SELECTIVE ETCHING OF SILICON IN PREFERENCE TO GERMANIUM AND SI$_{0.5}$GE$_{0.5}$.

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INTRODUCTION

As CMOS technology is scaled to < 10 nm, new MOSFET architectures are required for the gate to maintain control of the device. The ideal architecture for such a device is the gate-all-around (GAA) structure.[1] While in previous device generations MOSFETs were planar structures, the cylindrical geometry of the GAA structure makes highly selective isotropic etching a requirement for device fabrication.

Bright et al.[2] reported that selective reactive ion etching (RIE) of Si versus Ge can be achieved using an RIE H$_2$/CF$_4$ plasma at 25 mTorr and a plasma power of 200 W. The selectivity was extremely sensitive to the H$_2$ composition of the gas mixture, with the optimal composition being ~37.5% H$_2$. Bright et al. attributed the selectivity to the formation of a carbonaceous film on both the Si and Ge surfaces which protected the Ge from etching but did not protect the Si surface. In a follow-up investigation, they showed that the fluorocarbon layer is actually thicker on Si than on Ge during steady-state etching.[3] These studies employed RIE, and it is was not shown whether their results would also apply to isotropic etching conditions which are required for GAA structures. Selective isotropic etching of Si in preference to Si$_{0.8}$Ge$_{0.2}$ with a Si:SiGe ERR > 100:1 has more recently been accomplished using a CF$_4$/O$_2$/N$_2$ plasma.[4] However the CF$_4$/O$_2$/N$_2$ gas mixture deposits a highly fluorinated C$_x$F$_y$ layer which is subsequently difficult to remove from the surface.

In this report, a downstream H$_2$/CF$_4$/Ar plasma chemistry is described which etches Si but induces net deposition of sub-nanometer thickness carbon on Ge and Si$_{0.5}$Ge$_{0.5}$. Even for Si$_{0.5}$Ge$_{0.5}$, this plasma chemistry has a Si:SiGe ERR > 100:1 at 22 °C. The high selectivity is obtained by using a low surface temperature which is enabled by the surface temperature being independent of the downstream plasma operation. Since a downstream plasma was employed at 0.1 torr or higher pressure, the etching does not have an ion component and should be isotropic which is ideal for selective etching of nanowires. XPS studies show that the plasma produces an approximately 2 monolayers (ML) thick C$_x$F$_y$ film on both Si and Si$_{0.5}$Ge$_{0.5}$ but the carbon has a stronger interaction with SiGe than Si.

RESULTS

Silicon versus Germanium
Figure 1 shows the effects of pressure and CF$_4$ flow rate 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 is recorded under nearly steady state conditions. The etch rates (ERs) plotted in Figure 1a&1b are the results of single experiments whereas each of the ERs plotted in Fig. 1c is the average of three separate experiments performed under nearly identical conditions. The error bars in Fig. 1c represent the standard deviation of the etch rates recorded from three experiments performed under nearly identical conditions.

The The etch rates of Si and Ge should largely depend on the flux of F radicals as well as on the flux of carbon radicals (C$_x$H$_y$F$_z$(g)) onto the surfaces. The F radicals react with the surface to produce volatile etch products (SiF$_4$ and GeF$_4$) while the C$_x$H$_y$F$_z$(g) radicals are

expected to react with the surface and form surface-bound *C$_x$H$_y$F$_z$ which inhibit the approach of F radicals to the Si and Ge.[5] The CF$_4$ flux affects both these processes: as the CF$_4$ flux is increased, there is sufficient *C$_x$H$_y$F$_z$ to slow down the etching of Si. Since the surface-bound *C$_x$H$_y$F$_z$ species form on both the Si and Ge surfaces, the selectivity can be attributed to more efficient passivation of the surface by Ge*C$_x$H$_y$F$_z$ species compared to Si*C$_x$H$_y$F$_z$. This difference may be related to the difference in the Si-F bond strength (565 kJ/mol) versus the Ge-F bond strength (481 kJ/mol).[6]

Figure 1. Si and Ge etch rates. Si and Ge etch rates versus (a) reaction pressure, (b) CF$_4$ flow rate at 180 mTorr and (c) CF$_4$ flow rate at 760 mTorr. The reaction conditions are: (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 (a) and (b) are the results of single experiments while the data points in (c) are the average of three separate experiments performed under identical conditions. The error bars in (c) represent the standard deviation of the three experiments.

To further optimize the Si:Ge selectivity, the CF$_4$ flow rate was varied at high pressure (760 mTorr) since at this pressure the highest Si:Ge selectivity was observed (net deposition on Ge). Figure 1c shows the effect of just changing the CF$_4$ flow rate at high pressure (760 mTorr); no etching of Ge is observed (only deposition); therefore, an infinite Si:Ge ERR can be achieved so long as the CF$_4$ flow rate is > 0.

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 Si versus Si$_{0.5}$Ge$_{0.5}$, and the temperature was varied (Fig. 2a&b). The Si and Si$_{0.5}$Ge$_{0.5}$ etch rates increase exponentially with increasing temperature (Fig. 2c). From an Arrhenius plot, the

effective activation energies for Si and $Si_{0.5}Ge_{0.5}$ are 0.54 eV and 1.47 eV, respectively. The higher effective activation energy for etching $Si_{0.5}Ge_{0.5}$ than for Si suggests that high selectivity should be achievable at low temperature. This is verified at 22 °C where no etching of $Si_{0.5}Ge_{0.5}$ is observed, only deposition. The effect of pressure at low temperature (30 °C) was studied (Fig. 2d&e). It is found that the Si etch rate decreases with increasing pressure at 30 °C. A similar, more modest, effect is observed in the experiment for Si vs Ge etching at higher CF_4 flow rate and higher temperature (50 °C, Fig. 1a). This is consistent with an increase in the thickness of the carbonaceous passivation layer or a decrease in the concentration of free radicals due to faster gas phase recombination at higher pressure.
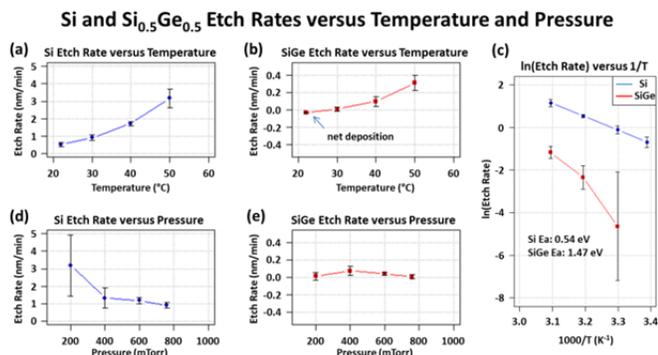
Figure 2. Si and $Si_{0.5}Ge_{0.5}$ etch rates. (a&b) Si and $Si_{0.5}Ge_{0.5}$ etch rates versus temperature. The reaction conditions are: $H_2/CF_4/Ar/purge$ = 100/18/40/5 sccm, P = 760mTorr, T = **X** °C, Power = 40 W. (c) Arrhenius plot showing the effective activation energies for the etching of Si and $Si_{0.5}Ge0.5$. The $Si_{0.5}Ge_{0.5}$ etch rate at 22 °C in (b) was < 0 and so it was not used in this plot. (d&e) Si and $Si_{0.5}Ge_{0.5}$ etch rates versus pressure. The reaction conditions are: $H_2/CF_4/Ar/purge$ = 100/18/40/5 sccm, P = **X** mTorr, T = 30 °C, Power = 40 W. The data points in this figure are the average of three experiments performed under nearly identical conditions. The error bars represent the standard deviation of the three experiments.

Kinetic Isotope Effect

To gain insight into the mechanism of etching of Si and SiGe by a $H_2/CF_4/Ar$ plasma, H_2 was replaced with D_2 in the feed gas. Chemical reactions in which the rate-limiting step involves the breaking of a bond to hydrogen (deuterium) tend to be slower when hydrogen is replaced with deuterium.[7] Conversely, the formation of a bond to D is more exothermic than the formation of a bond to H; therefore, if the rate limiting step is formation of a X-H bond then an inverse kinetic isotope effect is expected.
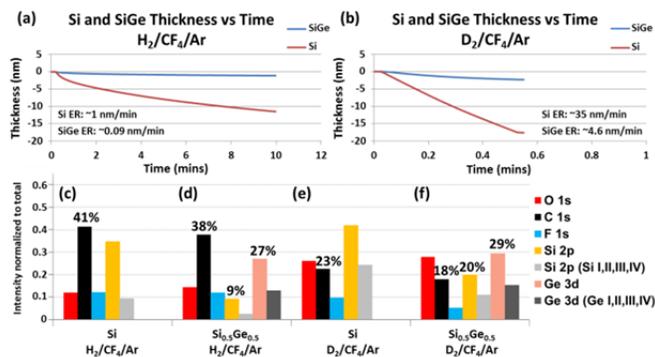
Figure 3. Si and $Si_{0.5}Ge_{0.5}$ post etch XPS analysis. (a&b) Raw QCM data for the etching of Si and $Si_{0.5}Ge_{0.5}$ subjected to (a) a $H_2/CF_4/Ar$ plasma and (b) a $D_2/CF_4/Ar$ plasma. The reaction conditions are: $H_2(D_2)/CF_4/Ar/purge$ = 100/18/40/5 sccm, P = 760 mTorr, T = 30 °C, Power = 40 W. (c-f) XPS compositional analysis of Si and $Si_{0.5}Ge_{0.5}$ after etching with a $H_2/CF_4/Ar$ plasma (c and d) versus with a $D_2/CF_4/Ar$ plasma (e and f).

Figure 3a&b shows a plot of the thickness versus time for Si and $Si_{0.5}Ge_{0.5}$ subjected to a $H_2/CF_4/Ar$ plasma (Fig. 3a) and a $D_2/CF_4/Ar$ plasma (Fig. 3b) under identical conditions. When $H_2/CF_4/Ar$ is employed, the Si and $Si_{0.5}Ge_{0.5}$ etch rates are 1 nm/min and 0.09 nm/min respectively. When $D_2/CF_4/Ar$ is employed, the Si etch rate increases by a factor of 36 and the $Si_{0.5}Ge_{0.5}$ etch rate increases by a factor of 51. The observation of an inverse KIE proves that H is involved in the rate limiting step for etching of Si and SiGe with a $H_2/CF_4/Ar$ plasma under the conditions described.

Figure 3c-4f shows the results of XPS measurements of the surface composition of Si and $Si_{0.5}Ge_{0.5}$ after etching 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 is assumed to be from air exposure. The XPS measurements show that the same amount of carbon is deposited on Si and SiGe. The thickness of the carbon layer is estimated to be ~ 2 ML on both Si and SiGe due to the finite escape depth of the electrons from the substrate and films. 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 since reactants and products must diffuse through the same film on Si as well as on SiGe. Instead the carbon film has a differential effect on Si vs SiGe; it is effective at suppressing etching of SiGe but not on Si. As shown in Fig 3d, the $Si_{0.5}Ge_{0.5}$ has become Ge-enriched, and its composition after etching is closer to $Si_{0.25}Ge_{0.75}$. This is consistent with the Si being etched faster than the Ge.

Figure 3e&f shows the atomic composition of the Si and $Si_{0.5}Ge_{0.5}$ surfaces after etching with a $D_2/CF_4/Ar$ plasma. When D_2 is employed, there is approximately half as much carbon deposited on Si and SiGe compared to when H_2 is employed. Additionally, there is less Ge-enrichment of the $Si_{0.5}Ge_{0.5}$; after etching 2.3 nm of material with $D_2/CF_4/Ar$, the SiGe is approximately $Si_{0.4}Ge_{0.6}$, while after etching 1.1 nm of material with $H_2/CF_4/Ar$, the SiGe is approximately $Si_{0.25}Ge_{0.75}$. The fact that there is less Ge enrichment of the $Si_{0.5}Ge_{0.5}$ suggests that the Ge may actually experience a larger KIE than the Si.

SUMMARY

At 50 °C and 760 mTorr, Si may be etched in preference to Ge and $Si_{0.5}Ge_{0.5}$ with an essentially infinite Si:Ge etch rate ratio (ERR), while for Si:$Si_{0.5}Ge_{0.5}$, the ERR is also infinite at 22 °C and 760 mTorr. XPS data shows the selectivity is due to 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 and Ge or $Si_{0.5}Ge_{0.5}$. The data is 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, while 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 results in an inverse kinetic isotope effect (IKIE) where the Si and $Si_{0.5}Ge_{0.5}$ etch rates are increased by ~42x with retention of significant etch selectivity. The use of $D_2/CF_4/Ar$ instead of $H_2/CF_4/Ar$ results in less total carbon deposition and eliminates fluorocarbon deposition on Si and $Si_{0.5}Ge_{0.5}$, and gives less Ge enrichment of $Si_{0.5}Ge_{0.5}$. This is consistent with the selectivity being due to the differential suppression of etching by an angstrom scale carbon layer.

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