Porous Structure of Anodized p-type 6H SiC

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Abstract. Porous silicon carbide is obtained from p-type 6H SiC wafers by electrochemical etching in hydrofluoric aqueous electrolyte. The porous structures are studied depending on wafer polarity and the applied current density. The porosity is estimated from the SEM images as well as from charge transfer calculations.

Introduction

The first report on porous p-type 6H silicon carbide was published about ten years ago by Shor *et. al.* [1]. The interpore spacing as determined by TEM images was in the range from 1 to 10 nanometers. The diffraction patterns indicated that the porous films were single crystal 6H SiC. Since then, not much effort has been put into developing porous structures formed from p-type SiC. Here we present our results on the investigation of the pore morphology obtained by electrochemical etching of p-type 6H SiC. The dependence of the pore size and interpore spacing on the anodization conditions is discussed. We estimate the porosity by using charge transfer calculation as well as by digital analysis of the cross-sectional SEM images.

Experimental

The samples are Cree 6H vicinal basal plane p-type SiC crystals doped at about $2{\cdot}10^{18}$ cm^{-3}. The wafers are oriented with a 3.5-degree off-cut angle toward a $<1\bar{2}10>$ direction. The experiments were performed on both the vicinal (0001) Si-face and the vicinal $(000\bar{1})$ C-face. In order to obtain a smooth carbon face the samples were polished with diamond paste down to one micron. Aluminum was deposited on the back of the samples to provide an ohmic contact. The electrochemical etching is done in aqueous HF solution mixed with ethanol. A standard three-electrode cell configuration is used with SiC serving as the working electrode. Electrical current density through the cell was maintained by a PAR 263A galvanostat and was set between 0.5 and 60 mA/cm^2. A platinum plate is used as the counter electrode, and a saturated calomel electrode as the reference. The etching is conducted anodically corresponding to the forward bias regime of a p-type semiconductor/ electrolyte junction. The forward biases applied to the working electrode ranged from 2.0 to 2.5 Volts. After the etching, samples are carefully removed from the bath and cleaned in acetone to prepare them for plan-view and cross-sectional SEM imaging, which are performed using a Philips XL 30 FEG scanning electron microscope.

Results and Discussion

The electrochemical dissolution of a semiconductor must be conducted in the anodic regime which necessitates holes to be collected at the interface with the electrolyte. Similar to p-type silicon, the anodization of p-type SiC may be performed in the dark because the material itself is a source of holes. Positive (forward) bias is needed to bend the bands upwards near the SiC/electrolyte junction in order to provide the flux of holes for the electrochemical reaction. Figure 1 shows a rectifying current-voltage characteristic of a p-type 6H SiC C-face crystal in a 5% HF (measured by weight)

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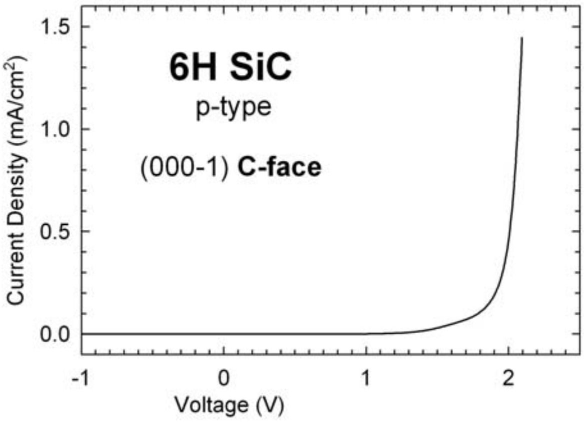

Figure 1. The current density vs. applied bias dependence of a C-face p-type 6H SiC sample in 5% HF solution. The data obtained for the (0001) Si-face looks similar.

aqueous solution mixed with 5% ethanol. From the curve one can see that the currents reach the milliampere range indicating intense electrochemical reaction at voltages above 2.0 Volts. The current-voltage curves for (0001) Si-face samples anodized in the same electrolyte are very similar to the C-face crystals. Regardless of the initial SiC substrate orientation, none of the I-V characteristics we have observed so far on our p-type SiC/electrolyte junctions have shown a typical p-type Si/electrolyte behavior in which one can clearly distinguish different regimes attributed to porous silicon formation and electropolishing, i.e., complete dissolution [2]. Unlike in p-type silicon, one of the major criteria for the formation of a porous structure in p-type SiC is the correct choice of the substrate polarity. When the Si-face of a sample is exposed to the anodizing conditions, electropolishing of the crystal is achieved for the HF concentration in the range from 1 to 20%. On the contrary, porous structures are formed on the C-face provided the HF concentration exceeds 1%. The origins of the completely different behavior of the two polar surfaces likely are the differences in the respective oxidation properties for the carbon-rich and silicon-rich surfaces.

Figure 2 shows an SEM image of the surface of a p-type SiC C-face sample which was electrochemically etched at 0.5 mA/cm^2 current density. Before the electrochemical processing, the sample on Figure 2 was polished with diamond paste down to one micron. It can be seen that, at the surface, the bulk porous network is overlaid by structures, left undissolved, of roughly 100 to 150 nm in diameter. In fact, other samples exhibited surface features up to 500 nm in width (not shown). Since the average width of a scratch on a polished surface is thought to be approximately one fourth of the size of a particle of the polishing agent, we believe the surface of the etched p-type SiC C-face samples is comprised of etch-resistant structures which formed upon the scratches left after the mechanical polishing. This is supported by Figure 3, which shows the surface of a porous sample whose front surface was polished prior to etching with diamond paste down to 250 nm. One can see that the dominating surface fiber width is 50 to 100 nm, roughly corresponding to a quarter of 250 nm size diamond particles.

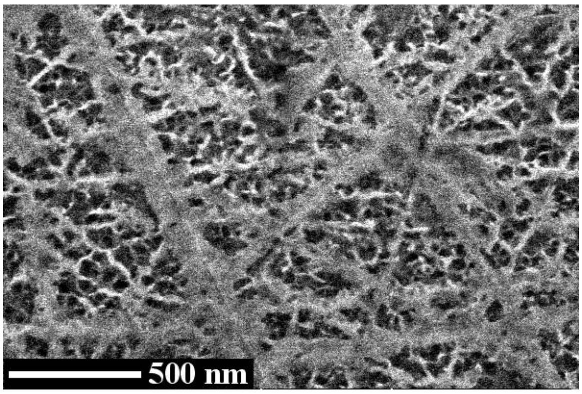

Figure 2. A plan-view SEM image of a porous C-face p-type 6H SiC sample polished down to one micron prior to the etching. The porous surface morphology is dominated by structures 100 to 150 nm in size.

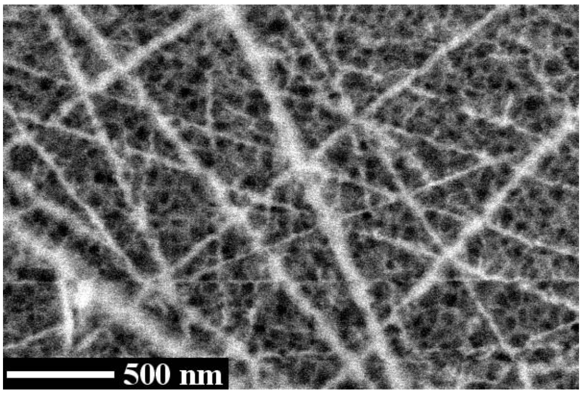

Figure 3. A plan-view SEM image of a porous C-face p-type 6H SiC sample polished down to a quarter micron prior to the etching. The porous surface morphology is dominated by structures 50 to 100 nm in size.

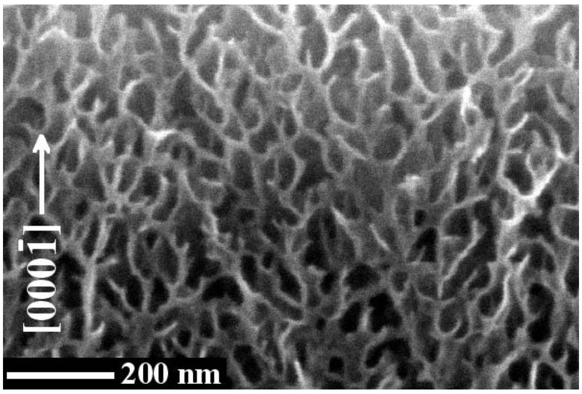

Figure 4. Cross-section of a porous p-type C-face 6H SiC sample electrochemically etched at 0.5 mA/cm^2. The pore wall thickness is 15 to 40 nm.

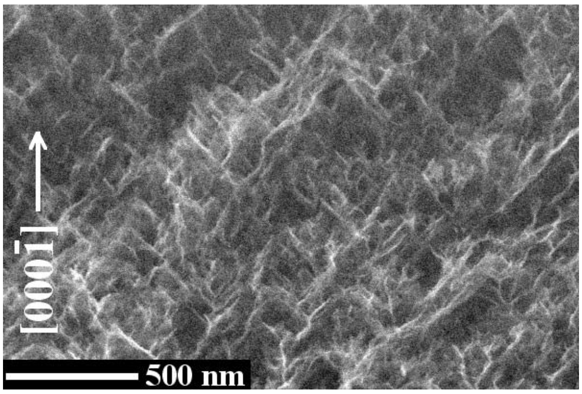

Figure 5. Cross-section of a porous p-type C-face 6H SiC sample electrochemically etched at 30 mA/cm^2. The pore wall thickness is 1 to 15 nm.

On Figure 4 one can see a cross-sectional SEM image of the bulk porous morphology obtained in the C-face sample whose front surface was shown on Figure 2. The etch rate at the current density of 0.5 mA/cm^2 is fairly low, less than one micron per hour. We estimate the thickness of the pore walls to be in the range from 15 to 40 nanometers. The "algae" type of morphology seen on the picture is characteristic for our highly doped p-type C-face 6H SiC samples anodized at current densities up to 15 mA/cm^2. The morphology does not change with increasing anodic current density but the thickness of the pore walls diminishes reaching 5 to 15 nanometers for samples etched at 15 mA/cm^2. The average size of the pores themselves does not seem to change. The forward bias required to achieve reasonable dissolution rates varies between 2.0 and 2.5 Volts depending on the desired current density.

When the current density is increased even further, the "algae" morphology changes into something which resembles a "cobweb" as seen on Figure 5. The sample shown in Figure 5 was etched at a current density of 30 mA/cm^2. The resolution of the SEM instrument does not allow us to accurately measure the size of the structures in the "cobweb" morphology. However, we estimate the pore wall thicknesses to reach the 1 nm range. This result correlates well with the interpore spacing obtained in [1] by TEM analysis. In that work, an anodic current density of 50 mA/cm^2 was used.

Despite the unequivocal dependence of the size of the interpore spacing on the dissolution current, there are general similarities for all p-type SiC porous C-face samples. First, unlike porous p-type Si, we have not observed any indication of preferential etching along specific crystallographic directions. Second, the porosity P, defined as the ratio of the volume of the void space V_p to the total volume V, is uniform throughout the porous film. This is not typical for n-type SiC samples where a porosity gradient is observed.

The porosity of the porous structures may be found by estimating the volume of the void space. This can be done by calculating the integrated charge Q_{int} transferred during the course of the reaction. For example, for the sample on Figure 4 etched for five hours one obtains about 3.15 Coulombs which correspond to roughly $1.96 \cdot 10^{19}$ holes. Knowing Q_{int}, the number of holes required to dissolve a single Si-C pair, and the lattice constants of 6H SiC (a = 3.08 Å, c = 15.12 Å) [3], it is possible to estimate the total volume of the semiconductor dissolved. Shor and Kurtz [4] reported that carbon dioxide, CO_2, and carbon monoxide, CO, bubbles had been observed during the electrochemical etching of SiC in HF. Assuming no SiO and SiO_2 present in the HF solution and taking into account that anodic etching of silicon in aqueous HF produces stable $(SiF_6)^{-2}$ ions [5], we believe the following reactions can take place:

$$\begin{aligned} &SiC + H_2O + 6F^- + 6\, h^+ = (SiF_6)^{-2} + CO + 2\, H^+, \\ &SiC + 2\, H_2O + 6F^- + 8\, h^+ = (SiF_6)^{-2} + CO_2 + 4\, H^+. \end{aligned} \qquad (1)$$

Accordingly, the numbers of holes required to dissolve one Si-C pair for the reactions (1) are 6 and 8, respectively. A value 6.9 has been obtained for the dissolution of 6H SiC [4]. Using 7 as the average number, which implies that the two reactions occur at equal rates, the total number of Si-C pairs can be found determining the dissolved volume of the SiC crystal V_p. The area of the sample exposed to etching was 0.32 cm^2 and the film thickness determined from SEM measurement is 3.6 microns. This gives the total volume of the porous film. Hence, the porosity expected from the charge transfer calculation for the sample shown on Figure 4 is found to be 0.51.

The value of porosity can also be estimated by analyzing the digital gray-scale SEM images. The pixels are subjected to a threshold in order to obtain values either 0 (black) or 255 (white). The white pixel corresponds to the solid part of the porous structure while the black one to a void. The two-dimensional porosity π is then just the ratio of the number of black pixels to the total number of pixels on the image. It is a rather complicated task to solve for the correct value of the volume porosity from its two-dimensional projection. We can, however, set a range of reasonable values for P, $P_{low} < P < P_{high}$. The lower limit is $P_{low} = \pi^{3/2}$, corresponding to the case when pores are approximated by non-interconnecting voids. The upper limit may be set for the case when the pores are fully interconnected, $P_{high} = \pi$. For the image on Figure 4 one obtains $\pi = 0.57$ which gives the volume porosity range $0.43 < P < 0.57$. The value of porosity obtained from the charge transfer calculation falls nicely in the middle of this range.

Finally, we have developed a technique for separating the p-type SiC porous layer from the original substrate. In this way, free-standing porous membranes of 20 to 110 μm thickness can be realized. Since SiC has been recognized as a biocompatible material, the p-type SiC membranes are being tested for medical applications. Brillouin scattering experiments and a study of the SiC/SiO_2 interface are also being carried out using our free-standing porous SiC membranes.

Conclusion

We have electrochemically etched p-type 6H silicon carbide in aqueous hydrofluoric acid solution. The etching is done in the anodic regime and results in porous layer formation when performed on the $(000\overline{1})$ basal plane, or C-face, and a complete dissolution of the crystal structure for the (0001) basal plane, or Si-face. It is found that in p-type SiC the surface morphology of the porous structure depends on the quality of the polishing prior to anodization while the bulk porous structure is independent of the surface treatment. The average pore size does not change with the applied current density up to at least 15 mA/cm^2 with the pore wall thickness decreasing along with increasing current density. For one of the samples, the bulk porosity is estimated using both charge transfer calculation and digital processing of the cross-sectional SEM images, and consistent values are obtained.

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