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Cite as: J. Vac. Sci. Technol. A **33**, 05E105 (2015); https://doi.org/10.1116/1.4921526 Submitted: 18 March 2015 • Accepted: 12 May 2015 • Published Online: 21 May 2015

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Hydrogen desorption from hydrogen fluoride and remote hydrogen plasma cleaned silicon carbide (0001) surfaces

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(Received 18 March 2015; accepted 12 May 2015; published 21 May 2015)

Due to the extreme chemical inertness of silicon carbide (SiC), in-situ thermal desorption is commonly utilized as a means to remove surface contamination prior to initiating critical semiconductor processing steps such as epitaxy, gate dielectric formation, and contact metallization. In-situ thermal desorption and silicon sublimation has also recently become a popular method for epitaxial growth of mono and few layer graphene. Accordingly, numerous thermal desorption experiments of various processed silicon carbide surfaces have been performed, but have ignored the presence of hydrogen, which is ubiquitous throughout semiconductor processing. In this regard, the authors have performed a combined temperature programmed desorption (TPD) and x-ray photoelectron spectroscopy (XPS) investigation of the desorption of molecular hydrogen (H₂) and various other oxygen, carbon, and fluorine related species from ex-situ aqueous hydrogen fluoride (HF) and in-situ remote hydrogen plasma cleaned 6H-SiC (0001) surfaces. Using XPS, the authors observed that temperatures on the order of 700-1000 °C are needed to fully desorb C-H, C-O and Si-O species from these surfaces. However, using TPD, the authors observed H₂ desorption at both lower temperatures (200–550 $^{\circ}$ C) as well as higher temperatures (>700 $^{\circ}$ C). The low temperature H₂ desorption was deconvoluted into multiple desorption states that, based on similarities to H_2 desorption from Si (111), were attributed to silicon mono, di, and trihydride surface species as well as hydrogen trapped by subsurface defects, steps, or dopants. The higher temperature H_2 desorption was similarly attributed to H_2 evolved from surface O-H groups at \sim 750 °C as well as the liberation of H₂ during Si-O desorption at temperatures >800 °C. These results indicate that while ex-situ aqueous HF processed 6H-SiC (0001) surfaces annealed at <700 °C remain terminated by some surface C–O and Si–O bonding, they may still exhibit significant chemical reactivity due to the creation of surface dangling bonds resulting from H₂ desorption from previously undetected silicon hydride and surface hydroxide species. © 2015 American Vacuum Society. [http://dx.doi.org/10.1116/1.4921526]

I. INTRODUCTION

Surface cleaning and preparation is an important consideration for numerous critical semiconductor fabrication processes including epitaxy, gate dielectric formation, and contact metallization.^{1,2} Nonoptimized surface cleaning can lead directly to decreased device performance and yield either through incomplete removal of particulate and other surface contamination that directly prohibit device operation,^{3–6} or through the formation of various point, line, and planar defects that degrade device performance.^{7–11} As the latter still limits the performance of silicon carbide (SiC) in various nuclear radiation detection,¹² and high power, frequency, and temperature device applications,¹³ the continued

development of optimized SiC surface cleaning processes offers the potential to further the advancement of SiC for these applications. Thermal desorption and Si sublimation from SiC surfaces has also recently become a popular means for the epitaxial growth of graphene^{14–17} and graphene nanoribbons.^{18–20} In this regard, numerous studies related to SiC surface cleaning and preparation have been reported and have focused primarily on carbon, oxygen, and fluorine related contamination species.^{21–27}

However, these studies have largely ignored the presence of hydrogen, which is ubiquitous throughout semiconductor processing,²⁸ and has been shown in many cases to have a profound effect on surface/interface reactivity^{29–33} and device performance.^{34,35} Thermally generated atomic hydrogen (H) is also one of the few known etchants for SiC (Refs. 36–38) and has recently proven useful for assisting epitaxial graphene growth on SiC (Refs. 39 and 40) as well as producing quasifree standing graphene on SiC (0001) surfaces via hydrogen intercaltion.^{41–45} Therefore, we have conducted a combined temperature programmed desorption (TPD) and x-ray photoelectron spectroscopy (XPS) investigation of the thermal desorption of molecular hydrogen (H₂) and various

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C, O, and F related surface species from *ex-situ* aqueous hydrogen fluoride (HF) and *in-situ* remote H-plasma cleaned 6H-SiC (0001) surfaces.

While numerous detailed investigations of H₂ desorption from the two elements that individually comprise SiC (i.e., silicon and carbon) have been conducted, relatively few such investigations for SiC surfaces have been reported.^{46–48} For Si (001) and (111) surfaces, multiple H₂ desorption states (β_{1-3}) have been observed at temperatures of ~330, 410, and 510 °C and attributed to H₂ desorption from silicon tri-(SiH₃), di- (SiH₂), and monohydride (SiH) surfaces species, respectively.^{49–54} In contrast, H₂ desorption from C/diamond (001) and (111) surfaces is observed to occur at significantly higher temperatures of 800-1000 °C and is attributed to species.^{55–58} primarily monohydride (C-H) surface Similarly, several studies of hydrogen terminated 3C-SiC (001) and 6H-SiC (0001) surfaces have indirectly observed that annealing at temperatures >700-900 °C results in complete hydrogen desorption.⁵⁹⁻⁶⁵ However, the few studies that have directly investigated H₂ desorption from SiC surfaces have pointed to results intermediate to those for Si and C.^{46–48} Specifically, recent results by the authors have shown that H₂ desorption can occur from atomically clean 6H-SiC (0001) surfaces at both low temperatures (200-500 °C) and high temperatures (650–850 °C).⁴⁷ Based on comparison to the prior Si and C studies, these observations suggested that the differing results for SiC may be due to H₂ desorption from both Si-H and C-H surface species and corresponding differences in surface stoichiometry and polarity.

As many of the prior studies of hydrogen adsorption and desorption kinetics from SiC were performed on surfaces prepared under ultrahigh vacuum (UHV) conditions that were nontypical for most SiC device fabrication,^{46–48} a key open question remains as to how hydrogen is bonded and desorbs from SiC surfaces prepared under non-UHV conditions. As we will show in this study, H₂ desorption from 6H-SiC (0001) surfaces prepared under more practical conditions occurs primarily from Si-H surface species at low temperatures (200–500 °C) and OH and SiO species at temperatures >700 °C.

II. EXPERIMENT

The substrates and sample preparation procedures used in these experiments have been described in detail elsewhere;^{66–68} however, a brief overview is presented herein. Polished *n*-type $(N_d = 10^{17-18}/\text{cm}^3)$ and *p*-type $(N_a = 10^{16-17}\text{cm}^3)$ 6H-SiC(0001) substrates were acquired from Cree, Inc. These substrates were 1 in. diameter, ultrasonically rinsed in acetone and methanol, dipped in a 10:1 buffered HF solution for 10 min, mounted to a molybdenum sample holder using tantalum wire, and immediately loaded into an UHV transfer line⁶⁹ having a base pressure of 9×10^{-10} Torr. This line connected to the XPS system, the TPD/SiC gas source molecular beam epitaxy (GSMBE) system, the remote hydrogen plasma system, and the low energy electron diffraction (LEED) unit utilized in this research. The capabilities of these UHV systems have been detailed elsewhere.⁷⁰ XPS spectra were collected using Al K α radiation (h ν = 1486.6 eV) and a 100 mm radius hemispherical electron energy analyzer (VG CLAM II).⁷¹ LEED utilized an 80 eV, 1 mA beam.⁶⁸ The TPD experiments were conducted in the SiC GSMBE system using a Hiden Analytical 0–200 amu quadrapole mass spectrometer (QMS) fitted inside a differentially pumped chamber having a 0.5 cm diameter opening.⁷² The sample holder/heater was positioned in front of this opening. The opening was located <2.5 cm from the sample surface. The TPD experiments were conducted to a maximum temperature of 1000 °C using a heating rate of 30–60 °C/min while sampling m/e⁻ 2 (H₂) with the QMS.⁴⁷

To ensure that the desorption features detected during TPD originated only from the 6H-SiC sample and not from the sample holder or heater, several additional TPD experiments were conducted. First, the TPD sample heater was always independently degassed prior to any TPD measurements. The degas procedure consisted of loading a separate sample holder containing a blank molybdenum disk and heating to 1000 °C for >5 min. TPD spectra collected from the blank Mo disk after this degassing procedure showed an essentially flat H₂ signal up to 1000 °C and was taken as the baseline H₂ background for the heater in these experiments. To further confirm that the detected H₂ signal was coming from the sample, TPD spectra were collected from both a hydrogenated Si sample and hydrogenated molybdenum disk but with the sample/heater rotated 180° from the QMS chamber. In these experiments, only a small linear rise in H₂ signal was observed, indicating that the amount of H₂ detected in our TPD experiments from nonline-of-sight desorbing H₂ was minimal. Finally, to rule out H₂ desorption from the Mo sample holder and Ta mounting wires, TPD spectra were collected from Si (111) and polycrystalline Mo disks exposed to a remote H-plasma. The spectra collected from these surfaces were compared to those collected from the SiC surfaces to ensure that the desorption features detected were unique to the SiC sample and not the Mo sample holder and tantalum mounting wire. In this regard, it is also important to note that the SiC samples utilized in these experiments were 2.54 cm in diameter whereas the opening to our mass spectrometer chamber was only 0.5 cm in diameter. This geometry helped to minimize the amount of line of sight H₂ desorption from the Mo sample holder and Ta mounting wire that could make it into the mass spectrometer chamber.

Additional spurious effects may also occur in TPD experiments such as electron stimulated desorption (ESD) of H caused by electrons from the mass spectrometer ionizer. While enclosing the mass spectrometer in the differentially pumped chamber may help to minimize this effect, we were not able to independently bias the chamber opening to completely eliminate it. Thus, some ESD effects may be present in our data. However, we feel this effect would only contribute to our background H_2 signal and not significantly alter our conclusions.

To calibrate the hydrogen desorption signal from the 6H-SiC(0001) surfaces, hydrogen desorption from a Si (111)-(7 \times 7)

surface exposed to a saturation dose of atomic hydrogen from a hot Rh filament was also examined.⁴⁷ The saturation surface coverage of hydrogen from a Si (111) surface has been previously determined to be 1.25 monolayer (ML = 7.8 $\times 10^{14}$ /cm²) by Culbertson *et al.*⁷³ By equilibrating the area under the H₂ TPD spectra from a saturated Si (111) surface to 9.75 $\times 10^{14}$ /cm², we were able to calibrate against a known standard the intensity of the desorption peaks from our 6H-SiC(0001) H₂ TPD spectra.

The *ex-situ* aqueous buffered HF cleaned 6H-SiC(0001) surfaces were also given in some cases an additional in-situ remote H-plasma clean. The remote H-plasma exposures were performed at 400 °C and approximately 40 cm downstream from a 13.56 MHz inductively coupled H₂ plasma. The H₂ plasma was operated at 20 W and 15 mTorr. At this pressure, the plasma was largely confined upstream of the sample, but a weak diffuse glow was observed in the sample vicinity. Prior characterization of the H₂ plasma has shown it to consist primarily of H, H^+ , H_2 , and electrons. H_2 to H dissociation efficiencies and H^+/H ratios of 50% and 10^{-4} , respectively, have been previously estimated for these plasma conditions. The energy of the ions in the plasma is low with an average characteristic energy of \sim 223 °C. Further details of the remote H-plasma treatment are described elsewhere.⁷⁴

III. RESULTS AND DISCUSSION

A. Aqueous HF clean—XPS

Figures 1–3 show XPS spectra of the C 1s, O 1s, and Si 2p core levels from a *p*-type 6H-SiC (0001) substrate after *ex-situ* surface oxide removal using a 10:1 buffered HF solution and subsequent *in-situ* thermal annealing at 800–1200 °C. After the *ex-situ* oxide removal, the C 1s spectrum shows two clear peaks [see Fig. 1(a)]. The first at 284.3 eV was attributed to C bonded to Si in the SiC substrate. The higher binding energy peak at 286.4 eV was attributed to adventitious carbon with a mix of C–H and C–O bonding.²⁷ Evidence for the latter was supported by Fig. 2(a), where the O 1s core level was clearly observed.



FIG. 1. (Color online) XPS spectrum of C 1s from a *p*-type 6H-SiC (0001) surface after (a) *ex-situ* oxide removal in 10:1 buffered HF and *in-situ* UHV annealing at (b) 800 °C for 30 min, (c) 1000 °C for 30 min, and (d) 1200 °C for 10 min.



FIG. 2. (Color online) XPS spectrum of O 1s from a *p*-type 6H-SiC (0001) surface after (a) *ex-situ* oxide removal in 10:1 buffered HF and *in-situ* UHV annealing at (b) 800 °C for 30 min, (c) 1000 °C for 30 min, and (d) 1200 °C for 10 min.

We have previously demonstrated this peak can be deconvoluted into two peaks attributable to C–O and Si–O bonding as shown in Fig. 2(a).⁶⁶ Evidence for Si–O bonding was supported by peak fitting of the Si 2p core level that revealed the presence of a small chemically shifted peak at ~103.9 eV relative to the primary Si 2p peak at ~102.3 eV that was attributed to Si–C bonding. Based on the relative intensities of these features, we have previously estimated the oxygen surface coverage for *ex-situ* HF cleaned 6H-SiC (0001) surfaces to be 0.75 ± 0.25 monolayer.⁶⁶ Despite the presence of the adventitious carbon and oxygen over layer, LEED displayed a strong (1 × 1) diffraction pattern.

After annealing at 800 °C for 30 min., the second C 1s peak at 286 eV completely disappeared, but a small peak at \sim 285.5 eV was still needed to completely fit the C 1s spectrum [see Fig. 1(b)]. The peak at 285.5 eV was attributed to C–C bonded clusters that formed during thermal desorption of the adventitious carbon layer. The C 1s and Si 2p peaks attributable to C–Si bonding correspondingly increased in intensity by 40%–50% after the anneal due to the removal of the adventitious carbon surface layer [see Figs. 1(b) and 3(b)]. The C 1s, O 1s, and Si 2p core levels were also all



FIG. 3. (Color online) XPS spectrum of Si 2p from a *p*-type 6H-SiC (0001) surface after (a) *ex-situ* oxide removal in 10:1 buffered HF and *in-situ* UHV annealing at (b) 800 °C for 30 min, (c) 1000 °C for 30 min, and (d) 1200 °C for 10 min.

observed to shift to lower binding energy by approximately 0.3 eV [see Figs. 1–3(b)]. This clearly indicates upward bending of the 6H-SiC (0001) surface valence and conduction bands by ~0.3 eV due to the thermal anneal. This is in contrast to thermal desorption studies of similarly processed *n*-type 6H-SiC (0001) surfaces where no change in bandbending has been reported after annealing at 700–900 °C.²¹ The observed upward band-bending after annealing the *p*-type 6H-SiC (0001) surface suggests that after HF oxide removal there is some slight downward band-bending and the 800 °C anneal produces upward band-bending and a more flat band condition.

Upward band bending has been previously observed for *n*-type 6H-SiC (0001) surfaces and attributed to both surface Si dangling bonds and Si adatom backbonds.^{75,76} Hydrogen termination of 6H-SiC (0001) surfaces and subsequent hydrogen desorption was not found to change the upward band bending.^{47,75} However, removal of Si adatoms via a remote H-plasma was shown to result in downward band bending of $\sim 0.5 \text{ eV}$.⁴⁷ For a *p*-type 6H-SiC (0001) surface, the presence of the same Si adatom state would produce downward band bending followed by upward band bending after removal of the adatom as observed previously by Benesch.⁷⁷ Unfortunately, the stoichiometry and chemistry of the *p*-type 6H-SiC surface after HF oxide removal suggests that the origin of the observed band bending in this case is not related to the presence and removal of Si adatoms. One alternate possibility is the adventitious surface carbon observed in XPS via the C 1s peak at 286.4 eV. The presence of this adventitious carbon could create carbon related adatom states that cause downward band bending on *p*-type surfaces. This would be consistent with the upward band bending observed to occur along with the disappearance of the adventitious surface carbon after annealing at 800 °C.

Annealing at 900 °C for 30 min produced relatively little changes in the XPS spectra. However, annealing at 1000 °C for 30 min resulted in a nearly complete disappearance of the O 1s core level from the 6H-SiC (0001) surface with relatively little changes in the position of the C 1s and Si 2p core levels or the LEED pattern [see Figs. 1-3(c)]. However, the intensity of the Si 2p peak at 103.7 eV previously attributed to Si–O bonding did decrease significantly in correspondence with the decrease in O 1s intensity. The C 1s peak at 285.5 eV also increased by 50% after the 1000 °C anneal.

The XPS spectra did not change significantly after annealing at 1100 °C for 30 min. However, a ($\sqrt{3} \times \sqrt{3}$)R30° LEED pattern did start to appear after annealing at this temperature. The ($\sqrt{3} \times \sqrt{3}$)R30° LEED pattern intensified after annealing at 1200 °C for 10 min, but XPS detected an increased intensity for the O 1s, suggesting an increased level of surface oxygen [see Fig. 2(d)]. The reappearance of oxygen was attributed to the reaction of the 6H-SiC surface with an increased background of H₂O that desorbed from the chamber walls due to heating of the internal UHV chambers surfaces during the high temperature anneal. The increased O 1s intensity also corresponded with a slight increase in intensity for the fitted Si 2p peak at 103.7 eV. In addition to the reappearance of surface oxygen, the C 1s peak detected at $\sim 285.5 \text{ eV}$ and attributed to C–C bonding⁶⁸ was observed to increase further by nearly 2X. The thermal desorption of oxygen at 1000 °C and appearance of C–C bonding at 1200 °C is consistent with the many previous UHV thermal annealing studies of *ex-situ* HF cleaned SiC surfaces that have shown similar behavior.²¹ The C–C bonding observed in XPS has also been shown to be the precursor to the eventual nucleation and growth of graphene on SiC (0001) surfaces via the Si sublimation method.^{22,63}

Attempts at performing TPD on p and n-type 6H-SiC (0001) surfaces given a similar ex-situ aqueous HF clean were, unfortunately, prohibited due to significant outgassing of the SiC substrate on initial heating that degraded the vacuum in the GSMBE from 10^{-10} Torr to $>10^{-5}$ Torr. This high level of outgassing prohibited operation of the QMS during the entire temperature ramp. However, the QMS was utilized to monitor the outgassing species during the initial ramp, which were determined to be primarily H₂O (m/e⁻ = 18) and HF (m/e⁻ 20). The latter was initially surprising as XPS did not detect the F 1s core level that would clearly signal the presence of fluorine related species. However, the 6H-SiC (0001) substrates utilized in this study did contain a high density of micropipe defects.^{78,79} As similar outgassing levels were not observed from similarly processed Si (111) substrates, the high outgassing of H₂O and HF from the 6H-SiC substrates was attributed to some of the 10:1 buffered HF cleaning solution being trapped in the micropipe defects due to capillary effects.

B. Remote H-plasma clean—XPS and TPD

In order to completely outgas the residual HF trapped in micropipes and simultaneously hydrogen passivate any surface dangling bond sites created by the outgassing procedure, the ex-situ aqueous HF processed 6H-SiC (0001) surfaces were given an in-situ remote H-plasma clean at 400 °C. Similar remote H-plasma cleaning conditions have been previously demonstrated to efficiently remove fluorine and carbon contamination and hydrogen terminate Si (111) and (001) surfaces.⁸⁰ As shown in Figs. 4(a) and 4(b), the 1 min remote H-plasma clean did remove some, but not all of the adventitious carbon remaining on an *n*-type 6H-SiC (0001) surface after the *ex-situ* aqueous HF clean. Other than a slight increase in the intensity for the substrate C 1s core level and Si 2p and O 1s core levels, no other significant changes were observed in the XPS spectra after the remote H-plasma exposure. The H₂O and HF outgassing from the 6H-SiC (0001) substrate during temperature ramping was, however, completely eliminated and allowed further H₂ TPD measurements to be performed.

Figure 5 shows the H₂ (m/e⁻ = 2) TPD spectrum acquired from a *n*-type 6H-SiC (0001) substrate that received an *ex-situ* aqueous HF clean followed by an *in-situ* 1 min, remote H-plasma exposure. Two broad desorption bands were observed ranging from 250 to 620 °C and 660 to 920 °C. The broad nature of these two H₂ desorption bands indicates the presence of multiple different desorption states



FIG. 4. (Color online) XPS spectrum of C 1s from a *n*-type 6H-SiC (0001) surface after (a) *ex-situ* oxide removal in 10:1 buffered HF, (b) *in-situ* remote H-plasma exposure for 1 min at 400 °C, and (c) *in-situ* TPD measurements to 950 °C.

and surface species. Unfortunately, this prohibits a detailed kinetic analysis as performed previously for desorption of hydrogen and other species from related surfaces.^{47,81} However, the general range of these two H₂ desorption bands is consistent with prior investigations of H₂ desorption from hydrogenated and oxidized Si (001) and (111) surfaces. As we will show next, the two observed H₂ desorption bands can be easily reproduced utilizing the previously determined kinetics for H₂, SiOH, and SiO desorption from Si surfaces.

In Fig. 6, we focus on the lower temperature H₂ desorption band ranging from 250 to 650 °C. The peak in H₂ desorption occurs at ~525 °C, which is in excellent agreement with numerous investigations of the β_1 H₂ desorption state attributed to surface silicon monohydride (Si-H) species on Si (111) and (001) surfaces. For H₂ desorption from Si (111) surface monohydride species, the kinetics have been previously determined to be second order with an activation energy of 2.6 ± 0.15 eV and pre-exponential of 1–200 cm²/s.⁴⁷ For fully hydrogenated Si (111) and (001) surfaces, lower temperature β_2 and β_3 desorption states have also been observed at ~410 and 330 °C, respectively.^{49–52} These states are consistent with the plateau in H₂ desorption at ~325 °C and the broad



FIG. 5. (Color online) H₂ (m/e⁻=2) TPD spectrum for *n*-type 6H-SiC (0001) after *ex-situ* oxide removal in 10:1 buffered HF and *in-situ* remote H-plasma exposure for 1 min at 400 °C (heating rate = 60 °C/min).



FIG. 6. (Color online) Low temperature portion of H_2 (m/e⁻ = 2) TPD spectrum for *n*-type 6H-SiC (0001) after *ex-situ* oxide removal in 10:1 buffered HF and *in-situ* remote H-plasma exposure. The symbols represent the experimental data and lines approximate fit to the experiment generated using the Polanyi–Wigner desorption rate equation and kinetic parameters previously determined for H_2 desorption from Si (111) and (001) surfaces.

desorption up to ~470 °C in Fig. 6. The β_2 and β_3 states have been previously attributed to H₂ desorption from dihydride (SiH₂) and trihydride (SiH₃) surface species, respectively.⁴⁷ For Si (111) and (001) surfaces, the activation energy for the β_2 and β_3 states have been determined to be 2.0 and 1.35 eV, respectively.^{50,51}

Using the previously determined kinetics for the β_{1-3} H₂ desorption states from Si surfaces, we can utilize the Polanyi–Wigner desorption rate equation⁸² to attempt to reproduce the H₂ TPD spectrum shown in Fig. 6. The Polanyi–Wigner desorption rate equation states that

$$-d\theta/dt = \text{desorption rate} (\text{DR}) = \nu_{\text{d}}\theta^{\text{n}} \exp\left(-\text{E}_{\text{d}}/\text{RT}\right), \tag{1}$$

where θ is the surface coverage, ν_{d} is the desorption jump frequency/pre-exponential, n is the rate order, and E_d is the desorption activation energy. In principal, ν_d , n, and E_d can all be dependent on θ ; however, most analyses assume these parameters to be independent of θ . As we show in Fig. 6, the low temperature H₂ desorption observed from the 6H-SiC (0001) surface can be reasonably well reproduced using the Polanyi-Wigner equation and the previously determined β_{1-3} kinetics for H₂ desorption from Si surfaces. However, to fully reproduce the spectrum, it was found necessary to add two additional desorption states (β_{1b} and β_{2b}) with activation energies slightly reduced from those for the β_1 and β_2 states (see Table I for summary of the full kinetic parameters utilized). This is consistent with a previous analysis of remote H-plasma treated Si (001) surfaces where additional desorption states were also needed to fully reproduce the H₂ TPD spectra from those surfaces.⁸³ In that case, the additional H₂ desorption states were attributed to hydrogen induced subsurface defect states and/or desorption from other surface facets/steps produced by the remote H-plasma exposure. For the 6H-SiC (0001) surfaces investigated in this study, we similarly attribute the additional $\beta_{1,2b}$ states to H₂ desorption from subsurface defects and/or surface steps.

State	Order	$T_{max}(^{\circ}C) \pm 5$	$E_d(eV)\pm 0.05$	$\nu_{\rm d} (\nu_2 {\rm cm}^2 / {\rm s}) (\nu_1 {\rm s}^{-1})$	Coverage (ML) ± 0.02	Assignment
β3	Second	320	1.35	$6.7\times10^{-5\pm1}$	0.14	SiH ₃
β_{2b}	Second	380	2.2	21 ± 10	0.16	Steps/defects
β_2	Second	420	2.35	16 ± 8	0.27	SiH ₂
β_{1b}	Second	470	2.4	2 ± 1	0.43	Steps/defects
β_1	Second	525	2.55	0.4 ± 0.2	0.91	SiH
<i>Y</i> 3	Second	735	3.4	22 ± 10	0.2	SiOH
δ_2	First	800	3.8	$2\pm2 imes10^{16}$	0.27	SiO
δ_3	First	840	3.95	$2\pm2 imes10^{16}$	0.18	SiO
δ_4	First	890	4.15	$2\pm2\times10^{16}$	0.8	SiO

TABLE I. Activation energies and pre-exponentials for H₂ desorption from 6H-SiC (0001) surfaces investigated in this study.

We do acknowledge the possibility that the $\beta_{1,2b}$ states may also originate from hydrogen released during the decomposition and desorption of the adventitious carbon on the SiC surface. Prior investigations of H₂ TPD of Si (111) and (001) surfaces have shown that organic contamination can also create an H₂ desorption signal in this temperature range.^{32,84} In particular, Kawase has shown a peak in CH₃ desorption at 450 °C for organic contaminated Si (001) surfaces.⁸⁴

Based on the ability to reasonably reproduce the observed low temperature H₂ TPD spectrum from 6H-SiC (0001) using primarily H₂ desorption kinetics previously determined for Si (111) and (001) surfaces, we attribute the observed H₂ desorption mainly to silicon mono, di, and trihydride surface species. This is consistent with the (0001) orientation of the 6H-SiC substrate that ideally should be silicon terminated. It also suggests that some of the observed adventitious carbon removed by the remote H-plasma passivates surface Si dangling bonds. As shown in Table I, the total hydrogen coverage desorbed from these low temperature states is ~ 1.9 ML (ML = 1.4×10^{15} atom/cm² for (0001) 6H-SiC). This value is in reasonable agreement with the time-of-flight elastic recoil detection measurements by Fujino et al. that determined a hydrogen coverage of 1.7 ML for a $(\sqrt{3} \times \sqrt{3})$ R30° surface exposed to a saturation exposure of thermally generated atomic hydrogen.⁸⁵

In Fig. 7, we next focus on the high temperature $(650-950 \,^{\circ}\text{C}) \,\text{H}_2$ desorption observed from the 6H-SiC (0001) surface. We show that this spectrum can also be reasonably well reproduced using the kinetics previously determined for H₂ liberated from surface silanol (Si-OH) groups and the sublimation of surface oxides (SiO) from oxidized Si (001) surfaces. Specifically, the shoulder at ~720 °C is consistent with the γ_3 H₂ desorption state previously observed from oxidized Si (001) surfaces and attributed to H₂ desorption from isolated surface SiOH species.⁸¹ As shown in Fig. 7, this shoulder is well reproduced using second order kinetics and the previously determined activation energy and pre-exponential of $3.4 \pm 0.05 \,\text{eV}$ and $22 \pm 10 \,\text{cm}^2/\text{s}.^{81}$

We do note that we have also previously observed H_2 desorption in this same temperature window from carbon rich 6H-SiC (0001) surfaces produced by exposing a Si rich (3 × 3) surface to a longer (5 min) remote H_2 plasma.⁴⁷ In that prior study, the H_2 desorption observed at 650–850 °C

(labeled $\alpha_{1,2}$) was attributed to C-H related surface species based primarily on both the carbon rich stoichiometry and the determined H₂ desorption activation energy of ~4.2 eV that was in close agreement with that for H₂ desorption from diamond (111) surfaces.⁴⁷ Although the desorption activation energies determined for the $\alpha_{1,2}$ state in the prior study and the γ_3 state in this study are significantly different, we can not rule out that some H₂ desorption from the observed γ_3 state is from C-H related surface species.

The higher temperature H_2 desorption observed at 810–900 °C in Fig. 7 is attributed to H_2 liberated during the sublimation of surface SiO species. This is based on prior TPD investigations of oxidized Si surfaces, where H_2 and SiO desorption were observed to occur at identical temperatures and kinetics.⁸³ As shown in Fig. 7, we were able to reproduce the remainder of the H_2 TPD spectrum in Fig. 7 using three desorption states with first order kinetics and activation energies of 3.8, 3.95, and 4.15 eV. The first order kinetics and activation energies for desorption from Si surfaces.^{86–90} However, the H_2 desorption activation energies are slightly higher than those recently determined for H_2 liberated during SiO desorption from Si surfaces.⁸³ This is consistent with the slightly higher temperatures needed to



FIG. 7. (Color online) High temperature portion of H_2 (m/e⁻ = 2) TPD spectrum for *n*-type 6H-SiC (0001) after *ex-situ* oxide removal in 10:1 buffered HF and *in-situ* remote H-plasma exposure. The symbols represent the experimental data and lines approximate fit to the experiment generated using the Polanyi–Wigner desorption rate equation and kinetic parameters previously determined for H₂ desorption from Si (111) and (001) surfaces.

thermally desorb oxygen from SiC surfaces versus Si and the higher energy of the Si–C bond that needs to be broken to liberate surface SiO from SiC versus the lower energy of the Si–Si bond that needs to be broken to liberate SiO from Si.⁶⁸ The multiple SiO desorption/H₂ liberation states (δ_{2-4}) needed to reproduce the high temperature portion of Fig. 7 are attributed to SiO/H₂ desorption from various surface site geometries such as steps and the perimeter versus the field of the surface oxide.^{91–94}

We note that the fitting at the highest temperature portion of Fig. 7 is not well reproduced. This is due to the H_2 TPD measurement being terminated at 900 °C prior to completion of SiO desorption. This was unfortunately forced by the limitation of using a K type chromel-alumel thermocouple in the TPD measurement for greater temperature measurement accuracy over the 200-900 °C range. (For the thermal desorption experiments described in Sec. III A, a type C tungsten-rhenium thermocouple was utilized that allowed operation of the sample heater at temperatures >1000 °C.) As shown in Fig. 2, oxygen is not completely removed until after UHV annealing at 1000 °C for 30 min. Also, XPS measurements after the TPD measurements still showed the presence of significant oxygen surface coverage (not shown). Thus, the H_2 TPD spectra in Figs. 5 and 7 would likely have continued to increase with temperature beyond ~1000 °C if not for the thermocouple limitation.

In Fig. 4(c), we show that after completion of the TPD experiment, the binding energy of the second C 1s core level attributed to the substrate Si–C bonding remains unshifted relative to its position after the *ex-situ* aqueous HF clean, *in-situ* remote H-plasma clean and TPD. This indicates no change in band-bending throughout the experiments for the *n*-type surface due to either desorption of adventitious carbon or hydrogen. However, a small fitted C 1s peak at 285.3 eV remains after the TPD measurements that can be attributed to C–C bonding as in Sec. III A. In this case, the C–C/C–Si C 1s ratio after TPD is roughly the same as after the 900 °C, 30 min anneal in Sec. III A.

As significant outgassing of H_2O and HF prior to the remote H-plasma exposure was attributed to micropipe defects, it is worth considering the possibility that some of the H_2 detected in the TPD measurements also originated from micropipes. In this regard, we are not able to exclude this as a possibility. However, due to the differences in the surface area of the micropipes versus the planar substrate surface, any H_2 desorption from the micropipe surface is believed to represent a small (<1%) contribution to the measured H_2 TPD spectrum.

IV. SUMMARY AND CONCLUSIONS

In summary, XPS and TPD were utilized to investigate desorption of various carbon, oxygen, fluorine, and hydrogen related surface species from *ex-situ* aqueous HF and *in-situ* remote H-plasma processed 6H-SiC (0001) surfaces. Desorption of adventitious carbon was observed to occur at temperatures $< 800 \,^{\circ}$ C while oxygen desorption occurred at $\geq 1000 \,^{\circ}$ C. Molecular hydrogen (H₂) desorption was

observed at both low (200–600 °C) and high (650–900 °C) temperatures. Based on similarities to hydrogen desorption from Si (111) and (001), the low temperature H₂ desorption from the *in-situ* remote H-plasma treated 6H-SiC (0001) surface was attributed primarily to surface silicon mono/di/tri-hydride species. The higher temperature H₂ desorption was similarly attributed to H₂ desorption from surface silanols (SiOH) and H₂ liberated during desorption of SiO.

ACKNOWLEDGMENTS

This work was supported by the ONR under Contracts Nos. N00014-91-J-1410 and N00014-92-J1477, and by the Department of Education through an Electronic Materials Fellowship.

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