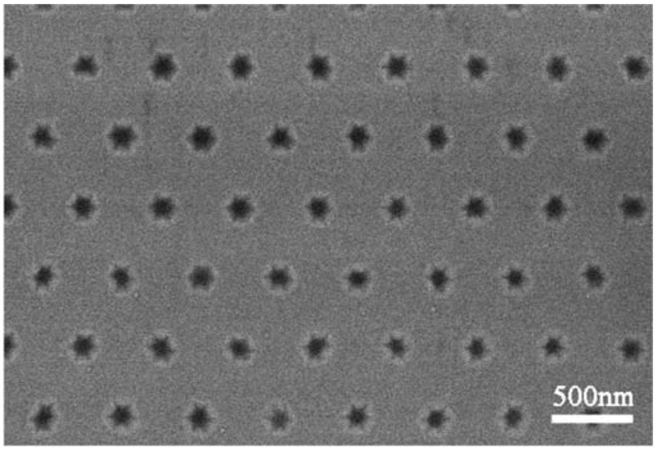

FIGURE 5 Scanning electron microscopy image of a periodic hole network in SiC after hydrogen etching. See text for comments

area representative of the whole nanopatterned surface. The pores are on a regular lattice, their size is well defined, while their shape is irregular, reflecting the properties of the membrane. The inset in Fig. 4 reproduces a fraction of the tube membrane used from the rear side in a bent form to obtain a better view of the topology. The morphological reorganization through hydrogen etching again leads to hexagonally shaped troughs as shown in Fig. 5. The monosize of the initial holes is reproduced and a small statistical spread of about 20 nm was observed for the pore diameter. With this process, ordered, mono-disperse pores of a well-defined hexagonal shape can be produced on large areas. Thus, the patterning and processing presented here is suitable for manufacturing large-area photonic crystals and sieves and templates for biological as well as electronic applications.

3 Conclusion

The realization of large-area vertical nanopatterning of SiC has been achieved by using Au-nanotube membranes as shadow masks for reactive ion etching. Well-organized hexagonal pores can be obtained in a subsequent hydrogen erosion. Depending on the depth of the initial pores after RIE, different nano-objects like facetted holes or nanotubes with flat and steep side walls can be fabricated. Their sizes and positioning in the SiC surface can be tuned via the membrane fabrication process. Large-area nanotube arrays will have potential applications in magnetism and electronic devices as well as in photonic crystals and biology.

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