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Wet Chemical Processing of $(0001)_{Si}$ 6H-SiC

Hydrophobic and Hydrophilic Surfaces

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The wetting characteristics of polished or polished and thermally oxidized, on- and off-axis $(0001)_{Si}$ 6H-SiC [the silicon-terminated surface of SiC] surfaces in selected acids and bases have been determined and compared with that of (111)Si. Auger electron and X-ray photoelectron spectroscopies and low energy electron diffraction were used to characterize the chemical state and order of these surfaces. The oxidized SiC surfaces were hydrophilic after oxide removal with a 10:1 HF solution and were terminated with approximately a monolayer containing OH, CO, CH, and F species. The same effects were observed for the similarly treated $(000\bar{1})_C$ [the carbon-terminated surface of SiC], $(11\bar{2}0)$, and $(10\bar{1}0)$ surfaces. The as-polished SiC surfaces were hydrophobic and covered with a thin (5-10 Å) contamination layer composed primarily of C-C, C-F, and Si-F bonded species. Removal of this layer using an RCA SC1 etch or Piranha clean resulted in a disordered hydrophilic SiC surface. A 20 Å amorphous Si capping layer both passivated the SiC surfaces and provided a better alternative to the aforementioned contamination layer for producing hydrophobic surfaces on this material.

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Preparation of clean, well-ordered surfaces is an important first step in all semiconductor fabrication processes.[1-3] The consequences of incomplete removal of all contaminants by nonoptimized surface cleaning processes are decreased device performance and yield.[4,5] The reasons for these two effects are the generation of increased densities of (*i*) electrically active defects which result in higher interface state densities, lower breakdown fields, and increased leakage currents[6-13] and (*ii*) structural defects including dislocations, twins, and stacking faults in the epitaxial layers.[14-25] Intensive efforts to understand the source(s) and nature of the surface contaminants accumulated during Si processing[26-49] have resulted in the development of numerous wet and dry (ex situ and in situ) surface cleaning processes specifically optimized for Si surfaces.[1,2,26-31,35-40]

Numerous studies have also been concerned with the nature and removal of native oxides and other contaminants on SiC surfaces.[50-63] Few of these studies[55-59] have investigated the effects of wet chemical processes on SiC surfaces and the differences between Si and SiC in the use of these processes. As such, several wet chemical processes optimized for Si have been implemented commonly for SiC device processing[50-63] despite the differences in the surface chemistry and the extreme chemical inertness of the latter material.[64,65] Reduction in the densities of aforementioned defects via proper surface cleaning techniques will assist the development and application of SiC as the semiconductor of choice for high-power and high-temperature electronic devices and as a substrate for III-nitride heteroepitaxy.[65,66]

In the present research, the effects on selected SiC surfaces of various wet chemical processes common to Si have been investigated. Emphasis was placed on HF processes which typically serve as one of the last steps in Si wet chemical processing and are primarily used for surface oxide removal.[31-49] A hydrogen terminated/hydrophobic (111)Si surface forms which is stable against oxidation in air for several hours/days.[38,45-49] By contrast, removal of the thermal oxide from $(0001)_{Si}$ [the silicon-terminated surface of SiC], $(000\bar{1})_C$ [the carbon-terminated surface of SiC], $(11\bar{2}0)$, and $(10\bar{1}0)$ 6H-SiC surfaces via exposure to HF in this study resulted in a hydrophilic surface. X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) studies revealed that HF processing leaves these SiC surfaces terminated predominantly with O (or OH) rather than H.

Wet chemical processing of hydrophobic surfaces of Si should lead to lower levels of particulate contamination due to the "snow plow" effect as the surface traverses the liquid/air interface. However, it has been empirically observed that particles are more attracted to hydrophobic than to hydrophilic surfaces during this processing because the latter acquires a negative charge in solution which repels negatively charged particles.[3,32-34] Hydrophobic surfaces are more passivated and develop less negative charge (or positive charge) in ionic solutions and do not sufficiently repel (or attract) the negatively charged particles in the solution.[3,32-34]

We have previously noted[67] that the hydrophilic nature of SiC surfaces produced in wet chemical processing leads to trapping of the chemicals in the micropipes of the wafers and the unwanted removal/outgassing of these chemicals in subsequent processing. Thus, we have additionally investigated alternative processes and passivation layers which would result in a hydrophobic $(0001)_{Si}$ 6H-SiC surface.

The following sections describe the experimental procedures and the results of the research noted above and provide a discussion and conclusions regarding the various topics.

Experimental

On axis and vicinal n-type (typically $N_d = 10^{18}/cm^3$) $(0001)_{Si}$ 6H-SiC wafers, without (as-polished) or with a 500-1000 Å thermally grown oxide, were used in these experiments. The oxidized $(000\bar{1})_C$, $(11\bar{2}0)$, and $(10\bar{1}0)$ surfaces of 6H-SiC were similarly but less extensively investigated. Both the as-polished and the oxidized wafers were ultrasonically cleaned/degreased in trichloroethylene, acetone, and methanol each for 10 min prior to any other wet chemical treatments. The thermally grown oxide was removed using a 10 min dip in a 10:1 HF solution, followed by rinsing in deionized (DI) water and N_2 blow drying. The wetting characteristics of this surface and the as-polished surfaces were then investigated by immersion in other acid/base solutions. The wet chemistries examined included 100:1 HF, 10:1 HF, 1:1 HF, 10:1 buffered HF (7:1 NH_4F:HF), 30:1 buffered HF, 40% NH_4F, 38% HCl, 70% HNO_3, piranha etch (7:3 H_2SO_4:H_2O_2 at 120°C), RCA SC1 and SC2 (1:1:5 NH_3OH:H_2O_2:H_2O at 85°C, and 1:1:5 HCl:H_2O_2:H_2O at 85°C), 100% $HC_2H_3O_2$, and 40% KOH. These chemistries were chosen primarily due to their extensive use in the Si microelectronics industry. Except where noted, the samples were rinsed in DI water (18 MΩ) and blown dry with N_2 after all wet chemical treatments. Each wafer was then visually inspected to determine if a hydrophobic or hydrophilic surface had been retained or obtained. On and off-axis (100) and (111)Si wafers were dipped in the same acid/base solution immediately after the SiC wafer and the wetting characteristics of the surfaces of both materials compared. All wet chemicals were of complementary metal oxide semiconductor (CMOS) grade purity (J. T. Baker).

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Wafers of $(0001)_{Si}$ 6H-SiC having a 200 Å amorphous (a) Si capping layer were prepared in the following manner. Each thermally oxidized $(0001)_{Si}$ 6H-SiC wafer was dipped in 10:1 HF for 10 min, rinsed in DI H_2O, and dried in flowing N_2. The samples were loaded into a Si-Ge molecular beam epitaxy system, degassed at 450°C and 10^{-10} Torr, and annealed at 1000°C for 20 min in a 10^{-6} Torr SiH_4 flux. This produced an oxygen-free, Si-rich (1×1) SiC surface. An $\approx$200 Å film of a-Si was subsequently deposited onto each (0001) SiC surface at room temperature via electron-beam evaporation. The samples were removed from the vacuum for wet chemical processing as described above for the oxidized and the as-polished SiC surfaces.

After each wet chemical treatment, the various 6H-SiC surfaces were analyzed via one or more of the following techniques: X-ray photoelectron spectroscopy (XPS) using a VG CLAM II electron energy analyzer and an Al anode ($h\nu = 1486.6$ eV) at 20 mA and 12 kV; Auger electron spectroscopy (AES) using a Perkin Elmer CMA at a beam voltage of 3 keV and an emission current of 1 mA; electron energy loss spectroscopy (EELS) using the same CMA but with a 100 eV electron beam and an emission current of 1 mA; and low energy electron diffraction (LEED) using Princeton Scientific rear view optics, a beam voltage of approximately 115 eV and an emission current of 1 mA. Calibration of the XPS binding energy scale was performed by measuring the position of the Au $4f_{7/2}$ and shifting the spectra such that the peak position occurred at 83.98 eV. These analytical techniques were contained in a single integrated and previously described[68] ultrahigh vacuum (UHV) system.

Results

Oxidized $(0001)_{Si}$ 6H-SiC surfaces.—In contrast to (100) and (111)Si, a 10:1 HF solution was observed to wet the surface of each $(0001)_{Si}$ 6H-SiC wafer as it was withdrawn from the solution after a 10 min dip (note: this is sufficient time to remove a 1000 Å thermal oxide, since the SiO_2 etch rate with 10:1 HF is $\approx$10 Å/s. [42-44]). The HF solution also slowly pooled on the SiC surface. After rinsing in DI water, the SiC surface was clearly wetted with no observed pooling of the H_2O. Figure 1a displays an AES survey spectrum taken from an off-axis $(0001)_{Si}$ 6H-SiC wafer after removal of the thermal oxide with a 10 min 10:1 HF dip. Similar results were obtained from on axis, $(0001)_{Si}$ 6H-SiC. Silicon, C, and significant amounts of oxygen were detected. Further analysis using XPS of the $(0001)_{Si}$ 6H-SiC surface after a 10:1 HF dip revealed $\approx$1/4 ML fluorine, (see Fig. 2a) which was not detected by AES due to a lower sensitivity to fluorine and possible electron-beam stimulated desorption effects.[69-73] The F 1s peak for intentionally fluorinated Si surfaces has been located at 685.9–686.2 eV [69-73]; the F 1s peak of the oxidized $(0001)_{Si}$ 6H-SiC surfaces after the HF dip was observed at 686.8 eV. These peaks were attributed to Si-F bonds. The fluorine surface coverage was initially observed to vary from 0–1/4 ML; however, further investigation revealed that the fluorine coverage was highly dependent on the DI rinsing procedure. Fluorine was not detected by XPS for surfaces dipped in HF and rigorously rinsed in DI water (see Fig. 2b).

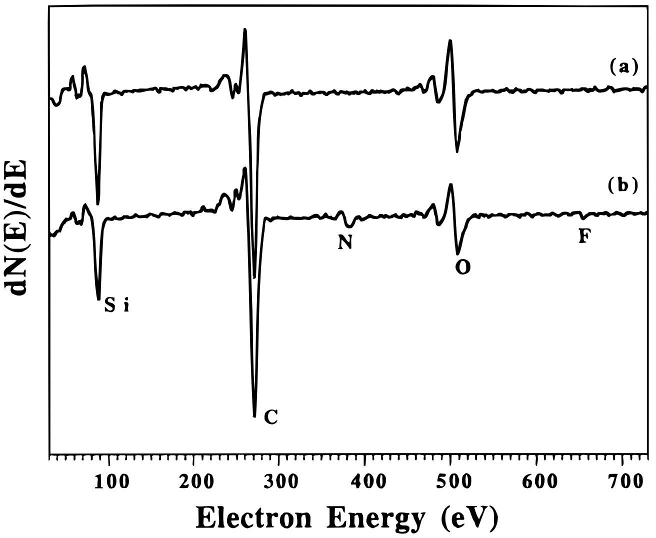

Figure 1. AES survey spectra of (a) $(0001)_{Si}$ 6H-SiC after thermal oxidation and removal of the oxide with 10:1 HF and (b) $(0001)_{Si}$ 6H-SiC as polished surfaces after solvent cleaning.

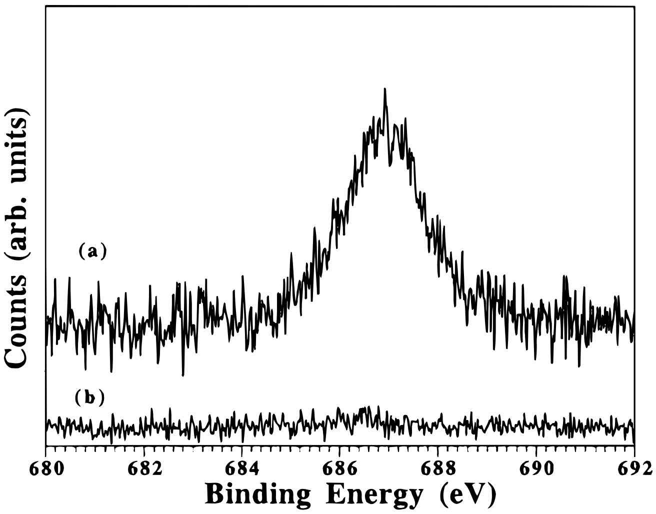

Figure 2. XPS spectra of the F 1s core level from an oxidized $(0001)_{Si}$ 6H-SiC surface after (a) oxide removal with 10:1 HF followed by (b) rigorous rinsing in running DI water.

Comparison of the relative intensities of the O KLL AES transition and the XPS O 1s core level after oxide removal with 10:1 HF from previously oxidized $(0001)_{Si}$ 6H-SiC and (100) and (111)Si surfaces indicated a significantly larger (five to ten times) residual surface concentration of oxygen on the SiC surfaces, as shown in Fig. 3 (XPS data only). The intensity of these two peaks/transitions were estimated to correspond to oxygen surface coverages of $\approx 3/4 \pm 1/4$ monolayer (ML) for $(0001)_{Si}$ 6H-SiC and <1/10 ML for (100) and (111)Si. This is in agreement with the observed hydrophilic and hydrophobic nature of these surfaces, respectively. More detailed analysis of the O 1s core level photoemission data of the

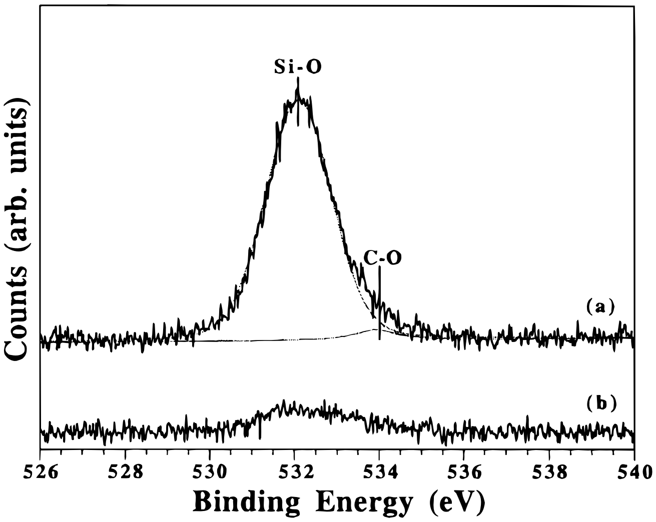

Figure 3. XPS spectra of the O 1s core level from (a) $(0001)_{Si}$ 6H-SiC after removal of a 750 Å thermal oxide with 10:1 HF and (b) (111)Si after a dip in 10:1 HF.

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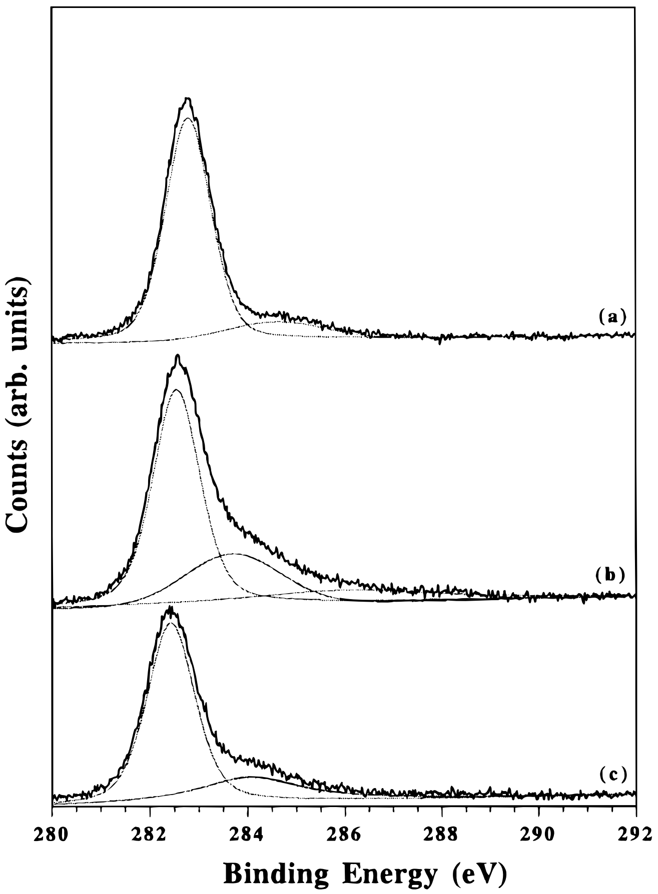

Figure 4. Typical XPS spectra of the C 1s core level from (a) oxidized $(0001)_{Si}$ 6H-SiC after oxide removal with 10:1 HF, (b) as-polished $(0001)_{Si}$ 6H-SiC after solvent cleaning, and (c) as-polished $(0001)_{Si}$ 6H-SiC after RCA SC1.

$(0001)_{Si}$ 6H-SiC surfaces indicated the presence of two peaks. The larger peak at 532.1 eV was indicative of Si-O or Si-OH bonded oxygen; the smaller peak at 533.5-533.9 eV was indicative of C-O bonding.[29,30,38,39] The intensity of the C-O O 1s bonding peak, like the F 1s Si-F bonding peak, depended on the DI rinsing procedure. The most C-O bonded oxygen was observed on the unrinsed surfaces. The presence of C-O bonded oxygen on the $(0001)_{Si}$ 6H-SiC surfaces was further supported by photoemission from the C 1s core level which revealed C 1s peaks at 282.8 eV, indicative of C-Si bonds, and at 284.7 eV, indicative of a mixture of C-H and C-O bonds,[19,20] as shown in Fig. 4. In contrast, EELS did not detect any π-π^* transitions (≈3–6 eV) typically observed from organic molecules and contamination. As mentioned by Mizokawa et al.,[57] the failure of EELS to detect adventitious surface carbon could be due to electron stimulated desorption.

It was difficult to accurately determine if a Si-O Si 2p bonding peak existed due to the inherent asymmetry of the XPS Si 2p core level arising from the unresolved Si $2p_{3/2,1/2}$ doublet. A second peak at ≈102.2 eV could be fitted to the spectrum, assuming a full width at half-maximum (FWHM) of 1.45 eV for the main Si-C Si 2p peak at 100.7 eV; however, the line width of this peak was <1.4 eV. The presence of significant amounts of Si-O bonded oxygen on the $(0001)_{Si}$ surface was supported by the Si KLL line shape in AES (see Fig. 1a) which as noted by Mizokawa is similar to that for oxidized Si surfaces.[57] The intensities of the Si-O O 1s or Si 2p bonding peaks were not observed to depend on the DI rinsing procedure with the O 1s (Si-O)/Si 2p (Si-C) intensity ratio remaining essentially constant and independent of wafer cut (off- or on-axis). Finally, these surfaces displayed intense (1 × 1) LEED patterns with broad dots which were clearly visible at beam energies (E_p) as low as 60–100 eV. The AES, XPS, and EELS results from the oxidized $(0001)_{Si}$ 6H-SiC surface are summarized in Tables I and II.

Following the 10:1 HF dip, the thermally oxidized $(0001)_{Si}$ 6H-SiC surfaces were dipped in a variety of different acids and bases, and the surface wetting characteristics visually noted. The results are summarized in Table III and illustrate that this surface was found to be hydrophilic in all acids and bases investigated. In all cases, the SiC surface was observed to retain a monolayer coverage of oxygen. For the oxidized $(0001)_{Si}$ 6H-SiC surface, the surface coverage of oxygen was not found to change appreciably with dipping time (1–24 h), HF concentration (1:1–1000:1), composition (HF-NH_4F), or pH (1–10).

Oxidized $(000\bar{1})_C$*,* $(11\bar{2}0)$*, and* $(10\bar{1}0)$ *6H-SiC surfaces.*—The thermally oxidized $(000\bar{1})_C$, $(11\bar{2}0)$, and $(10\bar{1}0)$ surfaces were similarly investigated after oxide removal with 10:1 HF and also observed to be hydrophilic in all acids and bases investigated. There was little difference in the AES spectra of these surfaces and that of samples having the $(0001)_{Si}$ orientation and shown in Fig. 1a. Table IV lists the Si/C, O/Si, and O/C peak-to-peak height (pph) ratios (uncorrected for differences in sensitivity) calculated for each surface. These results reveal that the O/C ratio is centered around 0.3 for all the different orientations. This similarity is surprising given that two of these surfaces are polar $[(0001)_{Si}$ and $(000\bar{1})_C]$, and the others are nonpolar $[(11\bar{2}0)$ and $(10\bar{1}0)]$. The Si/C pph ratio for the

Table I. Binding energy (in eV) of core level positions from $(0001)_{Si}$ 6H-SiC as polished and oxidized surfaces after various treatments. The full width half-maxima (Γ) of the peaks are also indicated.

Treatment	Si 2p, Γ	O 1s, Γ	C 1s, Γ	F 1s, Γ	N 1s, Γ
Oxidized					
10:1 HF	100.7, 1.4	532.1, 1.9 284.7, 2.1	282.8, 1.1		
As-polished					
Solvents	100.5, 1.4	531.9, 2.3 283.7, 2.7 286.0, 4.5	282.6, 1.1 687.5, 2.5	685.8, 1.9	398.2, 3.0
10:1 HF	100.5, 1.4	531.6, 2.4 283.6, 2.7 286.0, 4.4	282.5, 1.1 687.3, 2.5	685.6, 1.9	398.2, 3.0
H_2SO_4:H_2O_2	100.4, 1.4	531.5, 2.5 283.6, 2.7	283.5, 1.1	686.0, 3.0	398.2, 3.0
RCA SC1	100.3, 1.4	531.3, 2.8 283.9, 2.4	282.4, 1.1		
Aqua regia	100.5, 1.4	531.6, 2.3	282.6, 1.1 283.7, 2.7	685.5, 1.7 686.9, 3.2	398.2, 3.0

Table II. Summary of XPS Si 2p/O 1s, Si 2p/F 1s, C/C, and C-C data (uncorrected for sensitivity factors) for $(0001)_{Si}$ 6H-SiC surfaces.

Treatment	Si 2p/O 1s	Si 2p/F 1s	C/C	C-C (eV)
Oxidized				
10:1 HF	1.4	∞	6.65	1.9
As-Polished				
Solvents	1.2	1.6	1.1	1.3
10:1 HF	1.8	1.8	0.9	1.1
H_2SO_4:H_2O_2	0.9	4.0	1.1	1.1
RCA SC1	1.0	∞	2.2	1.5
Aqua regia	1.2	3.8	1.2	1.1

Table III. Summary of wetting characteristics of as polished and oxidized $(0001)_{Si}$ 6H-SiC and (111)Si.

Treatment	$(0001)_{Si}$ 6H-SiC (As-polished)	$(0001)_{Si}$ 6H-SiC (Thermally oxidized)	(111) Si and (a-Si passivated 6H-SiC)
None	Hydrophobic	Hydrophilic	Hydrophilic
10:1 HF	Phobic	Philic	Phobic
38% HCl	Phobic	Philic	Phobic
70% HNO_3	Phobic	Philic	Philic
RCA SC1	Philic	Philic	Philic
RCA SC2	Phobic	Philic	Philic
Piranha	Philic	Philic	Philic
Aqua regia	Phobic	Philic	Philic
Acetic	Phobic	Philic	Phobic
NH_4F	Phobic	Philic	Phobic
KOH	Phobic	Philic	Philic

$(0001)_{Si}$, $(11\bar{2}0)$, and $(10\bar{1}0)$ surfaces are all centered around 0.6 which is also surprising in that the ideal $(0001)_{Si}$ surface would be terminated exclusively with Si; whereas, the $(10\bar{1}0)$ and $(11\bar{2}0)$ surfaces, ideally, would be terminated with equal numbers of C and Si atoms. However, the Si/C ratio for the $(000\bar{1})_C$ surface is half that of the $(0001)_{Si}$ surface which is expected based on the differences in polarity for these two surfaces.

As-polished $(0001)_{Si}$ 6H-SiC surfaces.—As-received, commercially polished and nonthermally oxidized on- and off-axis $(0001)_{Si}$ 6H-SiC surfaces were hydrophobic. Figure 1b displays an AES survey spectrum obtained from an off-axis surface after ultrasonic degreasing in trichloroethylene, acetone, and methanol for 10 min each. Traces of N and F were detected, and subsequently confirmed on these surfaces by XPS analysis, in contrast to the hydrophilic SiC surfaces from which a thermally grown oxide had been removed with 10:1 HF. A more detailed analysis of the as-polished SiC surface revealed two F 1s peaks (see Fig. 5a) at 685.6 eV, indicative of Si-F bonding,[69-73] and at 687.3 eV, indicative of C-F, N-F, or SiF_x bonding.[72,73] The N 1s peak was observed at 398.2 eV and is indicative of Si-N bonding.[74,75] The surface concentrations of F and N from the XPS data were estimated to be ≈1 and <1/10 ML, respectively. These values did not change appreciably with subsequent HF processing.

Table IV. Peak-to-peak height ratios for various 6H-SiC surfaces (uncorrected for sensitivity factors).

	$(0001)_{Si}$	$(000\bar{1})_C$	$(11\bar{2}0)$	$(10\bar{1}0)$
Si/C	0.6	0.3	0.6	0.6
O/Si	0.5	1.0	0.4	0.4
O/C	0.3	0.3	0.2	0.3

Significant amounts of noncarbidic C were also detected via XPS on the solvent cleaned, as-polished, and unoxidized $(0001)_{Si}$ 6H-SiC surfaces, as shown in Fig. 4b. This spectrum was fitted to three peaks centered at 282.6, 283.7, and 286.0 eV and indicative of C-Si, C-C, and C-F bonding, respectively[72,73] (see Table I for the Si 2p, O 1s, C 1s, N 1s, and F 1s core level positions). A loss peak at 5-6 eV, indicative of the π-π* transition of graphite-like carbon, was also detected via EELS. The common (1 × 1) diffraction pattern was barely discernible in LEED at E_p = 100 eV; it was only clearly discernible at $E_p \approx 180$ eV. This is indicative of either a thin contamination layer, as suggested by the non-SiC C 1s peaks or to a disordered surface from subsurface defects or damage produced by the polishing treatment.[62]

As can be determined from Fig. 1a and b, the oxygen coverage is lower for the solvent cleaned, as-polished $(0001)_{Si}$ 6H-SiC surface than for the HF dipped, thermally oxidized SiC surface. However, the oxygen surface coverage based on the AES O KLL and XPS O 1s intensities is still ≈1/2 ML. The binding energy of the O 1s core level from the as-polished SiC surface (531.6 eV) is slightly larger than that from a SiC surface which has undergone an oxidation treatment (531.1). These differences in binding energy are most likely due to band bending. A small C-O O 1s peak was also detected from each of the as-polished SiC surfaces after wet chemical processing; however, it was not detected after solvent cleaning.

After dipping in 10:1 HF for 10 min, the as-polished surface remained hydrophobic when rinsed in DI water. Noncarbidic C, as well as F and N were still detected by XPS, AES, and EELS. The HF dip removed some oxygen from the surface, and the XPS Si 2p/O 1s ratio increased (see Table II); however, the coverage by this element remained ≈1/2 ML. The C 1s(Si-C)/C 1s(C-C) ratio decreased after the HF dip indicating that this procedure left more noncarbidic carbon on the surface. Additionally, the adventitious C 1s peak shifted from 283.9 to 283.6 eV (see Table I).

The as-polished $(0001)_{Si}$ 6H-SiC surfaces which had been dipped in 10:1 HF remained hydrophobic when subsequently dipped in various acids and bases. However, they become hydrophilic after extended dip/etches in RCA SC1 or H_2SO_4:H_2O_2 (Piranha etch). Subsequent XPS analysis revealed complete removal of F from those samples which had experienced prolonged immersion in RCA SC1 (see Fig. 5c) which was correlated with the permanent conversion of the surfaces to the hydrophilic state. In some samples, this hydrophilic surface could be again made hydrophobic by boiling in aqua regia (3:1 HCl:HNO_3) for 5–10 min. In these samples, XPS revealed incomplete removal of F by the RCA SC1 or Piranha etch treatment (see Fig. 5b). In addition, the third C 1s peak observed at 286.0 eV

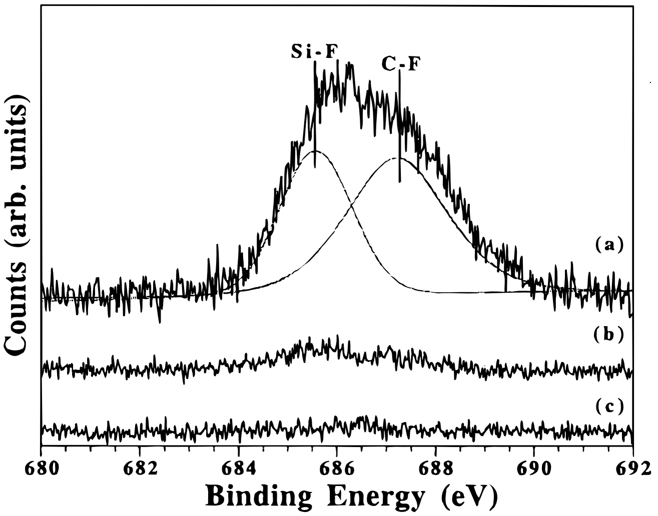

Figure 5. XPS spectra of the F 1s core level from as-polished $(0001)_{Si}$ 6H-SiC, (a) after solvent cleaning, (b) Piranha etch, and (c) RCA SC1.

tracked with the fluorine coverage, suggesting that this surface was terminated with a contamination layer of fluorocarbons. It should also be noted that none of the wet chemical processes employed here were successful in converting hydrophilic SiC surfaces to the hydrophobic state if the samples had previously undergone thermal oxidation and oxide removal with HF.

$(0001)_{Si}$ 6H-SiC surface with Si passivating layer.—The hydrophobic nature of as-received/polished SiC surfaces appeared to be related to a fluorocarbon contamination layer. As such, the use of a Si capping layer was investigated as a more controllable alternative hydrophobic passivation agent for $(0001)_{Si}$ 6H-SiC surfaces. Wafers terminated with an amorphous 200 Å Si passivation layer were observed to be hydrophobic after dipping in various HF and NH_4F solutions. This layer was subsequently thinned by repeated UV/O_3 oxidation and etching in 10:1 HF. The thinnest Si layers maintained a hydrophobic SiC surface to a thickness of ≈20 Å, below which the latter surface became increasingly hydrophilic. However, this effect could be partially related to nonuniformity in the thickness of the Si layer. The wetting characteristics of this Si passivated $(0001)_{Si}$ 6H-SiC surface in other acids and bases after an HF dip were similar to those of Si (see Table III).

Figure 6a shows an AES spectrum from a 20 Å Si/$(0001)_{Si}$ 6H-SiC surface after a 10:1 HF dip. Lower oxygen and non-SiC carbon levels were observed. The Si passivation layer was easily removed in vacuum by annealing at 1100°C for 5 min prior to epitaxy. A Si-rich, O-free, material (see Fig. 6b) having a (3×3) LEED pattern characteristic of a well-ordered surface was obtained. Figure 7 shows an XPS spectrum of the Si 2p core level from the same surface and further illustrates the loss of the Si passivation layer after the 1100°C anneal by the reduction in the Si–Si bonding peak at 99.5 eV. As previously noted,[67] the Si passivation layer also resulted in lower outgassing rates in vacuum due to lower levels of wet chemicals trapped in micropipes in the SiC wafer. Additional advantages and applications of the Si capping layer for the SiC surfaces will be more fully discussed in the following section.

Discussion

Oxidized $(0001)_{Si}$ 6H-SiC.—The significant coverage of oxygen and adventitious carbon for the thermally oxidized $(0001)_{Si}$ 6H-SiC surface relative to (111) and (100)Si after oxide removal using 10:1 HF or other HF/NH_4F solutions and the observation of a hydrophillic (0001) 6H-SiC surface as opposed to a hydrophobic surface illustrates that the chemistry occurring in HF at the SiC and Si surfaces are clearly different. The high levels of oxygen remaining on the SiC surfaces after an HF dip were significant given that concentrated HF is known to etch Si oxide from Si at rates as high as 1000 Å/s. [2] One explanation for the differences in residual oxygen coverage between Si and SiC is that the extra oxygen observed on surfaces of the latter is due to more strongly bound oxygen located at the steps of the SiC surface and which are bonded to both Si and C. If true, one would expect to observe via XPS and AES a difference in the O/Si ratio between on-axis and off-axis $(0001)_{Si}$ 6H-SiC surfaces. This was not observed; the O/Si ratios were essentially the same for both on- and off-axis wafers. Moreover, a maximum in the concentration of oxygen trapped at the SiC steps would still be insufficient to explain the observed 1 ML surface coverage.

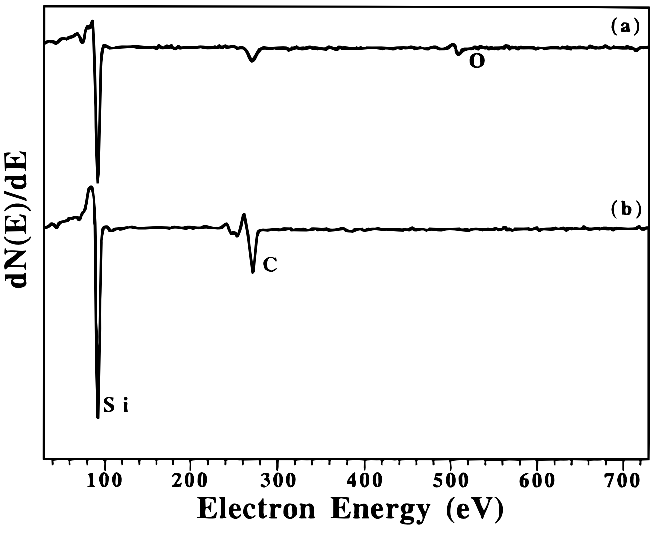

Figure 6. (a) AES spectrum from 20 Å a-Si/$(0001)_{Si}$ 6H-SiC after a 10:1 HF dip, and (b) after thermal desorption of Si passivation layer at 1100°C.

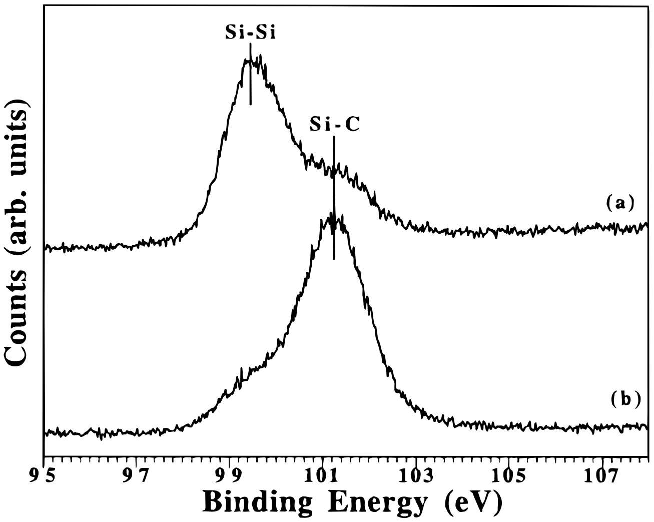

Figure 7. XPS spectra of Si 2p core level from Si passivated $(0001)_{Si}$ 6H-SiC (a) before thermal desorption and (b) after thermal desorption at 1100°C.

Another explanation for the observed differences between Si and SiC is that the residual oxygen is bonded to carbon. Evidence of C-O bonding at the SiC surface is seen in the C 1s and O 1s XPS spectra with peaks at 284.7 and 533.9 eV, respectively. However, XPS shows most of the oxygen to occur at 532.1 eV which is clearly indicative of Si-O or Si-OH bonding. This is further supported by the Si LVV line shape in Fig. 1 which is also indicative of Si-O bonding.

To explain the apparent oxygen or OH termination of oxidized $(0001)_{Si}$ 6H-SiC surfaces after an HF dip, it is necessary to first consider why hydrogen termination of Si is achieved with HF and, second, to account for the polar and ionic nature of (0001) SiC surfaces and HF solutions, respectively. In the case of Si, it was originally suggested that HF processes produced Si-F terminated surfaces due to the relatively large bond strength of Si-F compared to Si-H bonds (6 vs. 3.5 eV, respectively).[41] However, subsequent IR, TPD, and HREELS analysis showed that HF processed Si surfaces were terminated largely with hydrogen with <1/10 ML fluorine coverage.[42,43] Trucks et al.[45] explained the hydrogen termination as being a result of the instability of Si-F bonds due to the polarization of Si-Si backbonds by the strongly heteropolar Si-F bond (see Fig. 8a). Polarization of the Si backbonds leaves these bonds susceptible to the strongly polarized H^+F^- molecule which can then attack the backbond and fluorinate the Si surface atom and hydrogen terminate the nearby atom. This scenario eventually leads to removal of the Si surface atoms by complete fluorination (i.e., SiF_4), and only the Si-H species remain. The stability of the hydrogen-terminated Si surface in HF can be explained by comparison of the electronegativities of Si, H, and F which are 1.9, 2.2, and 4.0, respectively.[76] Due to the similarities in electronegativities of Si and H, the Si-H bond is nonpolar (as compared to Si-F) and is therefore, not attacked by HF. Trucks et al.[45] has additionally shown that the reverse reaction $\text{Si-H} + \text{HF} \rightarrow \text{Si-F} + H_2$ is energetically unfavorable.

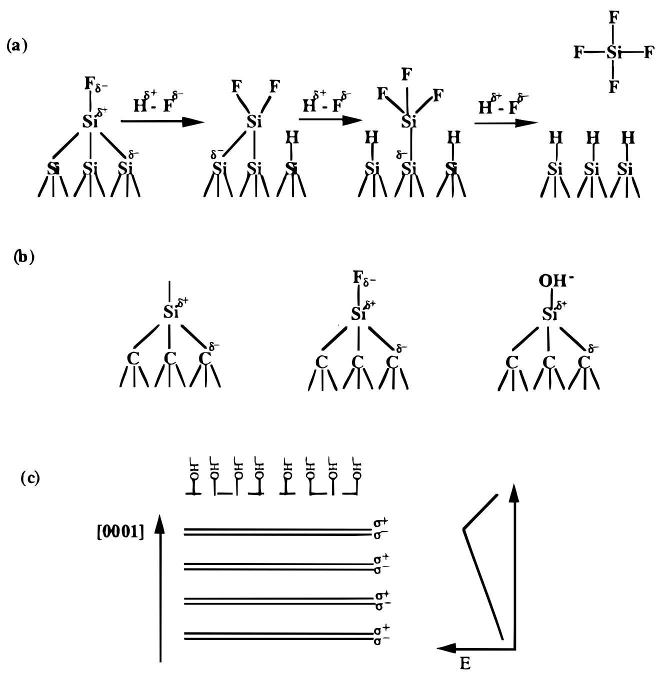

Figure 8. (a) Schematic diagram illustrating mechanism of hydrogen termination of silicon in HF solutions. (b) Schematic diagram illustrating stability of F^- or OH^- termination of SiC in HF solutions rather than H termination. (c) Schematic diagram illustration of crystal potential in SiC.

In the case of $(0001)_{Si}$ SiC surfaces, the underlying Si-C bonds are already polarized (see Fig. 8b) similar to Si-F bonds on Si due to the differences in electronegativity between Si and C (1.9 and 2.6, respectively). The polarization of the Si-C bonds due to the stacking sequence along the [0001] direction in SiC leads to the formation of a large crystal potential/field which must be canceled to stabilize the crystal (see Fig. 8c). [77] In vacuum, cancellation of this field is achieved by desorption of surface atoms which produces a compensating charge that cancels the internal field.[77] However, in an ionic solution such as HF, cancellation of this field can be achieved by simply adsorbing ionic species of opposite polarity/charge. For the $(0001)_{Si}$ SiC surface, this would require the adsorption of negatively charged ions such as OH^- or F^- instead of hydrogen which is what is observed. Termination of the SiC surface with OH^- is also supported by the recent high resolutions EELS (HREELS) studies of Starke et al.[58] which were able to identify the O-H stretch from HF processed (0001) 6H-SiC substrates.

By analogy to Si, [38,47-49] the observation that the fluorine coverage on SiC surfaces after an HF dip depends on the DI rinsing procedure suggests that the fluorine is located at defects sites on the SiC wafer. During the DI rinse, the fluorine is removed from the surface by saturation of these defect sites with OH^-. However, a change in the O/Si ratio with or without DI rinsing was not observed. This suggests that F either substitutes for H in the OH (i.e., Si-OF) instead of bonding directly with Si at the surface (i.e., Si-F) or the fluorine coverage is <1/4 ML such that a change in the O/Si ratio cannot be detected.

The OH^- termination of SiC wafers is important from the viewpoints of both chemical purity and particle contamination during wet chemical processing. The zeta potential of Si surfaces in acids is negative, and the particles in the solution are charged positively.[3,32-34] As a result, particles are electrostatically attracted to Si surfaces in acid processing and, consequently, these processes generally result in higher levels of particle accumulation.[3,32-34] To account for this, Si surfaces have to be cleaned in basic (high pH) solutions for particle removal where both Si surfaces and particles acquire the same negative charge and electrostatically repel one another.[3,32-34] It is expected that SiC surfaces exhibit a zeta potential pH dependence more similar to SiO_2 due to the OH termination. This has been observed in zeta potential measurements on SiC powders.[79-81] The importance of this is that the zeta potential pH dependence of SiO_2 and the SiC particles are very similar.[3,32-34] Therefore, particles should be repelled from SiC surfaces in both acids and bases.

As-polished $(0001)_{Si}$ 6H-SiC surfaces.—The results of the present research have shown that the $(0001)_{Si}$ 6H-SiC surfaces, which are not intentionally oxidized after polishing, are hydrophobic before and after dipping in 10:1 HF. However, only slightly smaller amounts of oxygen were detected on the as-polished surfaces even after an HF dip. As previously shown in Fig. 3, the oxygen surface coverage for both as-polished and oxidized SiC surfaces is five to ten times higher than that for hydrophobic, hydrogen-terminated Si surfaces. Thus, the hydrophobic, as-polished SiC surface observed in this study is not related to the hydrophobic, hydrogen-terminated Si surface, and chemical procedures effective for complete oxide removal from Si are not appropriate for SiC. This is evident simply from the observation that the as-polished $(0001)_{Si}$ 6H-SiC surface is hydrophobic in HNO_3 and H_2SO_4; whereas, the hydrogen-terminated (111)Si surface is not. The most significant difference observed between the oxidized and HF etched and the as-polished unoxidized SiC surfaces is the large amounts of fluorine (≈1–2 ML) on the latter. Thus, hydrophobic nature of polished/unoxidized surfaces is most likely related to fluorine termination (C-F or Si-F) instead of hydrogen termination.

As previously noted, two fluorine peaks were detected by XPS from the as-polished/unoxidized $(0001)_{Si}$ 6H-SiC surface after solvent cleaning, as shown in Fig. 5. The first peak was located at 685.8 eV and attributed to Si-F bonding based on previous examinations of fluorinated Si surfaces.[69-73] The second F 1s peak was detected at 687.5 eV and attributed to $C\text{-}F_x$, $N\text{-}F_x$, or SiF_x bonding.[72,73] Based on the observation of a broad C 1s peak at 286.0 eV (FWHM = 4.1 eV), the authors believe that the second F 1s peak is due to $C\text{-}F_x$ bonding. It is possible that the nitrogen detected by XPS and AES is derived from that incorporated during growth but which has segregated or which has remained at the SiC surface during polishing. Hence, we propose that the nitrogen is primarily bonded to Si (i.e., Si-N).

As a LEED pattern was only observable from as-polished SiC surfaces at beam energies of ≈200 eV, we believe these surfaces to be terminated with a thin (≈5–10 Å) contamination or a disordered/defective layer. This layer is composed primarily of a mixture of C-C, C-F, Si-F bonded species and is directly responsible for the hydrophobic nature of the as-polished SiC surfaces. Complete removal of this layer by oxidation of the C-C and C-F bonds causes the F 1s and C 1s peaks at 685–687 and 286.0 eV, respectively, to disappear and the C-C C 1s peak at 283.6 eV to shift to 283.9 eV indicative of more C-O bonding. After oxidation, this surface is irreversibly hydrophilic. The fact that some hydrophilic as-polished SiC surfaces revert back to being hydrophobic by boiling in aqua regia may be explained by the replacement of C-O bonds with C-H bonds.

Two possible sources of the fluorine detected on the as-polished SiC surfaces are the Fluoroware containers in which the SiC wafers are shipped and the initial polishing/etching procedure. The former are made of natural polypropylene which has a rather high outgassing rate for particles.[82] It has been previously noted[84] by others working on Si, that SiO_2 films stored in these containers for sufficiently long times can apparently become hydrophobic due the large concentrations of hydrophobic entities deposited on them. Discussions with the vendor revealed that they had already investigated this situation and found the polishing/etching procedure to be the only source of contamination. It should also be noted that we have observed similar contamination layers from Si surfaces etched in CF_4 reactive ion etching systems.[84]

In choosing between the two SiC surfaces for further wafer processing, it should be noted that the hydrophobic, as-polished surface has the advantages of minimizing the trapping of wet chemicals in the micropipes and reduced particulate contamination from wet chemical processing. However, all our data indicate that a thin contamination layer is responsible for the hydrophobic nature of this surface. The hydrophilic SiC surface produced by thermal oxidation followed by oxide removal with HF is most likely the more appropriate surface for devices due to the better crystallinity and surface order. Thermal oxidation of the as-polished SiC surfaces not only removes the thin contamination layer but also oxidizes and removes much of the subsurface damage present after polishing.[62]

$(000)_{Si}$ 6H-SiC surfaces with Si passivating layer.—As demonstrated above, the 20-200 Å amorphous Si capping layer behaved similarly in acids and bases to Si (111) surfaces and may be easily removed in situ by annealing in ultrahigh vacuum (UHV) at 1100°C without degradation of the SiC surface. Hence, the a-Si passivation allows the application of knowledge developed from ex situ processing of Si. The hydrophobic surface of this capping layer also resulted in lower outgassing rates in vacuum due to the production of a hydrophobic surface which prevented liquids from being trapped in the micropipes. Moreover, this layer could be deposited during cooling from SiC thin film CVD epitaxy. Rupp et al.[85] have demonstrated the ability to control the surface stoichiometry of SiC epitaxial films by controlling the gas-phase composition in their LPCVD system during cooling. Additional advantages are the protection of the SiC surface from contaminants during processing which could effect the quality of the SiC/SiO_2 interface and the capability for oxidation or nitridation to form the oxide/insulator for MOSFET/MISFET structures. Finally, the Si capping layer can be easily made hydrophilic by immersion in HNO_3 or H_2SO_4.

Conclusions

Removal of a thermal oxide from $(0001)_{Si}$, $(000\bar{1})_C$, $(11\bar{2}0)$, and $(10\bar{1}0)$, 6H-SiC surfaces using 10:1 HF leaves surfaces hydrophilic and terminated primarily with Si-OH and C-O species. In contrast, as-received nonoxidized/as-polished $(0001)_{Si}$ 6H-SiC surfaces were observed to be hydrophobic and terminated by a thin (5–10 Å) disordered contamination layer composed mainly of C-C, C-F, and Si-F species. Removal of this contamination layer using an RCA SC1 or Piranha etch resulted in a hydrophilic surface. The deposition of a 20–200 Å a-Si capping layer produced an alternative passivation layer and a hydrophobic SiC surface. This a-Si passivation layer was easily removed in situ via thermal desorption at 1100°C.

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