As the device dimensions are scaled for ultralarge scale integration (ULSI), silicon epitaxial growth offers new degrees of freedom in the fabrication of advanced semiconductor devices.\(^1\,^2\) One of the key challenges of silicon epitaxial growth in ULSI is to achieve defect-free thin films at low temperatures.\(^6\) As the thermal budget of epitaxial processes is reduced, surface preparation for epitaxial growth becomes especially critical. Achieving a silicon surface that is free of organic and metallic impurities is an essential requirement in silicon integrated circuit (IC) manufacturing. It is suggested that more than half of the yield losses in IC manufacturing today may be attributed to contamination.\(^7\)

Surface preparation prior to silicon epitaxial growth generally consists of two parts: wet chemical cleaning before the samples are loaded into the reactor (ex situ cleaning), and a surface treatment usually in the form of high temperature annealing, immediately before the epitaxial growth (in situ cleaning). In order to achieve atomically clean silicon surfaces for defect-free growth, while maintaining the thermal budget compatible with dopant diffusion requirements, both ex situ and in situ cleaning processes have to be optimized.

Ex situ surface preparation prior to silicon epitaxial growth has two objectives: (i) to remove the organic and metallic impurities from the wafer surface, and (ii) to passivate the surface against any contamination until the epitaxial growth is initiated. These objectives have been traditionally met by the RCA clean, which removes the organic and metallic impurities from the silicon surface by oxidizing the silicon surface and forming complexes with the contaminants, which become water soluble.\(^7\) After RCA clean, the silicon surface is left passivated with a chemical oxide, which protects the surface against recontamination. The oxide layer is removed to achieve an atomically clean silicon surface before epitaxial growth.

The conventional method of desorbing the native oxide from the silicon surface by high temperature anneal (>1000°C) is incompatible with ULSI.\(^8\) These concerns have resulted in the development of cleaning processes which removes the native oxide in a dilute HF etch, leaving the surface passivated with hydrogen. Hydrogen desorbs at lower temperatures (~400°C) which is compatible with low thermal budget requirements of ULSI.\(^9\) Using an HF dip to remove this protective oxide prior to loading the samples into the reactor has been used by several research groups both in molecular beam epitaxy (MBE) and chemical vapor deposition (CVD).\(^5,\,^9,\,^10\) However, hydrogen passivation is not as stable as the native oxide on a silicon surface. The stability of hydrogen passivation against oxidation is a function of exposure time and the humidity in the ambient. In addition, HF passivation has been demonstrated to be ineffective against hydrocarbon contamination.\(^11\)

In situ cleaning is the final step to remove the native or the chemical oxide layer as well as other contaminants from the silicon surface before epitaxial deposition. In situ cleaning in hydrogen yields good quality silicon epitaxial films. However, the adverse effects of this high temperature step, such as excessive dopant diffusion, silicon dioxide damage,\(^12\) and surface roughening\(^13\) make it an unlikely candidate for ULSI. Silvestri et al. demonstrated that, using an HF-last process, the prebake temperature could be reduced to 850°C for a 5 min hydrogen bake at 10 Torr to remove the residual oxide and other contaminants in a commercial cylindrical epitaxy reactor.\(^14\) Meyerson et al. proposed ultrahigh vacuum chemical vapor deposition (UHV-CVD), which reduces the epitaxial growth temperature to 550°C at which the surface is still protected by the hydrogen passivation.\(^9\) This method yielded good quality epitaxial layers without an in situ cleaning step. However, for this process, deionized (DI) water rinse step after the HF dip is eliminated, since the water rinse causes a partial loss of the hydrogen passivation and the desorption of the oxide requires temperatures well above 550°C. Racanelli et al. showed that in a UHV-CVD system, if the DI water rinse is used after an HF dip, a prebake at 800°C for 10 min in vacuum is needed to remove the oxygen from the surface.\(^15\)

Using a rapid thermal (RT) CVD reactor, Hsieh et al. demonstrated that good quality epitaxial films were deposited by a surface preparation method that consists of a dilute HF dip and DI water rinse followed by hydrogen bake for 60 s at 800°C.\(^3\) In 1995, using an ultrahigh vacuum rapid thermal CVD system and a similar ex situ clean, Sanganeria et al. showed that interfacial carbon and oxygen could be reduced below the secondary ion mass spectroscopy (SIMS) detection levels by an in situ clean at 800°C/10 s in an ambient free of any chlorinated residuals.\(^16\) In an earlier publication, we studied this surface preparation method in a chlorinated ambient for selective silicon epitaxial growth and demonstrated that a vacuum anneal at 800°C for 10 s was sufficient to reduce the oxygen and chlorine on Si(100) below the SIMS detection levels and significantly reduce the interfacial carbon.\(^17\)

Ghidini and Smith experimentally determined the critical partial pressures of oxygen and water vapor in the ambient to achieve a clean silicon surface at different temperatures.\(^18\) As the in situ cleaning temperature is reduced, the oxygen and water vapor background...
requirements to achieve a clean silicon surface become more stringent. Hence, in order to generalize our results to other RTCVD systems, less than ideal vacuum backgrounds must be studied to investigate the robustness of an in situ cleaning process with respect to the background pressure. Another motivation for this study comes from the need to determine the fundamental limits of the process in systems that do not rely on UHV conditions. Such systems are not only more difficult to maintain but they are also more expensive. In order to achieve low partial pressures of water vapor and oxygen, UHV systems have to be pumped out for extended periods of time before each growth. A good example of this process was given by Racanelli et al., reporting that the UHV-CVD system had to be baked and pumped out for 12 h before every epitaxial growth. In addition, if the UHV systems are exposed to atmosphere for any possible breakdown or maintenance work, they may have to be baked and pumped out for up to days to achieve background water vapor levels less than $1 \times 10^{-9}$ Torr.

When the wafers are passivated with hydrogen, they can be kept in vacuum at room temperature without any contamination for extended periods of time; Sanganeria et al. showed that no additional oxygen or carbon contamination was observed on hydrogen terminated silicon surfaces for up to 18 h. This is especially important for single-wafer cluster tools in which a cassette of wafers might be loaded into the reactor after ex situ cleaning and there may have been a lapse of time between processing of wafers. However, when the hydrogen passivation is removed from the surface, silicon surface is at a highly reactive state and it is prone to contamination from the ambient. Hence, if there were multiple epitaxial layers to be deposited on a substrate, between these cycles, wafer surface would be susceptible to contamination even in a UHV system.

In this study, we have explored surface preparation for silicon epitaxy by UHV-RTCVD. The work is focused on process variables that determine process robustness. Both in situ and ex situ variables that can lead to surface contamination are considered.

### Experimental

We used 100 mm, n-type (phosphorus doped), (100)-oriented Si wafers with a resistivity range of $3 \pm 4 \Omega \text{cm}$. The wafers were cleaned in the SC-1 solution ($5:1:1 \text{H}_2\text{O}:\text{H}_2\text{O}_2:\text{NH}_4\text{OH}$) for 5 min and were rinsed in DI water for 5 min, in the SC-2 solution ($5:1:1 \text{H}_2\text{O}:\text{H}_2\text{O}_2:\text{HC}l$) for 5 min and then again in DI water for 5 min. This wet cleaning step was followed by a 15 s dip in 5% HF to remove the native oxide as well as the chemical oxide grown during the SC-1 and SC-2 clean. At the end of this etch, all silicon active areas become hydrophobic, indicating that SiO$_2$ was etched completely from these areas. The wafers at this point were separated into different batches. The first batch of the wafers was rinsed in high purity DI water for varying times ranging from $10$ to $1000$ s to investigate the effect of the DI water rinse time on surface contamination. The DI water used in these experiments was generated by hydro Systems Picopure point of use purification system with a total organic content less than 20 ppm. The second set of the wafers was rinsed in DI water for 15 s. All of the wafers were dried at this point by blowing dry nitrogen obtained from a liquid source. The DI water exposure wafers were loaded into the UHV-RTCVD reactor. The second set of wafers was left in a controlled temperature and humidity ambient for various times ranging from $10$ to $100,000$ s. The temperature and the relative humidity during these exposures were $21.8 \pm 0.2^\circ C$ and $46.5 \pm 0.5\%$, respectively.

The vacuum system used in this work is a UHV-RTCVD reactor that was designed and constructed at North Carolina State University. It consists of a main process chamber, a sample entry chamber, and an intermediate chamber which serves as a vacuum buffer between the entry and main chambers. All three chambers are made of stainless steel. The main process chamber and the intermediate chamber rely on dedicated cryopumps which provide base pressures consistently in the $1-3 \times 10^{-9}$ Torr range. The base pressure of the main chamber goes up to $1 \times 10^{-7}$ Torr if the chlorine is added to the gas chemistry for selective deposition. Oil-free pumps are used to minimize the hydrocarbon contamination. A 35 kW PEAK Systems LXU-35 arc lamp is used to heat a 100 mm Si wafer through a quartz window. The temperature measurement was performed by an optical pyrometer ($\lambda = 2.2 \mu m$) through a quartz window focused on the wafer backside. The wafer is placed on a rotatable quartz sample holder. A detailed description of this system can be found elsewhere.

After the samples were loaded into the entry chamber, each wafer went through the same procedure. The entry chamber was pumped down to $1 \times 10^{-6}$ Torr in 10 min before the wafer was transferred to the intermediate chamber. This chamber was pumped down to $1 \times 10^{-9}$ Torr in 10 min by a cryopump. The wafer was transferred to the main process chamber which has a base pressure of $1 \times 10^{-8}$ Torr that is maintained by another cryopump. The arc lamp was turned on to heat the substrate at a ramp rate of $150^\circ C/s$. An epitaxial silicon cap layer with a thickness of 100 nm was deposited at $800^\circ C$ using 135 standard cubic centimeters per minute (sccm) at $10\% \text{Si}_2\text{H}_6-\text{He}$ gas mixture at a natural pressure of $38 \text{mTorr}$ without any in situ anneal to preserve the interfacial contamination. Without the cap layer, it was not possible to quantify the remaining surface contaminants accurately due to the surface effects that are involved in SIMS analysis. Note that these wafers did not receive any in situ cleaning treatment in order to cap the contamination at the epitaxy-substrate interface for the SIMS analysis. To investigate the effects of our typical in situ anneal on the air exposure wafers, another set of wafers was annealed for $10$ s in vacuum prior to the growth of a 100 nm epitaxial Si cap layer with the conditions given above. The SIMS analysis was used to quantify the oxygen and carbon concentrations at the epitaxy-substrate interface.

In the in situ cleaning robustness study, after a typical ex situ clean, hydrogen passivated wafers were loaded into the reactor as explained above. Oxygen or nitrogen was introduced into the reaction chamber via a high precision leak valve. In situ cleaning consisted of an anneal at $800^\circ C$ for $20$ s and the partial pressures of the contaminants were varied from $10^{-7}$ to $10^{-5}$ Torr. After a steady-state level of $N_2$ or $O_2$ partial pressure was achieved, the wafer temperature was elevated to the in situ cleaning temperature of $800^\circ C$ and held at that level for $20$ s. The arc lamp was turned off at the end of the process and the oxygen or nitrogen leak was terminated. This was followed by the deposition of the silicon cap layer for the SIMS analysis. An epitaxial silicon cap layer with a thickness of 200 nm was deposited at $800^\circ C$ using $135 \text{scm}$ of $10\% \text{Si}_2\text{H}_6-\text{He}$ gas mixture at a natural pressure of $38 \text{mTorr}$ to cap the surface contaminants.

In order to investigate the contamination level when the passivated silicon surfaces were left unprotected in the vacuum ambient at room temperature, a vacuum exposure experiment was performed. In this experiment, after a typical ex situ clean, the substrates were annealed in vacuum for $20$ s to desorb the hydrogen from the wafer surfaces. These wafers were kept in vacuum at room temperature for various times ranging from $10$ to $10,000$ s; this was followed by the growth of a silicon cap layer with a thickness of $200$ nm.

In this study, the SIMS analysis was performed at Charles Evans and Associates (CEA), Redwood City, CA, and North Carolina State University (NCSU) using Cameca 3F and Cameca 6f systems, respectively. Cesium ions ($\text{Cs}^+$) were used for the primary beams with an incident energy of $14.5 \text{kV}$ with a sputtering rate of 30-40 $\text{Å/s}$ at CEA and with an incident energy of $2.4 \text{kV}$ with a sputtering rate of 10-15 $\text{Å/s}$ at NCSU. The defect analysis was performed using dark fields and interference contrast optical microscopy and scanning electron microscopy (SEM). Surface roughness was quantified by atomic force microscopy (AFM).

**DI water exposure.**—In order to investigate the stability of hydrogen passivation against carbon and oxygen contamination in DI water, a series of experiments was performed using $\text{Si}(100)$ wafers. The ex situ clean on these wafers consisted of a standard RCA clean followed by a dilute HF dip and a high purity DI water rinse. The oxygen concentration at the epitaxy/substrate interface for samples with different DI water rinse times is given in Fig. 1. The DI water rinse times were varied from $10$ s (typical DI water rinse time in our
ex situ cleaning) to 1000 s. Note that there is a very slight increase in the oxygen peak when the duration of the rinse was varied from 10 to 1000 s. Sanganeria et al. showed that the formation of these bonds is almost instantaneous when a wafer is dipped in DI water.19 Graf et al. demonstrated that the oxygen on the silicon surface at this point is in the form of OH bonds attached to the hydrogen on the surface.21

Figure 2 shows the carbon concentration at the epitaxy/substrate interface for different waiting times in DI water after a dilute HF dip. Note that an in situ clean was not performed before the silicon cap layer was grown. Hence, the carbon observed at the epitaxy/substrate interface was on the wafer surface when the wafers were loaded into the reactor. These carbon atoms on the surface may be in the form of hydrocarbons physisorbed on the silicon surface.22 There are reports in the literature suggesting that HF may be partly responsible for this kind of carbon contamination;11 Kasi et al. showed that although HF forms a protective layer of hydrogen passivation against oxidation, this passivation layer is not effective against hydrocarbons. There are reports which suggest that this carbon contamination might originate from the aqueous HF solution.23 Our results also indicate that the initial interfacial carbon coverage for a 10 s DI water rinse does not increase significantly with increasing DI water rinse periods and the carbon contamination is established instantaneously.

Air exposure.—It has been shown that a Si(100) surface is covered by 85% hydrogen, 10% fluorine, and 5% oxide or hydroxide after a dilute HF dip without a water rinse.9 Although a DI water rinse following a dilute HF dip may increase the oxygen coverage on the surface, it has also been suggested that the DI water rinse might actually increase the hydrogen passivation by replacing the fluorine atoms with hydrogen.24 Morita demonstrated that this passivation layer is stable on Si(100) up to 200 min for moderate n- and high p-type doping. However, for high levels of n-type doping, wafers exhibit an enhanced oxidation possibly due to a built-in electric field.25 It has also been demonstrated that the oxidation rate of hydrogen terminated silicon surface is directly related to the humidity level in the ambient.25 The temperature and the relative humidity during our experiments were 21.8 ± 0.2°C and 46.6 ± 0.5%, respectively.

Figure 4 shows the oxygen levels at the epitaxy/substrate interface without an in situ clean for air exposure times varying from 10 (typical immediate loading time) to 10,000 s. The data reveals a two-fold increase in the oxygen coverage from 10 to 10,000 s. However, when the wait time was increased to 100,000 s (27.7 h), the high oxygen coverage on Si inhibited the epitaxial growth due to inherent selectivity of the epitaxial growth process using disilane.26 This resulted in a thinner silicon cap layer than expected which in turn made the SIMS measurement unreliable due to surface effects. (This data point is not shown in the plot.)

The effect of air exposure on carbon contamination was also investigated. Figure 5 illustrates the carbon concentration vs. depth profiles for different wait times in air. As the data shows, there is no measurable increase in carbon contamination due to prolonged wait.
times in air. The initial carbon contamination may be due to HF treatment as discussed before. Grundner et al. demonstrated that the carbon on silicon surface after HF treatment is in the form of CH$_x$–Si bonds. These findings are in agreement with the previous results of other research groups, which suggest that the carbon contamination is not caused by the air exposure unlike oxygen.$^{23}$

Figure 6 shows the monolayer coverage of oxygen and carbon in Si(100) as a function of wait time in air. The oxygen coverage increases steadily from 10 to 25% of a monolayer after 10,000 s, whereas carbon coverage stays at 2% of a monolayer. Therefore, the air exposure on the HF-treated samples results in a slight increase in oxygen coverage up to 10,000 s (2.78 h). However, much longer air exposure times resulted in an oxide coverage level which inhibited growth, as mentioned before. These results are in agreement with previous reports by Morita et al. In their experiments, the oxide coverage on silicon was measured as approximately 2 Å (less than a monolayer of oxide) for wait times up to 12,000 s (200 min) when the HF-treated samples were exposed to air.

The defect densities were measured by dark field microscopy. Figure 7 shows the density of high contrast features observed in the epitaxial layers for varying wait times in air. The defect density increases exponentially with increasing wait time in air. The sample, which was kept in air for 10,000 s (27.7 h), was not included in this figure, since the sample exhibited a highly defective and a very rough surface. When these defects were etched in a dilute Schimmel etch,$^{27}$ the SEM studies revealed that these defects mainly consisted of isolated pyramidal shaped defects and etch pits. When the density of defects is plotted with respect to interfacial oxygen, as shown in Fig. 8, it is observed that the density of defects increases signifi-

In situ cleaning on samples exposed to air.—The limits of a typical in situ cleaning process were investigated by using samples contaminated by prolonged exposures to air and quantifying the residual interfacial contamination levels after a typical in situ cleaning cycle. The oxygen and carbon levels shown in the preceding figures were obtained without any in situ cleaning treatment. Figure 9 demonstrates the oxygen concentrations for samples with different wait times in air after a 10 s in situ clean in vacuum. As the figure illustrates, the oxygen coverage was reduced below the SIMS detection levels on samples with wait times up to 1000 s by performing a 10 s anneal at
800°C. For the 10,000 s (2.7 h) sample, the oxygen level at the interface was reduced from $1 \times 10^{20}$ cm$^{-2}$ to less than $2 \times 10^{18}$ cm$^{-2}$.

Carbon concentrations of the same samples are shown in Fig. 10. The carbon peaks at the epitaxy/substrate interface are reduced by approximately one order of magnitude as result of the in situ clean. However, it can be observed that the carbon levels in the epitaxial films increase with in situ cleaning before the epitaxial growth. This increase in the carbon level in the epitaxial film is attributed to the increase in the carbon background in the growth chamber at elevated temperatures. A detailed investigation of this phenomenon can be found in earlier publications from this laboratory.$^{17,29}$

Figure 11 shows the percent coverage of oxygen and carbon on Si(100) as a function of air exposure time after in situ cleaning at 800°C for 10 s. As shown, for samples which were exposed to air for up to 10,000 s (2.7 h), both carbon and oxygen levels at the epitaxy/interface were reduced to below 1% of a monolayer after an in situ clean (800°C/10 s). In this figure, it is also important to note that although the 100,000 s (27.7 h) sample has the highest contamination level, it was not even possible to grow an epitaxial layer for this exposure time without an in situ clean previously. Hence, it was observed that, even for relatively long air exposure times exceeding several hours, an in situ clean of 10 s/800°C is sufficient to significantly reduce the interfacial oxygen and carbon levels.

Addition of nitrogen and oxygen to the cleaning ambient.—Thermal desorption efficiency is directly related to the partial pressures of the contaminants in the ambient and the wafer temperature. In order to investigate the efficiency of in situ cleaning at different vacuum backgrounds, we have performed a series of experiments. In these experiments, oxygen and nitrogen were leaked into the in situ cleaning ambient via a high precision leak valve. Using very large scale integrated grade nitrogen and oxygen, as well as baking the gas delivery lines, the partial pressures of nitrogen and oxygen were varied from $1 \times 10^{-5}$ to $1 \times 10^{-2}$ Torr while keeping the water vapor...
and hydrogen partial pressures at the same level. This procedure enabled us to decouple the effect of different contamination species on the cleaning efficiency.

Figure 12 demonstrates carbon, oxygen, and nitrogen levels at the interface for two different levels of nitrogen partial pressure. As shown, the concentrations of carbon and oxygen at the epitaxy/substrate interface are independent of the nitrogen background. The nitrogen level at the interface was found to be below the SIMS detection levels for both levels. Therefore, we conclude that oxygen removal from the silicon surface was not affected by the nitrogen background pressure even when it was increased to $1 \times 10^{-6}$ Torr; residual oxides on the surface were effectively removed by an in situ clean ($800^\circ\text{C}/20$ s). The carbon levels measured at the epitaxy/substrate interface were typical for our system with temperature switching between the thermal cycles. Carbon peaks at the epitaxy/substrate interface with temperature switching is attributed to the fact that the substrate is cooled to room temperature between the in situ clean and the deposition cycle during which the surface is left unpassivated and prone to any contamination in the chamber. A detailed comparison of gas switching vs. temperature switching and its impact on interfacial carbon can be found in a previous publication from this laboratory.19

Figure 13 illustrates the oxygen concentration at the epitaxy/substrate interface for two different partial pressures of oxygen. With an oxygen partial pressure of $1 \times 10^{-6}$ Torr in the cleaning ambient, a residual oxide was observed on the surface even after an $800^\circ\text{C}/20$ s in situ clean. The peak oxygen concentration at the epitaxy/substrate interface for this sample is $2 \times 10^{18}$ cm$^{-3}$, which corresponds to less than 1% of a monolayer coverage. This level does not result in a higher defect density as observed under dark field microscopy. With oxygen partial pressures at and below $1 \times 10^{-7}$ Torr, residual oxide on the surface was reduced below the SIMS detection levels by in situ cleaning at $800^\circ\text{C}$. When Ghidini and Smith’s results correlating the oxygen partial pressure to wafer temperature to achieve oxide-free silicon are extrapolated to $800^\circ\text{C}$, we observe that the oxide free silicon could be achieved below $1 \times 10^{-6}$ Torr. Therefore, our results appear to be in good agreement with the predicted values.30

Ghidini and Smith also demonstrated that the water vapor partial pressure requirement is more stringent than that for dry oxygen for vacuum systems, and that the partial pressure of water vapor has to be lower than the oxygen partial pressure for the same temperature. In this study, we have attempted to form water vapor by introducing oxygen and hydrogen and elevating the wafer temperature. However, the residual gas analysis measurements revealed that it was not easy to increase the partial pressure of water vapor in the ambient in a controllable manner by this method. This may be due to the fact that the reactor used in these experiments is cold-walled and the only hot body in the ambient is the wafer itself. Nevertheless, if the Ghidini and Smith results are extrapolated to $800^\circ\text{C}$, the water vapor partial pressure should be below $1 \times 10^{-7}$ Torr to achieve an oxide-free silicon surface which is above the water vapor background of the vacuum system employed in this study.

When the high partial pressures of oxygen exist in the ambient, there is a concern that the surface roughness might increase with the substrate temperature is increased to high temperatures. There are reports in the literature suggesting a surface roughness increase with high levels of oxygen in the cleaning ambient; Roberge et al. reported that when oxygen was added during heat-up of the epitaxial deposition in a conventional Gemini-type reactor, rough and defective films were observed.31 Figure 14 shows the root-mean-square (rms) surface roughness of samples annealed in different backgrounds of oxygen. The control sample in this case was a silicon wafer cleaned by a typical ex situ clean (SC1 + SC2 + 5% HF dip + DI water rinse). As illustrated, the rms roughness for all the in situ cleaned cases was less than that of the control sample (1.73 Å).

Figure 15 illustrates a typical AFM micrograph of a substrate, which was in situ cleaned for $20$ s at $800^\circ\text{C}$ with a background partial pressure of $10^{-5}$ Torr of oxygen. The rms roughness for this sample was less than 1 Å over a $5 \times 5$ μm scan area. Therefore, under the experimental conditions used in this study, we did not observe a surface degradation with different levels of O$_2$. The discrepancy between these results and the results of Roberge et al. may be attributed to high partial pressures of water vapor in a conventional reactor in the latter case. In this experiment, the water vapor partial pressure was measured to be less than $10^{-9}$ Torr for any of the different oxygen leak settings.

Chamber background.—A hydrogen passivated silicon surface under high vacuum has been shown to be stable against any oxygen
or carbon contamination for up to 18 h. In UHV-RTCVD, it is possible to deposit multiple layers of epitaxial silicon with different doping concentrations. This is performed by extinguishing the arc lamp and changing the dopant gas (diborane or phosphine) levels in the reaction chamber. This is typically carried out in several minutes. During this period, the silicon surface is prone to contamination. In this experiment, the substrates were annealed in the main chamber for 20 s in vacuum to desorb the hydrogen from the surface. When the hydrogen passivation is removed from the surface, the silicon surface is highly reactive and prone to any contamination in the chamber background. These substrates were then exposed to the vacuum ambient for different periods varying from 10 to 10,000 s.

Figure 16 shows the oxygen concentration at the epitaxy/substrate interface for various exposure times in vacuum. As shown in this figure, there is no observable oxygen contamination on the surface up to 1000 s. Even after 10,000 s, the oxygen concentration at the epitaxy/substrate interface is $3 \times 10^{19}$ cm$^{-2}$, which corresponds to less than 2% of a monolayer of surface coverage. This is due to low partial pressures of (10$^{-2}$ Torr) oxygen and water vapor in the ambient.

Figure 17 demonstrates the carbon concentration at the interface for various wait times in vacuum. The initial carbon concentration occurs as soon as the arc lamp is extinguished. A detailed investigation of this contamination phenomenon can be found elsewhere. As shown, there is no significant increase in the carbon level from 10 to 10,000 s. It is important to note that the vacuum system used in this experiment employed oil-free vacuum pumps, eliminating a major source of carbon contamination. Hence, after the initial contamination, carbon level at the surface does not increase by prolonged wait times.

The defect analysis was performed by using dark field microscopy. The measurements showed that although the oxygen at the epitaxy/substrate interface increased for more than one order of magnitude, all the defect density values were in the range of 1-2 ×
10^3 cm^-2, and there was no apparent increase in the defect density up to 10,000 s (2.78 h). Note that even for the sample with the longest exposure period, the oxygen coverage on the surface was less than 2% of a monolayer.

Conclusions

The wafers were kept in DI water for different times and there was no significant increase observed in the oxygen and carbon coverage on the silicon surface for up to 1000 s. When the wafers were exposed to air, it was observed that carbon contamination levels stayed steady, whereas the oxygen coverage on Si(100) increased up to 25% of a monolayer after 10,000 s. The oxide coverage on the sample which was exposed to air for longer times was sufficiently high to hinder epitaxial growth and the films were highly defective. The defect density was obtained using dark field microscopy and a significant increase in defect formation was observed with increasing air exposure. A relation is observed between interfacial oxygen and defect density. Wafers contaminated by exposure to air for different times were in situ cleaned to study the limits of the process, and it was observed that on the sample with air exposure up to 1000 s, the oxygen level at the epitaxy/substrate interface was reduced below the SIMS detection levels by an in situ clean of 800°C/10 s.

In situ cleaning was studied in an ambient with different partial pressures of oxygen and nitrogen. These contaminants were introduced into the ambient in varying amounts during in situ anneal and the contaminant levels at the epitaxy/substrate interface were correlated to the partial pressures. In situ cleaning was performed at 800°C for 20 s. The results indicate that the oxygen removal from Si (100) was not affected by the high nitrogen partial pressure in the cleaning ambient up to 1 × 10^-6 Torr and oxygen at the epitaxy/substrate interface was reduced below the SIMS detection levels after an in situ clean. There was also no apparent nitrogen at the epitaxy/substrate interface.

Oxygen removal from the epitaxy/substrate interface was also investigated in different oxygen backgrounds. It was demonstrated that when the oxygen partial pressure in the ambient was sufficiently high, oxygen removal from the surface was limited. With an oxygen partial pressure of 1 × 10^-6 Torr in the cleaning ambient, a residual oxide was obtained on the surface even after an 800°C/20 s in situ clean cycle. No increased level of defect density was observed under dark field microscopy. Moreover, any residual oxide on the surface was removed in other samples by in situ cleaning at 800°C with oxygen partial pressures at or below 1 × 10^-7 Torr. The samples annealed in different vacuum backgrounds were analyzed by AFM and there was no observable increase in the rms surface roughness. This is attributed to low water vapor partial pressures (<10^-9 Torr) in the cleaning ambient.

Combination of an unpassivated silicon surface was studied by removing the protective hydrogen coverage and exposing the substrate to vacuum at room temperature for different times. There was no observable oxygen contamination on the surface up to 100 s. Even after 10,000 s, the oxygen coverage at the epitaxy/substrate interface was below 2% of a monolayer. The carbon contamination on the surface was instantaneous and no additional carbon accumulation on the surface was observed up to 10,000 s (2.78 h). There was no apparent increase in the defect density for these wait times.

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