Ex Situ and In Situ Methods for Complete Oxygen and Non-Carbidic Carbon Removal from $(0001)_{Si}$ 6H-SiC Surfaces

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ABSTRACT

Comparisons between the wetting characteristics of $(0001)_{Si}$ 6H-SiC and (111) Si surfaces in various acids and bases were made. It was found that 10:1 HF dipped Si (111) surfaces were hydrophobic where as the $(0001)_{Si}$ 6H-SiC surfaces were hydrophilic. $(0001)_{Si}$ 6H-SiC surfaces capped with a 20Å Si layer, however, were hydrophobic after HF dipping and exhibited outgassing levels on annealing which were several orders of magnitude lower than SiC wafers dipped in HF without the capping layer. Annealing the Si capped $(0001)_{Si}$ 6H-SiC surfaces in UHV at 1100°C for 5 min. was found to be sufficient to thermally desorb the Si capping layer and produce a (3x3) Si rich, oxygen free $(0001)_{Si}$ 6H-SiC surface.

INTRODUCTION

For SiC to succeed as the substrate/semiconductor of choice for high frequency/ high temperature, high power devices and III-N heteroepitaxy, a considerable reduction in defects (line, planar, point, etc.) must be achieved. Following Si technology, where surface cleaning and preparation are critical first step in all processes [1], a continued reduction in defects in SiC should be expected as a result of improved SiC wafer surface cleaning techniques. In Si technology for example, improper removal of surface contamination and oxides prior to Si homoepitaxy has been shown to result in an increase in the density of line and planar defects in epitaxial films from $< 10^4/cm^2$ to $> 10^{10}/cm^2$ [2-5] and an associated drop in device yield [2].

Typically SiC ex situ cleaning consists of solvent degreasing and RCA cleaning with the last step usually a 5-10 min. dip in an HF solution (composition ranging from 0.1-50%) [6-8]. The HF dip is intended to remove any native or intentionally grown (dry or thermal) oxides formed on the SiC surface. For silicon, the HF etch has been found to be beneficial in that it not only removes oxides (SiO_2 or SiO_x) from the surface but also passivates the surface by terminating all the dangling bonds with hydrogen [9-11]. The hydrogen termination inhibits re-oxidation of the silicon surface on removal from the HF solution and produces a hydrophobic surface [11]. For $(0001)_{Si}$ 6H-SiC this has not been found to be the case. Surface analysis by the authors and others (see Figure 1a) has revealed that the SiC surface is still terminated with an ≈ 10 Å layer of carbonaceous material (consisting or C-C, C-O, C=O, and C-H bonding) after HF dipping [7-9]. Thermal desorption of this non-carbidic carbon can be easily achieved by annealing at temperatures as low as 500-700°C. However, unlike Si, approximately 1/2 to 3/4 monolayer of oxide remains at the surface (see Figure 2a-b), and thermal desorption of this oxide in UHV requires temperatures in excess of 1000°C [12]. As shown in Figure 1c, removal of the oxide by this method can result in the formation of some non-carbidic/graphitic carbon at the SiC surface. To combat this, others have followed the pioneering work of Kaplan [13] and employed in situ techniques in which the SiC surface is annealed in a flux of Si (solid or gas source) which allows thermal desorption of the oxide at lower temperatures (< 900°C) while maintaining a Si rich surface [12,14]. In this paper, we report on our efforts to use a Si capping layer to provide both a hydrophobic surface during ex situ processing and a Si rich surface during in situ processing.

EXPERIMENTAL

The vicinal n-type (typically $N_d = 10^{18}/cm^3$) $(0001)_{Si}$ 6H-SiC wafers used in these experiments contained an n type epilayer (typically $N_d = 10^{17}/cm^3$) and 500-1000Å of thermally grown oxide. They were supplied by Cree Research, Inc. The thermal oxide was removed using a 5-10 min. dip

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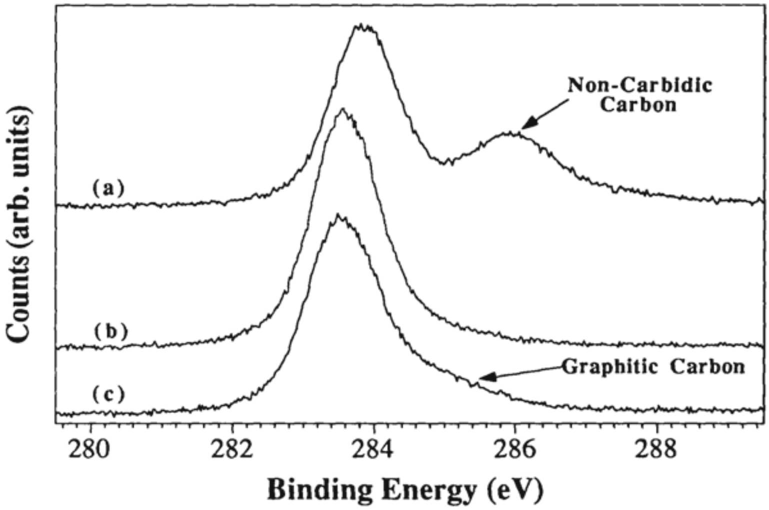

Figure 1. XPS of C 1s from $(0001)_{Si}$ 6H-SiC surface after: (a) 5 min. 10:1 HF dip, (b) after thermal annealing at 800°C, and (c) after annealing at 1200°C in UHV.[8]

in a 10:1 HF dip (CMOS grade, J.T. Baker). Further cleaning of this surface was then investigated by immersion in other acid/base solutions or by reoxidizing the SiC surface using a UV/O_3 treatment followed by a wet chemical treatment. The UV/O_3 treatments described in this study employed a box in which was positioned a high intensity Hg lamp in close proximity to the SiC wafer. The details of this process have been described previously [15]. The wet chemistries examined included 10:1 HF, 10:1 buffered HF (7:1 NH_4F:HF), 40% NH_4F, HCl:HF, and NH_3OH:HF solutions, HNO_3, H_2SO_4, acetic, and lactic acid. Except where noted, after all wet chemical cleans the samples were rinsed in DI water (18 MΩ) and blown dry with N_2 (UHP). All wet chemicals were of CMOS grade purity (J.T. Baker).

The in situ cleaning and the surface analyses of the samples subjected to ex situ and in situ cleaning were conducted in a unique ultra-high vacuum (UHV) system consisting of a 36 ft. long UHV transfer line to which were connected several surface analysis and thin film deposition units. The details of each and the transfer line have been described elsewhere [15]. Surfaces prepared in the above manner were then subsequently mounted to a molybdenum sample holder and loaded into the loadlock for subsequent analysis by AES, XPS, EELS, and LEED. XPS analysis was performed using the Al anode (hυ = 1486.6 eV) at 20 mA and 10kV. AES spectra were obtained using a beam voltage of 3 keV and an emission current of 1 mA. LEED was performed using rear view optics, a beam voltage of approximately 100 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. All sample temperatures quoted here were measured using an optical pyrometer and an emissivity of 0.5.

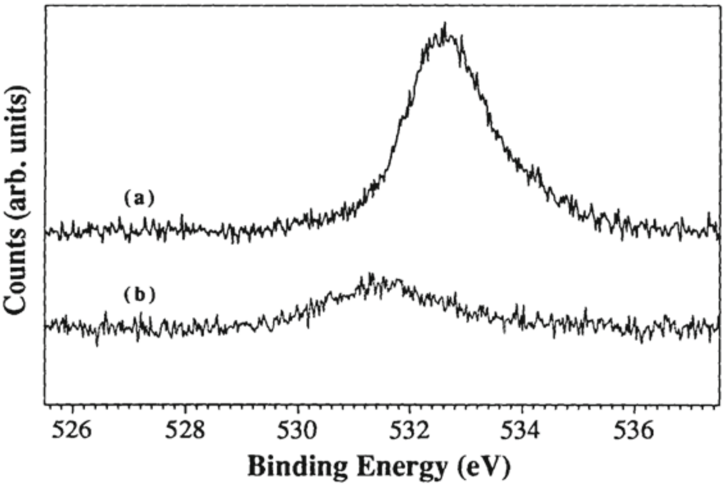

Figure 2. XPS of O 1s from (a) $(0001)_{Si}$ 6H-SiC and (b) Si (111) wafers after dipping in 10:1 HF for 5 min.[12]

RESULTS

Si and SiC wetting experiments. As previously mentioned, oxide removal from (0001) 6H-SiC surfaces using HF leaves a hydrophilic surface containing significant amounts of oxide surface (see Fig. 3a). To determine a wet chemistry which produces a more hydrophobic SiC surface, several $(0001)_{Si}$ 6H-SiC wafers were dipped in HF, NH_4F, NH_3OH, HCl, HNO_3, H_2O_2, H_2SO_4, acetic acid, and lactic acid and the wetting characteristics of these surfaces in these acids and bases and de-ionized water monitored visually. For comparison purposes, Si (111) and Si (100) wafers were also dipped simultaneously in each acid with the SiC wafer. All wafers (Si or SiC) were initially dipped in 10% HF to remove any native oxides from the surfaces before dipping in the acids and bases of interest. For Si, the surfaces remained hydrophobic when dipped in NH_3OH, HCl, or H_2O_2. Dipping the Si wafers in HNO_3 or H_2SO_4 removed the hydrophobic nature of the surface. Dipping Si in the organic acids resulted in a strongly adhering thin film of the acid to the silicon surface which could be removed in DI H_2O leaving a hydrophobic surface. For SiC, all acids and bases wetted the surface and none were found to produce a hydrophobic SiC surface. 10% HF solutions with pH's adjusted from strongly acidic, neutral, and to strongly basic using HCl, NH_4F, and NH_3OH, respectively, were also examined as they have been reported to produce better hydrogen termination of Si (111) surfaces [17,18]. In these experiments, the dipping times were held constant at 10 min. No changes in the wetting characteristics of the $(0001)_{Si}$ SiC surface in HF solutions with the different pH's were found. In an additional experiment, the dipping time was varied from 5 min. to 1 hr.; however, no difference was found. Additionally, neither XPS nor AES indicated a significant change (within AES and XPS experimental accuracy) in the amount of surface oxygen on $(0001)_{Si}$ SiC wafers after dipping in HF solutions of various pH. No differences were observed between on axis and vicinal surfaces, as well.

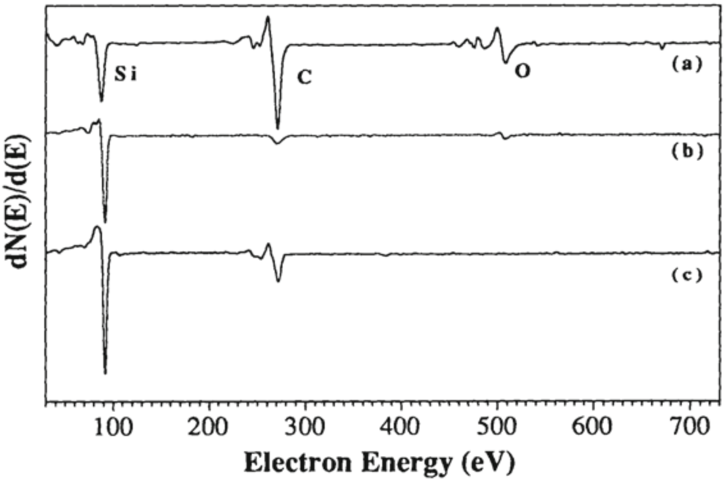

Figure 3. (a) AES of (0001)Si 6H-SiC surface after dipping in 10:1 HF for 5 min., (b) $(0001)_{Si}$ 6H-SiC with a 20Å Si capping layer after dipping in 10:1 HF, 5min., (c) $(0001)_{Si}$ 6H-SiC after hermal desorption of the Si capping layer at 1100°C for 5 min.

Si capping layer. A new technique for in situ oxide removal rapidly gaining acceptance consists of annealing SiC in a flux of silicon at temperatures > 900°C [13,14]. Since wet chemical cleaning of Si was found to more readily produce hydrophobic and cleaner surfaces, the use of a 20Å Si capping layer on $(0001)_{Si}$ 6H-SiC was investigated. The following procedure was used to prepare the Si capping layer. Firstly, the (0001) 6H-SiC wafer was given a 5 min. dip in 10:1 HF, DI rinsed, N_2 blow dried and loaded into vacuum. The 6H-SiC was then degassed and annealed in a SiH_4 flux (10^{-6} Torr) at 950°C for 20 min. in the GSMBE. This produced an oxygen free Si rich (1x1) SiC surface. Next, a Si-Ge electron beam MBE was used to deposit 200Å of Si on the SiC at room temperature in situ. The Si/SiC sample was then given two UV/O_3 treatments followed by dips in 10:1 HF to thin the Si capping layer down to 20Å. After each HF dip, the polished face of the Si/SiC wafer was found to be hydrophobic as with Si wafers. AES of this surface after HF dipping showed only small amounts of oxygen and carbon contamination (see Figure 3b). XPS of this surface after HF exposure showed a Si 2p peak at 99.5 eV with a shoulder at 101.5 eV indicating that the surface consisted of an ≈ 20 Å Si film on top of the SiC. On annealing this surface to desorb the Si capping layer, it was observed that the outgassing from the wafer was several orders of magnitude lower than that typical for other HF dipped SiC wafers (10^{-7} Torr ax vs. 10^{-5} Torr typical). In fact, the outgassing levels were typical for those observed from Si (111) wafers. The reason's for these higher and lower outgassing rates will be discussed later.

Following annealing of the Si/SiC wafer at 1100°C for 5 min., LEED showed a sharp (3x3) reconstructed surface commonly observed for surfaces prepared via annealing in Si fluxes [12]. XPS of this surface, now shows a Si 2p peak located at 101.5 eV with a shoulder at 99.5 eV indicating that the 3x3 surface is due to the presence of a Si bilayer. Continued annealing at 1100°C resulted in further desorption of Si which resulted in first a (1x1) and then a $(\sqrt{3}x\sqrt{3})R30°$ LEED pattern. AES of the (3x3) surface showed no oxygen within the detection limits of AES and

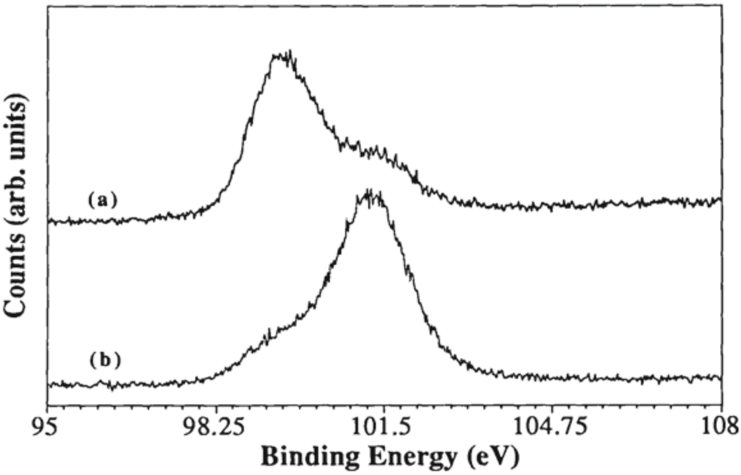

Figure 4. XPS of Si 2p from a $(0001)_{Si}$ 6H-SiC with a 20Å Si capping layer after: (a) 5 min. dip in 10:1 HF, and (b) after thermal desorption of the Si capping layer at 1100°C for 5 min.

a Si/C ratio of 3/1. It should be pointed out that (3x3) surfaces have been previously prepared, removed from vacuum, dipped in HF, and the wetting characteristics observed. In this case, the surfaces were hydrophilic indicating that the Si bilayer is readily removed by the combination of air exposure and HF dipping. As such, 15-20 Å probably represents the optimum thickness for the Si capping layer.

DISCUSSION

One frequently noted problem with (0001) 6H-SiC wafers is the existence of internal micro-pipes. Aside from being potential device killers, the authors have frequently experienced other problems during processing of SiC wafers which can be attributed to the micro-pipes as well. The authors have frequently observed that these entities can harbor HF and H_2O after HF dipping and N_2 drying. Presumably, this is due to capillary action. This conclusion is based primarily on the observation that during annealing/thermal desorption in UHV of HF dipped SiC wafers phenomenally high outgassing rates have been observed (i.e. 10^{-5} Torr). RGA analysis of the background vacuum during thermal annealing of the SiC wafer reveals that HF and H_2O are the two main constituents outgassing from the wafers. As outgassing rates for Si wafers which have experienced an HF dip & N_2 dry are several orders of magnitude lower (10^{-8} to 10^{-7} Torr), we suggest that HF/H_2O trapped in the micro-pipes due to capillary action are the source of the extremely high outgassing. The importance of this observation is that the high outgassing can lead to difficulties in completely removing the oxide from the SiC surface as well as creating a large background of H_2O and HF in the growth system. The H_2O/HF levels can subsequently result in an increase of background oxygen or fluorine in epitaxial films. Owing to the observed change from a hydrophilic to a hydrophobic surface with the addition of the Si capping layer, it is not surprising that lower outgassing rates were observed for the SiC surface with the Si capping layer.

In addition to the oxide removal and the lower outgassing rates, another advantage of the use of the Si capping layer is the potential for its incorporation into already existing processing routes. Potentially, the Si capping layer could be deposited during cooling from SiC thin film CVD epitaxy. Currently, the SiC wafer/film assemblies are cooled in H_2 which produces a carbon rich layer which must be removed by a second processing step of thermal oxidation [9,18]. Unfortunately, high quality SiC CVD epitaxial deposition typically occurs at temperatures higher than the Si melting point (1440°C) and hence results in the deposition of Si droplets instead of a continuous film of Si [19]. However, the authors have initially found that this approach can still eliminate the need for oxidation as the Si droplets can be etched away (15 HNO_3: 2 HF: 5 CH_3COOH) leaving a surface concentration equal (by XPS and AES) to that produced by thermal oxidation and oxide removal by HF. Perhaps, the Si capping layer can best be utilized with 3C-SiC surfaces where epitaxy can occur at lower temperatures.

CONCLUSIONS

The wetting characteristics of (0001) 6H-SiC surfaces in HF and other acids were found to be hydrophilic. Hydrophobic surfaces could be achieved by use of a thin 20 Å Si capping layer. The use of the capping layer also resulted in lower outgassing rates during thermal annealing during in situ processing. Annealing the Si capping layer/SiC wafer at 1100°C for 5 min. resulted in the desorbtion of the excess silicon and a (3x3) reconstructed SiC surface.

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