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Chemical Vapor Cleaning of 6H-SiC Surfaces

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The techniques (temperature range of study) of *in situ* thermal desorption (500–1100°C) and chemical vapor cleaning (CVC) via exposure to SiH_4 and/or C_2H_4 (750–1100°C) have been investigated for preparing 6H SiC [$(0001)_{Si}$, $(000\bar{1})_C$, $(11\bar{2}0)$, and $(10\bar{1}0)$] surfaces suitable for epitaxial growth of SiC and III-nitride films, and are compared with regard to surface purity, stoichiometry, and structural order. Oxide removal below the detection limits of Auger electron spectroscopy was achieved for all orientations via annealing in 200 L SiH_4 at 850–900°C or ≈200° lower than necessary by thermal desorption. No non-SiC carbon was detected on the surface by X-ray photoelectron spectroscopy. An approximately one-tenth of a monolayer of oxygen coverage and significant quantities of non-SiC carbon were detected for all 6H-SiC surfaces prepared by thermal desorption. In contrast to the predominantly non-SiC carbon-rich surfaces prepared by thermal desorption, the stoichiometry of the SiC surfaces prepared by CVC could be manipulated from Si-rich to C-rich without non-SiC carbon formation by either extending the SiH_4 exposures or by following with C_2H_4 exposure. The latter surfaces also had lower concentrations of both oxygen and non-SiC carbon and increased surface order.

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Preparation of clean, structurally well-ordered surfaces is an important first step in all semiconductor microelectronic fabrication processes.[1-3] Surface cleaning prior to epitaxy is particularly important, as improper removal of surface oxides and organic contaminants has been shown in Si homoepitaxy to result in an increase in the density of stacking faults and dislocations from $<10^4/cm^2$ to $>10^{10}/cm^2$ [4-15] and a concomitant decrease in device performance and yield.[16-22] Studies of the heteroepitaxial growth of Si_xGe_{1-x} alloys on Si have also shown that residual oxide and organic contaminants act as the preferred sites for nucleation of misfit dislocations.[15] The control of defects is of paramount importance in epitaxial films of SiC, as a range of structural and electrical defects are currently limiting the application of this material for several types of high power, and high temperature electronic devices and for substrates for III-N nitride heteroepitaxy.[23-25] Powell *et al.*[26] and Burk and Rowland[27] have shown that surface pretreatments are instrumental in the control of the deposited polytype[26] and the reduction of interfacial Al [27] for growth of SiC by atmospheric chemical vapor deposition or vapor phase epitaxy.

We have shown in a separate study[28,29] that a monolayer of oxygen and the presence of adventitious/surface carbon remain on $(0001)_{Si}$ 6H-SiC surfaces following the use of wet chemical cleaning processes employed in silicon technology. *In situ* removal of these contaminants has been previously achieved via thermal desorption,[30-46] sputtering/ion bombardment,[47-50] electron cyclotron resonance (ECR) H_2 plasma cleaning,[51-54] and annealing in a Si flux.[55-62] Thermal desorption of the monolayer of oxide from SiC occurs at ≈1000°C [34,35,55] which is ≈200°C higher than that required for silicon.[63] However, the loss of the oxide from the SiC surface as a result of the use of this technique has been reported to result in the formation of graphite (C-C) bonded surface structures.[33-36,38,39] This is primarily due to the fact that surface oxides on Si and SiC desorb not as O_2, but as SiO, which depletes the surface of Si for SiC. The employment of an ECR H_2 plasma clean has been shown previously to be useful for removing C-C, C-F, and C-O bonded contaminants; however, the technique is inefficient and/or incomplete with regard to removing Si-O. [51] As others[52-54] have shown in separate studies, atomic H also selectively removes Si from the SiC surface producing a carbon-rich surface. Ion bombardment or sputtering inherently induces surface damage and disorder which must be removed via high temperature annealing. This will also lead to both a loss of silicon and the possibility of graphitic bonding at the surface.[49]

An alternative technique is to anneal a SiC wafer in a flux of material in which the oxide or suboxide of the flux is more volatile than SiO_2. As the atoms of the flux react with the surface oxide, the products desorb and this desorption occurs at significantly lower temperatures than thermal desorption in vacuum. The advantage of this technique is that the oxide may be chemically removed at lower temperatures and without physically bombarding or damaging the surface with high energy ions. Fluxes of Ga, [63] Ge, [64] GeH_4, [65] SiH_4, [66,67] and Si_2H_6 [68] have been used successfully to chemically reduce and remove oxides on silicon surfaces. Kaplan and Parrill[55-57] have demonstrated that evaporated Ga or Si will reduce and remove, respectively, oxides from SiC surfaces at ≈850°C which is ≈100–200°C lower than the temperature necessary to thermally desorb the oxide from this compound.[34,35] The technique of Kaplan[55] has been recently implemented by Fissel *et al.*[62] in solid source molecular beam epitaxy (MBE) growth of SiC on $(0001)_{Si}$ 6H-SiC. Alternatively, the use of a gaseous source of silicon, *e.g.*, SiH_4 or Si_2H_6, would allow this technique to be extended to lower vacuum growth techniques. In the present research, we have demonstrated that using SiH_4 for the preparation of silicon-terminated $(0001)_{Si}$ 6H-SiC surface, achieves similar results to that obtained using evaporated silicon. This chemical vapor cleaning (CVC) procedure is compatible with both gas source MBE and low pressure chemical vapor deposition (LPCVD) growth processes. We have also demonstrated that the sequential use of SiH_4 and C_2H_4 can be used for the preparation of carbon terminated $(000\bar{1})_C$ and nonpolar $(11\bar{2}0)$ and $(10\bar{1}0)$ 6H-SiC surfaces of varying stoichiometry without the presence of non-SiC carbon.

In this paper, we examine and compare two of the most popular methods for preparing SiC surfaces prior to epitaxial growth of SiC or III-nitride materials. Direct comparison with thermal desorption shows the CVC technique to be superior for preparing SiC surfaces free of oxide and carbon-carbon bonded contaminants without the depletion of Si. Further, the CVC technique allows the preparation of surfaces with a full range of stoichiometries and surface structures not achieved by other *in situ* cleaning processes.

Experimental

Integrated surface preparation and analysis system.—All experiments described below were conducted using an integrated, multichambered, ultrahigh vacuum (UHV) configuration containing several completely independent UHV surface preparation and surface characterization systems[69-73] and connected by a transfer line. The experiments described in this paper employed SiC atomic layer epitaxy (ALE), Auger electron spectroscopy (AES), electron energy

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loss spectroscopy (EELS), low energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS), and remote H_2/SiH_4 plasma CVD. Descriptions of these systems are provided below.

Atomic layer epitaxy of SiC films was achieved within a chamber having a base pressure of 3×10^{-10} Torr and equipped with a variety of gas dosers. The sample heating stage in the ALE system consisted of a wound tungsten heating filament positioned close to the back of the sample and mounted on a boron nitride disk.[69] A W/6%Re-W/26%Re thermocouple was employed to measure the temperature of the back side of the wafer. The surface temperatures and heating profiles to 1100°C were easily achieved using a programmable microprocessor and 20 A SCR power supply. The surface or sample temperatures (reported herein) were determined using an infrared pyrometer with a spectral response of 0.8 to 1.1 μm. An emissivity setting of 0.5 was used, and the experimental accuracy for the reported temperatures was estimated to be ±25°C. The gas sources in the ALE system included SiH_4 (99.995%) and C_2H_4 (99.995%). Sample exposure to these gases was obtained using "molecular beam" dosers similar to the design of Bozack *et al.*[73]

The remote plasma CVD system consisted of a metal seal stainless steel vacuum chamber pumped by a turbomolecular pump with a base pressure of 4×10^{-9} Torr. The hydrogen and silane process gases flowed through a quartz tube mounted at the top of the chamber. The sample was located 40 cm below the center of the radio frequency (rf) coil which was wrapped around the quartz tube. Sample heating in the plasma system was achieved using a sample heater similar in design to the one previously described in the ALE system.

XPS experiments were performed within a chamber having a base pressure of 2×10^{-10} Torr and equipped with a dual anode (Mg/Al) X-ray source and a 100 mm hemispherical electron energy analyzer (VG CLAM II). All XPS spectra reported herein were obtained using Al Kα radiation ($h\nu = 1486.6$ eV) at 15 kV and 20 mA emission current. Calibration of the binding energy scale was achieved by periodically taking scans of the Au $4f_{7/2}$ and Cu $2p_{3/2}$ peaks from standards and correcting for the discrepancies in the measured and known values of these two peaks (83.98 and 932.67 eV, respectively.[74]) A combination Gaussian-Lorentzian curve shape with a linear background was found to best represent the data.

The Auger electron spectrometer and the rear view, low energy electron diffraction optics were mounted on a six-way cross off the transfer line and pumped through the transfer line. A 3 keV, 1 mA beam was used in the AES analysis. Each Auger electron spectrum was collected in the undifferentiated mode and numerically differentiated. An 80 eV, 1 mA beam was used in the LEED studies.

Substrate and thin film preparation and analysis.—Various orientations of 6H-SiC substrates supplied by Cree Research, Inc., were examined in this research including on-axis and vicinal (4° off-axis toward $(11\bar{2}0)$) $(0001)_{Si}$, on axis and vicinal $(000\bar{1})_C$, and on-axis $(11\bar{2}0)$, and $(10\bar{1}0)$. The sizes of these substrates ranged from ≈1.5 cm^2 for $(0001)_{Si}$ and $(000\bar{1})_C$ orientations to 5 mm^2 for the $(11\bar{2}0)$ and $(10\bar{1}0)$ samples. All substrates were nitrogen doped n-type with a carrier concentration, N_D–N_A, of $\approx 10^{18}/cm^3$. An ≈1 μm n-type epitaxial layer ($N_d = 5 \times 10^{17}/cm^3$) was deposited on the off axis $(0001)_{Si}$ and $(000\bar{1})_C$ substrates. All wafer surfaces were prepared with a 500–1000 Å dry oxidation which was removed using a 10 min dip in 10:1 HF. The unpolished back side of each SiC wafer was subsequently coated with tungsten using rf sputtering to increase the efficiency of heating these wafers, since they are transparent to the infrared radiation emitted from the tungsten filament heaters. Finally, the SiC wafers were ultrasonically rinsed in trichloroethylene, acetone, and methanol for 5 min each; exposed to the vapor from a 10:1 buffered HF solution for 10 min; and mounted to a 1 in. diam Mo disk using Ta wire.[29] Each wafer and Mo disk assembly was fastened to a ring-shaped Mo sample holder using Ta wire and inserted into the load lock of the transfer line.

Results

$(0001)_{Si}$ 6H-SiC.—Figure 1 shows a series of AES spectra acquired from a vicinal $(0001)_{Si}$ 6H-SiC surface after a 200 langmuir (L) exposure of SiH_4 at 750, 820, and 880°C. Exposure to SiH_4 at 750°C resulted in little change in the amount of surface oxide relative to that observed at room temperature. Removal of the oxygen below the detection limits of both AES and XPS was achieved at temperatures of 880°C and above. This temperature is 100–200°C lower than the temperature at which the oxide was observed to thermally desorb in UHV in this study. Sharp (1 × 1) LEED patterns were obtained; whereas, prior to CVC, (1 × 1) patterns with broad diffraction spots were observed, as shown in Fig. 2a and b. The SiC surfaces prepared in this manner were slightly silicon rich as observed by the ratio of the Si KLL/C KLL AES peak-to-peak heights (pph) and the XPS Si 2p/C 1s intensity ratios of ≈3 and 1.1, respectively (uncorrected for differences in sensitivity factors). Similar results were obtained from on-axis $(0001)_{Si}$ 6H-SiC surfaces.

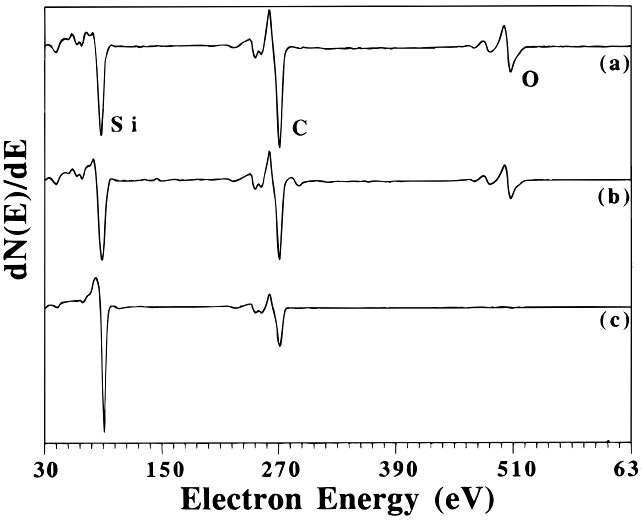

Figure 1. AES scans of a vicinal $(0001)_{Si}$ 6H-SiC surface after 200 L exposure of SiH_4 at (a) 750°C, (b) 820°C, and (c) 880°C.

If a larger SiH_4 exposure was employed, the (3 × 3) surface reconstruction was observed with LEED, as shown in Fig. 2c. In this case, the XPS analysis of the Si 2p core level from this surface revealed two Si 2p peaks at 99.5 and 101.3 eV (see Fig. 3) that are indicative of Si-Si and Si-C bonding, respectively. A detailed analysis of the intensity of these two peaks based on the attenuation of the Si-C Si 2p peak indicated that the (3 × 3) reconstruction corresponds to a silicon coverage of ≈1.5 monolayers, *i.e.*, an incomplete bilayer. Increased SiH_4 exposures did not commonly result in additional reconstructions.

Annealing of the (3 × 3) surface at 1000°C in vacuum resulted in the loss of the excess Si (see Fig. 4) and the reversion to the (1 × 1) LEED pattern. Additional annealing at 1000–1100°C resulted in the $(\sqrt{3} \times \sqrt{3})R30°$ reconstruction, as shown in Fig. 2d. Accounting for the approximately 2:1 difference in AES sensitivity to Si and C, [55] the $(\sqrt{3} \times \sqrt{3})R30°$ surface appears to be the closest to bulk stoichiometry. These results are in excellent agreement with the study of Kaplan and Parrill[55] that also determined that the surface oxide could be removed at 850°C and that (3 × 3) and $(\sqrt{3} \times \sqrt{3})R30°$ reconstructions could be obtained via annealing in a flux of evaporated silicon followed by annealing in UHV. Other previously reported[38,39] reconstructions, including the $(6\sqrt{3} \times 6\sqrt{3})R30°$ and (6 × 6), were not observed with extended annealing within this temperature range.

For comparison purposes, $(\sqrt{3} \times \sqrt{3})R30°$ 6H-SiC $(0001)_{Si}$ surfaces were also prepared by thermal desorption at 1000°C. A comparison of the AES survey spectra acquired from these surfaces is presented in Fig. 5. It is clearly evident that the Si KKL/C KLL pph ratio is <1 for the thermal desorption surface and >1 for the SiH_4 CVC prepared surface. This suggests that the $(\sqrt{3} \times \sqrt{3})R30°$ surface prepared by thermal desorption is more carbon rich (or Si deficient) than the $(\sqrt{3} \times \sqrt{3})R30°$ surface prepared by CVC. This observation was supported by the results of the XPS analysis of the C 1s core

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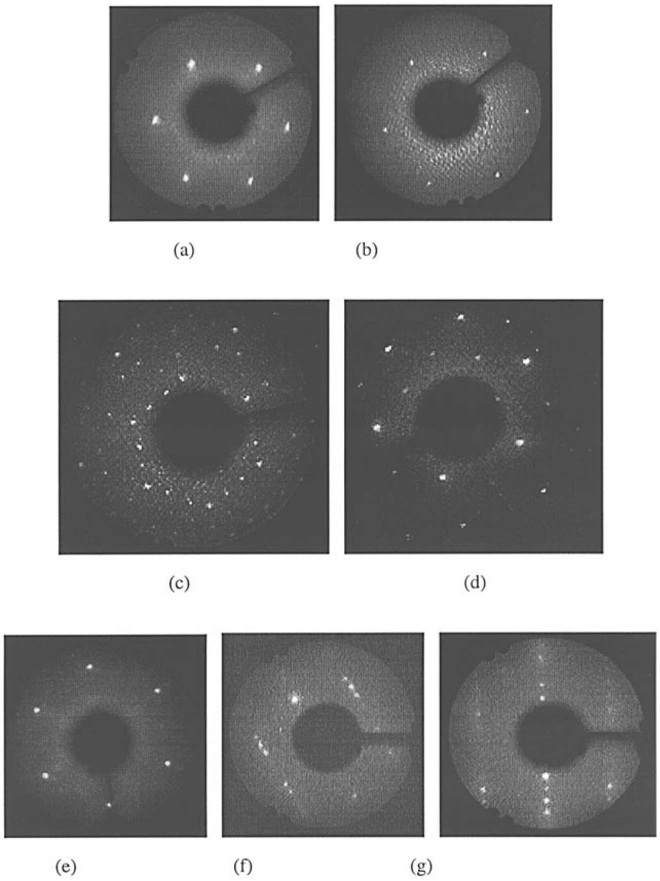

Figure 2. Observed LEED patterns: (a) (1 × 1) after HF dipped $(0001)_{Si}$ 6H-SiC, (b) (1 × 1) $(0001)_{Si}$ 6H-SiC, (c) (3 × 3) $(0001)_{Si}$ 6H-SiC, (d) $(\sqrt{3} \times \sqrt{3})$R30° $(0001)_{Si}$ 6H-SiC, (e) (1 × 1) $(000\bar{1})_C$ 6H-SiC, (f) $(11\bar{2}0)$ 6H-SiC, (g)$(10\bar{1}0)$ 6H-SiC.

level from these two surfaces as shown in Fig. 6. The spectra display a second C-C C 1s peak in the thermal desorption spectrum that is not observed from the CVC surface. It should also be noted that removal of oxygen below the AES and XPS detection limits was never achieved using thermal desorption. Finally, the $(\sqrt{3} \times \sqrt{3})$R30°

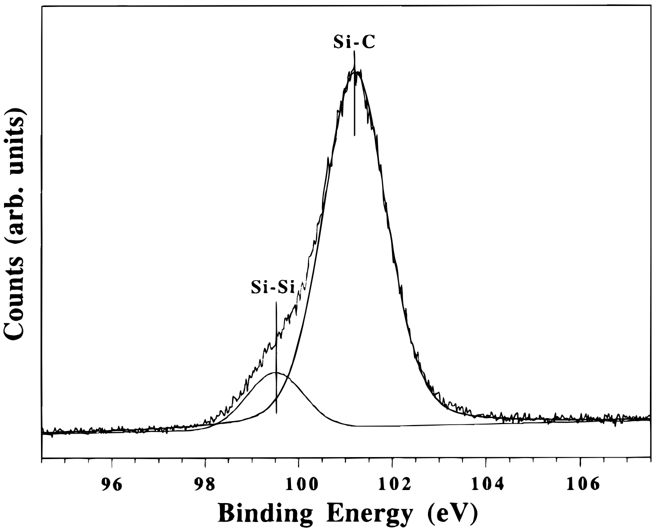

Figure 3. The XPS spectra of the Si 2p core level from a (3 × 3) reconstructed $(0001)_{Si}$ 6H–SiC surface prepared by annealing in 500 L SiH_4 at 1050°C. The deconvolution identifies Si-C and Si-Si related features.

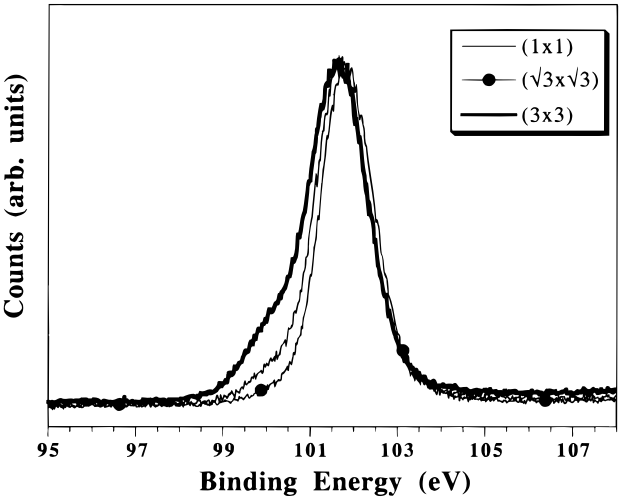

Figure 4. The XPS spectra of the Si 2p core level from (3 × 3), (1 × 1), and $(\sqrt{3} \times \sqrt{3})$R30° reconstructed $(0001)_{Si}$ 6H-SiC surfaces prepared at 1050°C.

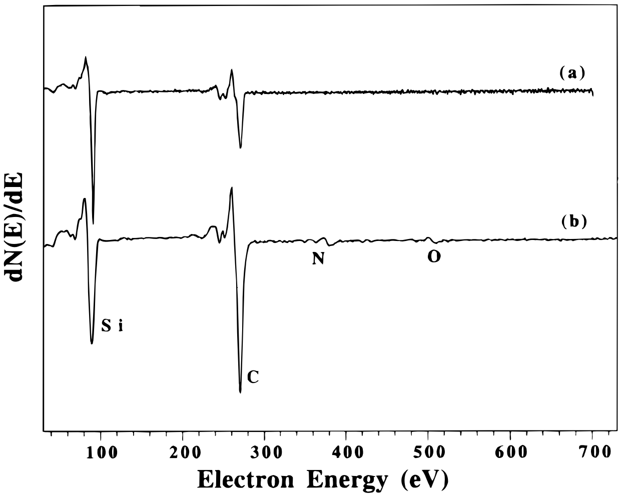

Figure 5. The AES survey spectra from $(\sqrt{3} \times \sqrt{3})$R30° reconstructed $(0001)_{Si}$ 6H-SiC surfaces prepared by (a) SiH_4 CVC, and (b) thermal desorption at 1050°C.

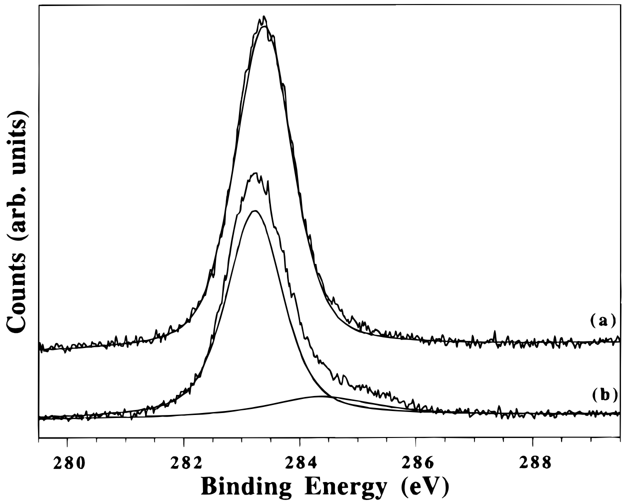

Figure 6. The XPS spectra of the C 1s core level from $(\sqrt{3} \times \sqrt{3})$R30° reconstructed $(0001)_{Si}$ 6H-SiC surfaces prepared by (a) SiH_4 CVC, and (b) thermal desorption at 1050°C. The solid lines show a deconvolution of the C ls core level indicating the formation of C-C bonds.

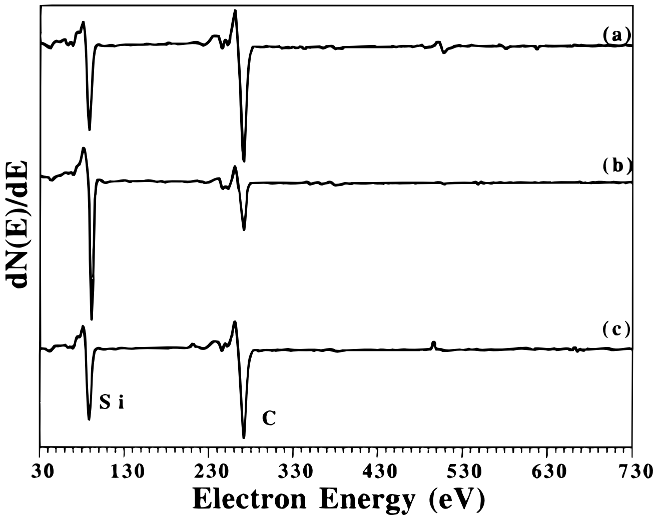

Figure 7. The AES survey spectra from $(000\bar{1})_C$ 6H-SiC surfaces prepared by (a) thermal desorption at 1050°C, (b) SiH_4 CVC at 1050°C, and (c) SiH_4/C_2H_4 CVC at 950°C.

surfaces prepared by CVC displayed sharp dots with very little background; whereas, the $(\sqrt{3} \times \sqrt{3})R30°$ surfaces prepared by thermal desorption showed a very diffuse background.

$(0001)_C$ 6H-SiC.—Oxide removal from $(000\bar{1})_C$ 6H-SiC surfaces via annealing in SiH_4 was observed to exhibit a similar temperature dependence as the $(0001)_{Si}$ surfaces with temperatures >850°C being generally required for complete removal. A (1×1) LEED pattern was observed from $(000\bar{1})_C$ surfaces for all processes investigated, as shown in Fig. 2e. The (3×3) reconstruction was not observed from these CVC cleaned surfaces despite the observations of AES Si KLL/C KLL pph ratios as large as 3–5 and a Si-Si bonding Si 2p peak in the XPS spectra. The $(\sqrt{3} \times \sqrt{3})R30°$ reconstruction was also not observed despite extended annealing (≈1 h) at 1100°C. These observations may be related to the trace amounts of nitrogen consistently observed from the $(000\bar{1})_C$ wafers after either CVC cleaning or thermal desorption, see Fig. 7a. Similar persistent traces of nitrogen have also been observed from these surfaces by Bermudez[61] and attributed to preventing the reconstruction of this surface.

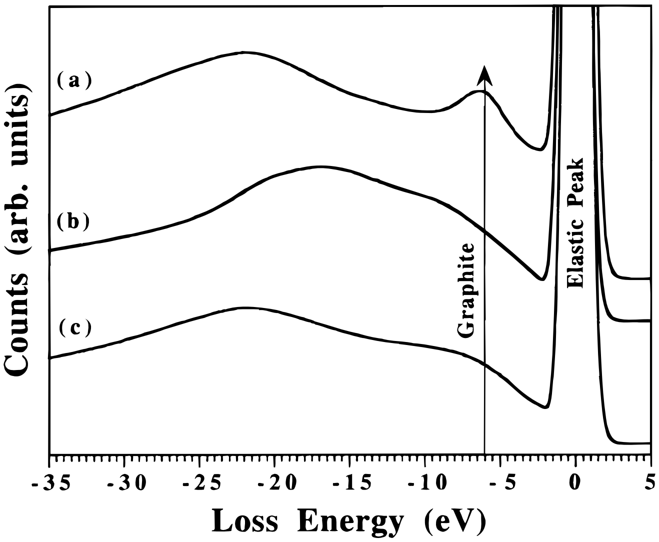

Figure 8. The EELS spectra from $(000\bar{1})_C$ 6H-SiC surfaces after (a) annealing in UHV at 1050°C, (b) 200 L exposure of SiH_4 at 1050°C followed by (c) 200 L exposure of C_2H_4 at 950°C.

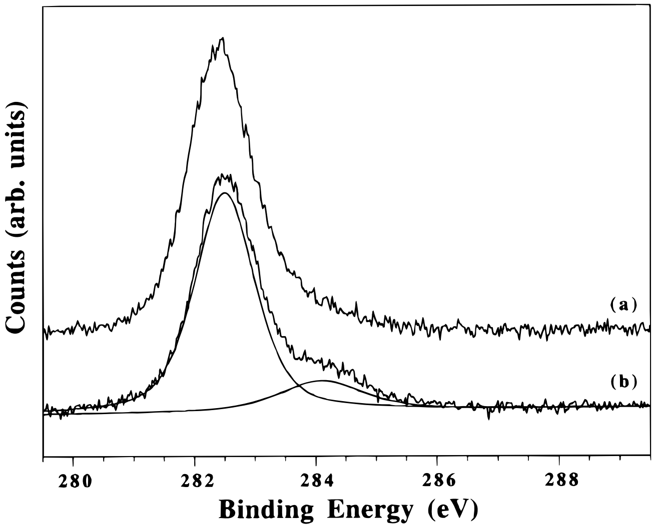

Figure 9. The XPS spectra of the C 1s core level from $(000\bar{1})_C$ 6H-SiC surfaces after (a) 200 L exposure of SiH_4 at 1050°C and (b) annealing in UHV at 1050°C. The solid lines show a deconvolution of the C ls core level indicating the formation of C-C bonds.

Comparisons between SiH_4 CVC and thermal desorption cleaned $(000\bar{1})_C$ surfaces were also made, as shown in Fig. 7a and b. First, similar traces of oxygen were observed from $(0001)_{Si}$ and $(000\bar{1})_C$ surfaces prepared by annealing in UHV at 1050°C for 15 min. Significant amounts of graphitic C-C bonding were also observed to form on the $(000\bar{1})_C$ surface after this anneal, as clearly indicated in the EELS and XPS spectra by the characteristic 6eV loss peak (see Fig. 8a), and a second C 1s peak at 284.5 eV (see Fig. 9a), respectively. A second C 1s XPS peak was also observed from the $(\sqrt{3} \times \sqrt{3})R30°$ reconstructed $(0001)_{Si}$ surfaces prepared via thermal desorption; however, the 6 eV loss peak in EELS was not observed (see Fig. 10). No graphite bonded C was observed in EELS (see Fig. 8b) and no C-C bonding was observed in the C 1s XPS (see Fig. 9b) from a $(000\bar{1})_C$ surface which was exposed to SiH_4. The SiH_4 CVC treatment also converted to SiC the graphite bonded C that formed on the $(000\bar{1})_C$ surfaces after thermal desorption.

An interesting characteristic of the SiH_4 CVC treated $(000\bar{1})_C$ surfaces was their inability to be regraphitized via high temperature annealing in UHV. After annealing at 1100°C for ≈1-2 h, neither a 6 eV loss peak in EELS nor evidence of C-C bonding in the XPS C

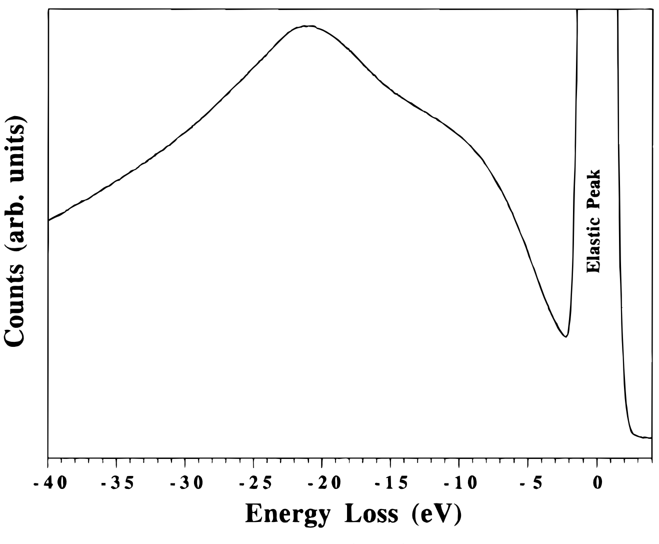

Figure 10. The EELS spectrum from a $(\sqrt{3} \times \sqrt{3})R30°$ reconstructed $(0001)_{Si}$ 6H-SiC surface prepared by annealing in UHV at 1050°C.

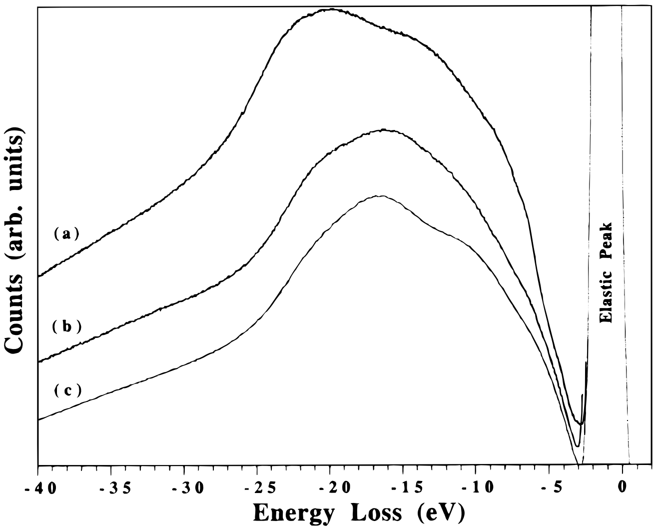

Figure 11. The EELS spectra of (3 × 3), (1 × 1), and (√3 × √3)R30° reconstructed $(0001)_{Si}$ 6H-SiC surfaces prepared via SiH_4 CVC at 1050°C.

1s peak were obtained. A Si KLL/C KLL pph ratio of >1 was also maintained for surfaces annealed at 1100°C. The Si KLL/C KLL ratio of >1 and similarities between the EELS spectra of SiH_4 CVC treated $(0001)_{Si}$ (see Fig. 11) and $(000\bar{1})_C$ (see Fig. 8b) surfaces suggest that despite high temperature annealing, SiH_4 CVC treated $(000\bar{1})_C$ surfaces are still silicon terminated. However, exposure of these surfaces to C_2H_4 resulted in a reduction of the Si KLL/C KLL ratio to <1, as shown in Fig. 7c, suggesting that the surface exhibits carbon termination. Exposure to C_2H_4 at temperatures >950°C resulted in regraphitization of the $(000\bar{1})_C$ surfaces, as shown in Fig. 8c. To reduce the Si KLL/C KLL ratio to <1 and avoid graphite formation, it was found necessary to heat the surfaces to 850°C in C_2H_4 (see Fig. 12). However, at these lower temperatures, sharp (1 × 1) LEED patterns were not obtained.

$(10\bar{1}0)$ and $(11\bar{2}0)$ 6H-SiC.—Oxide removal from $(10\bar{1}0)$ and $(11\bar{2}0)$ 6H-SiC surfaces via the SiH_4 CVC process exhibited a similar temperature dependence to the $(0001)_{Si}$ and $(000\bar{1})_C$ surfaces. Analogous vicinal surfaces were not investigated. The LEED patterns displayed by these formations were observed to intensify and sharpen after the SiH_4 clean, however, reconstructions were not observed as a result of either the clean or the deposition of excess silicon, see Fig. 2f and g. The SiH_4 clean again resulted in Si KLL/C KLL ratios >1 which could not be reduced to <1 by annealing at 1100°C. This ratio was reduced to <1 by annealing in C_2H_4 at 900–1000°C; however, a 6 eV loss peak, characteristic of graphite bonding, was not observed from either surface. A C-C bonding C 1s bonding peak was detected by XPS for large C_2H_4 exposures. Thermal desorption of the oxide from these two surfaces at 1050°C resulted in incomplete thermal desorption and the observation of a C-C bonded C 1s peak in XPS, similar to that observed for the $(0001)_{Si}$ and $(000\bar{1})_C$ surfaces.

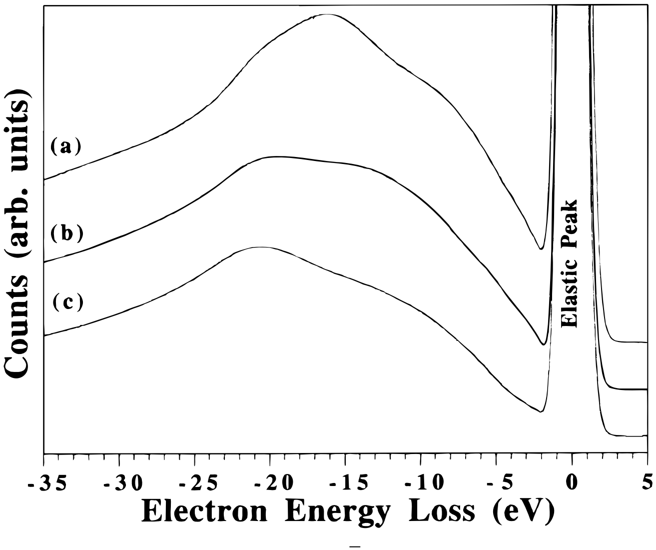

Figure 12. The EELS spectra from $(000\bar{1})_C$ 6H-SiC surfaces after (a) 200 L exposure of SiH_4 at 1000°C, (b) 400 L exposure of C_2H_4 at 850°C, and (c) 800 L exposure of C_2H_4 at 850°C.

Low vacuum CVC/LPCVD clean.—To simulate conditions in lower vacuum processes (*i.e.* CVD or organometallic vapor phase epitaxy), $(0001)_{Si}$ 6H-SiC wafers were exposed to various fluxes of a 1% SiH_4/H_2 mixture in the plasma cleaning system. Oxygen free, (3 × 3) reconstructed $(0001)_{Si}$ 6H-SiC surfaces were attained via annealing the wafers in 70 standard cubic centimeters per minute of the 1% H_2/SiH_4 mixture (10–15 mTorr) at 900°C.

Discussion

$(0001)_{Si}$ 6H-SiC.—The results presented above show that the application of SiH_4 CVC for $(0001)_{Si}$ 6H-SiC surfaces yields results similar to those achieved by the Si evaporation technique of Kaplan and Parrill.[55] This is important, as the method of Kaplan and Parrill is applicable only to SiC in MBE and other high vacuum processes. Our demonstration of CVC for SiC surfaces at both high and low vacuums allows this method to be extended to pre-epitaxial cleaning for low pressure and possibly atmospheric CVD growth processes. Application of SiH_4 CVC to the latter should be particularly advantageous due to the relatively high temperatures used (1100-1400°C) which can lead to loss of Si from the SiC surface.[26-28] Addition of SiH_4 to the gas phase chemistry during the ramp up to temperature in CVD processing should prevent the loss of silicon.

Optimum solid source MBE on $(0001)_{Si}$ 6H-SiC has been reported to occur with the (3 × 3) reconstruction. The structure of the (3 × 3) reconstruction has been recently solved using a combination of scanning tunneling microscopy (STM), conventional LEED, LEED holography, and density functional theory.[75] The deduced structure consists of a Si tetramer on a twisted, complete Si adlayer with clover-like rings on top of bulklike SiC. Our Si 2p XPS spectra indicate an ≈1.5 monolayer coverage of Si for the (3 × 3) reconstructed surface generated via the SiH_4 CVC clean. This result is consistent with the previously reported AES results of Kaplan and Parrill[55] and the solution for the (3 × 3) reconstruction by Starke *et al.*[75] indicating that the (3 × 3) reconstruction obtained by SiH_4 CVC is similar to that prepared by Si evaporation.

As previously noted, the Si KLL/C KLL pph ratio in AES was <1 for the (√3 × √3)R30° surface prepared by thermal desorption; whereas, the SiH_4 CVC (√3 × √3)R30° surface was observed to have a Si KLL/C KLL ratio >1. Further, a C-C bonding C 1s peak not present for the CVC prepared surface was observed in XPS for the thermal desorption prepared (√3 × √3)R30° surface. The C-C bonding, Si/C ratio <1, and poorer quality LEED pattern observed for the (√3 × √3)R30° reconstruction prepared by thermal desorption could be due to the simultaneous formation of higher order reconstructions. The STM analysis by Owman and Martensson[44,45] of (√3 × √3)R30° surfaces produced by thermal desorption also showed the presence of (6 × 6) reconstructions which increased in density with annealing time and temperature. The surface XPS studies of Johansson *et al.*[38,39] have shown that the (6 × 6) reconstruction is accompanied by formation of significant amounts of C-C bonded carbon at the surface. The excess silicon on the (√3 × √3)R30° surface prepared by SiH_4 CVC followed by annealing may stabilize this structure and prevent the simultaneous formation of higher order reconstructions.

Additional proof of the effectiveness of the SiH_4 CVC cleaning procedure is provided by secondary ion mass spectroscopy (SIMS) analysis which did not detect oxygen at the interface between a 6H-SiC wafer which had been cleaned by this procedure and a 3C-SiC

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film epitaxial grown on the wafer.[58] The detection limit for O of AES and XPS is typically 0.1 atom %; that of SIMS is in the ppm range.

$(000\bar{1})_C$ 6H-SiC.—The superiority of the CVC process compared to that of thermal desorption was again proved during the examination of the $(000\bar{1})_C$ surface. The SiH_4 exposure successfully stabilized the $(000\bar{1})_C$ surface against graphite formation, and when followed by a C_2H_4 exposure, allowed the preparation of either silicon- or carbon-rich surfaces without graphite formation. The observation of graphite in EELS from $(000\bar{1})_C$ surfaces prepared via thermal desorption at 1000°C but not from similarly prepared $(0001)_{Si}$ surfaces is consistent with the observations of Muehlhoff *et al.*[32] where carbon segregation for the former surface was observed to occur $\approx$300°C lower than that for the latter face. However, the inability to regraphitize $(000\bar{1})_C$ surfaces via annealing in UHV after a SiH_4 CVC treatment was surprising, given the relative ease with which this occurred when this SiH_4 CVC treated surface was exposed to C_2H_4. These results indicate that the addition of a monolayer of Si somehow stabilizes the $(000\bar{1})_C$ surface against graphitization. However, this surface termination is highly unstable in the presence of excess or free carbon and immediately forms graphite. These results indicate that a silicon-rich surface should be maintained to avoid graphite formation during high temperature cleaning and epilayer growth on $(000\bar{1})_C$ surfaces. Finally, it is noted that C_2H_4 has been used for the preparation of carbon-terminated c(2 × 2) reconstructed (001) 3C-SiC surfaces.[76,77] In our case, it was found necessary to use relatively low temperature C_2H_4 exposures (850°C) to suppress graphite formation. However, surfaces prepared in such a manner exhibited diffuse (1 × 1) LEED patterns suggesting disorder.

As noted above, we were unable to observe any surface reconstructions from the $(000\bar{1})_C$ surface for wafers undergoing either thermal desorption or SiH_4 CVC treatments. This is in contrast to the results of Nakanishi *et al.*[33] and others[60,78,79] who have observed (3 × 3) and $(\sqrt{3} \times \sqrt{3})R30°$ reconstructions in STM and LEED studies of this surface after thermal desorption or annealing in a Si flux in the range of 900–1400°C. Particularly interesting is the observation of a (3 × 3) reconstruction on $(000\bar{1})_C$ by Johansson *et al.*[78] using thermal desorption and by Hoster *et al.*[79] using Si flux annealing. In these cases, (3 × 3) reconstructions were observed for Si/C ratios both <1 and >1, respectively. In the former case, the (3 × 3) reconstruction was observed to occur at 1050°C and degrade at higher temperatures. In the latter case, the (3 × 3) was not observed until 1200°C. In the present study, the authors' inability to observe any of these reconstructions may be related to the trace amounts of nitrogen consistently observed from the $(000\bar{1})_C$ wafers after either CVC cleaning or thermal desorption, as shown in Fig. 7a. However, the authors have observed larger concentrations of nitrogen on $(0001)_{Si}$ surfaces which have displayed (3 × 3) and $(\sqrt{3} \times \sqrt{3})R30°$ reconstructions. In the SiH_4 CVC case, the inability to observe the (3 × 3) reconstruction may actually be due to using too low a temperature. As noted above, Hoster *et al.*[79] reported that the use of temperatures of >1200°C were necessary to form this reconstruction using Si flux annealing. In our case, 1100°C was the maximum temperature investigated. In the case of thermal desorption, the (3 × 3) reconstruction may have been missed by simply annealing past the formation and degradation temperature.

Alternatively, the authors' inability to observe surface reconstructions from the $(000\bar{1})_C$ surface with LEED may be related to the source of the wafers. Nakanishi *et al.*[33] and Hoster *et al.*[79] used the natural faces of Acheson crystals, and Johansson *et al.*[78] used 6H epi layers grown on Si. In our case, the wafers were cut from a SiC ingot and polished to remove sawing damage. The increased surface roughness and or damage induced by the polishing procedure may have prohibited the formation of any reconstructions or the observation of these reconstructions due to the large spot size of the LEED beam. The ability to produce several high-quality reconstructions on the $(0001)_{Si}$ surface indicates that difficulties on the $(000\bar{1})_C$ surface are most likely wafer related and not due to the technique or the substrate orientation.

Despite the inability to produce reconstructions on the $(000\bar{1})_C$ surface, this study clearly shows the utility of using the CVC technique over simple thermal desorption in terms of preparing SiC surfaces of high purity, variable stoichiometries, and surface order. Oxygen removal was incomplete using thermal desorption and not without the formation of C-C bonded entities. By contrast, oxygen removal via SiH_4 CVC was complete and without formation of C-C bonded entities. Further, the surface could be adjusted from Si- to C-rich by appropriate postexposures to C_2H_4.

$(11\bar{2}0)$, and $(10\bar{1}0)$ 6H-SiC.—The $(11\bar{2}0)$, and $(10\bar{1}0)$ orientations of 6H-SiC are nonpolar surfaces with an equal number of carbon and silicon atoms at the outermost surface. It may be expected that these surfaces would exhibit properties intermediate to those of the $(0001)_{Si}$ and $(000\bar{1})_C$ orientations. However, our limited studies revealed that the $(11\bar{2}0)$ and $(10\bar{1}0)$ orientations behave almost exactly like the $(0001)_{Si}$ face of 6H-SiC. These results of the first reported examinations of these orientations emphasize the need for more detailed studies of these surfaces. In particular, a more detailed examination of the electronic structure of the $(11\bar{2}0)$, and $(10\bar{1}0)$ surfaces would be most beneficial, and these results should lead to a better understanding of the polar $(0001)_{Si}$ and $(000\bar{1})_C$ orientations.

Conclusion

Successful CVC procedures based on annealing in fluxes of SiH_4 or C_2H_4 have been demonstrated for $(0001)_{Si}$, $(000\bar{1})_C$, $(11\bar{2}0)$, and $(10\bar{1}0)$ 6H-SiC surfaces. Surfaces prepared via CVC were compared directly to those prepared by thermal desorption; the latter were found to be of higher purity in that they were free of both oxides and C-C bonded carbon/graphite. For the $(0001)_{Si}$ orientation, both (3 × 3) and $(\sqrt{3} \times \sqrt{3})R30°$ reconstructions were achieved using the SiH_4 CVC procedure; whereas, only $(\sqrt{3} \times \sqrt{3})R30°$ reconstructed surfaces of lower quality were achieved via thermal desorption. In contrast, no reconstructions were observed for SiH_4 CVC prepared $(000\bar{1})_C$, $(11\bar{2}0)$, and $(10\bar{1}0)$ 6H-SiC surfaces. The SiH_4 CVC procedure was particularly effective in preventing the formation of graphitic bonded C on $(000\bar{1})_C$ surfaces, as well as the removal of C once formed. The stoichiometry of the $(000\bar{1})_C$, $(11\bar{2}0)$, and $(10\bar{1}0)$ surfaces was easily controlled via exposure to SiH_4 followed by C_2H_4. The procedures demonstrated here are applicable for processes that operate in pressure ranges associated with both MBE and CVD. As such, they should be widely applicable for SiC epitaxial film growth and other interface formation processes.

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