Selective Etching of Native Silicon Oxide in Preference to Silicon Oxide and Silicon

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ABSTRACT

An in-situ dry clean which removes native SiO_x and flowable oxide but does not etch the underlying silicon, thermal SiO_2 or SiN_x is reported. This process utilized a remote $NF_3/NH_3/Ar$ plasma, and the selectivity was studied as a function of temperature and time. Under the optimized conditions, the native SiO_x on Si was removed after ~15 seconds of plasma exposure whereas the etching of as-sputtered SiO_2 was zero within this time period. Selectivity on a nanometer scale was confirmed by TEM of a patterned Si wafer showing that the optimized dry clean removed flowable SiO_2 but does not etch Si and leaves SiN_x/thermal SiO_2 fins undamaged. Furthermore, this cleaning procedure was used to remove the native oxide on a SiGe-based patterned sample containing SiO_2/SiN_x fins in preparation for $MoSi_x$ atomic layer deposition (ALD). The selectivity between two types of silica relied on defective or weak Si-O bonds in native SiO_x compared to SiO_2.

INTRODUCTION

As devices are scaled to sub 5nm, it is critical to prepare clean and atomically flat surfaces. The traditional aqueous HF clean for removal of native Si oxide suffers from an inevitable air exposure resulting in re-oxidation of the Si surface as well as carbon contamination.[1] The Siconi™ process is a dry clean which utilizes a low temperature (<30°C) NF_3/NH_3 based plasma to selectively etch the native oxide layer on Si without significantly etching the underlying Si layer.[2] However, unlike aqueous HF, the Siconi™ process leaves behind an ammonium hexafluorosilicate salt, $(NH_4)_2SiF_6(s)$, which must be removed in a subsequent anneal. Furthermore, the selectivity of this process for various forms of SiO_2 is not known. Miki et al.[3] found that native Si oxide could be selectively etched with respect to various other silicon oxides using anhydrous HF(g). The selectivity was attributed to different oxides having different amounts of physisorbed H_2O, and this surface H_2O helped to dissociate HF(g) and promote etching. However, they found that the dry etching of native silicon oxide with HF(g) leaves the surface Si-F terminated, and this surface termination has detrimental effects on subsequent processing steps. In this work a process is reported which selectively etches native SiO_x and flowable SiO_2 in preference to Si, thermal SiO_2 and SiN_x. This process utilizes a downstream $NF_3/NH_3/Ar$ plasma which avoids the use of toxic anhydrous HF(g) and does not leave the surface Si-F terminated. The insulator selectivity is consistent with the contrast between weak bonding in native oxide and flowable oxide versus strong bonding in thermal SiO_2 and SiN_x.

RESULTS

The etching of native SiO_x and SiO_2 was studied in-situ using a pair of quartz-crystal microbalances (QCMs). A Si-sputtered quartz crystal containing native oxide and a SiO_2-sputtered quartz crystal were loaded on two different QCMs in the same chamber and subjected to the same plasma conditions ($NF_3:NH_3:Ar$ = 1:10:1.5, chamber pressure of 190 mTorr, and a plasma power of 100W for 2 minutes at 45 °C; Figure 1). In this experiment, the samples were subjected to two consecutive plasma pulses separated by approximately 20 minutes to observe the difference in Si etch rate with and without native oxide. The samples were not exposed to air between the first and second plasma pulses and, therefore, should not have reformed a native oxide (Fig. 1a). It was observed that the first 2-minute plasma rapidly etched the native oxide on Si while no etching of Si was observed during the second 2-minute plasma. As shown in Fig 1b, the native oxide on Si was rapidly etched during the first ~15 seconds of the plasma exposure, after which only deposition was observed.

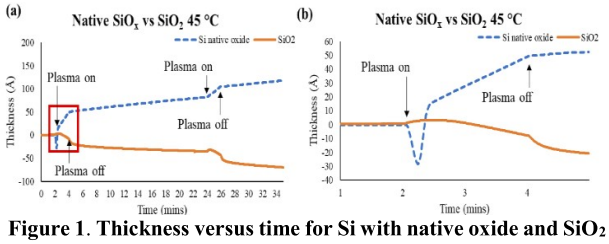

Figure 1. Thickness versus time for Si with native oxide and SiO_2 subjected to two consecutive $NF_3/NH_3/Ar$ plasma doses at 45 °C. (a) The thickness versus time data is shown for both consecutive plasmas separated by approximately 20 minutes. **(b)** An expansion of the region outlined by the red box in Fig. 1a is shown. This data showed that the first plasma removed the native SiO_x on Si and did not etch the underlying Si. The onset for etching of SiO_2 began at around 1 minute of plasma exposure. The process parameters were: $NF_3:NH_3:Ar$ = 1:10:1.5 at a chamber pressure of 190 mTorr and a plasma power of 100W for 2 minutes.

This etching process was tested on crystalline Si (001) to determine the process parameters for selective native SiO_x etching vs crystalline Si (001). A Si coupon was degreased and loaded into the UHV chamber for XPS analysis (see Figure 2a). The degreased Si sample had 37% O and 8% C contamination. After the dry clean, all of the O was removed, and the sample surface consisted of 11% C, 43% F, 30% Si (of which 20% was Si^0 and 10% was oxidized Si) and 15% N. The XPS was consistent with a clean Si^0 surface covered with a layer of $(NH_4)_2SiF_6(s)$ salt. It is known that the $(NH_4)_2SiF_6(s)$ salt

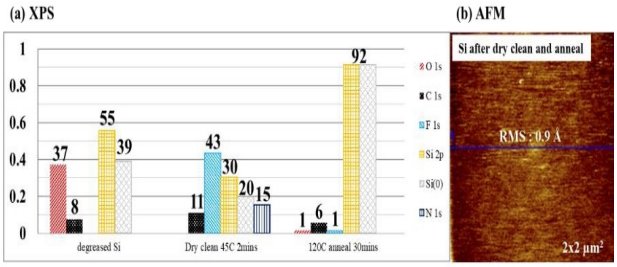

Figure 2. Chemical composition and surface topography of Si(001) subjected to the dry clean and anneal. (a) XPS of Si before and after the dry clean and a subsequent 120 °C anneal. The conditions for the dry clean were: $NF_3:NH_3:Ar$ = 1:10:1.5 at a chamber pressure of 190 mTorr and a plasma power of 100W for 2 minutes at 45 °C. The 120 °C anneal was performed for 30 minutes. **(b)** AFM of the Si surface after the dry clean and anneal at 120 °C. The Si surface has an RMS roughness of 0.9 Å.

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must be removed in a subsequent anneal step[4]; therefore, the sample was annealed at 120 °C for 30 minutes in the UHV chamber. After the anneal, XPS showed that the Si surface consisted of 92% Si (all of which was Si^0) along with 1% O, 6% C and 1% F contamination (Figure 2a). The AFM images of dry cleaned and annealed Si sample shows that the Si surface had an RMS roughness of <1 Å (Fig. 2b).

To determine the selectivity on the nanoscale, the dry clean was performed on a nanoscale patterned sample (Figure 3). The patterned sample was a Si substrate with poly-Si fins coated with SiN_x on the top and sides, and thermal SiO_2 in between the poly-Si and Si substrate (schematic shown in Fig. 3a). The entire patterned sample was coated with a layer of flowable SiO_2. A TEM image of the patterned sample before any plasma treatment is shown in Fig. 3b. The patterned sample was subjected to two 30-second plasma pulses using the standard conditions and TEM was performed (Fig. 3c and 3d). It can be seen that the dry clean etched all of the flowable SiO_2 but did not etch the fins or the Si substrate. The collapse of three of the fins in Fig. 3c is believed to be due to mechanical damage during the sample cleaving process in preparation for TEM. Fig. 3d shows a higher magnification TEM of the region shown in Fig. 3c. Upon closer inspection it is seen that the fins remain intact and the thermal SiO_2 layer was not etched.

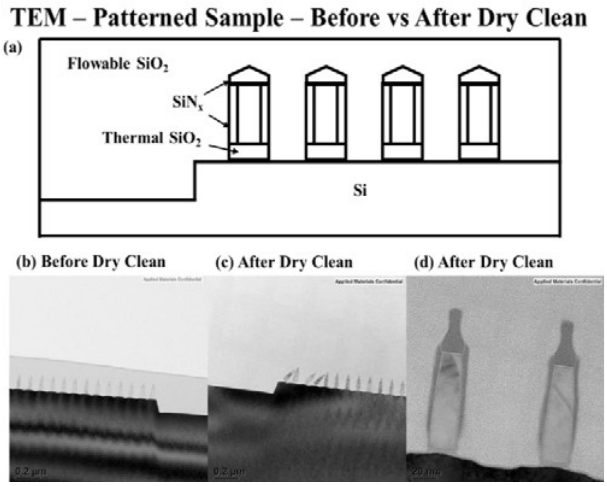

Figure 3. Selective Clean on NanoScale Patterned Sample. Two 30-second plasma pulses were employed using the standard conditions: NF_3:NH_3:Ar = 1:10:1.5 at a chamber pressure of 190 mTorr and a plasma power of 100W at 45 °C. **(a)** Schematic representation of the patterned sample. **(b)** TEM image at 13,000 x magnification of a patterned sample with no plasma treatment. **(c)** TEM image at 13,000 x magnification shows that the flowable oxide has been completely etched by the dry clean, while the fins and Si substrate remain unetched. **(d)** TEM image at 135,000 x magnification shows that the fins, including the thermal SiO_2 and SiN_x, were not etched.

This process was used to remove the native oxide from a patterned sample in preparation for atomic layer deposition (ALD) of a $MoSi_x$ film. $MoSi_x$ ALD is known to deposit selectively on Si but not SiO_2 or SiN, and it has been shown that when aqueous HF is used to remove the native SiO_x, there always exists an ~2.8 nm thick interfacial oxide layer between the Si and ALD $MoSi_x$.[5] A cross sectional STEM EELS study after ALD of a $MoSi_x$ layer on the dry cleaned pattern sample shows that the native oxide was removed while leaving the Si, SiN and SiO_2 not etched (Figure 4a). EELS elemental mapping shows that the $MoSi_x$ deposited selectively on the SiGe substrate, showing that the dry clean did not negatively affect the inherent selectivity of this process. Figure 4c shows an overlay of the elemental mapping. It can be seen that there is no oxygen at the

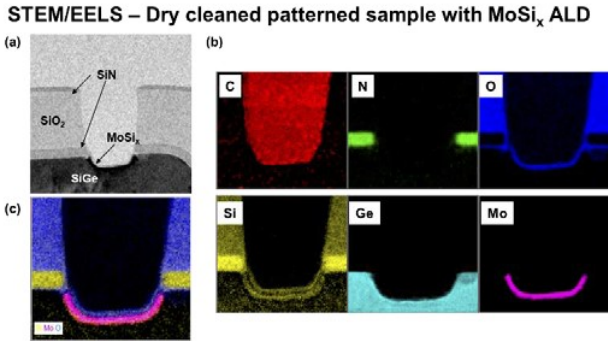

Figure 4. TEM images of a patterned sample subjected to a 1-minute plasma clean followed by $MoSi_x$ ALD. The dry clean was performed under the standard conditions: NF3:NH3:Ar = 1:10:1.5 at a chamber pressure of 190 mTorr and a plasma power of 100W at 45 °C for 1 minute. **(a)** TEM shows the structure of the patterned sample. **(b)** Elemental mapping showing the distribution of C, N, O, Si, Ge and Mo. **(c)** An overlay of the Si, Mo and O distribution shows that there is no interfacial oxide in between the SiGe and $MoSi_x$.

$MoSi_x$/SiGe interface, showing that the dry clean is superior to the traditional aqueous HF clean in that it does not lead to an interfacial oxide layer in this ALD process.

Conclusion

In conclusion, an in-situ dry clean has been developed which removed the native oxide from silicon and etched flowable SiO_2 but did not etch the underlying Si, bulk SiO_2 or SiN_x. It was found that careful control of the temperature was crucial in order to control the selectivity, and at 45 °C the native SiO_x on Si was removed with no etching of the underlying Si, and no etching of sputtered SiO_2 in this time period. XPS showed that the dry clean produced a very clean Si surface with only 6% carbon, <1% oxygen and <1% fluorine contamination. AFM showed that the dry-cleaned Si surface was atomically flat with an RMS roughness of ~1 Å. TEM images showed that the dry clean did not damage thermal SiO_2 or SiN_x features, however flowable SiO_2 was rapidly etched under these same conditions. This shows that this plasma process may be used to selectively etch flowable SiO_2 in the presence of Si, thermal SiO_2 and SiN_x. TEM and EELS measurements showed that the dry clean produced a cleaner Si surface than ex-situ HF(aq) because it eliminated the interfacial SiO_x layer in between Si and ALD $MoSi_x$. This showed that this dry clean should find applications in the preparation of patterned Si samples for selective ALD.

Acknowledgements

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