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Selective Etching of Silicon in Preference to Germanium and Si_{0.5}Ge_{0.5}

Christopher F. Ahles,[†] Jong Youn Choi,[†] Steven Wolf,[†] and Andrew C. Kummel^{*,‡}

[†]Materials Science and Engineering Program and [‡]Department of Chemistry and Biochemistry, University of California-San Diego, La Jolla, California 92093, United States

Supporting Information

ABSTRACT: The selective etching characteristics of silicon, germanium, and $Si_{0.5}Ge_{0.5}$ subjected to a downstream $H_2/CF_4/Ar$ plasma have been studied using a pair of in situ quartz crystal microbalances (QCMs) and X-ray photoelectron spectroscopy (XPS). At 50 °C and 760 mTorr, Si can be etched in preference to Ge and $Si_{0.5}Ge_{0.5}$, with an essentially infinite Si/Ge etch-rate ratio (ERR), whereas for $Si/Si_{0.5}Ge_{0.5}$, the ERR is infinite at 22 °C and 760 mTorr. XPS data showed that the selectivity is due to the



differential suppression of etching by a ~2 ML thick $C_xH_yF_z$ layer formed by the $H_2/CF_4/Ar$ plasma on Si, Ge, and $Si_{0.5}Ge_{0.5}$. The data are consistent with the less exothermic reaction of fluorine radicals with Ge or $Si_{0.5}Ge_{0.5}$ being strongly suppressed by the $C_xH_yF_z$ layer, whereas, on Si, the $C_xH_yF_z$ layer is not sufficient to completely suppress etching. Replacing H_2 with D_2 in the feed gas resulted in an inverse kinetic isotope effect (IKIE) where the Si and $Si_{0.5}Ge_{0.5}$ etch rates were increased by ~30 times with retention of significant etch selectivity. The use of $D_2/CF_4/Ar$ instead of $H_2/CF_4/Ar$ resulted in less total carbon deposition on Si and $Si_{0.5}Ge_{0.5}$ and gave less Ge enrichment of $Si_{0.5}Ge_{0.5}$. These results are consistent with the selectivity being due to the differential suppression of etching by an angstrom-scale carbon layer.

KEYWORDS: selective etching, plasma etching, isotropic etching, downstream plasma, kinetic isotope effect, inverse kinetic isotope effect, deuterium etching, silicon and germanium etching

1. INTRODUCTION

As complementary metal–oxide–semiconductor (CMOS) technology is scaled to length scales of <10 nm, new metal–oxide–semiconductor field-effect transistor (MOSFET) architectures are required for the gate to maintain control of the device. The ideal architecture for such a device is the gate-allaround (GAA) structure.¹ Whereas MOSFETs in previous device generations were planar structures, the cylindrical geometry of the GAA structure makes highly selective isotropic etching a requirement for device fabrication.

Fluorocarbon-based plasmas deposit a Teflon-like fluorocarbon film on the substrate, and the nature of this fluorocarbon film can affect the etching characteristics of the substrate.^{$2-\epsilon$} The Bosch process, for example, utilizes a fluorocarbon-based plasma to passivate the side walls of trenches against chemical etching during deep reactive-ion etching (DRIE). Bright et al. reported that selective reactive-ion etching (RIE) of Si versus Ge can be achieved using a H₂/CF₄ plasma at 25 mTorr and a plasma power of 200 W.7 The selectivity was found to be extremely sensitive to the H₂ composition of the gas mixture, with the optimal composition being $\sim 37.5\%$ H₂. Bright et al. attributed the selectivity to the formation of a carbonaceous film on both the Si and Ge surfaces that protected the Ge from etching but did not protect the Si surface. Even though RIE was used, so that the energetic ions could be expected to remove the carbonaceous film from Si and Ge, it appears that, if the ion energy were low enough, the carbonaceous layer could remain on the Si and Ge surfaces and give the desired selectivity. In a follow-up investigation, the same group showed that the fluorocarbon layer was actually thicker on Si than on Ge during steady-state etching.⁸ These studies employed RIE, and it is was not shown whether their results would also be applicable under the isotropic etching conditions that are required for GAA structures.

Oehrlein et al.⁹ reported a highly selective isotropic etching of Si in preference to Ge using a SF₆/H₂/CF₄ plasma at 150 mTorr. A selectivity greater than ~10:1 Si/Ge required the addition of CF4 to the SF6/H2 gas mixture, and a selectivity greater than 80:1 Si/Ge could be obtained at a $SF_6/H_2/CF_4$ ratio of 7:13:16. X-ray photoelectron spectroscopy (XPS) showed that the Ge surface was composed primarily of a $GeS_xC_yF_z$ layer in addition to a polymeric carbonaceous film. Shang et al.¹⁰ found that the $GeS_xC_vF_z$ layer left behind by a $SF_6/H_2/CF_4$ plasma was highly resistive and could not be removed by an O_2 plasma. Therefore, the $SF_6/H_2/CF_4$ plasma chemistry is undesirable from a manufacturing standpoint. Previously, high-speed selective etching was demonstrated for Si versus SiGe/Ge using RIE;¹¹ however, RIE is anisotropic, and an isotropic process is needed for the fabrication of nanowires and gate-all-around (GAA) transistors. In addition, thermal etching eliminates the damage often induced by RIE of channel materials. Selective isotropic etching of Si in preference to $Si_{0.8}Ge_{0.2}$ with a Si/SiGe etch-rate ratio (ERR) greater than 100:1 has more recently been accomplished using a $CF_4/O_2/$ N_2 plasma.¹² However, the $CF_4/O_2/N_2$ gas mixture deposits a

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Reactor Chamber Design

Figure 1. Schematic diagram of the reactor chamber.

highly fluorinated C_xF_y layer (of undetermined thickness) that is subsequently difficult to remove from the surface.

In this report, a downstream $H_2/CF_4/Ar$ plasma chemistry is described that etches Si but induces net deposition of a subnanometer-thick carbon layer on Ge and Si_{0.5}Ge_{0.5}. Even for Si_{0.5}Ge_{0.5}, this plasma chemistry has an essentially infinite Si/ SiGe ERR. The high selectivity is obtained by using a low surface temperature, which is enabled by the fact that the surface temperature is independent of the downstream plasma operation. Because a downstream plasma was employed at 180 mTorr or higher pressures and because the quartz crystal microbalance (QCM) samples were not biased, the etching did not have an ion component and was expected to be isotropic, which is ideal for the selective etching of nanowires. XPS studies showed that the plasma produced an approximately two monolayer (2 ML) thick $C_x H_y F_z$ film on both Si and Si_{0.5}Ge_{0.5}; however, the carbonaceous film was sufficient to arrest etching on SiGe but not on Si. The use of a $D_2/CF_4/Ar$ plasma increased the Si and Si_{0.5}Ge_{0.5} etch rates by more than 30 times, deposited less total carbon and eliminated any fluorocarbon deposition, and gave less Ge enrichment of SiGe than did a $H_2/$ CF₄/Ar plasma.

2. EXPERIMENTAL SECTION

A custom reactor chamber was employed for the etching experiments (schematic shown in Figure 1). To protect the QCM feedthroughs and electronics from the corrosive gases generated by the plasma, two custom Teflon sleeves were fitted around the QCMs that allowed a purge of argon gas (5 sccm Ar) to be flowed through each of the nipples to the chamber. The base pressure of the chamber was ~ 20 mTorr, and the chamber was pumped with a scroll pump. During an etching experiment, two 5 sccm Ar purges (one through each nipple) were first established, which brought the chamber pressure to 130 mTorr. Subsequently, the desired gas mixture was flowed into the chamber through a 13-mm-diameter sapphire tube, and the chamber pressure was controlled using the throttle valves. After a steady flow/ pressure had been established, the water-cooled QCMs were heated to the desired temperature. After stabilization of the QCM thickness readings to ± 0.01 Å/s, the plasma was lit. The plasma was generated using a McCarroll cavity powered by a 2.45 GHz microwave plasma generator and initiated by an electric discharge from a Tesla coil.

Before each etching experiment, the samples were exposed to a $H_2/NF_3/Ar$ plasma to remove any native oxide as well as residual fluorocarbon deposited from previous experiments.^{13,14} The samples were etched until >1 nm of material had been removed. The typical etching parameters used in the cleaning step were as follows: $H_2/NF_3/Ar/purge = 100:30:300:3$ sccm, P = 180 mTorr, T = 50 °C, power =



Si and Ge Etch Rates versus Pressure and CF₄:H₂

Figure 2. Si and Ge etch rates versus (a) reaction pressure, (b) CF₄ flow rate at 180 mTorr, and (c) CF₄ flow rate at 760 mTorr. The reaction conditions were as follows: (a) $H_2/CF_4/Ar/purge = 100:120:40:5$ sccm, P = X mTorr, T = 50 °C, power = 40 W; (b) $H_2/CF_4/Ar/purge = 100:X:40:5$ sccm, P = 180 mTorr, T = 50 °C, power = 40 W; (c) $H_2/CF_4/Ar/purge = 100:X:40:5$ sccm, P = 760 mTorr, T = 50 °C, power = 40 W. The data points in panels a and b are the results of single experiments, whereas the data points in panel c are the averages of three separate experiments performed under identical conditions. The error bars in panel c represent the standard deviations of the three experiments.

40 W. The base pressure of the chamber with two 3 sccm Ar purges was 100 mTorr. XPS measurements on a nominally Si_{0.5}Ge_{0.5} sample before the H₂/NF₃/Ar plasma clean as well as on another nominally Si_{0.5}Ge_{0.5} sample after the H₂/NF₃/Ar plasma clean showed that the cleaning step did not enrich the Si_{0.5}Ge_{0.5} sample in either silicon or germanium (Figure S5). The Si_{0.5}Ge_{0.5} sample that had not been exposed to the H₂/NF₃/Ar plasma clean contained 10% carbon on the surface, whereas the sample that had been exposed to the H₂/NF₃/Ar plasma clean contained 12% carbon. Therefore, in analyzing the amount of carbon deposited by the H₂/CF₄/Ar plasma, we assumed that 10–12% carbon corresponded to the amount of adventitious carbon present on our samples and that any additional carbon was deposited by the H₂/CF₄/Ar plasma.

The XPS experiments were performed ex situ using a monochromatic Al K α source (1486.7 eV) on an XM 1000 MkII/SPHERA spectrometer from Omicron Nanotechnology. All spectra were measured with constant analyzer energy (CAE) with a pass energy of 50 eV and a step width of 0.1 eV. The takeoff angle between the analyzer axis and the sample normal was 60°, and the analyzer acceptance angle was 7°. Peak-shape analysis was performed with the CASA XPS v.2.3 program and utilized a Shirley background subtraction.

The QCMs used in this study were purchased from Colnatec (Tempe sensor head and Eon film-thickness controller) and used RCcut Inficon (TAN06RCG, Phillip Technologies) quartz crystals with a resonance frequency of 6 MHz. The Si and SiGe were sputtered onto the quartz crystals using an AJA radio-frequency (RF) sputter deposition tool, and the Ge was sputtered using an AJA direct-current (dc) sputter deposition tool. For the SiGe film, a Si_{0.5}Ge_{0.5} target was employed. All of the gases were purchased and used without further purification: deuterium (99.9%, Sigma-Aldrich), hydrogen (99.999%, Praxair), tetrafluoromethane (99.999%, Praxair), argon (99.999%, Praxair), and nitrogen trifluoride (99.999%, Advanced Specialty Gases).

3. RESULTS AND DISCUSSION

3.1. Silicon versus Germanium. Figure 2 shows the effects of pressure and CF₄/H₂ ratio on the Si and Ge etch rates. The $H_2/CF_4/Ar$ plasma can etch the surfaces (reduce the mass) or deposit a carbonaceous film (increase the mass). The data were recorded under near-steady-state conditions. The etch rates (ERs) plotted in Figure 2a,b are the results of single experiments, whereas each of the ERs plotted in Figure 2c represents the average of three separate experiments performed under nearly identical conditions. The error bars in Figure 2c correspond to the standard deviations of the etch rates recorded from three experiments performed under nearly identical conditions. It is believed that the major source of variation in the measurements of the ERs was the variability in the sample surface roughness from experiment to experiment. For this reason, the standard deviation was chosen as a metric for the reproducibility of the measured ERs. Because the results in Figure 2a,b are from single experiments, no standard deviations can be calculated for them.

As shown in Figure 2a, the Ge etch rate was ~ 0 nm/min at all of the pressures studied. The Si etch rate, however, decreased with increasing pressure. These results are consistent





Figure 3. (a) Freshly loaded samples of Si and Ge were first subjected to a NF₃/H₂/Ar plasma. Conditions: NF₃/H₂/Ar = 20:135:100 sccm, Ar purge = 5 sccm, P = 180 mTorr, T = 50 °C, power = 40 W. (b) A H₂/CF₄/Ar plasma etch was performed with the CF₄ flow rate increased at various time intervals. Conditions: H₂/CF₄/Ar = 100:(30, 60, 120, 180):40 sccm, Ar purge = 5 sccm, P = 180 mTorr, T = 50 °C, power = 40 W. (c) Subsequent exposure of the samples to a NF₃/H₂/Ar plasma showed that the Ge sample was protected from any etching for the first 10 min of the experiments, during which time ~110 nm of Si was removed. Conditions: NF₃/H₂/Ar = 25:100:100 sccm, Ar purge = 5 sccm, P = 180 mTorr, T = 50 °C, power = 40 W.



Figure 4. Si and Si_{0.5}Ge_{0.5} etch rates. (a,b) Etch rates as functions of temperature for (a) Si and (b) Si_{0.5}Ge_{0.5}. Reaction conditions: H₂/CF₄/Ar/ purge = 100:18:40:5 sccm, *P* = 760 mTorr, *T* = X °C, power = 40 W. (c) Arrhenius plot showing that effective activation energies for the etching of Si and Si_{0.5}Ge_{0.5} of 0.54 and 1.47 eV, respectively. The Si_{0.5}Ge_{0.5} etch rate at 22 °C in panel b was negative, so this data point was not used in this plot. (d,e) Etch rates versus pressure for (d) Si and (e) Si_{0.5}Ge_{0.5}. Reaction conditions: H₂/CF₄/Ar/purge = 100:18:40:5 sccm, *P* = *X* mTorr, *T* = 30 °C, power = 40 W. Note that all data points in this figure represent the averages of three experiments performed under nearly identical conditions. The error bars represent the standard deviations of the three experiments.

with a decrease in the radical concentration at higher pressure due to faster recombination. As shown in Figure 2b, the etch rate of Si was highly sensitive to the CF_4/H_2 ratio. The Ge etch rate, however, was very low over the range of CF_4/H_2 ratios studied. The etch rates of Si and Ge should largely depend on the fluxes of F radicals and carbon radicals $[C_xH_yF_z(g)]$ onto the surfaces. The F radicals react with the surface to produce volatile etch products (SiF₄ and GeF₄), whereas the $C_xH_yF_z(g)$ radicals are expected to react with the surface and form surface-bound $*C_xH_yF_z$ species that inhibit the approach of the F



Figure 5. Si and Si_{0.5}Ge_{0.5} post-etch XPS analysis. (a,b) Raw QCM data for the etching of Si and Si_{0.5}Ge_{0.5} subjected to (a) a $H_2/CF_4/Ar$ plasma and (b) a $D_2/CF_4/Ar$ plasma. Reaction conditions: H_2 (D_2)/ CF_4/Ar /purge = 100:18:40:5 sccm, P = 760 mTorr, T = 30 °C, power = 40 W. (c–f) XPS compositional analysis of Si and Si_{0.5}Ge_{0.5} after etching with (c,d) a $H_2/CF_4/Ar$ plasma versus (e,f) a $D_2/CF_4/Ar$ plasma.

radicals to the surface Si and Ge atoms.¹⁵ The CF₄/H₂ ratio affects both of these processes: As the CF₄/H₂ ratio was increased, there was sufficient $C_xH_yF_z$ to slow the etching of Si. Because the surface-bound $C_xH_yF_z$ species formed on both the Si and Ge surfaces, the selectivity can be attributed to more efficient passivation of the surface by Ge*C_xH_yF_z species than by Si*C_xH_yF_z species.

Further experiments showed that there was only moderate Si/Ge etch selectivity when the samples were subjected to a nonpolymerizing F-based plasma etch consisting of H₂, NF₃, and Ar gases (Figure 3). Figure 3a shows the raw QCM data for Si and Ge subjected to a H₂/NF₃/Ar plasma. It can be seen that, in the absence of a carbonaceous passivation layer, the Si/ Ge ERR was ~2.3. The Si/Ge selectivity increased dramatically, however, when the samples were subjected first to a H₂/CF₄/ Ar plasma and then to a H₂/NF₃/Ar plasma (Figures 3b and 3c). This enhancement of the Si/Ge selectivity after the samples had been subjected to a H₂/CF₄/Ar plasma further demonstrates that the selectivity was due to differential passivation by a C,H,F, film. This difference is consistent with the difference in the Si–F bond strength $(5.86 \text{ eV})^{16}$ and the Ge-F bond strength (4.99 eV).¹⁶ The stronger Si-F bond means that there is a larger driving force for the reaction of atomic F with surface species to form SiF₄ compared to GeF₄, which are the expected etch products of Si and Ge, respectively.

To further optimize the Si/Ge selectivity, the CF_4/H_2 ratio was varied at high pressure (760 mTorr) because the highest Si/Ge selectivity was observed at this pressure (net deposition on Ge). Figure 2c shows the effect of changing the CF_4/H_2 ratio at high pressure (760 mTorr): No etching of Ge was observed (only deposition). Therefore, an infinite Si/Ge ERR can be achieved as long as the CF_4 flow rate is greater than 0 sccm.

3.2. Silicon versus Si_{0.5}Ge_{0.5}. The optimized pressure (760 mTorr) and $H_2/CF_4/Ar$ gas flow ratio (100:18:40) for selective

etching of Si in preference to Ge were applied to the etching of Si in comparison with Si_{0.5}Ge_{0.5}, and the temperature was varied. Figure 4a,b shows the effects of temperature on the Si and Si_{0.5}Ge_{0.5} etch rates. The data were recorded under near-steady-state conditions. The Si and Si_{0.5}Ge_{0.5} etch rates increased exponentially with increasing temperature (Figure 4a,b). From an Arrhenius plot, the effective activation energies for the etching of Si and Si_{0.5}Ge_{0.5} were determined to be 0.54 and 1.47 eV, respectively (Figure 4c). The higher effective activation energy for etching Si_{0.5}Ge_{0.5} than Si suggests that high selectivity should be achievable at low temperature. This is verified in Figure 3b: At 22 °C, no etching of Si_{0.5}Ge_{0.5} was observed, only deposition.

The effects of pressure at low temperature (30 °C) are shown in Figure 4d. It can be seen that the Si etch rate decreased with increasing pressure at 30 °C. A similar, more modest, effect was observed in the experiment on Si versus Ge etching at higher CF_4 flow rate and higher temperature (50 °C; Figure 2a). These results are consistent with a decrease in the concentration of free radicals due to faster gas-phase recombination at higher pressure.

3.3. Kinetic Isotope Effect. To gain insight into the mechanism of the etching of Si and SiGe by a $H_2/CF_4/Ar$ plasma, H_2 was replaced by D_2 in the feed gas. Bonds to deuterium are expected to have a smaller vibrational frequency than bonds to hydrogen, resulting in a lower zero-point energy for deuterium bonds compared to hydrogen bonds and a higher activation energy for the breaking of the deuterium bonds. Chemical reactions in which the rate-limiting step involves the breaking of a bond to hydrogen tend to be slower when hydrogen is replaced by deuterium.¹⁷ The magnitude of the kinetic isotope effect is defined by the ratio k_H/k_D , where k_H and k_D are the rate constants for the chemical reaction with H and D, respectively; the ratio rarely exceeds a factor of 10.^{17,18} For an inverse kinetic isotope effect, $k_H/k_D < 1$.



Figure 6. Si and Si_{0.5}Ge_{0.5} post-etch XPS chemical-shift analysis. (a) XPS spectra of the C 1s, F 1s, and Si 2p orbitals on the Si sample after exposure to a $H_2/CF_4/Ar$ plasma (black) and a $D_2/CF_4/Ar$ plasma (blue). (b) XPS spectra of the C 1s, F 1s, Si 2p and Ge 3d orbitals on the Si_{0.5}Ge_{0.5} sample after exposure to a $H_2/CF_4/Ar$ plasma (black) and a $D_2/CF_4/Ar$ plasma (blue).

Figure 5 shows plots of the thickness versus time for Si and $Si_{0.5}Ge_{0.5}$ subjected to a $H_2/CF_4/Ar$ plasma (Figure 5a) and a $D_2/CF_4/Ar$ plasma (Figure 5b) under identical conditions: H_2 $(D_2)/CF_4/Ar/purge = 100:18:40:5 \text{ sccm}, P = 760 \text{ mTorr}, T =$ 30 $^{\circ}$ C, power = 40 W. In these experiments, the average Si and $Si_{0.5}Ge_{0.5}$ etch rates were found to be 0.9 ± 0.1 and (3 ± 4) × 10^{-2} nm/min respectively, where the average etch rates and standard deviations of four experiments were used to estimate the errors of the measurements. The error in the Si_{0.5}Ge_{0.5} ER is larger than the Si_{0.5}Ge_{0.5} ER itself because the SiGe ER was very low under these conditions. When D₂/CF₄/Ar was employed (Figure 5b), the Si etch rate increased to 37 ± 7 nm/min, and the Si_{0.5}Ge_{0.5} etch rate increased to 3 ± 2 nm/min (ERs averaged over three experiments). This corresponds to a D₂ enhancement of the etch rate of 40 ± 9 for Si and of 104 ± 177 for Si_{0.5}Ge₅. Again, the large uncertainty in the SiGe etch-rate enhancement is due to the large relative error in the etching experiments of SiGe with $H_2/CF_4/Ar$. Regardless of the magnitude of the inverse KIE, the observation that the Si and SiGe ERs changed when H₂ was replaced with D₂ confirms that

H is involved in the rate-limiting step for the etching of Si and SiGe with a $H_2/CF_4/Ar$ plasma under the conditions described.

Figure 5c-f shows the results of XPS measurements of the surface compositions of Si and Si_{0.5}Ge_{0.5} after they had been etched with a $H_2/CF_4/Ar$ plasma and with a $D_2/CF_4/Ar$ plasma. These XPS measurements were performed ex situ, and so, the oxygen on the surfaces was assumed to be from air exposure. Air exposure was also assumed to have deposited \sim 10% carbon on the surfaces (as discussed in the Experimental Section and shown in Figure S5). As a result, there is an inverse relationship between the amounts of O and C on the Si and SiGe surfaces: A thinner carbonaceous film gave rise to more surface oxidation during the ex situ transfer of the samples to the XPS chamber. The XPS measurements show that the same amounts of carbon were deposited on the Si and SiGe surfaces. The thickness of the carbon layer was estimated to be \sim 2 ML on both Si and SiGe based on the attenuation of the substrate signals. Therefore, the selectivity is not due to selective deposition of the carbonaceous film. Furthermore, the etch rate is not likely to be limited by diffusion through the carbonaceous film because reactants and products must diffuse through the same film on both Si and SiGe. Instead, the carbon film has a differential effect on Si versus SiGe; that is, it is effective at suppressing the etching of SiGe but not the etching of Si. As shown in Figure 5d, the $Si_{0.5}Ge_{0.5}$ surface became Ge-enriched, and its composition after etching was closer to $Si_{0.25}Ge_{0.75}$. This is consistent with the Si being etched faster than the Ge.

Figure 5e,f shows the atomic compositions of the Si and $Si_{0.5}Ge_{0.5}$ surfaces after they had been etched with a $D_2/CF_4/Ar$ plasma. When D_2 was employed, approximately half as much carbon was deposited on Si and SiGe compared to when H_2 was employed. Additionally, there was less Ge enrichment of the $Si_{0.5}Ge_{0.5}$ surface: After 2.3 nm of material had been etched with $D_2/CF_4/Ar$, the composition of the SiGe sample was approximately $Si_{0.4}Ge_{0.6}$, whereas after 1.1 nm of material had been etched with $H_2/CF_4/Ar$, the SiGe sample composition was approximately $Si_{0.25}Ge_{0.75}$. The fact that there was less Ge enrichment of $Si_{0.5}Ge_{0.5}$ suggests that the Ge might actually have experienced a larger KIE than the Si.

Figure 6 shows the XPS spectra of the Si and SiGe samples after they had been etched with $H_2/CF_4/Ar$ or $D_2/CF_4/Ar$ plasmas. When either H_2 or D_2 was used, all of the carbon on Si appeared at a binding energy of 284.6 eV, which is characteristic of hydrocarbons and suggests that no C-F bonds were present. On SiGe, however, when H₂ was used the C 1s peak had a clear shoulder at high binding energy (290 eV), which is characteristic of C-F bonds.¹⁹ When D₂ was employed, this high-binding-energy shoulder on SiGe was not present. On Si, when D2 is used, the F 1s peak had two components: a low-binding-energy component that was centered at the same binding energy as the F 1s peak when H₂ was used and a high-binding-energy component. Additionally, the Si 2p peak showed a broadening of the high-bindingenergy Si component for D₂ compared to H₂. This broadening of the high-energy Si peaks and the higher-binding-energy F component is consistent with the presence of higher silicon fluorides under steady-state etching conditions for D₂ compared to H₂. Alternatively, these high-binding-energy Si and F peaks could suggest the presence of SiO_xF_y (likely containing -OF groups) formed either as a result of contamination or post-etch oxidation because the XPS measurements were performed ex situ. On SiGe, when D₂ was employed, there was less fluorine than when H₂ was employed, and approximately half of the Si signal was shifted to higher energy. This increase in the amount of higher-bindingenergy Si also suggests the presence of higher silicon fluorides during steady-state etching of SiGe with D₂. It can also be seen that the oxidized Ge XPS component was shifted to higher binding energy when D₂ was used compared to H₂. This is consistent with there being a higher etch rate of the Ge in SiGe and the presence of higher germanium fluorides under steadystate etching conditions when D_2 was used compared to H_2 .

The observation of a strong inverse kinetic isotope effect indicates that H (D) is involved in the rate-limiting step. It is possible that the role of H₂ is to scavenge F in the gas phase and create HF, which does not etch Si at an appreciable rate. If this were the case, then the reaction D₂ + F \rightarrow DF + D should be slower than the reaction H₂ + F \rightarrow HF + H, and so, more free atomic F should be present when D₂ was used compared to H₂. This could give rise to a higher Si etch rate with D₂ compared to H₂ and the observation of an "inverse" KIE. However, if the scavenging of F radicals by H₂ were ratelimiting, then the etch rates of Si and SiGe should either (i) show no dependence on the substrate temperature (because this would be a gas-phase process) or (ii) show the same dependence on the substrate temperature [if this radical scavenging were occurring close enough to the substrate surface for the $H_2(g)$ and/or F(g) to be heated]. However, two different effective activation energies were measured for Si and SiGe, indicating that the natures of the rate-limiting steps were different for the two substrates.

The dependence of the Si and SiGe ERs on the substrate temperature is consistent with the rate-limiting step occurring on the surface and not in the plasma or in the gaseous phase. However, the fact that the Si ER was at a minimum in a solely H_2/Ar plasma (Figure 2c) shows that F is required for the etching to proceed at an appreciable rate. These data are consistent with the role of H being to initiate the etching, likely by inserting into surface Si-C or Si-Si bonds to create dangling bonds that then react rapidly with atomic F to complete the etching. In this case, the effective activation energies reported herein might correspond to the activation energies for the insertion of H into Si-C, Si-Si, or Si-Ge bonds under conditions of high carbon coverage. These results are consistent with those of previous investigations. Iwakuro et al.²⁰ found that, for RIE etching of Si with pure H_2 versus pure D_2 , the etch rate of Si subjected to the pure D_2 plasma was 34 times greater than that observed when pure H₂ was used and the etch rate of Si exhibited no dependence on the sample bias for either H₂ or D₂ plasma etching. Jasinski also showed that the etching of chemical vapor deposition (CVD) Si is at least 9 times faster with D_2 than with H_2 .²¹

4. CONCLUSIONS

In this work, it was found that $H_2/CF_4/Ar$ downstream plasma deposits a carbonaceous film on Ge that is effective in passivating the Ge surface over the range of CF₄/H₂ ratios studied. Conversely, the Si surface is less effectively passivated by a carbonaceous layer at optimal CF_4/H_2 ratio. At 50 °C, 760 mTorr, and a plasma power of 40 W, a range of CF_4/H_2 ratios were found to give net deposition on Ge, and hence, very high Si/Ge ERRs were observed. The same plasma chemistry can be applied to the selective etching of Si in preference to $Si_{0.5}Ge_{0.5}$ and under optimized conditions $(H_2/CF_4/Ar/purge =$ 100:18:40:5 sccm, P = 760 mTorr, T = 22 °C, power = 40 W), no etching of SiGe was observed whereas Si exhibited an etch rate of ~0.5 nm/min. Compared to $H_2/CF_4/Ar$, the use of a $D_2/CF_4/Ar$ plasma greatly enhanced both the Si and SiGe etch rates (>30 times), gave less Ge enrichment of SiGe, deposited less total carbon, and eliminated any fluorocarbon deposition.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b02060.

All XPS spectra with peak fitting. Atomic composition of the $Si_{0.5}Ge_{0.5}$ surface with and without $H_2/NF_3/Ar$ plasma clean (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: akummel@ucsd.edu.

ORCID [©]

Andrew C. Kummel: 0000-0001-8301-9855

Notes

The authors declare no competing financial interest.

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