Published in J. Electron. Mater. 27, 308 (1998).

Preparation of atomically flat surfaces on silicon carbide using hydrogen etching

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Abstract

Hydrogen etching of 6H- and 4H-SiC(0001) surfaces is studied. The as-polished substrates contain a large number of scratches arising from the polishing process which are eliminated by hydrogen etching. Etching is carried out in a flow of hydrogen gas at atmospheric pressure and temperatures around 1600-1700° C attained on a tantalum strip heater. Post-etching atomic force microscopy (AFM) images show periodic arrays of atomically flat terraces that are a few thousand Å wide. These terraces are separated by steps 15 Å high in the <1$\bar{1}$00> directions. Often, the surface is seen to be faceted with steps on neighbouring facets forming 60° angles and offset in the c-direction by half a unit cell. Images of incompletely etched surfaces show early stages of etching where one can see remnants of surface damage in the form of arrays of hexagonal pits. On the larger scale, the surface has a hill-and-valley type morphology. The observed features are interpreted in a model based on the symmetry of the SiC unit cell and crystal miscut.

1 Introduction

Epitaxial growth on a substrate is highly dependent on the surface quality of the substrate, since even minor defects may propagate into the film being grown and degrade its quality. There have been speculations that this may be a reason why gallium nitride thin films grown on silicon carbide substrates have properties much inferior to those grown on sapphire substrates in spite of the more favorable lattice mismatch in the case of SiC [1]. Commercially available SiC substrates grown by the Lely or Modified Lely process are found to have a large number of deep scratches arising from polishing damage. Other bulk defects that manifest themselves on the surface such as micropipes are produced during growth of the substrate[2]. In order to use these substrates for epitaxial growth, it is necessary to remove these defects. Hydrogen etching has been proposed as one effective method of obtaining a surface that is more suitable for growth in that surface scratches are minimized and large atomically flat terraces are obtained [3,4]. The method involves exposing the growth surface to hydrogen flow at high temperatures.

In our experiments, we have used hydrogen etching on a strip heater to produce surfaces suitable for epitaxial growth. By varying the time of etching we have obtained the SiC(0001) surface at various stages of being etched and then observed these stages by contact mode atomic force microscopy(AFM) and optical microscopy.

2 Experimental Details

The 6H- and 4H-SiC substrates used for these studies are (0001) oriented with nominally no miscut, obtained from Cree Research Inc. and designated Research Grade. We use the Si-terminated face for our studies, as polished by the supplier. The wafers are n-type doped and have a doping density of about 10^{18} cm^{-3}.

We use a simple strip-heating arrangement to perform our hydrogen etching experiments. The strip is made from tantalum foil $0.001\times0.25\times1$ in^3 and requires 40–45 A of current to heat to operating temperatures. Etching involves heating the wafer at 1600° C to 1700° C (temperature is measured by a disappearing filament pyrometer without emissivity correction) for about 15 minutes on this strip while passing pre-purified hydrogen gas at a rate of 14 lpm over it. The pressure in the etching chamber is atmospheric. Hydrogen flow over the SiC starts prior to the rise in temperature and ends after the wafer is cool. Measurements on the surfaces were made using a Park Scientific atomic force microscope (AFM), imaging in contact mode.

3 Results and Discussion

The as-polished, solvent cleaned 4H- and 6H-SiC (0001) substrates studied by AFM show a large number of deep (about 75 Å), irregularly directed scratches all over the surface with breadth in the nanometer range, as seen in Fig. 1 . Hydrogen etching at about 1630° C is seen to produce regular arrays of wide (few thousand angstroms) atomically flat terraces separated by steps of unit cell height as can be seen in Fig. [Ref: steps] . (One unit cell of 6-H SiC is 15.12 Å high in the c-direction , i.e. perpendicular to the (0001) plane. A unit cell of 4H-SiC is 10.08 Å [5]). The steps are found to lie along the $<1\bar{1}00>$ family of directions. The inset of Fig. 2 shows steps arranged around an etch pit or micropipe, to be discussed in more detail below. The substrates become more transparent with increased etching which we attribute to the diminished number of scratches causing a reduction in the amount of diffuse reflection of light.

The surface produced on 6H-SiC(0001) is faceted, and the facets form a shallow undulation (facet angle ~ 0.1°) on the surface as shown in the large-scale image of Fig. 3 (a). These shallow facets have been observed to exist on all the samples we have etched. Figures 3 (b) and (c) show the arrangement of steps at the intersection of two facets. Steps on neighboring facets are directed differently: the two sets of steps always have an angle of 60° between them, and they have an offset in height in the (0001) direction of 7.5 Å. This height is half a unit cell of 6H-SiC and describes the plane in the unit cell where there is a change in the stacking sequence [5,6]. Hence, we conclude that the surfaces of the terraces on the two facets have different orientations. In general, facets with steps directed differently also have different terrace widths, implying that the angle made by these facets with the (0001) plane is different.

Based on these observations, we propose inverse step flow as a mechanism for the etching process. There are two kinds of steps that can form on the SiC(0001) surface (Fig. 4 (b)) in the $<1\bar{1}00>$ family of directions, one being of lower energy than the other. On Si(111), these are referred to as S_N and S_D steps by Pechman et al. [7]. The structure of the SiC(0001) surface is quite different, yet it is expected that the two kinds of steps will also have different energies thus implying different etch rates for them. These two kinds of steps have an angle of 60° between them.

Etching causes the disappearance of higher energy steps, and as etching proceeds, more material is taken off such steps, making the directions perpendicular to these step-edges the “fast-etch” directions. Across two facets, there is a displacement of half a unit cell in the c-direction between steps, indicative of an orientation rotation of 60° between terraces on the two facets (Fig. 4 (a)). This means that the “fast-etch” directions and the steps are rotated by 60°. As mentioned above, that is what we see in our AFM data across two facets.

Hydrogen etching experiments with 4H-SiC also lead to similar results. In this polytype, steps in a facet have a height of 10 Å and the offset in step height between neighbouring facets rotated over by 60° is 5 Å. The 4H-SiC unit cell with a height of 10.08 Å has a change in stacking sequence at half that height, 5.04 Å. While imaging on the hydrogen-etched 4H-SiC surface, we often find large hexagonal faceted features, whose cores are associated with screw-type burgers vectors. In the inset of Fig. 2, we show one such feature, which is associated with a screw burgers vector of magnitude 10 Å. Closer examination of the center of the feature shows the presence of a deep hole whose bottom is not seen by the AFM. This feature is either an etch pit associated with a dislocation or a micropipe; we cannot distinguish between these possibilities using our measurements. However, the screw burgers vector of 10 Å is a factor of 4 to 13 times smaller than the values noted on micropipes by other workers [8]. We do note that such etch pit (or micropipe) features are seen on only a few of the samples which we etched, indicating that the hydrogen etching process is not highly preferential towards etching near dislocations.

We believe that the the origin of the large-scale faceting seen on the surface of these crystals lies in the miscut that inadvertently arises when these wafers are cut from a bulk crystal. The orientation for these wafers is specified as 0°±0.5° so we may expect up to a 0.5° deviation in any direction away from (0001). In general, this miscut is not exactly towards a <$1\bar{1}00$> direction. The miscut surface decomposes into two sets of facets, so that steps are allowed to lie along <$1\bar{1}00$> directions [9]. If $\hat{n}_1$ and $\hat{n}_2$ are the normals to these facets and the fractional area occupied by the facets are f_1 and f_2 respectively, then $f_1 + f_2 = 1$ and $\hat{n} = f_1\,\hat{n}_1 + f_2\,\hat{n}_2$ where $\hat{n}$ is the normal to the wafer (i.e. normal to the plane of miscut). The (0001) planar component of $\hat{n}$ gives the tangent of the angle of miscut. The surface free energy γ_{tot} of this morphology is given by

$$\gamma_{tot} = f_1\,\gamma_1 + f_2\,\gamma_2$$

where γ_i is the surface free energy of the ith facet and can be written as a function of the facet angle of the facet. The surface arranges itself into the morphology which minimizes γ_{tot}. This leads to a particular choice of facets and hence step spacings. The direction of the hill-and-valley features seen in Fig. 3(a) can be determined entirely from the step separations on the two different kinds of facets. If α_1 is the angle made by the facet ridges and valleys to the direction in which the step separation is L_1 (while step separation in the other direction is L_2), we find that

$$L_1/L_2 = \cos(\alpha_1)/\cos(60° - \alpha_1).$$

Analysis has been done on Fig. 3(a) producing a value of 0.25° for the miscut of the wafer which is well within the specifications of the supplier. The (0001) in-plane component of the miscut is shown as $\hat{n}_{||}$ in the figure. For this sample, this vector is only 2.23° off from the [$1\bar{2}10$] direction.

The calculated direction of the hill-and-valley features is also shown on Fig. 3(a) as a dashed arrow, and is seen to be reasonably consistent with the data.

In Fig. 5, we show an atomic force micrograph of a 6H-SiC sample that was hydrogen etched for 1 minute. This is a picture of an early stage of etching. The unit-cell-high steps are seen to be rough. Triangular peninsulas of height half a unit cell protrude from the steps onto the terraces below them. The triangles are observed to have 60° angles at their vertices. These peninsulas can also be understood in terms of "fast-etch" and "slow-etch" directions of the (0001) surface. The etching proceeds in the "fast-etch" direction of one set of bilayers allowing only the more stable steps to survive along one of the slow etch directions. But half a unit cell below (or above), because of the change in stacking, this slow-etch direction becomes a fast-etch direction. Steps in this direction vanish faster leaving behind steps at angles of 60° to it. This leads to the appearance of the triangles with included angles of 60°. The kink at the apex of such a triangle is another instability which leads to preferential etching of these triangles, eventually leaving an array of unit-cell-high steps. The deep depressions seen on this partially etched surface are probably remnants of surface damage that was previously on the surface. Such a surface may later develop into one similar to that in Fig. 6, (which is an area close to that where Fig. 5 was taken) where the depressions have grown smaller and the steps have become smoother. This is expected since if the scratches were made on the surface, they would be widest at the top and as etching proceeds further down, the width of damage should reduce. Eventually the remnants of surface damage vanish entirely leaving surfaces looking like Figs. 2 and 3.

4 Conclusion

From the results above, we infer that hydrogen etching indeed improves the quality of SiC surfaces, with polish damage being replaced by uniform arrays of large terraces. The steps that form prefer to lie in the $\langle 1\bar{1}00 \rangle$ directions. We have also observed the evolution of the etching process, obtaining images of the elimination of surface damage. Interferometric measurements show that we etch about 2000 Å of material during 15 minutes of etching. On a larger scale, the etching leaves behind a faceted surface morphology, which, we believe, arises from the miscut of the wafers. The spacing or steps on these facets as well as the area covered by these facets is determined by the surface miscut and minimization of surface free energy. The mechanism which determines the extent of each individual facet is not clear yet, and we speculate that this may have to do with parameters such as etching time and temperature.

The fact that steps prefer to lie along $\langle 1\bar{1}00 \rangle$ directions has implications for cutting off-axis wafers, in that a miscut towards $\langle 1\bar{1}00 \rangle$ directions will lead to shallower facets than a miscut towards $\langle 11\bar{2}0 \rangle$ directions. This may prove significant for subsequent epitaxy by minimizing planar defects which may originate at facet boundaries.

We believe that the chemical reactions leading to etching involve the reaction of surface silicon with hydrogen to form various silanes and carbon to form hydrocarbons both of which are volatile at the temperatures at which etching is done. We see no Si droplet formation as reported in [10], perhaps because of residual oxygen in our etching chamber or the etchant itself which would oxidize the excess Si leading to its removal. The strip annealer used here is considerably simpler than the hot-wall CVD reactor used in [3,11] although the results obtained here are of similar quality to those reported previously [3]. Few etch pits or other signs of preferential etching are seen upon completion of etching.

This work has been made possible by the support of the Office of Naval Research under grant N00014-96-1-0214.

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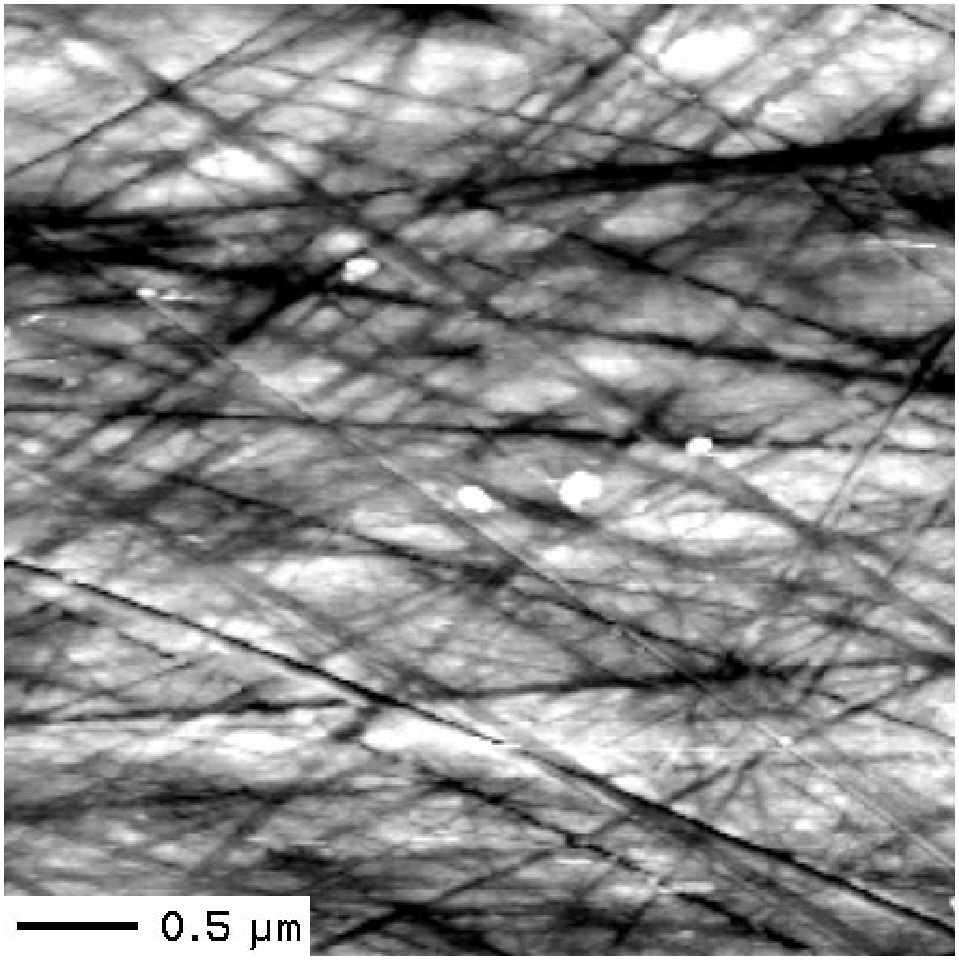

Figure 1 4 µm x 4 µm contact mode AFM image of an as-received 6H-SiC (0001) wafer. 4H-SiC surfaces look similar. Note the high density of scratches on the surface. The greyscale on this image corresponds to a height range of 75 Å.

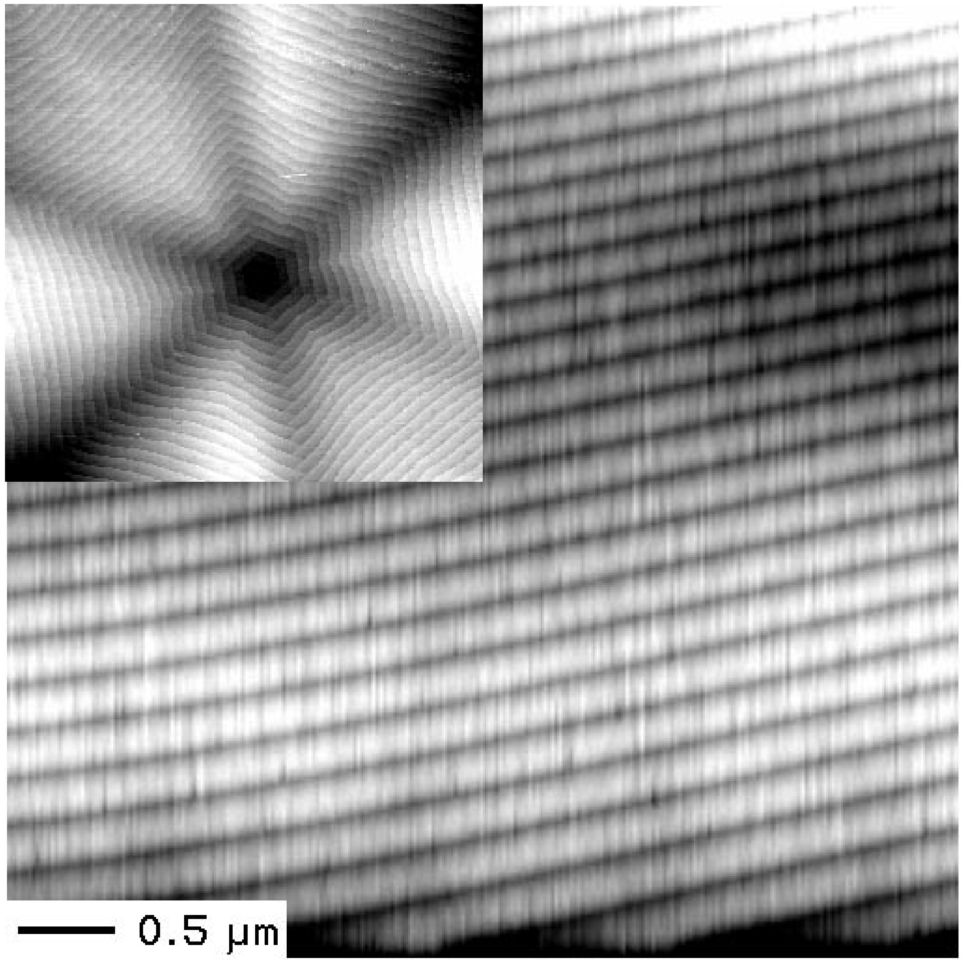

Figure 2 AFM image of a hydrogen etched 6H-SiC (0001) surface. The terraces are about 2500 Å wide and the steps are 15 Å high. The 20 µm x 20 µm inset shows the etched surface of a 4H-SiC wafer. Arrays of steps can be seen on this surface too. These arrays are arranged in a hexagonal pattern around a core that is associated with a 10 Å screw burgers vector. The greyscale ranges for this figure and inset are 5 and 9 Å respectively.

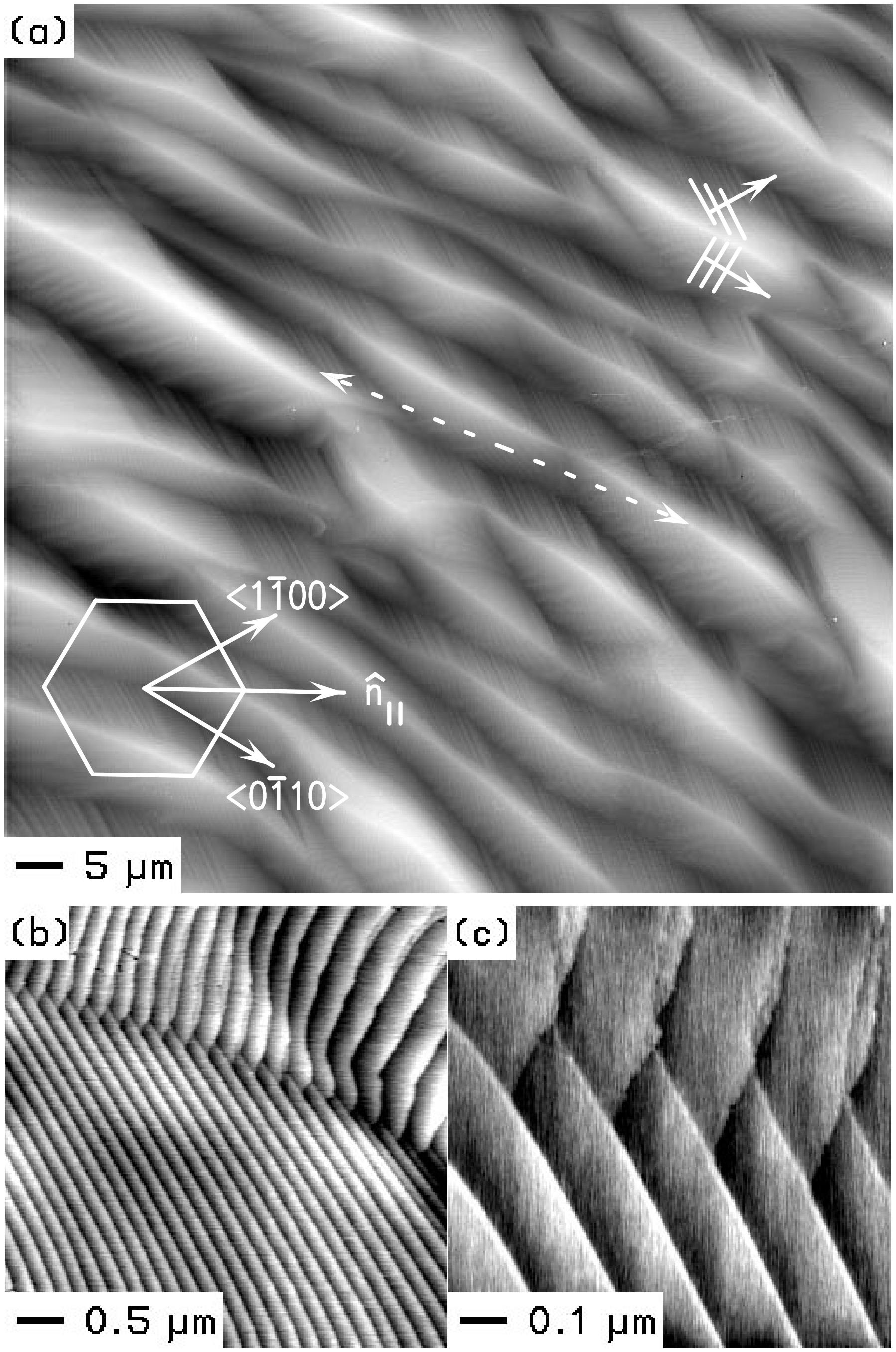

Figure 3 (a)AFM image of a hydrogen etched 6H-SiC (0001) surface showing facets leading to an undulating surface. The faceting arises from the miscut not being directed along a direction in which stable steps exist. Indicated on the image are various step directions on the surface and the (0001) in-plane component of the wafer miscut, $\hat{n}_{||}$. (b) Two arrays of steps intersecting at a facet boundary. (c) Close-up of the facet boundary showing the 60° relationship between steps on neighbouring facets. Greyscale ranges are 236, 15 and 14 Å for (a),(b) and (c).

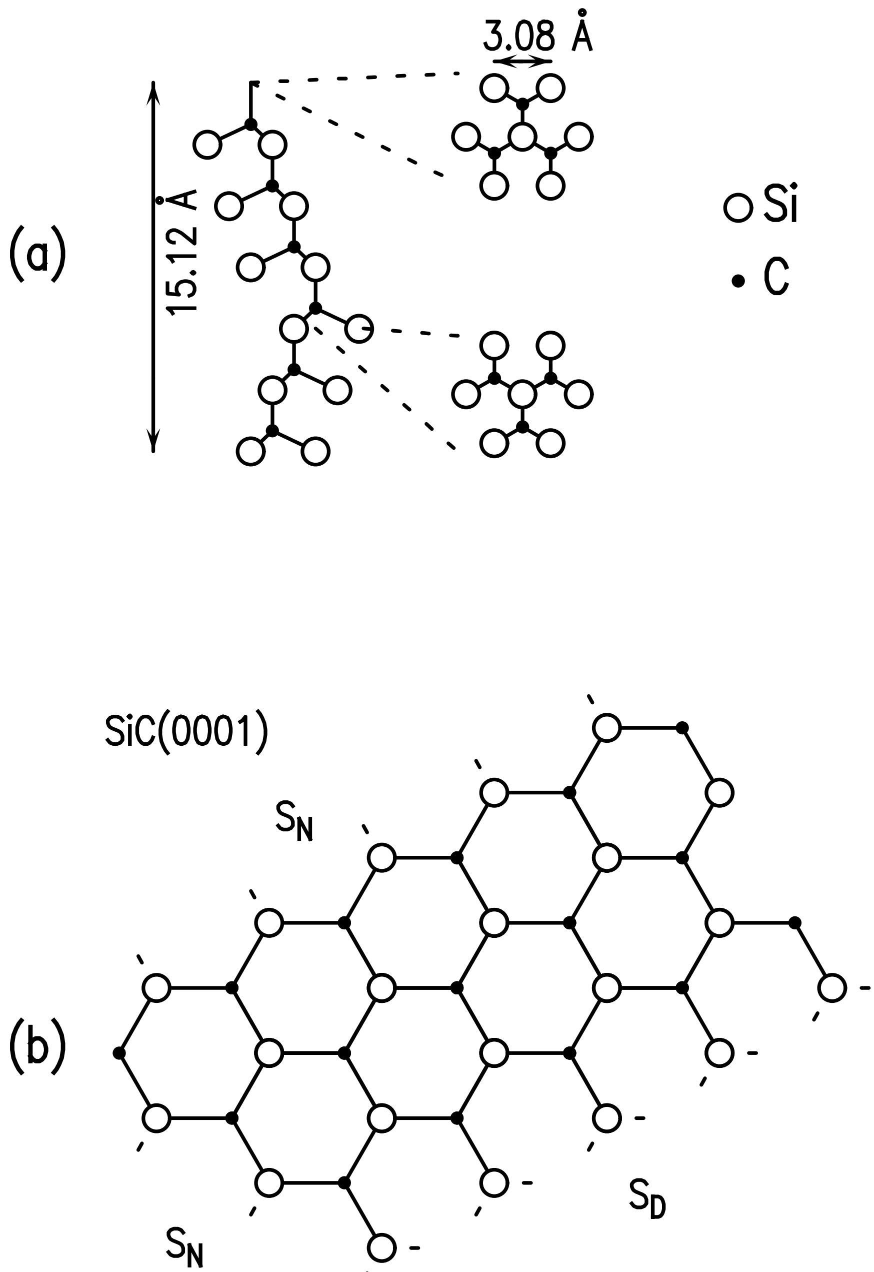

Figure 4 (a)Unit cell of 6H-SiC showing the stacking sequence on the left. A change in stacking sequence can be seen after the third Si-C bilayer. To the right of this unit cell are plan views of the (0001) surface as seen at the third bilayer (below) and the sixth bilayer (top). In these views it is clear that the unit cell has threefold symmetry in the (0001) plane. Also, it can be seen that the (0001) plane on the sixth bilayer is rotated by 60° relative to the third bilayer. (b) Plan view of the SiC(0001) surface showing S_N and S_D (nomenclature according to Pechman et al) steps. The dotted lines are dangling bonds at the step edge. It is expected that these two kinds of steps have different energies and hence different etch rates.

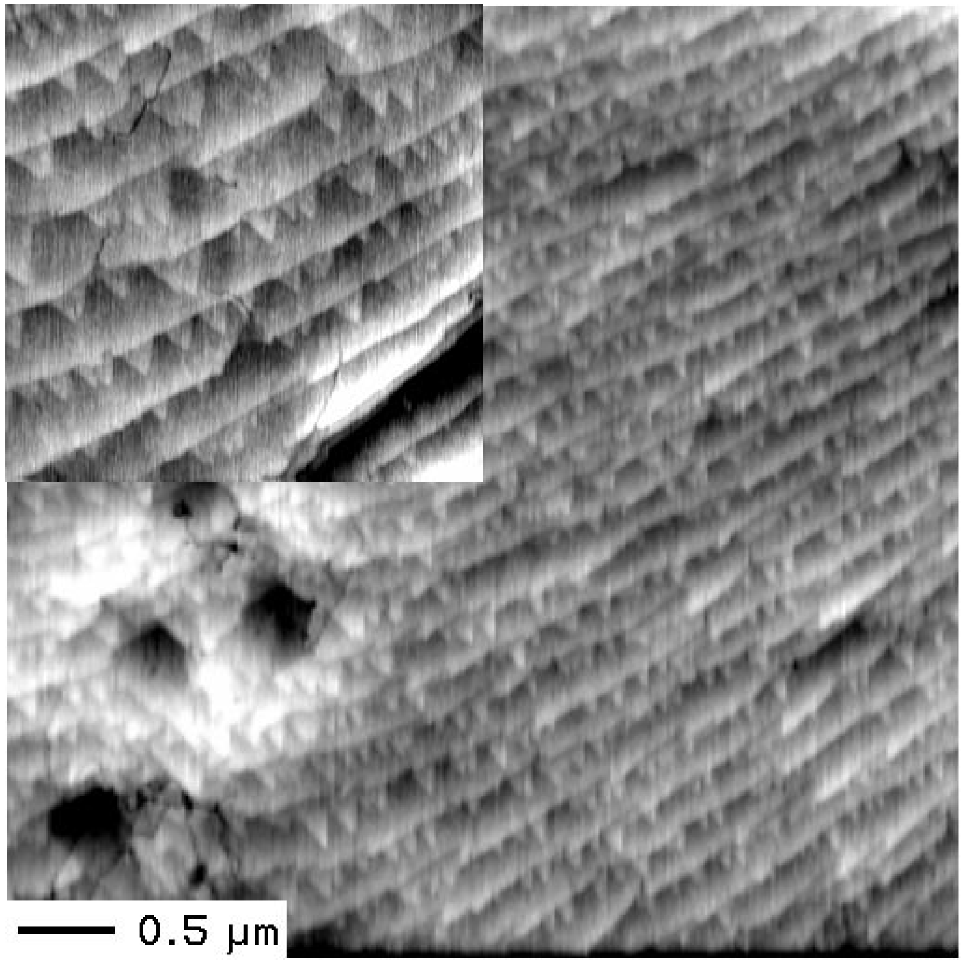

Figure 5 AFM image of an early stage of etching showing rough steps and triangular outgrowths from the steps onto terraces below. Some deep depressions can be seen towards the left which are presumably remnants of deep scratches. The inset is a 2 μm x 2 μm close up of a similar area showing the steps and peninsulas in greater detail. Greyscale corresponds to a height range of 15.5 Å in the figure and 18.2Å in the inset.

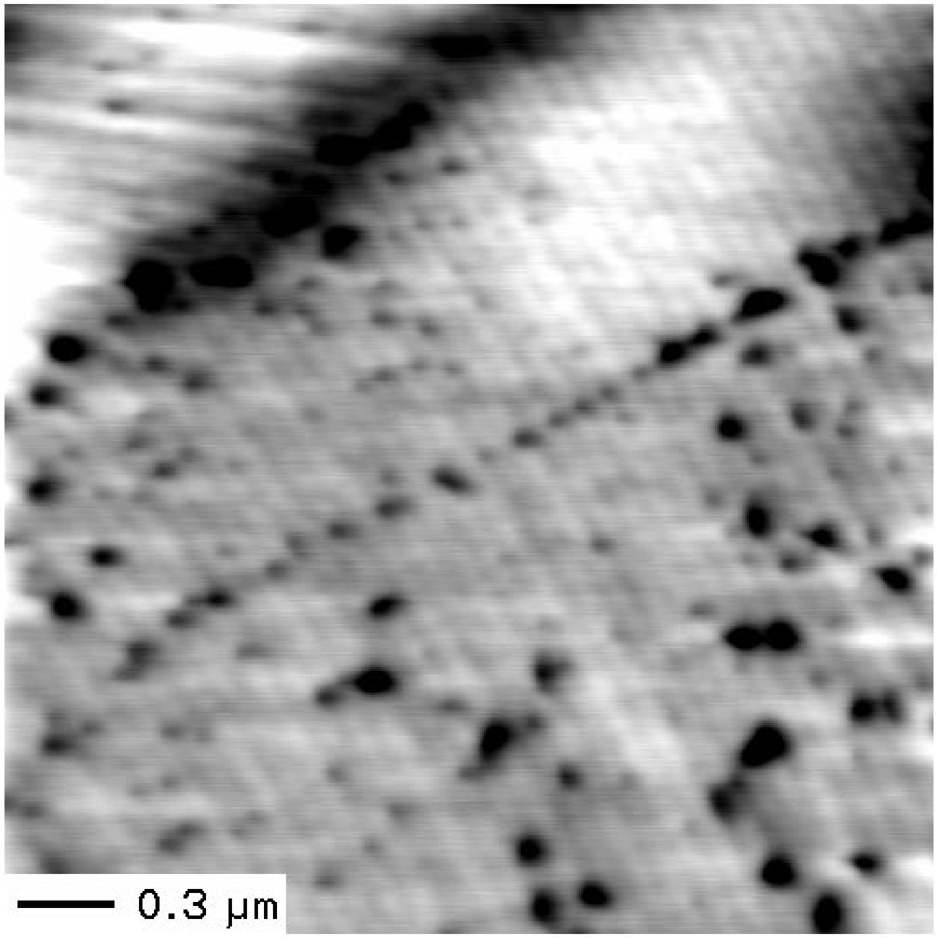

Figure 6 SiC (0001) surface showing incomplete etching. An array of straight, parallel steps is clearly visible.Remnants of scratch marks can be seen as sets of pits arranged in lines cutting across the steps. The greyscale range is 21.2 Å.