

Preferential carbon etching by hydrogen inside hexagonal voids of 6H-SiC(0001)

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6H-SiC(0001) samples have been etched in a hot-wall chemical vapor deposition reactor at a hydrogen pressure of 13 mbar at 1800 °C. The surface morphology and elemental composition have been studied by scanning electron microscopy and micro-Auger analysis. Stoichiometric etching of SiC with equal atomic concentrations of Si and C is found on the flat sections of the surface, but in hexagonal voids of the SiC samples, a selective removal of C, leading to a pure Si surface at the bottom of the voids, is observed. Fast gas diffusion is the main transport mechanism for etching of the flat surface, while Knudsen diffusion becomes important inside the voids. It is proposed that the lower diffusion constant of reaction products containing Si compared to those containing C, leads to a preferential removal of C and a Si enrichment inside the voids. © 2002 American Institute of Physics. [DOI: 10.1063/1.1519962]

The application of SiC for devices relies heavily on the removal of the abundant defects, which are generally found on SiC surfaces. The hydrogen etching of SiC is an indispensable tool to remove the inherent defects and polishing scratches from SiC samples. It is well established that atomically flat SiC surfaces with terraces, which are separated by single unit cell high steps (15 Å) can be obtained after hydrogen etching.^{1,2} The scanning tunneling microscopy, atomic force microscopy, and low energy electron diffraction experiments of these studies indicate an atomic structure near the surface region, which corresponds to a truncation of the hexagonal SiC substrate. Consequently, both elements Si and C are expected to be present near the surface region in equal concentrations.

In this study we report on a different etching behavior in the interior of hexagonal voids, which are common defects on SiC substrates,³ compared to flat parts of the SiC samples. We performed a chemical analysis of the SiC surface with high spatial resolution before and after hydrogen etching, and we identify a preferred removal of C from the interior of hexagonal voids, where only Si is detected.

It is proposed that different diffusion mechanisms of the gas phase reaction products in the void as compared to flat surface regions are responsible for this behavior. This argument relies on the fact that the lateral dimensions of the voids (approximately 10 μm) are considerably smaller than the mean free path of the gas species under our low pressure etching conditions.

The samples were cut from an on-axis, nitrogen-doped, *n*-type (resistivity 0.03–0.12 Ω m⁻¹) 6H-SiC(0001) wafer.⁴ Prior to hydrogen etching the samples were cleaned in methanol in an ultrasonic bath. Hydrogen etching of the cut samples was performed in a horizontal graphite hot-wall chemical vapor deposition reactor⁵ at a hydrogen 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 up and cooling down. The exposure to hydrogen at 1800 °C lasted for 20 min. One sample was subsequently etched at a reduced temperature of 1775 °C for an additional 40 min. We estimate a SiC etch rate of approximately 10 μm/h for these experiments. We have chosen these conditions based on our previous experiments on concave-shaped SiC surfaces, where we concluded that a lower temperature of 1700 °C was not sufficient to establish an equilibrium surface morphology in the concave areas.⁶ After hydrogen etching, the samples were analyzed by scanning electron microscopy (SEM) in topological and elemental contrast mode. Energy dispersive spectroscopy of x-ray intensities (EDS) has been performed to characterize the elemental composition within the imaged areas. In a second UHV chamber, SEM and micro-Auger spectroscopy have been performed to get an independent chemical analysis of the surface composition within the voids and on the flat surface areas. The micro-Auger data presented in Fig. 2(c) are taken from an area of approximately 500 nm in diameter.

Before we discuss our results on the different etching behavior inside and outside of voids in SiC, we give in Fig. 1 a brief flavor of what hydrogen etching does to the surface morphology of a void. Figure 1 shows SEM images of a SiC sample with voids, imaged as black depressions, before [(a) and (c)] and after [(b) and (d)] hydrogen etching. Before etching, two voids, one with an elliptical and one with a needle-like perimeter can be identified. The zoom-in of Fig. 1(c) shows that the elliptical void has a diameter of roughly

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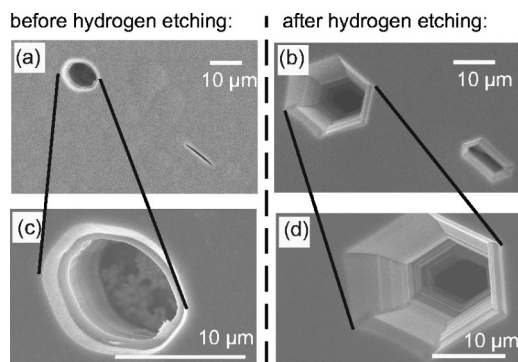


FIG. 1. SEM images of a 6H-SiC(0001) sample with voids—imaged as darker depressions which are bound by brighter sidewalls—before hydrogen etching on the left in (a) and (c), and after hydrogen etching on the right hand side in (b) and (d). Images (c) and (d) show the large void of the upper images in higher magnification. The brighter structures near the bottom in (c) are ascribed to a corrugated uneven bottom surface. Etching induces a faceted structure of the perimeter and of the inner sidewalls of the voids. The diameter of the void increases more near the surface as compared to the bottom of the void. This sample has been etched in 13 mbar hydrogen for 20 min at 1800 °C, and then for 40 min at 1775 °C.

10 μm . The bottom is filled, and the sidewalls are almost perpendicular to the surface.

After etching, the same surface area has been found by SEM due to the characteristic voids. Figures 1(b) and 1(d) reveal that hydrogen etching changes the perimeters of the voids to a more hexagonal pattern. We ascribe this to the hexagonal structure of the SiC sample. The perimeter and the sidewalls of the voids are now oriented along well defined directions. This transition from an almost isotropic rounded shape for the not etched samples to this hexagonal pattern reflects the hexagonal symmetry of the SiC sample. At these experimental conditions, the anisotropy of the surface free energy of SiC seems to play an important role for the resulting morphology.

The diameter of the void has increased considerably, as can be seen by comparing Figs. 1(c) with 1(d). After etching, the diameter has increased from roughly 10 to 22 μm . The sidewalls are no longer vertical, but they are inclined, leading to a smaller inside diameter with increasing depth within the void. This is a first indication of a nonuniform etch rate. Etching seems to be faster near the surface, whereas it is slower near the bottom of the void. We come back to the issue of nonuniform etching later.

Figure 2 shows a SEM image of a hexagonal void after hydrogen etching in two different contrast modes. Figure 2(a) is an “ordinary” SEM image and the contrast is determined by the secondary electron intensity. It reflects the topology of the void. The sidewalls, which are inclined with respect to the surface normal, appear brighter in contrast, parallel, and flat surface areas outside and inside the void show the same brightness. The maximal diameter of the void near the surface is of the order of 14 μm . We conclude from images of the tilted sample—not shown—that the bottom of the void is approximately 5 μm below the surface. Figure 2(b) is obtained with a detector for backscattered electrons. In contrast to (a), brighter areas indicate the presence of heavier elements. Note that here the contrast between the surface area (1) and the sidewalls is much less pronounced, whereas the bottom (2) is much brighter than the surface (1).

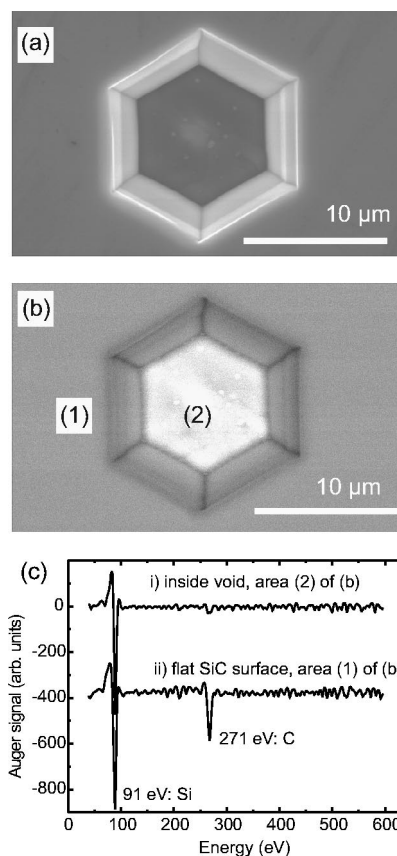


FIG. 2. SEM image of a hexagonal void taken with a secondary electron detector in (a). Brighter areas indicate inclined surfaces. The same void is imaged in (b) with a detector for backscattered electrons. Brighter areas indicate the presence of heavier elements. The brighter interior (2) is ascribed to a higher concentration of Si as compared to the flat surface area (1), where Si and C are present in equal concentrations, as deduced from EDS and Auger spectroscopy. (c) Micro-Auger electron spectroscopy of the sample of (a), (b). AES data are taken at the bottom of a void—upper curve—and in the flat region—lower curve. Hydrogen etching leads to a depletion of C at the bottom of the void, as deduced from the absence of a clear 271 eV C Auger signal in the upper curve. The sample has been etched in 13 mbar hydrogen for 20 minutes at 1800 °C.

This identifies a change of the chemical composition of the bottom of the void as compared to the surrounding surface. We propose that the bottom is enriched in Si as compared to the flat surface, and the higher backscattering power of Si ($Z=14$) as compared to C ($Z=6$) is responsible for the contrast.

We performed EDS measurements inside the void at (2) and outside at (1). No C is found at (2), but both elements Si and C are detected with comparable intensities at (1). Additional depth-profiling experiments are called for to map the elemental composition below the surface region at (2). We performed Auger electron spectroscopy (AES) with high lateral resolution to identify the elemental composition in areas (1) and (2). The result is shown in Fig. 2(c).

Figure 2(c) presents the AES data, which were measured on the sample of Fig. 2. The upper curve was taken inside the void at position (2), and the lower curve was taken on the flat surface at (1). Prior to taking the AES data, the sample has been bombarded by 5 keV Ar ions for 7 min to remove surface contaminants, which would contribute erroneously to the true inherent elemental composition near the surface region. Figure 2(c) shows, that AES signals at 91 and 271 eV, Downloaded 05 Nov 2002 to 195.37.184.165. Redistribution subject to AIP license or copyright, see <http://ojps.aip.org/aplo/aplcr.jsp>

which identify Si and C, respectively, are detected on the flat surface area, see lower curve. However, the AES signal of C has dropped to the noise level inside of the void, see upper curve of Fig. 2(c). We conclude that all three techniques EDS, backscattered intensity, and AES confirm a depletion of C at the bottom of a void after hydrogen etching. On flat parts of the surface, however, the concentrations of Si and C remain at their original levels, which is expected to be a one-to-one ratio for the two elements due to the stoichiometry of SiC.

The same investigation has been performed on samples with voids, which have not been etched. There, we find no indication of a loss of the stoichiometric ratio between Si and C within the voids, as compared to the flat surface areas. Thus, the depletion of C within the void is ascribed to a non-stoichiometric etching.

Our results of preferential removal of C inside the void indicate immediately that the supply of hydrogen to the interior of the void is abundant. In case of a hydrogen deficiency, one would expect a C enrichment,⁷ which is not observed.

In the following we propose a simple model which ascribes the nonstoichiometric etching of SiC near the bottom of a void leading to the depletion of C to the specific interplay between the relevant gas species in the void of small lateral dimensions. An important quantity in this model is the mean free path λ of a gas molecule at the pressure of the etching process. For the applied etching conditions of $p(\text{H}_2) = 13$ mbar and $T = 1800^\circ\text{C}$, hydrogen is by far the most abundant gas species and we estimate λ to be approximately $60\ \mu\text{m}$.⁸ This estimate shows that λ exceeds the dimensions of a void and we conclude that the flow of gas molecules in the void is determined by Knudsen diffusion, i.e., ballistic motion of the gas particles from wall to wall of the void. By contrast, the etching of flat surface areas is determined by gas diffusion with intermolecular collisions as the main scattering mechanism.

To explain the preferential etching of C in the voids, let us first concentrate on the question, whether the reaction rate or mass transfer limits the rate of etching. On the flat areas, no preferential etching is observed and C and Si are etched with the same rate. Under equilibrium conditions at an hydrogen pressure of 13 mbar and 1800°C , the pressure of the most important reaction products (i.e., Si, C_2H_2 , CH_4) in the gas phase is of the order of 10^{-2} mbar.⁹ At this partial pressure, the molecular flux due to the Maxwell distribution of velocities in the gas phase is of the order of 100 molecules/ $(\text{\AA}^2\ \text{s})$. This flux gives the upper limit for diffusion of the reaction products away from the surface and corresponds to a maximum etching rate of the order of $60\ \mu\text{m}/\text{h}$. Experimentally we observe an etch rate of a similar magnitude of $10\ \mu\text{m}/\text{h}$. This comparison indicates that the etch rate under these experimental conditions is limited by the diffusion of

the reaction products away from the surface, and not by the supply of hydrogen nor the surface reaction rate. Under these circumstances, the gas in front of the surface and the surface are in local thermodynamic equilibrium and the partial pressures of the reaction products are the equilibrium pressures for stoichiometric SiC.

Inside the voids, however, diffusion is hindered by the small lateral dimensions of the void compared to the mean free path λ . The diffusion constant D in this regime is given by the mean thermal velocity c of the gas molecules and the diameter L of the void; $D = cL/3$ compared to $D = c\lambda/3$ in the free gas. That means, that the out diffusion of reaction products from the void to the free gas is strongly hampered by a factor of approximately 5. As the mean thermal velocity of a molecule is proportional to $m^{-1/2}$, where m is the mass of the molecule, the out diffusion of the heavier reaction products is slowed down more than that of the lighter. In general, the reaction products of Si (dominant species Si) are heavier than that of C (dominant species CH_4 , C_2H_2) and a preferential etching of C in the voids occurs. The difference of the diffusivities as given by the different molecular weight of the Si versus the C gas species may lead to an enrichment of Si species in the gas phase inside the void. This increases the partial pressure of Si reaction products inside the void even above the equilibrium partial pressure of Si droplets. However, in front of the surface the partial pressure of Si is in equilibrium with SiC, and it does not exceed the partial pressure for droplet formation.

The reduced diffusivity of the reaction products inside the voids offers a natural explanation for the observed inclined sidewalls after etching. The reduced diffusivity due to Knudsen diffusion gets more pronounced deeper inside the void and leads to an etch rate which decreases with increasing depth.

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