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Self-organization in porous 6H-SiC

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Pores in porous 6H-SiC were found to propagate first nearly parallel with the basal plane and gradually change direction and align with the *c* axis. As a consequence, well-defined columnar pores were formed. It was shown that the rate of change of propagation directions was influenced by the etching parameters, such as hydrofluoric acid concentration and current density. Larger currents resulted in formation of larger pores. Pore sizes were found to increase with depth due to a decrease of the acid concentration. In addition, due to chemical etching effects, larger pore sizes were obtained close to the sample surface.

SiC is a promising candidate material for high-power, high-temperature, high-frequency, and optical device applications. These are mainly due to the high-saturation electron drift velocity, thermal conductivity, and breakdown field of the material.¹ A spin off from SiC materials research results from the high surface area material obtained by electrochemical dissolution of the crystalline bulk material in hydrofluoric acid (HF) solutions.²⁻⁵ The resulting structures may find applications in disciplines such as sensor technologies, considering the superior mechanical, thermal, and electronic properties, as well as long time stability of the materials compared with other porous structures such as porous silicon (PS).⁶ In addition, creating quantum wires through the etching process resulting in an increase of the band gap compared with the bulk material may provide future optoelectronics application possibilities. Strong photo- and electroluminescence above the band gap and in the blue and ultraviolet (UV) part of the spectrum has also been reported.^{7,8} Therefore, an accurate understanding of the influence of the etching conditions on the morphological properties of the material is required. In a recent report we emphasized the anisotropy in pore propagation in nitrogen-doped 4H-SiC.⁹ Pores were found to initially propagate nearly parallel to the sample surface and gradually change direction and follow planes such as ($\bar{1}104$), ($\bar{1}103$), and ($\bar{1}102$). A similar phenomenon is also observed in nitrogen-doped 6H-SiC, as will be shown below. In ad-

dition, variations in pore morphology with depth and its dependence on the anodization conditions (i.e., current density and HF-concentration) will be discussed.

Porous SiC (PSC) samples were prepared using *n*-type 6H-SiC wafers from CREE Research, Inc., Durham, NC with a nitrogen-doping level of approximately $4.3 \times 10^{18} \text{ cm}^{-3}$. The 3.5° off-cut is neglected in the following discussions. Photoassisted electrochemical etching was performed on the polished silicon face of the samples using a 24-W UV light source in a mixture of HF, water, and ethanol. The applied current densities were in the range of 25 to 100 mA/cm². Prior to etching, samples were suspended vertically in the etch solution for 3 min to remove the native oxide. The counter-electrode was a platinum wire positioned about 2 cm from the SiC sample. After anodization, samples were placed in ethanol for 10 min and finally blown dry in nitrogen. Scanning electron microscopy (SEM) studies were done using a 1550 FEG instrument from LEO GmbH, Germany. The image contrast was obtained using the secondary electron mode with an accelerating voltage of 5 kV. Cross-sectional SEM (XSEM) studies were realized by cleaving the samples along the ($1\bar{1}20$) plane. The morphology at the PSC/SiC interface of a few samples was studied by electrochemically destabilizing (see below) the porous layers, sticking the PSC layers from the sample surfaces onto a conducting carbon tape, and finally lifting off the SiC substrates mechanically.

Characteristic sample surface morphology was circular-shaped holes with diameters on the order of 20 nm or less, surrounded by rosettelike structures, as can be seen in the SEM surface image of a sample of type A (low HF

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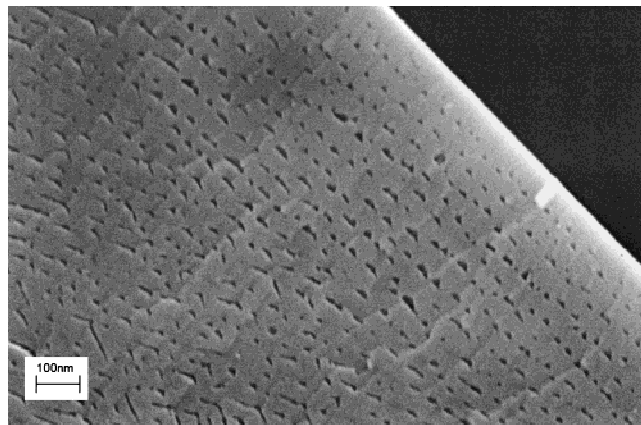
concentration) in Fig. 1. The concentration of the pore openings did not seem to be affected by the etching conditions. However, increasing the HF concentration as well as current density resulted in an increase in size of the pore openings (see also below). Furthermore, the surfaces appeared to be divided into closely situated domains. These structures could not be observed using lower accelerating voltages, indicating that they are fingerprints from underlying channels which propagate nearly parallel with the sample surface. The image indicates that no unique propagation directions can be identified close to the interface. In general, increasing the HF concentration resulted in separation of the domains, which is an indication of a faster change in the pore propagation directions with etching time and sample thickness. A similar phenomenon could also be observed by increasing the current density.

The pore morphology of two samples (type A and type B) at the PSC/ambient interface is shown in Figs. 2(a) and 2(b). Close to the interface the pore cross sections are isolated with shapes both nearly circular but also triangular. It provides evidence for existence of pore propagation in directions other than the c axis. Note also the lack of pores in a relatively thin region at the PSC/ambient interface. Further down, they appear V shaped in a manner similar to 4H-PSC.⁹ At higher HF concentration [Fig. 2(b)], the V-shaped pores appear closer to the PSC/ambient interface and are larger in size. The larger size of the pores is most probably related to the chemical-etching effects in a manner similar to PS.^{10,11} This could also be discerned by the decrease in pore sizes with depth, followed by an increase of pore sizes toward the PSC/SiC interface in thicker samples. This phenomenon is most probably related to a decrease in the HF concentration with depth. This phenomenon was also employed as a preparation step for the SEM investigation of the PSC/SiC interfaces (see above). It has to be noted that the phenomenon shown in Figs. 2(a) and 2(b) could also be

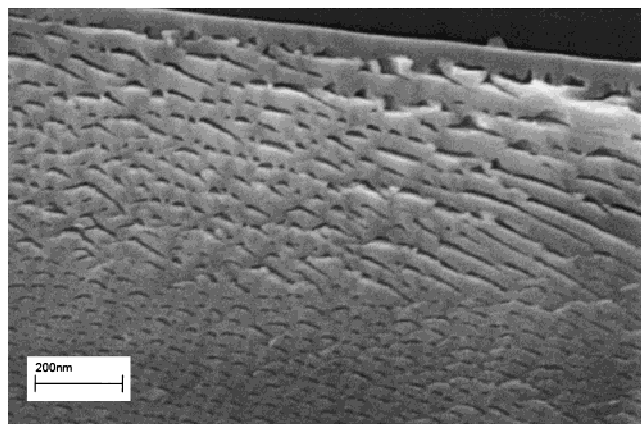


FIG. 1. Surface morphology of a type-A sample with a current density of 25 mA/cm^2 and an etching time of 5 min.

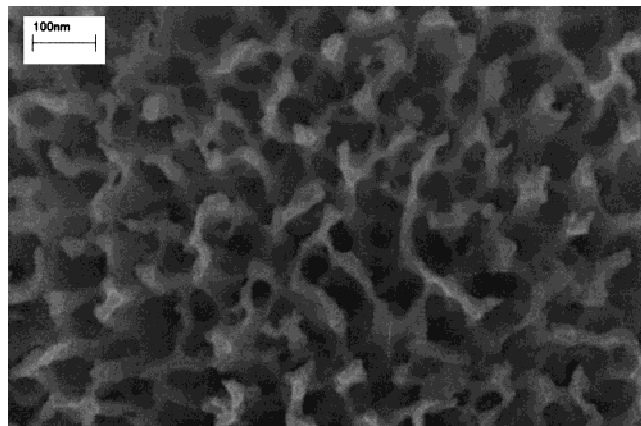
observed when larger current densities were used. It is thus likely that the porosity and pore sizes are affected by the HF concentration and current density in a manner similar to PS.⁶ Figure 2(c) illustrates the pore morphol-



(a)



(b)

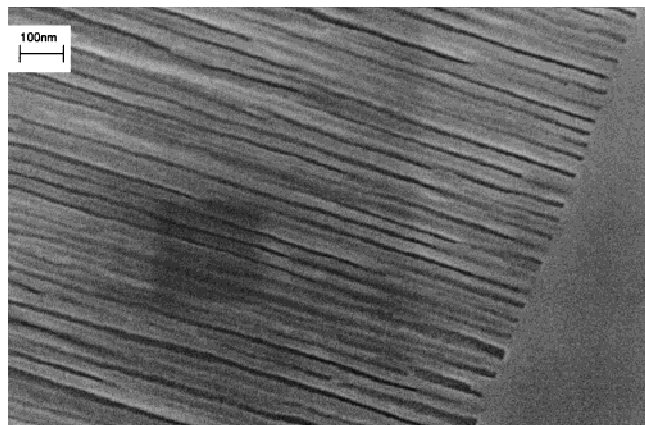


(c)

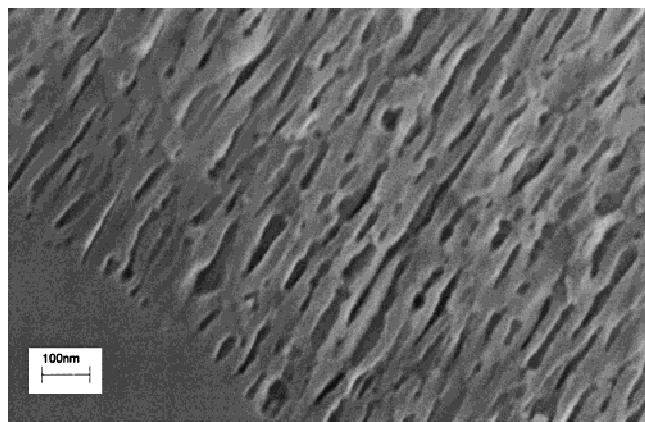
FIG. 2. (a) XSEM image of the sample shown in Fig. 1 at the PSC/ambient interface. (b) XSEM image of a type-B sample with a current density of 25 mA/cm^2 and an etching time of 5 min at the PSC/ambient interface. (c) Plane view image of the PSC/SiC interface of a type-A sample with an etching time of 5 min and a current density of 75 mA/cm^2 .

ogy of a type-A sample at the PSC/SiC interface. Although the surface morphology resembled the structure shown in Fig. 1(a), a considerably different microstructure is found further down in the material. The increase of the pore sizes with depth can be clearly discerned from the image.

Under certain conditions, and relatively far from the PSC/ambient interface, channels are found to propagate nearly parallel with the direction of the c axis [Fig. 3(a)]. Note that the samples shown in Figs. 2(c) and 3(a), although fabricated using different current densities, belong to the same group (type A). A similar phenomenon is encountered within samples fabricated using etching solutions containing relatively large HF concentration [Fig. 3(b)]. Lack of side pores is an indication that etching is completely limited to the etch pits.¹² The columnar structures encountered here resemble the well-defined pores formed in alumina.¹³ Even in that case a transitional irregular porous layer is formed at the porous alumina/ambient interface. Furthermore, Leh-



(a)



(b)

FIG. 3. (a) XSEM image of 38- μm -thick sample (type A) with an etching time of 5 min and a current density of 50 mA/cm^2 near the PSC/SiC interface. (b) XSEM image of a 24- μm -thick sample (type C) with an etching time of 5 min and a current density of 25 mA/cm^2 near the PSC/SiC interface.

mann and Föll¹² reported formation of similar trenches in silicon. Thus, pores in 6H-SiC tend to propagate first nearly parallel with the basal plane and gradually change direction and align with the c axis. Depending on the etching conditions, the columnar structures can be formed closer to the PSC/ambient interface. It may therefore be possible to initiate the columnar structure from the PSC/ambient interface using proper etching conditions.

The gradual change of pore propagation from near normal to directions parallel to the c axis may be explained in terms of the Si-C stacking sequence in the bulk SiC. The anisotropy can be understood if the Si-Si bonds are broken much easier than the Si-C bonds. Hence, the C layers act as protective layers. Thus, the electrochemical etching is anisotropic and proceeds at a much higher rate perpendicular to the c axis than along the c axis in a bulk phase. Initially, pores are formed only along the surface and then only at sites with defects¹⁴ allowing the etch solution to penetrate into the surface. The channel directions change with depth and etching time following more closely the direction of the applied current.¹⁵

In conclusion, it is shown that the propagation direction of pores in 6H-PSC depends on a number of etching parameters such as thickness, etching time, current density, and HF concentration. Larger current densities resulted in formation of larger pores. Increasing the HF concentration caused an increase of pore sizes close to the PSC/ambient interface. This phenomenon was related to chemical etching of regions and a longer exposure time to HF. Due to a decrease in HF concentration with depth, the pore sizes were found to increase toward the PSC/SiC interface.

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