Direct observation of porous SiC formed by anodization in HF

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A process for forming porous SiC from single-crystal SiC wafers has been demonstrated. Porous SiC can be fabricated by anodizing n-type 6H-SiC in HF under UV illumination. Transmission electron microscopy reveals pores of sizes 10-30 nm with interpore spacings ranging from \( \approx 5 \) to 150 nm. This is the first reported direct observation of porous SiC formation.

Silicon carbide is a useful material for high-temperature and high-frequency electronics due to its wide band gap, high breakdown electric field, and high melting point. Recently, several breakthroughs in crystal growth have led to high-temperature SiC devices, such as p-n junction diodes and field-effect transistors. In addition, SiC exhibits interesting optical properties which have been used in blue light emitting diodes and ultraviolet photodetectors.

In other semiconductor materials, specifically Si, a porous structure can cause changes in the optical, electronic, and oxidation properties of the material. For example, visible luminescence has been observed in porous Si and has been attributed to either quantum structures in the material or enhanced surface chemistry. This luminescence is of interest because of its potential to be the basis for Si optoelectronics. In addition, the large surface area of porous Si has been useful in the fabrication of dielectrically isolated electronic devices due to its enhanced oxidation properties.

There have been limited reports on the electrochemistry of SiC. In a series of papers, it has been demonstrated that patterns could be rapidly etched into \( \beta \)-SiC using UV-assisted electrochemistry. Carrabba used photoelectrochemistry to etch diffraction gratings into epitaxial \( \beta \)-SiC and polycrystalline 6H-SiC. Gierria characterized the electrochemical parameters, such as the flat-band voltage and \( I-V \) characteristics for SiC Lely crystals. Lauermann investigated the potential of SiC as a photoelectrochemical electrode. However, porous SiC formation was not explicitly demonstrated in any of the previous reports, to the authors’ best knowledge.

In this letter, it is demonstrated that porous n-type 6H-SiC can be fabricated by photoelectrochemistry. This material may exhibit optical and electronic properties which are different from bulk 6H-SiC and therefore may prove to be a potentially useful material for device applications.

The experiments were carried out on single-crystal n-type 6H-SiC \( (N_D=3\times10^{14}, \text{Si face}) \) supplied by Cree Research, Durham, NC. The SiC wafers were cut into small pieces (6 mm \( \times \) 6 mm), and ohmic contacts were deposited on the edge of these samples. External lead wires were attached to the contacts. Semiconductor electrodes were formed by encapsulating the samples in black wax, such that only the semiconductor surface was exposed. The area of the exposed SiC was measured with an accuracy of \( \approx 10\% \). The SiC electrode was placed into a Teflon electrochemical cell, along with a Pt wire counter electrode and a saturated calomel reference electrode. Dilute HF (2.5\% in \( \text{H}_2\text{O} \)) was used as the electrolyte and was pumped rapidly across the sample surface to prevent heating due to the UV beam. The pumping speed had no effect on the magnitude of the anodic currents. The range of potentials applied was 0–4 V\text{sc} (see refers to the saturated calomel reference electrode; all potentials were applied to the SiC working electrode with respect to the reference electrode). The light source used was a 200-W Hg arc lamp with the wave lengths outside the band 250–400 nm filtered out. Large UV power densities could be achieved by focusing the beam. At 300 mW/cm\(^2\), the variation in the beam intensity across a 1-cm\(^2\) area was roughly 20\%.

Large anodic photocurrents \( (10-30\text{ mA/cm}^2) \) were observed in n-type 6H-SiC at potentials above 0 V\text{sc} for UV intensities of 150–700 mW/cm\(^2\). The \( I-V \) curves and electrochemistry of the process will be reported elsewhere. Under all conditions studied, the surface of the anodized SiC appeared very rough, and shallow depressions \( (<150 \text{ nm}) \) were formed. Considering the large amount of charge that passed between the SiC and the HF, these depressions were very small if etching was the only process occurring. In a separate study, Lauermann did not observe \( \text{O}_2 \) formation during the anodization of 6H-SiC, which rules out that the large currents were due to the oxidation of water. Thus, it was reasonable to assume that the currents may have been due to porous layers forming on the surface.

To test this hypothesis, anodized SiC samples were thermally oxidized in a steam ambient for 4 h at 1150 °C. Under these conditions, bulk 6H-SiC will oxidize to a SiO\(_2\) thickness of less than 60 nm. However, after a short HF dip to remove the oxide, deep cavities (several micrometers) were observed on the anodized layers. This indicates that the layer produced by anodization oxidized at a rate.
much faster than bulk SiC. A sufficiently porous material would behave in this manner due to its large surface area.

In order to prove that pore formation was occurring, anodized SiC samples were prepared for TEM analysis. The samples were anodized for 31 min at a potential of 1.4 $V_{\text{sc}}$ under a UV intensity of 300 mW/cm$^2$. The total charge (expressed as a charge density) that passed the semiconductor/electrolyte junction was 19.6 C/cm$^2$. Planar-view transmission electron microscopy (TEM) samples were prepared by polishing and ion milling the anodized specimen from the substrate side.

Figure 1 is a bright-field TEM micrograph of the anodized layer. The existence of pores (the bright areas of Fig. 1) is confirmed by the absence of microdiffraction from similar bright areas observed under higher magnification. There was also no noticeable change in the pore morphology or density when the sample was tilted, and no illumination could be obtained from these bright features using dark-field image techniques. All these effects indicate that the bright areas are devoid of any matter, and are indeed pores.

Figure 2 is a higher magnification image of the porous SiC layer. In this micrograph, it appears that there exist central pores, which branch out into smaller pores. These branches resemble the dendritic structures observed in metals and are similar to pore morphologies that have been observed in porous Si. The pore sizes vary between 10 and 30 nm. The spacing between central pores appears to be less than 150 nm, and adjacent branches, as shown in Fig. 2, appear to be separated by just several nanometers.

The pore morphology varied somewhat across the surface of the sample, from the semi-equiaxed shape to the branched structure as seen in Figs. 1 and 2. This may be due to variations in the pore morphology as a function of thickness of the porous layer or may be attributed to non-uniformities in the photoelectrochemical process, such as the UV intensity or the localized electrode potential.

Figure 3(a) presents a selected area diffraction (SAD) pattern of a porous area from the sample of Fig. 1. The analysis of this SAD Fig. 3(b) indicates that the anodized layer is single-crystal 6H-SiC.

The exact chemical nature of SiC anodization has not yet been determined, to the author's best knowledge; therefore, it is difficult to speculate about the cause of pore formation. Nevertheless, it seems that the large amount of defects found in sublimation-grown 6H-SiC (Ref. 3) could act as chemical centers where pores initiate. Alternatively, pores may begin to form due to variations in surface chemistry. Once pores are formed, they may propagate through chemical nonuniformities between the pore tips and pore walls, as has been suggested for porous Si.*

The UV wavelengths used in these experiments may not have been deep enough to be absorbed efficiently in the bulk, and a large degree of absorption may have occurred along defect sites, causing pores to initiate. However, this would not explain the formation of similar layers in the dark anodization of p-SiC, which have been observed by the authors.

It is possible that microcrystallites exist within the porous SiC which are small enough to satisfy the conditions for quantum confinement (i.e., with dimensions of 2–5 nm). For example, Fig. 2 shows very small spacings between adjacent pore branches which may approach this condition. In porous Si, quantum confinement has been suggested as a possible mechanism to allow band-gap widening and direct-gap transitions, the combination of which
FIG. 3. (a) Selected area diffraction pattern of the sample of Fig. 1 and (b) analysis of the SAD pattern showing that the material is single-crystal 6H-SiC.

might explain the efficient visible luminescence in the material. In SiC ($E_g = 3$ eV), such quantum structures might facilitate luminescence in the UV. Preliminary low-temperature cathodoluminescence measurements indicate a luminescence tail between 300 and 410 nm. However, this UV luminescence was too weak to draw any firm conclusions from at this time.

Micropore formation has been observed in SiC for the first time. Porous films are fabricated on $n$-type 6H-SiC by anodizing the material in HF under UV illumination. TEM analysis indicates that the pore sizes vary from 10 to 30 nm with pore spacings between 5 and 150 nm. Selected area diffraction patterns show that the layers are single-crystal SiC. In order to fully characterize and understand pore formation and propagation in SiC, it is necessary to study the pore morphology and size as a function of the process conditions. However, the data presented in this letter show clearly that porous SiC formation is possible and merits further study.

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