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Highly regular nanometer-sized hexagonal pipes in 6H-SiC(0001)

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ABSTRACT An array of troughs was prepared on a 6H-SiC(0001) surface using focused ion beam (FIB) patterning. Troughs were etched with various ion doses and close-to-circular voids of increasing depths for larger ion doses were obtained. The samples were then etched in a hot-wall reactor at a hydrogen partial pressure of 13 mbar at 1800 °C. The resulting morphological reorganizations have been studied by scanning electron and atomic force microscopy. Very regular hexagonal voids with facets oriented perpendicular to the surface were obtained after hydrogen etching. The voids were surrounded by regular secondary facets of lower inclination. Whereas the depth of the voids increases with ion dose, the void diameter and facet sizes stay constant. This effect is explained by surface diffusion during hydrogen etching. The FIB technique in combination with hydrogen etching allows the preparation of very regular surface patterns and highly ordered wells and tubes for nanometer-sized sieves and photonic crystals.

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Silicon carbide (SiC) is known as an interesting semiconductor material due to its characteristic electrical and mechanical properties. Introducing material porosity to standard semiconductors has turned out to be a promising approach to obtain new physical properties for applications like photonic crystals [1]. The preparation of pipes has been reported for materials like silicon, alumina or gallium phosphide [2–5]. Their applications as membranes, sieves or photonic crystals, for example, has been discussed during the last years. The preparation of the pipes generally consists of complex, multiple-step methods. The spatial distribution of the pipes is often only poorly ordered and the tubes obtained frequently show an irregular morphology [6]. The side walls of the pipes are not always smooth and the alignment of the pipes vertical to the initial surface is difficult to obtain. An ordered spatial distribution of the pipes is of crucial importance for photonic applications. We report the fabrication and characterization of a highly regular network of nanometer-sized pipes on a 6H-SiC(0001) surface. The combination of this versatile semiconductor material with an array of regular perforations is expected to lead to interesting potential applications. We present a preparation technique to obtain a regular network of pipes with flat and steep side walls. The diameter, chosen to be several hundred nanometers in this experiment, can easily be tuned, as can be the pipe arrangements. The evolution of the structures during the different processes, i.e. focused ion beam (FIB) sputtering and H_2 erosion, has been followed by scanning electron microscopy (SEM) and atomic force microscopy (AFM).

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 [7]. An array of 10×10 circular holes each 200-nm wide was prepared by FIB in the area mode. The beam voltage was 30 keV and the beam current 200 pA. The pitch between the holes was 3 μm in the x and 2 μm in the y direction. The ion dose used for etching the first hole was $1.5 \times 10^3\ C/m^2$ and this value was systematically increased by a factor of 1.2 from one hole to the next in the x direction and by an additional factor of 1.5 for the holes in the y direction. Increased etching leads to depressions with increasing depth. The so-prepared samples were imaged with SEM before and after additional hydrogen erosion. Figure 1a reproduces a SEM overview of the array after etching. Clearly, the regularly spaced holes are visible. The depressions of the lowest sputter dose are in the upper left and the ones of the highest in the lower right corner. Figure 1b shows a selected area of the array (white box in Fig. 1a) before etching. Slightly irregular holes with diameters of 200 nm can be seen. After FIB preparation and SEM imaging, hydrogen etching was performed in a horizontal graphite hot-wall chemical vapor deposition (CVD) reactor [8] at a hydrogen partial pressure of 13 mbar, with no other gas added. The samples were heated

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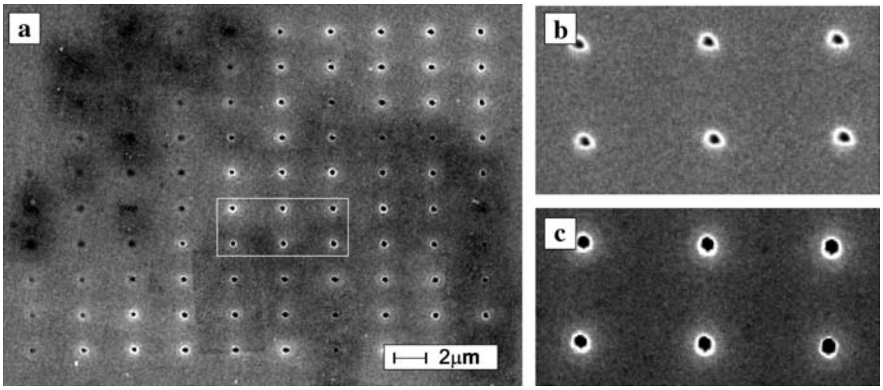

FIGURE 1 SEM images of the FIB patterned depressions after (**a**, **c**) and before hydrogen etching (**b**). **b**, **c** are zoomed in as indicated by the *white box* in (**a**)

for 5 min to 1800 °C at a hydrogen flux of 6 l/min. This flux was also applied during heating and cooling. We estimate a SiC etch rate of approximately 10 μm/h for these experiments. These conditions have been chosen based on our previous experiments on concave-shaped SiC surfaces [9, 10] and on the etching behavior of micropipes [11]. The etching results in the formation of flat surfaces on SiC(0001) [12, 13]. The array of holes was imaged again after etching and a magnified image of six holes is depicted in Fig. 1c. The regular positions of the holes remain, but their diameter slightly increased. Also, their shape has become more regular.

Figure 2a–c show three individual holes with increasing dose from the left to the right. They represent the three typical morphologies that were observed. For doses below $11 \times 10^3\,C/m^2$ the holes reorganize to simple depressions of hexagonal shape. The outer diameter of the hexagonal depressions varies only a little from 650 nm for a dose of $1.5 \times 10^3\,C/m^2$ to 750 nm for a dose of $10.5 \times 10^3\,C/m^2$. The diameter is much larger than the initial hole after FIB of 200 nm. This reorganization can be explained by etching at high temperatures, which drives the surface to its lowest-energy state, i.e. the flat surface. The hole is smoothed out and the surface area around the hole approaches the (0001) orientation. In the center of the depression, a flat (0001)-oriented area can be found for the very low doses. Besides removal of material due to etching, surface diffusion is the most important mechanism for the expansion of the whole diameter of the depressions. The almost constant diameter is most likely related to the limited surface-diffusion length during the etching. Furthermore, the shape of the depressions changes from nearly circular to hexagonal. This is in agreement with surface diffusion, as the thermodynamics of the step edges should reflect the hexagonal crystal structure of SiC. The sides of the hexagon run along $\langle 11\overline{2}0 \rangle$ directions. Steps along these directions are close packed and minimize the step energy, i.e. they reflect the Wulff construction. This indicates that step-edge diffusion is active on the length scale of the facets of the hexagon, in agreement with the previous consideration on the surface-diffusion length. For the critical dose of $11 \times 10^3\,C/m^2$, the depression consists of six facets without a flat area in the center. When the dose is increased further, the structure of the voids becomes more complex. In the center of the void, a secondary hexagonal hole is found, as depicted in Fig. 2b. The diameter of this central hole is ≈ 275 nm, while the outer diameter of the total structure stays unchanged. With increasing dose, the central hole gets deeper. The sides of the hole are perpendicular to the SiC(0001) surface, i.e. hexagonal pipes evolve. The diameter of the pipes is independent of the dose and varies only slightly with a statistical spread of 20 nm. Also, the outer diameter of the whole structure stays unchanged over the full range of the studied dose.

Figure 3a and b show SEM images with the sample tilted with respect to the electron beam to get a three-

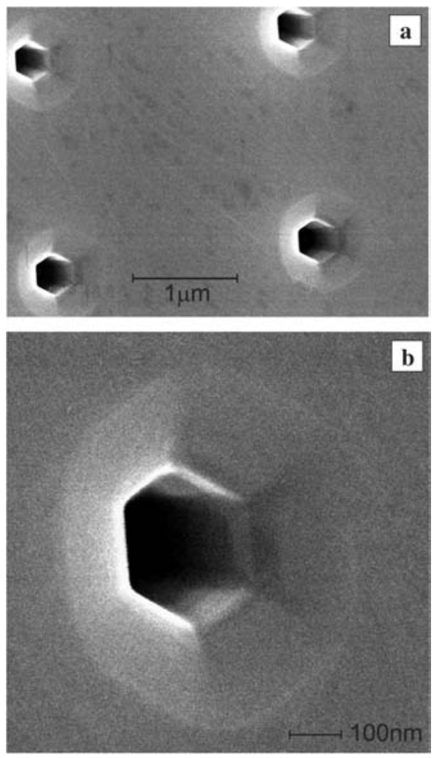

FIGURE 3 Inclined SEM view of **a** several nano-pipes and **b** a close up of one nano-pipe after hydrogen etching. The nano-pipes are highly regular and six well-oriented facets are clearly visible surrounding the central holes

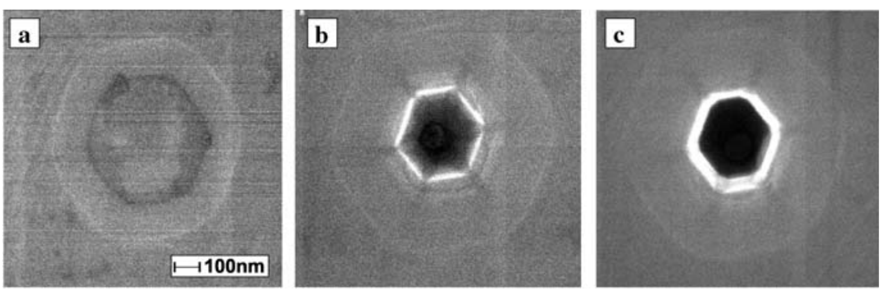

FIGURE 2 SEM images of the patterned depressions after hydrogen etching. The FIB dose varied between **a** 1.5, **b** 11.2 and **c** $150 \times 10^3\,C/m^2$. For the lowest dose, only a smooth depression is observed while, for the higher doses, the depression consists of an outer set of six facets and a hexagonal central hole with perpendicular side walls

dimensional impression of the holes. The sharp and perpendicular walls of the inner pipe are clearly visible. Around the central pipe, six facets can be seen. We studied these facets in more detail with AFM and found that above the critical dose of $11 \times 10^3\,\mathrm{C/m^2}$, the facets have a constant angle of 24° with respect to the (0001) surface. For smaller doses, the facet is less inclined. For higher doses, the central pipe evolves. This hints at the formation mechanism of the pipes. Initially, the increasing depth of the sputtered hole just leads to an increasing depth of the depression of the hole, while the outer diameter of the depression stays unchanged due to the limitation of surface diffusion. At a critical dose, the facets reach an angle which represents a stable or low-energy facet. We suggest that instead of a further increase of the facet's slope with increasing dose, it is more favorable to split the total depth of the depression into two stable facets, one of 24° inclination and the other, steeper one, of the low-energy $[11\bar{2}0]$ facets. In this way, the inner pipes are formed. With further increase of the FIB dose, only the depth of the pipes is increased. Unfortunately, we were unable to image the bottom of the pipes with our AFM, as the tips were not sharp enough to reach the bottom. From the AFM and the SEM images, however, a minimum depth of 300 nm of the pipes has been observed.

The formation of very regular pipes with perpendicular walls is related to the symmetry of the directional surface free energy of hexagonal or hcp crystals. Hexagonal columns are energetically favored due to the minimum surface free energy of their facets. Analogously, the growths of hcp materials often leads to the formation of long, hexagonal needles. The same mechanism may be used to produce regular and very deep pipes in SiC(0001), e.g. for photonic applications, micropipes and sieves or nozzles. We have demonstrated that these pipes can be formed with diameters of less than 300 nm. We, however, think that this is not the minimum diameter. Pipes with a smaller diameter, possibly 100 nm, may be obtained when the initial holes are fine enough and the etching temperature is slightly decreased.

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