

Formation of Excess Silicon on 6H-SiC(0001) during Hydrogen Etching

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The surface of 6H-SiC(0001) samples was subjected to etching under H₂/Ar gas mixture in a cold-wall tubular furnace. Its topography and properties were characterized by atomic force microscopy and X-ray photoelectron spectroscopy before and after hydrogen etching. The conditions have been found, under which surface polishing-related damages could be removed. Si droplets were observed under certain etching conditions. The effect of the samples' cooling rate on the obtained surface morphology and chemistry was investigated to unveil the mechanism of Si recrystallization onto the crystal surface upon etching.

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1. Introduction

Vapor-phase epitaxial growth is the most practical means for fabricating devices from modern, high temperature stable materials such as silicon carbide SiC [1, 2]. Properties of both hetero- and homo-epitaxial films are highly dependent on the original surface condition of the substrate. Surface morphology of commercially available SiC wafers is mostly poor, with a considerable amount of polishing-induced defects. Hence, a special preparation of the crystalline substrate before growing the films is a very important step. The most effective method of the semiconductor's surface preparation is hydrogen etching [3, 4]. The process, depending on the working conditions, may lead to different end forms of both atomically perfect surfaces and quite non-uniform ones [5]. The final composition of the surface layers may be different. In some cases the Si:C ratio can be raised, with excess silicon segregating as congealed droplets on the surface [6]. This agent is highly undesirable from the technological point of view because silicon islands affect the homo- and heteroepitaxy processes, which leads to deterioration of physical properties of the final electronic device or component.

Factors affecting the surface accumulation of excess silicon during hydrogen etching are not well known. Those authors refer to the cooling rate of samples in the final stage of hydrogen etching as crucial to this harmful effect. The aim of this work was to look at the recrystallization process of Si in order to recognize the conditions and factors responsible for deterioration of the SiC surface properties during the hydrogen-etching preparation stage. This could enable one to avoid some undesired

effects of quenching type like a secondary recrystallization leading to a malleable state of the 6H-SiC(0001) surface, and attain it suitable to use as the substrate in technology.

2. Experimental details

Hydrogen etching was performed in a cold-wall tubular furnace in dynamic gas-supply mode with entry pressure 0.4 atm. The working gas was a mixture of 35% H₂ and 65% Ar at a flow rate of 5 lpm through the quartz reaction tube of 4 cm diameter. The samples, around 3 × 10 mm² in size, were cut out of the nitrogen-doped *n*-type (resistivity 0.1 Ω cm) 6H-SiC single crystal on-axis, (0001)-face of Si oriented, 0.25 mm thick wafer (Cree Research Inc.), polished by the supplier. During etching, samples were resistively heated by passing the current directly through the sample. Etching times ranged from 10 to 40 min at temperatures from 1450 to 1650°C as measured by means of optical pyrometer. Prior to etching, the samples were ultrasonically degreased in alcohol. The sample was kept in the flux of H₂/Ar mixture during both heating and cooling stages. The effect of etching on the topography of samples was examined with the air atomic force microscope (AFM) operating in contact mode. Additionally, chemical analysis of the sample surface was carried out by X-ray photoelectron spectroscopy (XPS) using Mg *K*_α non-monochromatized radiation ($h\nu = 1253.6$ eV). Photoelectrons from the Si-2*p*, C-1*s*, and O-1*s* core levels were recorded using a hemispherical analyzer with the 30 eV pass energy and 0.1 eV steps.

3. Results and discussion

AFM topography of as-received 6H-SiC(0001) samples taken in the air shows mechanical scratches randomly

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distributed on the surface of depth up to 15 nm and width to 150 nm, which arose in the polishing process. Any step structures cannot be observed, the surface is apparently amorphous [5].

The effect of hydrogen etching was studied as a function of temperature and time for a fixed gas-flow ratio of the gas mixture. It was investigated how the post-etch cooling rate affected the quality and stoichiometry of the surfaces under processing. This factor was confirmed to largely be deciding in the final stage of hydrogen etching. The best surface quality was obtained for a sample heated at 1550°C. Upon heating for above 25 min no evidence of the scratches was found and the etched surface showed a high degree of smoothness (Fig. 1). The steps displayed are 1.5 nm in height which corresponds to the height of the 6H-SiC lattice in the [0001] direction [7]. Such substrate surfaces were prepared by slow cooling down, with a post-etch cooling rate of below approximately 15°C/min. Examination of XPS peak areas revealed the stoichiometric composition with the Si:C ratio equal to 1. The residual contaminant left was oxygen that was due to the air exposure during transportation of samples into the XPS measurement chamber. Position of the main XPS peaks was typical of SiC samples with the binding energy (BE) 283.7 eV for C-1s peak, 101.5 eV for Si-2p and 532.8 eV for O-1s peaks.

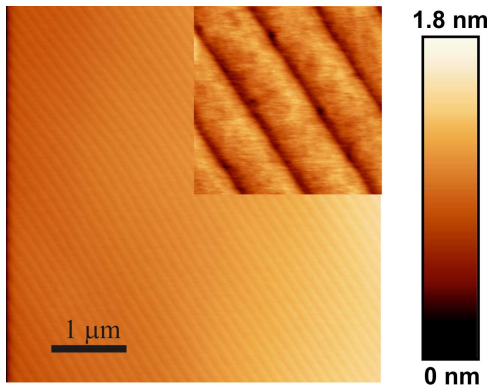


Fig. 1. AFM image of the 6H-SiC (0001) surface optimally hydrogen-etched (slow post-etch cooling rate). The $2 \mu\text{m} \times 2 \mu\text{m}$ inset shows the clean, atomically smooth surface with a perfect regular arrangement of steps whose height is equal to the lattice parameter $1c$ (1.5 nm).

It has been found, for a sample etched under the same conditions as for those of Fig. 1 (gas flow rate, increase in temperature, working gas pressure), but at the high post-etch cooling rate higher than 100°C/min, that a quench of the crystal results in an essential change in topography of the surface (Fig. 2). The presence of terraces and islands is revealed with, however, no evidence of original scratches. Chemical composition of the surface layers alters, showing the Si:C ratio 1.3. Samples rapidly cooled during etching show changed shapes of the Si-2p and C-1s peaks (Figs. 3, 4). The full width at half-

-maximum (FWHM) 1.7 eV of the Si-2p core level peak increases to 3.15 eV. Likewise, the FWHM of C-1s peak broadens from 1.4 to 1.7 eV. The position of the Si-2p peak does not change while the C-1s peak is shifted by ≈ 0.2 eV toward low energy.

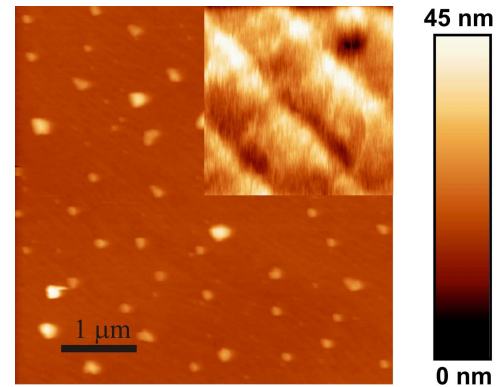


Fig. 2. AFM image of a hydrogen-etched 6H-SiC (0001) surface with Si islands (fast post-etch cooling rate). The $2 \mu\text{m} \times 2 \mu\text{m}$ inset shows a rough region of steps with their height of ≈ 1.5 nm.

Deconvolution of major XPS spectra provides more details. The evolution of the XPS Si-2p core level is shown in Fig. 3. The Si-2p spectrum of the samples with islands is resolved into three Gaussian components after subtracting the background using a conventional method [8]. The first peak located at 99.9 eV is due to an Si-Si bond, which suggests that the imaged islands were silicon based. The second one at 101.5 eV is due to an Si-C bond and the third one at 103.7 eV is due to the SiO₂ compound [9]. This indicates that the contaminant oxygen could react with silicon to form silicon dioxide. The Si-2p spectrum of the samples with a smooth surface is resolved into two major components. The first component is located at 101.4 eV, which is shifted by 0.1 eV toward the low energy side in comparison to the samples with islands, due to the Si-C bond. The second one at 102.6 eV is due to silicon oxides [9]. Figure 4 shows changes in XPS C-1s core level, with the spectra resolved into two major components. Primary peaks at 283.5 eV and 283.6 eV are due to the Si-C bond [10]. The minor peak located at 284.55 eV is due to C-C bonds. On the samples with Si islands this peak is more distinct and narrow, and we believe that it is rather related to the graphite phase formed at high temperatures that became frozen after rapidly cooling. On smooth samples, which we assume as clean, the same peak is much lower and wider and it clearly comes from traces of organic contaminations which could be adsorbed on the samples when they were exposed to air before XPS measurements.

We have analyzed the distribution of diameters and heights of the islands without accounting of tip size (Fig. 5). The mean diameter of Si islands amounts to ≈ 117 nm and the maximum diameter of an island observed is below 400 nm. The mean island height is 26 nm.

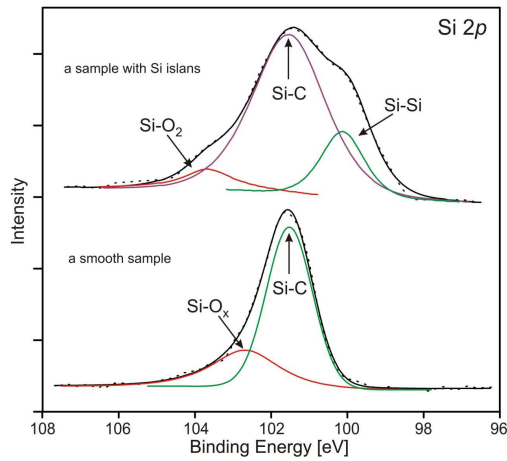


Fig. 3. Si-2*p* XPS spectrum recorded at the hydrogen-etched smooth 6H-SiC (0001) surface and at the surface with Si islands (dotted lines). Solid-line curves through the data points show the results of deconvolution procedure.

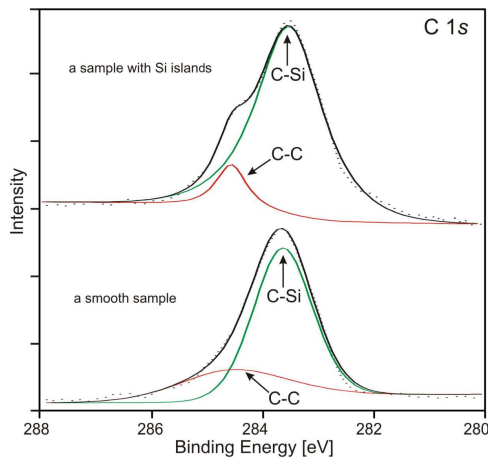


Fig. 4. As in Fig. 3, but for C-1*s*.

Most islands are of 5 nm height; the maximum island height is below 35 nm. As it was described above we have found that upon rapid cooling below the melting point of silicon (MP_{Si}), 1410°C, certain amount of silicon crystallizes from liquid phase on the surface (Fig. 2). If, after the crossing of the melting point, further cooling proceeds, fast population of the frozen islands is high and their average diameter is small. If the further cooling down proceeds slowly, Si diffusion over the surface allows the formation of large Si islands. The latter merge to form agglomerates as shown in Fig. 6a; these are several times larger than islands of Fig. 2.

The results allow for better understanding the very process of hydrogen-etching the 6H-SiC crystals. Mechanism of removing carbon and silicon atoms depends on the temperature of the sample, the gas flow rate, and the working-gas pressure, i.e. the partial pressure of hy-

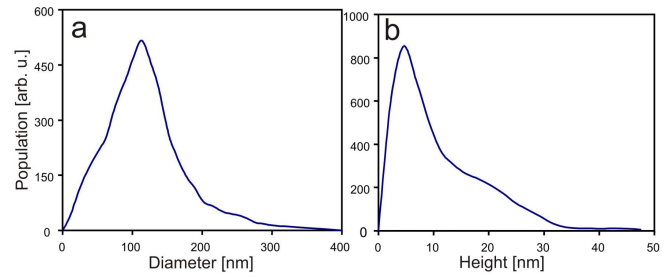


Fig. 5. Distribution of diameters (a) and heights (b) of Si islands on a hydrogen-etched 6H-SiC (0001) surface (fast post-etch cooling rate).

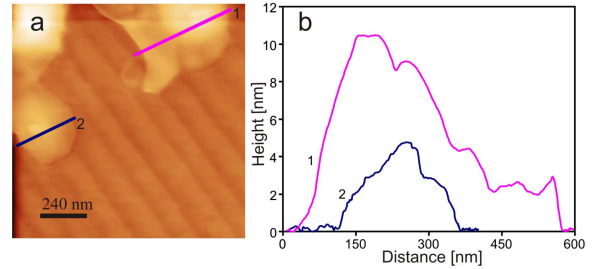


Fig. 6. (a) AFM image of the hydrogen-etched 6H-SiC (0001) surface with Si islands. (b) Profiles of the islands as taken along the lines marked on the topography shown in (a).

drogen. Consequently, it consists in chemical reaction between the hydrogen and the atoms present on the surface, which results in gaseous hydrocarbons and silanes. Temperature is the primary factor in the etching process, as we have observed. The removal rate of the substrate surface components is essentially temperature dependent. For temperatures lower than the MP_{Si} , the etching process proceeds relatively slow, and the resultant surface appears stoichiometric with no evidence of the presence of silicon islands. In contrast, when the temperature of the crystal under etching exceeds the MP_{Si} , we believe that what we observe is the occurrence of two phases of a liquid Si and a graphite-like phase of carbon. During etching, the removal rate for both these components settles at the same level, however, if a rapid drop in temperature is admitted to below the MP_{Si} , then a “freezing” of both species appears and the Si:C ratio becomes spoilt. The Si atoms of surface liquid phase would be trapped on the surface (i.e. crystallized), which is revealed in the XPS spectra (Fig. 3), and such a surface will be silicon-rich in the form of islands (Fig. 2). Next, if the sample after such a rapid pass down the MP_{Si} is still being under etching, hydrogen may react with the excess silicon as well as with the Si-C species removing those from the surface, but the etching rate is not enough high to eliminate the Si from the sample’s surface. In such a case, the sample temperature is not sufficiently high for Si evaporation, but the excess Si can diffuse over the surface to form larger islands (Fig. 6). The condition for

obtaining a stoichiometric surface of the carbide during etching can be expressed as dynamic equilibrium between the amounts of carbon and silicon atoms being removed. Consequently, to obtain the stoichiometric surface of SiC the sample must be cooled very slowly while passing the MP_{Si} because this is the point of a rapid change in removal mechanism of the crystal's components.

4. Conclusions

Certain surface detrimental factors have been recognized in this investigation of Si recrystallization process. The appearance of excess silicon on the SiC sample surface is attributed to the fast post-etch cooling rates. Therefore, to obtain the stoichiometric surface the sample must be cooled very slowly (here, with a post-etch cooling rate of below $\approx 15^\circ\text{C}/\text{min}$ under the flowing gas mixture 35% $\text{H}_2/65\%$ Ar). The hydrogen etching process should be controlled so that the dynamic equilibrium between removal of Si and C should be ensured. The critical stage is the moment of passing through the melting point of silicon. If the sample is being cooled sufficiently slow during approaching and passing the MP_{Si} , then the surface of such samples will be free of Si droplets.

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