Journal of The Electrochemical
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To cite this article: R. J. Carter *et al* 1994 *J. Electrochem. Soc.* **141** 3136

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In Situ Remote H-Plasma Cleaning of Patterned Si-SiO$_2$ Surfaces

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ABSTRACT

A RF H-plasma exposure was used to clean the surface of Si-SiO$_2$ patterned wafers. The areal coverage of SiO$_2$ to bare Si was 4 to 1, and the patterns were long strips, small squares, and large open regions. The plasma-surface etching was monitored by residual gas analysis (RGA). The RGA spectra indicated etching of the Si surface at temperatures below 400°C and no detectable by-products due to interactions with the SiO$_2$ regions for temperatures <450°C. The patterned surfaces were characterized with low energy electron diffraction (LEED) (from the bare Si regions) and atomic force microscopy (AFM). The LEED patterns indicate 1 × 1 and 2 × 1 surface symmetries at 300 and 450°C, respectively. The sharpness of the LEED patterns as well as the 2 × 1 reconstruction indicated that the H-plasma cleaned the bare Si regions. In addition, AFM measurements indicated that the Si and SiO$_2$ surface rms roughnesses do not vary significantly due to the H-plasma exposure. It can be concluded from the RGA and AFM data that the remote H-plasma process at 450°C cleaned the surface and did not significantly react with either the Si or SiO$_2$ regions.

With the continued demands to decrease device geometries and increase packing densities in silicon-based integrated circuits, issues related to contamination become increasingly important. This results in the need to address complicated issues related to surface contamination.[1] One approach is to combine processing with surface preparation. As such, *in situ* cleaning of semiconductor surfaces has become an area of increased interest. The motivation is to remove particulates and contaminants from semiconductor surfaces in order to produce smooth and atomically clean surfaces immediately prior to next step processing. Two approaches are often considered: (*i*) clustering the process and preparation chambers and (*ii*) developing systems which can sustain both a surface preparation and process in the same chamber. A smooth and atomically clean surface is favorable for subsequent processing steps in device manufacturing. A trend in clean surface technology is the evaluation of dry phase processes as alternatives to wet chemical processes. It has previously been established that hydrogen plasma (H-plasma) processing is capable of removing some surface contaminants and controlling the surface termination and passivation.[2-5]

In previous studies, H-plasma processing has been applied as a subsequent step following wet chemical treatments. An example is the surface preparation for either epitaxial Si growth or oxide formation on Si (100). The process sequence is typically an RCA (or HF-based) wet chemical clean followed by an *in situ* H-plasma clean.[2-9] In another related study it was demonstrated that an electron cyclotron resonance (ECR) H-plasma exposure can be effective without a requiring a wet chemical preparation.[10] Comparing the Auger electron spectroscopy (AES) data before and after H-plasma exposure, the resulting surface exhibits reduced concentrations of carbon and oxygen.[2-4,8,9] The hydrogen-terminated surface symmetry can be 1 × 1, 3 × 1, or 2 × 1 depending on the H-plasma processing conditions.[3,5,8,11] Therefore, the structure and chemistry of the Si (100) surface following H-plasma processing is suitable for subsequent epitaxial or oxide growth.

H-plasma exposure of Si surfaces has been employed for the removal of the native oxide. In these studies a threshold ion density of ~10^{10} cm^{-3} was found to be necessary for etching the SiO$_2$.[2,12] To achieve this plasma density, ECR is

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coupled with a microwave discharge of 2.45 GHz. One study indicates a relationship between the threshold density and the system base pressure.[12] Another study indicates that the plasma emission can be used to monitor the surface chemistry during the etching.[2] A key result of the studies is that the SiO_2 etching is H^+ ion assisted.[2,12] In a related study, an ECR H-plasma was used to hydrogenate an SiO_2 film and to terminate the surface with atomic H bonded predominantly to Si.[13] Adsorbed H on Si has been demonstrated to be a suitable surfactant which suppresses island growth during Ge deposition.[14] In addition to the threshold density for removing native oxide, previous research has indicated that the removal process is enhanced at temperatures >350°C.[15]

Two of the problems of H-plasma processing are (*i*) the potential for etching of the Si surface and (*ii*) the diffusion of H into the subsurface region. The surface etching can result in a rough surface and the H diffusion can lead to subsurface defects.[6,7,16-18] Si surface etching depends on exposure duration and substrate temperature.[6,7,19] The etching occurs for exposure durations >5 min[5] and at temperatures <450°C.[6,19] In a previous study, Si (100) surfaces were exposed to a H-plasma at temperatures between 150 and 450°C for durations between 1.0 and 60 min.[6] The AFM results indicated that the rms surface roughness was greater for Si (100) surfaces processed at 150°C as compared to 450°C processing. Also, the AFM data indicated that the rms surface roughness was greater for exposure durations of 60 min compared to 1.0 min for 150°C processing. Previous results have also indicated that the formation of H induced subsurface defects are related to H diffusion into the Si.[16] It has also been shown that low energy H^+ ions can potentially result in smoothing of an SiO_2 surface.[20] The smoothing rate was also shown to increase with increasing incident H^+ ion energy in the range 0.2 to 1.0 keV.[20] The diffusion of H into the subsurface region is also a temperature-time process.[16,18] High resolution transmission electron microscopy (TEM) has indicated the presence of subsurface defects for the 60 min, 150°C processing. In contrast, defects were not detected in the TEM of the samples processed for even the long time exposures of 60 min at 450°C.[6] In a related study, H was implanted into damaged regions in a p-type Si (100) surface.[21] A four-decade change in the free-carrier concentration was observed which was stable for annealing of the samples at temperatures up to 800°C for 1 min. This effect is attributed to deactivation of the acceptors due to the hydrogen and reduced diffusion of the H in the disordered regions.

Previous research[22,23] has indicated that smooth, defect-free surfaces are necessary for reasonable values of the minority carrier lifetime. This is supported by the correlation between the atomic structure and electronic properties from the work of Hahn and Henzeler.[24] The researchers measured the Hall mobility of Si (111) p-channel metal oxide semiconductor field effect transistor (MOSFET) devices and related their data to the roughness of the Si-SiO_2 interface. The conclusion is that the roughness at the Si-SiO_2 interface degrades the Hall mobility. It is clear that *in situ* surface preparation processes are required to maintain a smooth Si surface. The motivation for the present work is to clean Si-SiO_2 patterned surfaces without damaging the bare Si or oxide regions. The *in situ* clean studied in this report is directed toward the preclean for the gate oxidation step in transistor device processing. The H-plasma cleaning process is investigated as a precursor for removing hydrocarbon and residual oxide contamination whereas more complicated multistep processes may be required for residual metal removal. In this study, the plasma and surface characterizations are combined to develop an understanding of the plasma-surface interaction in the remote H-plasma cleaning process.

Experimental

The original surfaces of the patterned structures studied were 25 mm diam, Si (100), phosphorus-doped (n-type) wafers with a resistivity of 5 to 10 Ω-cm. Prior to oxidation the wafers were prepared via an *ex situ* process described as follows: (*i*) the samples were exposed to a UV-excited air ambient which generates ozone to remove the surface hydrocarbons, and (*ii*) the samples were processed with an HF-based spin etch {HF:H_2O:ethanol::(1:1:10)} to remove the oxide layer grown during the UV-ozone exposure.[25] Following the *ex situ* clean, the samples were then transferred to a chemical vapor deposition (CVD) system. A 3500 Å oxide layer was grown in a wet-dry-wet oxidation process at 1000°C for 60 min. The samples were patterned and etched via a contact UV-photolithography process. The process involved 8000 Å (positive) photoresist spin, soft bake 95°C, UV-exposure, development, hard bake at 120°C, oxide removal with 10:1 buffered oxide etch (BOE), photoresist removal, and an RCA clean. The mask for patterning the wafers is divided into four quadrants: (*i*) two quadrants with graduated features, (*ii*) one quadrant completely open (a square of side 5 mm of bare Si), and (*iii*) one quadrant closed for providing a completely oxidized region of the wafer. The center of the mask has an open square of bare Si of side 3 mm. The structured regions are comprised of strips, graduated from 500 μm to 3 μm, and squares, graduated from 250 μm to 3 μm. the strips and squares are regions of exposed or bare Si. The ratio of areal coverage between the SiO_2 to Si regions for all of the square and graduated features was 4 to 1.

Prior to insertion into the vacuum system for the *in situ* cleaning, the patterned surfaces were prepared with the two-step UV/ozone followed by HF-based spin etch. The only difference in this step compared to the above preclean was that more ethanol was required to spread the HF-based etchant over the oxidized wafer during the spin. The ethanol was introduced from a separate bottle and not mixed in the original HF-based solution. This wet chemical cleaning step removes the native oxide and results in a predominantly H-terminated surface.[25]

The samples were inserted into the UHV surface analytical system through a loadlock for characterization prior to the plasma cleaning. The base pressure of the surface analytical system is $>1.0 \times 10^{-9}$ Torr. Following the initial characterization, the patterned surfaces were then transferred into the H-plasma cleaning system (Fig. 1). The base pressure of the plasma system is $\sim 7 \times 10^{-9}$ Torr. The plasma is created by direct excitation of molecular hydrogen flowing through a quartz tube with a 12-turn copper coil encircling it. The application of 13.56 MHz RF power to the coil created atomic, ionized, and excited H and H_2 species. The applied RF power used in this study was 20 W. The gas purity is 99.9995%. The RGA traces obtained while the system is at base pressure have been previously presented.[5] A brief description of the base spectra of the plasma clean-

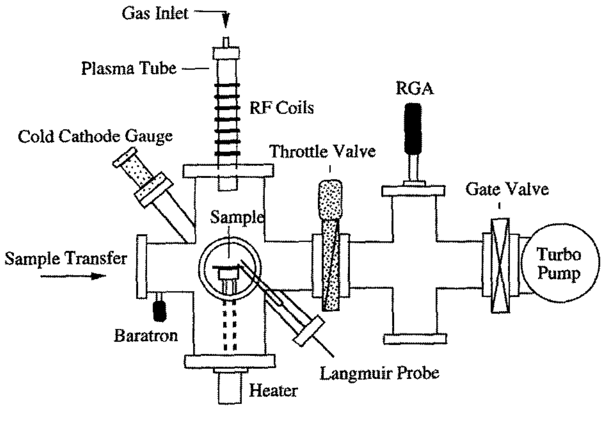


Fig. 1. A schematic of the chamber used for remote H-plasma exposure. The plasma is essentially confined to the quartz plasma tube region. The position of the Langmuir probe is indicated. The RGA is downstream from the plasma excitation chamber allowing operation at processing pressures. Pressure was maintained by control of the gas flow and the throttle valve.

ing system with the improved base pressure is presented in the next section.

The samples were located 40 cm downstream from the center of the coil and at the center of the cylindrically symmetric stainless steel chamber (Fig. 1). The process pressure was maintained with a throttle valve, capacitance manometer, and turbo pump and the gas flow was controlled with mass flow controllers. By varying the process pressure and RF power, the plasma could extend into the chamber and immerse the sample region or become largely confined to the tube and therefore is remote from the sample surface. For the pressure used in this study (15 mTorr), the plasma glow was largely confined to the coil region but a weak, diffuse glow was observed in the sample vicinity. The sample temperature was established by radiative heating from a tungsten filament wound into a coil and located behind the sample. The temperature measurement was made with a thermocouple located directly behind the center of the sample. To calibrate this temperature measurement system, the thermocouple measurement was compared to an optical pyrometer measurement in the range 600 to 1000°C. The measurements were then extrapolated into the range 20 to 600°C. The difference in the upper range was $\sim \pm 20$°C which extrapolated to the lower range as $\sim \pm 15$°C. In other experiments from this laboratory,[11] observed H-plasma induced surface symmetry transitions occur at temperatures consistent with previous studies.[3,5,9]

The surface etching processes were characterized with a residual gas analyzer (RGA). The RGA was operated in the Faraday cup mode, and the sensor was located between the throttle valve and the turbo pump. For our system and pumping configuration, the molecular hydrogen flow could not exceed 5.0 sccm to operate the RGA at its maximum pressure of 5×10^{-4} Torr. The sensitivity of the RGA at the process pressure of 15 mTorr is determined by the location in the system. The present location is between the throttle valve and the turbo pump but not colinear with the two. This results in an apparent stagnant flow condition from the RGA samples which leads to the problem of reduced sensitivity to changes in the plasma chemistry. To eliminate this problem the flow is reduced to 5 sccm H_2 during processing which results in a pressure in the region of the RGA of $\sim 4 \times 10^{-4}$ Torr. At this pressure, the sensitivity of the RGA is $\sim 5 \times 10^{-7}$ Torr. Operating the RGA in this pressure range preludes accurate absolute measurements of peak intensities from one process run to another, however, the trend of the peak intensities within a single process run are accurate and repeatable.

The process sequence for the H-plasma clean is as follows: the substrate temperature was ramped 50°C/min to 150°C. When the substrate temperature reached 150°C, it was held there for 2 min. The 2 min at 150°C was intended for desorbing any remaining wet chemical residue on the sample surface. The next step in the temperature sequence was a ramp to 450°C, at the same rate, and held for 3 min. For the first 2 min at 450°C, the H-plasma was activated (20 W, 15 mTorr). After 2 min of plasma exposure, the RF power and H_2 gas were switched off. Then the sample was held at 450°C for the final minute. Holding the temperature constant at 450°C for the extra minute prevented the sample from cooling in a H-H_2 ambient, possibly leading to a H-saturated surface. The plasma system recovery time prior to UHV transfer to the analysis system was approximately 5 min. The base pressure of the transfer system was 1.0×10^{-9} Torr.

The LEED diffraction patterns were obtained, before and after H-plasma processing, at a beam energy of 60.8 eV. The samples were also characterized with Auger electron spectroscopy (AES) for detection of surface contaminants.

After processing and surface characterization, the samples were removed from the vacuum system and the surface morphology was studied with AFM. AFM was used to study the topography of both the field oxide and bare Si regions before and after H-plasma processing. The AFM analysis was performed with an ambient Park Scientific System that employed a 10 μm × 10 μm scanner and silicon nitride tips.

Results

In previous publications from this laboratory,[6] the plasma density was determined from double Langmuir probe measurements. For the H-plasma process parameters of 15 mTorr and 5 sccm, the plasma density is $\sim 10^{8}$ cm^{-3}. The plasma density is converted to an ion flux of $\sim 10^{12}$ cm^{-2} s^{-1}. *In addition, catalytic probe measurements* indicate that for the H-plasma process conditions of the present work, the H flux to the surface is $\sim 10^{16}$ cm^{-2} s^{-1}. A theoretical calculation using the geometry of the plasma system also indicated similar values of the atomic and ion fluxes.[26] We note that as expected the plasma densities are much lower than the densities required for native oxide removal.

The RGA measurements were used to determine when surface reactions were occurring and data was obtained over the atomic mass range of 1.0 to 70 amu. The baseline RGA spectra is described as follows. Appearing at 1 and 2 amu are features associated with hydrogen, at 17 and 18 amu are features associated with water, a feature at 28 amu is associated with CO, and the feature at 32 amu is due to trace oxygen in the system. When the H-plasma is activated and no sample is present in the system, the RGA spectra contains an additional peak at 44 amu associated with CO_2. The peaks at 1, 2, 17, 18, and 28 amu increase when the H-plasma is activated. The origin of the increased intensities of the peaks during the plasma activation compared to the peaks observed in the base spectra is plasma-wall interactions.[5] When a bare Si sample is introduced to the H-plasma system, the RGA contains additional peaks at 29, 30, and 31 amu. These peaks are associated with the formation of SiH_4 [3,5,27] and the liberation of Si from the surface. These peaks correspond to SiH, SiH_2, and SiH_3, respectively, which are attributed to silane (SiH_4) fragmentation and Si since the relative abundance of Si is ^{28}Si:^{29}Si:^{30}Si is 92:5:3. To be more specific, the 30 amu peak is comprised of $^{30}Si + {}^{29}SiH + {}^{28}SiH_2$. The 30 amu peak is the largest in the fragmentation pattern and is therefore a traceable feature for the surface etching. The etching of SiO_2 is expected to display RGA peaks appear near 17, 18 amu (OH and H_2O), 29, 30, and 31 amu (SiH, SiH_2, SiH_3), and 44 amu (SiO). Unfortunately some of these signals are difficult to sense because of the common background signals from the plasma system. Water is always present and CO_2 exhibits a peak at 44 amu. The Si-H features cannot be used to distinguish Si or SiO_2. RGA trends of 45 amu (SiOH), 60 amu (SiO_2), and 61 amu (SiO_2H) indicate no observable molecules from the plasma-oxide surface reactions.

The plasma-surface interactions for the different wafer surfaces were sequentially investigated. First, a bare Si (100) wafer was exposed to the H-plasma. In this case, the peaks in the RGA spectra indicated SiH_4 fragmentation. The strongest feature was at 30 amu. The substrate temperature dependence of the 30 amu peak intensity is displayed in Fig. 2. The trend in Fig. 2 indicates that surface etching decreases with increasing temperature. Second, a completely oxidized surface of an Si (100) wafer was exposed to the H-plasma over the range of temperature 40 to 600°C. In this case, no SiH_4 fragmentation was detected and while signals due to water (17, 18 amu) and CO (44 amu) were always present in the RGA spectra, no significant increase in these peaks was observed.

Last, a patterned Si/SiO_2 surface was exposed to the H-plasma over the range of temperature 40 to 600°C. As noted, the surface was prepared with the *ex situ* clean prior to loading. The RGA spectra of this wafer indicated the same trend as the bare Si (100) for SiH_4 fragmentation.

Following the 300°C, 1.0 min H-plasma exposure of the patterned surface, LEED patterns were detected which exhibited the 1 × 1 pattern (Fig. 3a). Following a 450°C, 1.0 min H-plasma exposure a 2 × 1 LEED pattern is observed (Fig. 3b). In prevous work on n-type (1 Ω-cm) Si

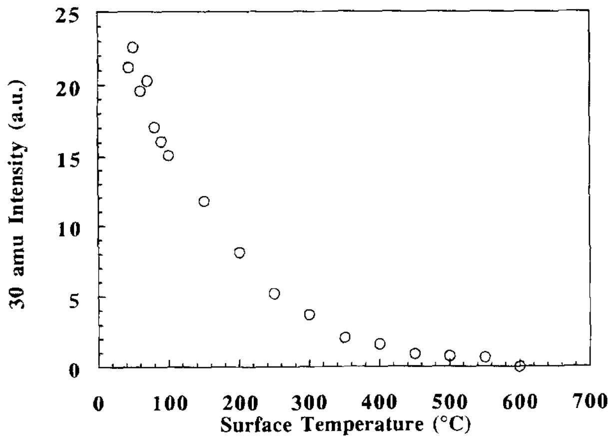
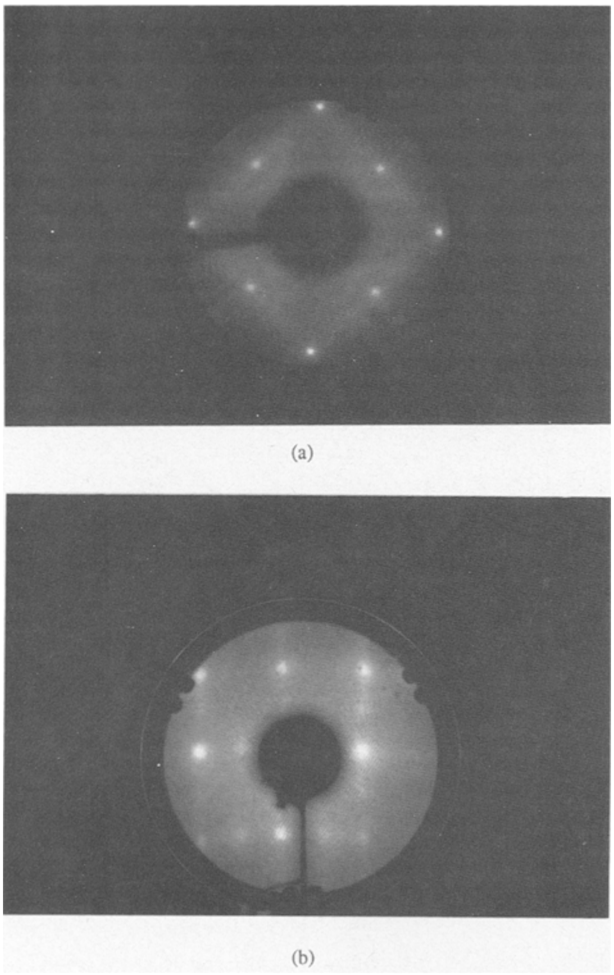


Fig. 2. The substrate temprature dependence of the 30 amu signal (SiH_2) obtained during H-plasma processing of a Si (100) surface. The signal is attributed to the generation of SiH_4 from the interactions of atomic H with the Si surface.

(100) surfaces the 2 × 1 LEED pattern was observed for H-plasma exposure at as low as 300°C.[5] At this time we cannot determine whether the slightly higher temperature for obtaining the 2 × 1 reconstruction is attributed to different doping levels or to the patterned surface.

The surface chemical concentration was determined using AES with detection limits of ~0.5 atom percent. Following the *ex situ* cleaning process, the AES data indicates less than 0.1 monolayer C and O contamination only with the dominant spectral feature being due to Si. These results are consistent with AES data obtained from unpatterned Si (100) surfaces in this laboratory and reported in previous research.[3] These contaminants are residuals due either to the wet chemical clean or from the atmospheric exposure following the wet chemical clean. Immediately following the H-plasma exposure, the AES spectra (of the exposed Si regions) indicates a reduction in the O peak and no detectable peak for the C. Again, this is consistent with previous AES[3,4,8,9] and x-ray photoemission spectroscopy (XPS)[10] studies of the H-plasma cleaning process.


(a)

(b)

Fig. 3. LEED patterns from bare Si regions of oxide patterned Si (100) surfaces obtained with a beam energy of 60.8 eV: (a) 1 × 1 pattern after 300°C, 2 min H-plasma clean; and (b) 2 × 1 after 450°C, 2 min H-plasma clean.

In a further attempt to characterize the surface, AFM was employed to measure the surface roughness. Applying this technique to the Si/SiO_2 patterned surfaces, the AFM scans were obtained for scan ranges of 2 to 5 μm with ~1000 × 1000 pt images. The root mean square roughness from the average surface plane was determined using the AFM system software (Park Science). The rms roughness on the oxide regions before and after H-plasma exposure is ~2.5 Å. This data indicates that the oxide regions were not significantly roughened by the H-plasma. In a previous study AFM measurements on H-plasma processed Si (100) surfaces were reported.[7] The results indicate a significant dependence of the surface roughness on substrate temperature. For samples processed with an H plasma at 150°C an rms roughness of >20 Å was observed for a 10.0 min exposure. Increased roughness was observed for extended 60 min H-plasma exposures. In contrast for H-plasma exposures at 450°C, the rms roughness was <2 Å which is essentially the same as the original wafer surface. Therefore, in this process region (15 mTorr, 20 W, 450°C) the H-plasma exposure does not significantly roughen either the oxide or Si surface.

The results raise the issue as to whether surface roughness is related to surface etching. A previous report from this laboratory investigated the relationship between surface etching and surface topography.[6] The surface etching was characterized by observing the trends in the SiH_4 pattern in the RGA spectra (Fig. 2). The surface roughness was characterized via AFM. The data correlated such that the increased etching at low temperature (<150°C) was coincident with an increased surface rms roughness.[6] These results were repeatable and are consistent from wafer to wafer for similar process conditions. Therefore, in the case of H-plasma interactions with Si (100) surfaces, surface etching is related to surface roughness such that etching produces roughness. At this time we cannot be assured that the same conclusion is true for the oxide regions. However, evidence of etching was not observed in these measurements and the observed flat surface is at least consistent with no etching for the low ion density H-plasma processes employed in this study.

Discussion

In a previous study by Veprek *et al.*,[19] the etch rates of Si (100) and SiO_2 surfaces exposed to an immersed H-plasma were measured. Similar to the RGA measurements presented here, their data indicates that the Si (100) etch rate decreases with increasing temperature. According to the study, the Si (100) etch rate is maximized at 60 to 80°C and is near zero at <400°C depending on the discharge current.[19] The decreased etch rate of Si (100) with increasing surface temperature in a H-plasma is also reported in another previous study.[28] The 300 and 450°C etch rates in Ref. 19, 28 correlate well with the inability to observe SiH_4 fragments in the RGA spectra during H-plasma processing presented here. In contrast to the Si (100) etch rate, the SiO_2 etch rate in an immersed H-plasma increases with increasing sample temperature.[19] Furthermore, the SiO_2 etch rate is near zero at 350°C and increases significantly at 600°C.[19] To avoid surface etching of both the oxide and Si surfaces, the optimal temperature for the H-plasma cleaning process is ~450°C.

The LEED patterns displayed in Fig. 3 indicate that the bare Si regions are well ordered. The 2 × 1 structure in

Fig. 3b is an indication that the surface is atomically clean since the formation of dimers requires the joining of dangling bonds. If C or O surface contamination is present on the surface during dimer formation, the C or O would insert and therefore block the dimers from forming. The reduction in the C and O concentrations, observed in the before and after H-plasma AES spectra, also indicates that the H-plasma has removed surface contaminants from the Si (100) surface.

The last point to be discussed in the interaction of the plasma ions and electrons and the patterned oxide surface. In this study, at 15 mTorr, the ratio of the ion flux to the atomic H flux is $\sim 10^{-4}$. This indicates that the concentration of H^+ ions is minor compared to the concentration of the atomic H at the sample surface. For the pressures employed, the H ions would have an average energy characteristic of $\sim$500 K. In contrast, electrons are accelerated to the plasma potential of $\sim$50 V. The plasma potential was determined from the Langmuir probe measurements. Hence, for the remote H-plasma exposure, the combination of low density and low energy of ions and electrons will likely limit damage due to charged species. This is to be contrasted with ECR plasmas which would exhibit substantially higher ion and electron densities, and because of the lower pressure, a higher ion temperature.

Furthermore, the observation of clean Si regions indicates that if any Si-O bonds were broken, the oxygen was apparently not able to diffuse over to the bare Si regions. Earlier work[29] proposed that H_2 acts as a carrier gas flushing away any sputtered oxygen clusters; so if any oxygen moved over to the bare Si regions, it is likely bonded to the hydrogen covering the Si and leaves the surface as H_2O and OH species.

A parallel study has examined whether the H-plasma results in degradation of the electrical properties of MOS devices.[7] Devices were prepared with an *in situ* H-plasma clean at different temperatures prior to gate oxide formation. The processes were carried out in a cluster module system, and the oxide and poly-Si were deposited by rapid thermal chemical vapor deposition. The details are described elsewhere.[7] The results indicate that devices produced with H-plasma clean at ≤300°C exhibited a reduced mobility and lower threshold voltage, while the mobility and threshold voltage for the devices produced with H-plasma at ≥400°C were essentially identical to devices prepared with an RCA clean prior to oxide deposition.

Conclusion

The RGA data indicate no observable etching of patterned Si-SiO_2 surfaces during a H-plasma exposure at 450°C. The AFM scans indicate that the rms surface roughness is unchanged when comparing the before and after H-plasma processed surfaces. RGA and AFM measurements indicate that H-plasma processing of patterned Si-SiO_2 wafers is suitable for smooth and clean surfaces. LEED patterns observed before and after H-plasma processing indicate that the surface becomes well ordered following the H-plasma exposure. Collectively, H-plasma induced damage to both regions can be minimal, and efficient cleaning of the wafer has been demonstrated.

Acknowledgments

We acknowledge helpful discussions with Y. L. Chen and J. Barnak. We also acknowledge E. Condon for help with designing the mask. This work has been supported by the NSF Engineering Research Centers Program through the Center for Advanced Electronic Materials Processing (Grant CDR 8721505).

Manuscript submitted Jan. 28, 1994; revised manuscript received June 10, 1994.

North Carolina State University assisted in meeting the publication costs of this article.

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