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Carbon and oxygen removal from silicon (100) surfaces by remote plasma cleaning techniques

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A hydrogen plasma-based technique for carbon removal has been combined with a modest anneal for oxide desorption at 720 °C to produce atomically clean Si(100)2×1 surfaces. Carbon and oxygen contamination can be removed from silicon surfaces by a 30 s hydrogen plasma exposure at 480 °C (for carbon removal) followed by a 5 min anneal in molecular hydrogen at 720 °C (for oxygen removal). Surface hydrocarbon removal is thought to occur by volatilization through hydrogenation. The mechanism for oxygen removal is believed to be more straightforward and consist of thermal desorption of SiO at approximately 700 °C. Hydrogen plasma exposures on the order of 5 min are seen to induce microscopic surface roughness without complete oxygen elimination. Samples which are devoid of oxygen following the 720 °C anneal are found to reoxidize upon re-exposure to the hydrogen plasma. The origin of the oxygenating species is unclear, but likely sources include, SiO or OH from tube wall erosion, or contamination produced by interactions of atomic hydrogen with the chamber walls. A subsequent anneal at 720 °C effectively removes any surface reoxidation. Anneals at 720 °C with carbon present on the surface results in a surface reaction which complexes the carbon and oxygen on the surface, rendering the surface contamination resistant, under nominal conditions, to subsequent plasma processing or annealing.

1. INTRODUCTION

Plasma based cleaning techniques are currently being pursued by a number of researchers as part of a general effort to develop single-wafer processing technologies and more extensive in situ processing capabilities. In situ cleaning techniques must also be adapted to meet the growing demand for low-temperature processes which leave surfaces with a minimum of process induced damage. Demands for low temperature processes and minimal surface damage are driven in turn by the constraints of subhalf-micron device scaling and the requirements for defect-free surfaces essential for active interface formation. In designing a hydrogen based plasma cleaning process, there are several competing reactions in progress which have to be balanced. Silicon surfaces are etched upon exposure to the atomic hydrogen. Small quantities of process generated oxygen containing species can chemisorb on the surface upon exposure to the hydrogen plasma. Finally, carbon and oxygen are removed from the surface, although the oxygen removal rate appears much slower than the carbon removal rate. All of the above reactions are temperature dependent of course; the silicon etch rate tends to decrease as the sample temperature increases, and the other reaction rates increase with temperature. A further consideration in designing a cleaning process is the identity of the molecule carrying the oxygen and carbon contamination to the surface. One expects oxygen contained in methanol to be easier to remove from the surface than oxygen bonded directly to the silicon. In many cases, however, the nature of the contamination on the surface is not well characterized and, furthermore, can be altered by the cleaning process itself.

The use of hydrogen plasmas to clean semiconductors has been reported by a number of groups and includes atomic hydrogen generation by radio frequency (rf) remote plasma sources, rf plasma sources, and microwave electron cyclotron resonance (ECR) sources. In general, removal of carbon contamination from the surface has proved easier than oxygen removal; primarily due to the relatively slow etch rate of silicon oxides by atomic hydrogen. Tasch et al. have reported using a remote plasma rf source, operating at 9 W of power, to reduce carbon to levels below the detectability limit as measured by Auger electron spectroscopy (AES). Yamada has reported on ECR techniques to remove carbon from the silicon surface by atomic hydrogen exposure at 650 °C. Contamination levels were measured by secondary ion mass spectroscopy (SIMS).

Removal of oxygen in the form of suboxides appears to be a more difficult task. In one case, samples were exposed to a rf remote hydrogen plasma for 45 min at 305 °C to remove the oxygen from the surface. Furthermore, wafers exposed to ambient for 120 min could not be deoxygenated, while samples exposed to ambient for 15 min were cleaned to below the Auger detection limit. It appears that the structure of the oxide, which is related to the thickness, is the major factor in determining ease of removal. In the second case, Nakashima et al. have also reported a reduction to background levels in the Si 2p peak associated with the Si 2p x-ray photoelectron spectroscopy (XPS) peak following cleaning with a hydrogen ECR source.

Silicon has also been very effectively cleaned by simple thermal annealing. Although oxygen is removed after an anneal at 830 °C, temperatures over 1100 °C are required to remove carbon from the surface. Ishizaka et al. have demonstrated a thermal process for cleaning silicon at consid-
erably lower temperatures through careful wet chemistry to remove carbon from the surface and an anneal at 800 °C to remove the remaining oxide from the surface. They found that if the oxide layers were thin enough following the wet chemistry the desorption temperature was lowered from 1000 °C for a full oxide to less than 800 °C. The correlation between oxide thickness and desorption temperature is supported in a recent study by Engstrom et al. of thermal desorption from oxygen dosed silicon surfaces. At submonolayer coverages SiO desorbs from the surface at approximately 700 °C. The desorption temperature rises as the oxide thickness increases to a maximum of 1000 °C for the fully developed dioxide.

In the present work, we have applied sequential processing steps to reduce both the carbon and oxygen on the silicon surface. We found that a combination of steps tailored to the removal of carbon and oxygen, respectively, gave the best results. A brief exposure to the remote hydrogen plasma to reduce the residual surface carbon, followed by a brief thermal anneal to remove the remaining oxygen left the surface with carbon and oxygen levels below the limit of detectability by XPS.

II. EXPERIMENTAL PROCEDURES

The cleaning chamber that was used in the present work is shown in Fig. 1. The chamber is pumped by a cryogenic pump while in standby mode and a 500 /s turbomolecular pump while process gas is flowing. After baking, the chamber typically achieves an ultimate pressure of 5 × 10⁻¹⁰ Torr. The plasma is generated by rf excitation of a five-turn coil located approximately 45 cm from the sample position. rf power is supplied to the excitation coil at 13.56 MHz with an available power range of up to 100 W. Tube conditioning is performed prior to sample introduction by running a hydrogen plasma discharge. Hydrogen is injected into the system via a ring feed located approximately 5 cm below the sample, and all cleans are performed with hydrogen as the sole feed gas. The sample is radiantly heated by a tantalum filament located approximately 1 cm behind the sample. A sheathed reference thermocouple is positioned in close proximity to the coils of the filament heater and is used for routine determination of the sample temperature. The temperature offset of the reference thermocouple relative to the sample temperature was calibrated by introducing a silicon wafer with a thermocouple attached to the front face by a high-temperature ceramic adhesive. Calibration of the reference thermocouple was performed while flowing hydrogen through the chamber. We estimate an accuracy of 20 °C for the sample temperature with this measuring arrangement. Very large scale integrated (VLSI) grade hydrogen, further purified with a Nanochem filter, was used for all cleans. A differentially pumped quadrupole mass spectrometer (QMS) is located beside the main chamber to sample gasses during processing.

Silicon samples used in the study consisted of 2.5 cm diam, (100), p-type, 10 Ω cm wafers. All samples receive a modified RCA clean prior to introduction to the cleaning system with final buffered HF dip immediately before loading into the transfer system.

Low-energy electron diffraction (LEED), XPS, and AES are available via ultrahigh vacuum (UHV) transfer from the cleaning chamber to the respective analytical facilities. Transfers can be accomplished in approximately 5 min with a background pressure of about 1 × 10⁻⁹ Torr. All samples are mounted on molybdenum carriers.

III. EXPERIMENTAL RESULTS

Figures 2 and 3 show XPS results from two silicon samples which were given hydrogen plasma cleans at 480 °C for 5 min followed by 5 min anneals at 720 °C in flowing molecular hydrogen. The samples were treated identically except that one of the samples, Fig. 2, was loaded into the vacuum system immediately after HF cleaning (approximately 7 min exposure to air), and the second sample, Fig.
was exposed to laboratory ambient for 120 min prior to insertion into the vacuum system. Figures 2(a) and 3(a) give XPS spectra of the samples as introduced to the chamber. Both carbon and oxygen are evident on the surface of the samples. The first step of the cleaning process consisted of exposing the samples to a hydrogen plasma for 5 min at 480 °C to remove carbon. Figures 2(b) and 3(b) show the samples after exposure to the hydrogen plasma. No evidence of carbon is seen on the surface for either sample, even with an expanded scale. However the oxygen peak is still present, and in some cases is slightly higher. Figures 2(c) and 3(c) show XPS spectra of the samples after the second step in the cleaning process, a 5 min anneal at 720 °C in flowing molecular hydrogen at 5 mTorr. After annealing the samples were cooled in flowing hydrogen. No plasma was used during the anneal or during the cooldown phase. Although the second sample, due to a longer ambient exposure time, had slightly higher levels of carbon and oxygen on the surface as loaded, the same cleaning sequence removed all traces of both contaminants.

Additional experiments were performed to investigate the minimum operating parameters required to remove carbon and oxygen from a sample surface. Figures 4(a)–4(c) show XPS spectra for a cleaning process where the plasma-processing time was reduced from 5 min to 30 s and where the desorption anneal was reduced from 720 to
600 °C. Figure 4(a) shows an XPS spectra from the sample as loaded. Results in Fig. 4(b) show that a 30 s exposure to the hydrogen plasma was sufficient to reduce the carbon to levels below detectability. However, annealing at 600 °C did not prove effective at removing oxygen from the surface, as shown in Fig. 4(c).

LEED was performed on the samples at intervals during the cleaning process. Samples cooled from 720 °C to room temperature in molecular hydrogen exhibited a 2 × 1, 1 × 2 LEED pattern. Samples in the 2 × 1, 1 × 2 state were easily converted to the 1 × 1 state by a 2 s exposure at room temperature to the hydrogen plasma. These results are consistent with previous studies on hydrogen adsorption and desorption from the silicon(100) surface. A hydrogen terminated silicon 1 × 1 surface will reconstruct to the 2 × 1 configuration upon heating to approximately 450 °C. Annealing to this temperature results in a surface where each silicon atom is terminated by one hydrogen atom. Annealing to approximately 550 °C results in the desorption of the remaining hydrogen from the surface as molecular hydrogen. Reexposure of the clean 2 × 1 surface to atomic hydrogen at a temperature below the first desorption temperature of 425 °C results in a 1 × 1 hydrogen terminated surface again.

Atomic hydrogen is known to etch silicon relatively easily, 10 and comparisons were therefore made of the surface morphology as a function of processing parameters. Figure 5 shows scanning electron micrographs of three surfaces: before in situ cleaning, after in situ cleaning with a 5 min plasma exposure, and after in situ cleaning with a 30 s plasma exposure. The first sample which was exposed for 5 min has been severely etched. The second sample exposed for 30 s shows no evidence of surface damage, and has a surface morphology comparable to the sample before cleaning.

Although carbon was removed by exposure to the hydrogen plasma at 480 °C, many of the samples showed slight increases in the O 1s XPS peaks. Examination of the Si 2p peak intensities revealed a similar increase after carbon removal. It is likely that a substantial percentage of the differences in oxygen and silicon peak intensities seen can be attributed to carbon attenuation of both the oxygen and silicon signals. However, in order to determine the role of the plasma in producing oxygen contamination of the surface, samples were cleaned and then reexposed to the plasma under the conditions used to remove carbon. Figure 6 shows XPS spectra for a sample after cleaning and then after exposure to the plasma at 400 °C for 5 min. At the power levels and pressures used here, we find that subsequent exposure to the plasma adsorbs oxygen onto what had previously been an oxygen-free silicon surface. Annealing the sample to 720 °C, once again, easily removes the oxygen.

Tests were also made to ascertain the importance of carbon removal prior to desorbing oxides from the surface. Samples were heated to 720 °C without first exposing the surfaces to a hydrogen plasma for carbon removal. XPS spectra taken after plasma treatment showed that oxygen was not removed from the surface. Samples were then exposed to the hydrogen plasma for 5 min at 480 °C. XPS spectra in this case revealed that little if any carbon was removed from the surface by the plasma. It appears that if samples are annealed at 720 °C with both carbon and oxygen on the surface, the oxygen will not desorb. Subsequent hydrogen plasma processing is rendered ineffective at carbon removal.

IV. DISCUSSION

Although carbon removal from the silicon surface has been reported by a number of research groups, the exact mechanism is still unclear. It is thought to be by hydrogenation to form volatile hydrocarbons. Removal of oxygen from the surface by hydrogen plasma cleaning has proved to be more difficult. 4,5,11 It is not clear if oxygen removal occurs by etching back the silicon or by direct attack of the Si-O bonds by the atomic hydrogen. Certainly the Si-Si

\[ \text{Si-Si} \]

\[ \text{Si-O} \]
bonds are much weaker, and perhaps are easier for the atomic hydrogen to break than the Si-O bonds.

The mechanism for oxygen removal in the cleaning process reported here is relatively easy to understand. For submonolayer coverages of oxygen on silicon, the desorption temperature of the oxide, as SiO, has been reported as approximately 700 °C. This was found for a heating rate of 6 °C/s, presumably a longer time at a lower temperature would achieve the same effect. As the oxygen coverage is increased the desorption temperature increases to a maximum beyond 1000 °C for a fully developed oxide. One key to minimizing the oxide desorption temperature is to start the in situ cleaning process with as little adsorbed oxygen as possible.

Reoxidation of clean surfaces upon exposure to the plasma is observed to occur at a slow rate. No evidence of oxygen adsorption is seen when clean samples are simply exposed to flowing molecular hydrogen, so we can assume the plasma is activating some species or process. Possibilities include residual gases in the cleaning chamber, and etching of the quartz plasma tube. No evidence is seen for contamination of the hydrogen with the quadrupole mass spectrometer while the plasma is off. Base pressure for the system is 5 × 10⁻¹⁰ Torr, of which a significant component is mass 18, or water. The plasma could easily transform a portion of the residual water vapor into OH radicals, which could then chemisorb on the silicon surface. A concurrent process may be etching of the quartz plasma tube to form SiO, which again would adsorb on the surface.

Of particular interest in this work is the observation that if carbon and oxygen are left on the surface prior the the 720 °C anneal, neither species are removed during the high-temperature anneal, and, furthermore, subsequent processing by either plasma treatment or thermal desorption has no effect. The presence of carbon on the surface appears to prevent the desorption of suboxides of silicon from the surface at 720 °C, and, in turn, the carbon species on the surface seem to be altered by the anneal. It is unlikely that the carbon on the surface initially exists as pure carbon bonded to silicon. A more likely form is a hydrocarbon physisorbed or partially chemisorbed on the silicon. Bozack et al. have studied the relationship between hydrocarbon species and desorption products from the silicon surface. In general, higher molecular weight hydrocarbons adsorb more easily on the silicon surface and will tend to decompose as the temperature is increased, eventually forming silicon carbide. Correlations were also found between number of C-C bonds and reactivity with the silicon surface. For example, ethylene was found to desorb in greater quantities without decomposition than acetylene. However, hydrocarbons and perhaps halocarbons on the surface are apparently susceptible to attack by atomic hydrogen before they are thermally decomposed. Once the hydrocarbons have thermally decomposed on the surface, the desorption temperature is raised to well over 1000 °C.

Any oxygen remaining on the surface with the carbon can potentially be bound to the silicon, to the carbon or bridge the two atoms. One expects carbon to be bound to the silicon with two of four available bonds. The remaining
two bonds offer sites for carbon–oxygen bonds. Oxygen desorption from graphite has been measured to be approximately 800°C. This was for a heating rate of 50°C/s so it is not clear what the desorption rate would be for an isothermal anneal at a lower temperature. If the oxygen is thus bound preferentially to the carbon, the oxygen/graphite desorption results may account for the inability to desorb oxygen at 700°C from silicon surfaces which are contaminated with carbon.

V. CONCLUSIONS

A hydrogen plasma-based technique for carbon removal has been combined with a modest anneal for oxide desorption at 720°C to produce atomically clean Si(100) surfaces. Carbon and oxygen contamination can be removed from silicon surfaces by a 30 s hydrogen plasma exposure at 480°C (for carbon removal) followed by a 5 min anneal in molecular hydrogen at 720°C (for oxygen removal). Carbon removal is thought to occur by volatilization through hydrocarbonization. The mechanism for oxygen removal is believed to be more straightforward and consist of thermal desorption of SiO at approximately 700°C. Longer duration exposures to the hydrogen plasma, under the reported conditions, are seen to induce microscopic surface roughness without oxygen elimination. Samples which are devoid of oxygen following the 720°C anneal are found to reoxidize upon reexposure to the hydrogen plasma. It is not known at this time whether the oxidizing species originates as an impurity in the hydrogen gas, is present as a residual background impurity, or is generated from interactions between the hydrogen plasma and the quartz plasma tube. The effect of the oxidizing species, however, is clear. It compromises the plasma cleaning at 480°C. Hence, the hydrogen plasma cleaning process is seen to be a competition between silicon etching, hydrocarbonization of surface contaminants, and reoxidation of the silicon surface.

The approach taken here to obtain clean Si(100) surfaces was to first remove the surface carbon with a short plasma exposure to minimize surface damage and, second to thermally desorb the remaining oxygen from the surface in flowing hydrogen gas. Anneals at 720°C with carbon present on the surface results in a surface reaction which complexes the carbon and oxygen on the surface, rendering the surface contamination resistant to subsequent plasma processing or annealing.
