

Study of Oxygen and Carbon Species on Si Substrate during In-Situ Cleaning Prior to High-Quality Epitaxial Deposition

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We investigated the effect of in-situ cleaning with ECR (Electron Cyclotron Resonance) hydrogen plasma. This cleaning was effective in removing oxygen and carbon on the wafer surface because of its high density and low substrate damage and, thus, high quality epitaxial films were deposited. The contents of the oxygen or carbon species were correlated with the structural quality of the interface and film. The possible reaction mechanisms for the cleaning of oxygen and carbon species were scrutinized. The removal of oxygen rather than of carbon, was crucial in obtaining high quality epitaxial films.

Keywords : epitaxy, oxygen, carbon, chemical vapor deposition

1. INTRODUCTION

In recent years, surface preparation techniques that avoid surface contamination and generate very clean wafer surfaces have become of critical importance. It is reported that surface impurities are especially detrimental when they are present on the semiconductor surface and the potential sources of gases and vapors in a vacuum system [1,2]. In this study carbon and oxygen are taken into account as contaminants, since other contaminants such as metals can be suppressed to negligible levels through careful wafer handling and an established cleaning method [3]. Oxygen may originate from the natural oxide on the silicon surface, which may grow during exposure to air or the water rinsing process. Water vapor may enter into the chamber when the wafer is loaded. The internal surfaces of the main chamber should be evenly coated with layers of water molecules and may become a predominant residual gas [4]. Therefore, during heating, some water molecules may desorb and adsorb onto the wafer surface. To reduce this phenomenon, a Load Lock Chamber was installed in our CVD system. The bake-out treatment was performed to remove some of the water molecules. Carbon can originate from organic contaminants on the oxide layer, from the HF solution, and from DI water [5]. Vacuum pumps, including the turbomolecular and mechanical pumps can be a source of hydrocarbons Licciardello *et al.* suggested that, after HF dipping, organic compounds were chemically bonded to the silicon surface and this organic layer would not be affected by the

growth of a surface oxide layer [6]. An atomically clean surface can be generated by thermal treatment of the silicon surfaces at high temperature (~1250). At high temperatures surface oxides are reduced by the underlying silicon to produce a volatile silicon monoxide. Oxygen is removed after annealing at 830. Carbon is much more tenacious [7] and stable on the silicon surface. Temperatures over 1100 are required to remove carbon from the surface. Also during heating of the substrate, hydrocarbons form in their crystalline form, β -SiC [8]. This form is quite stable and difficult to remove.

To effectively remove the carbon and oxygen species at lower temperatures, hydrogen plasma was used to clean the semiconductor surfaces and the use of microwave electron cyclotron resonance (ECR) sources are reported in the literature [9,10]. Low temperature ($\leq 600^\circ\text{C}$) in-situ cleaning was performed in our experiments to reduce interfacial carbon and oxygen concentration. There are reports that the low temperature process is more effective in removing hydrocarbons from the surface [11,12]. Recent literature reports that lower temperature in-situ cleaning might be more efficient than higher temperature cleaning in removing oxygen contaminants because at higher temperatures the sticking coefficient of hydrogen to the silicon surface decreases; hydrogen atoms are easily desorbed and hydrogen passivation is lost [6]. In our study, the effect of the in-situ cleaning temperature on oxygen removal was investigated and the possible reactions are discussed.

2. EXPERIMENTAL PROCEDURE

The substrates were 4 inch, czochralski-grown, p-type <100> Silicon wafers with 0.5 -20 Ω -cm resistivity. The wafers were RCA cleaned and HF dipped for 20-30 seconds in 10:1 aqueous solutions and rinsed in DI (deionized) water and then dried by blowing nitrogen on them. All the processes were done inside a class 100 cleanroom and it took only 10 seconds to load the wafer into the Load Lock Chamber after the wafer was blow-dried. After the Load Lock Chamber was pumped down to about 1×10^{-7} Torr the wafer could be transferred to the main chamber by opening the gate valve. The hydrogen was kept flowing through the main chambers when the gate valve was opened to avoid cross contamination. After the wafers were transferred and loaded onto the heater stage, the main chamber was pumped down and ultimately $1-2 \times 10^{-8}$ Torr could be attained. In-situ pre-deposition wafer cleaning was performed using ECR hydrogen plasma, operated at the 2.45 GHz S-band microwave frequency. Depositions were done by flowing 10 sccm of SiH_4 without carrier gases, immediately after the plasma was extinguished. For the in-situ cleaning and deposition, the wafer was heated up to 600°C in a hydrogen flow rate of 20 sccm. It took about 7 min, which was a well-characterized deposition temperature in our system. Thermal heating (bakeout) was performed by using heating tapes outside the chambers. A QMS (Quadrupole Mass Spectroscopy) scan was done during bakeout to check for the appearance of water vapor. After bakeout treatment, a hydrogen plasma exposure was performed to provide energy to help remove the contaminants inside the chamber. Silane gas was introduced and kept flowing at 600°C for 20 minutes, mainly to pre-coat the wafer heating elements. The QMS was mounted on the CVD chamber [13]. The unit was differentially pumped

with an independent pumping system consisting of a 450 l/s turbomolecular pump backed by a mechanical pump. Gases were extracted from the wafer edge and then transported through the capillary to the analyzer and real time information on gas concentration was obtained. Cross-sectional transmission electron microscopy (XTEM) was used to observe the epitaxial layer and the epilayer/substrate interface. SIMS measurements were performed to detect interfacial oxygen and carbon. Cs^+ ion was used as the ion source for sputtering and the primary ion energy was 5 keV and beam current was 200 nA.

3. RESULTS AND DISCUSSION

Fig. 1 shows XTEM micrographs of epitaxial films, cleaned in-situ at 600°C : Samples A, B, C and D. Sample A received a standard in-situ plasma cleaning. Samples B, C, and D received the same in-situ cleaning as Sample A, except that in Sample B, the DC bias was set at 0V and in Sample C, the hydrogen pressure was set at 8mTorr and in Sample D, the cleaning time was set at 20 minutes (Table 1). The SIMS data of Samples A, B, C and D were investigated. The oxygen and carbon concentrations at the epilayer/substrate interface were listed in Table 2. Table 2 shows that the interfacial oxygen concentration of Sample A was less than 5×10^{13} atoms cm^{-2} , and less than those of Sample B, C and D. The structural qualities of the epitaxial layer and the epilayer/substrate interface were closely related to the interfacial oxygen concentration. Fig. 2 shows the SIMS data of Sample A, where the oxygen concentration inside the film was about $1-2 \times 10^{18}$ atoms/ cm^3 and almost the same level as the substrate concentration (1×10^{18} atoms/ cm^3). RBS channeling experiments confirmed that the epitaxial film had an almost perfect crystallinity. The χ_{min} was measured to be in the 3-4% range.

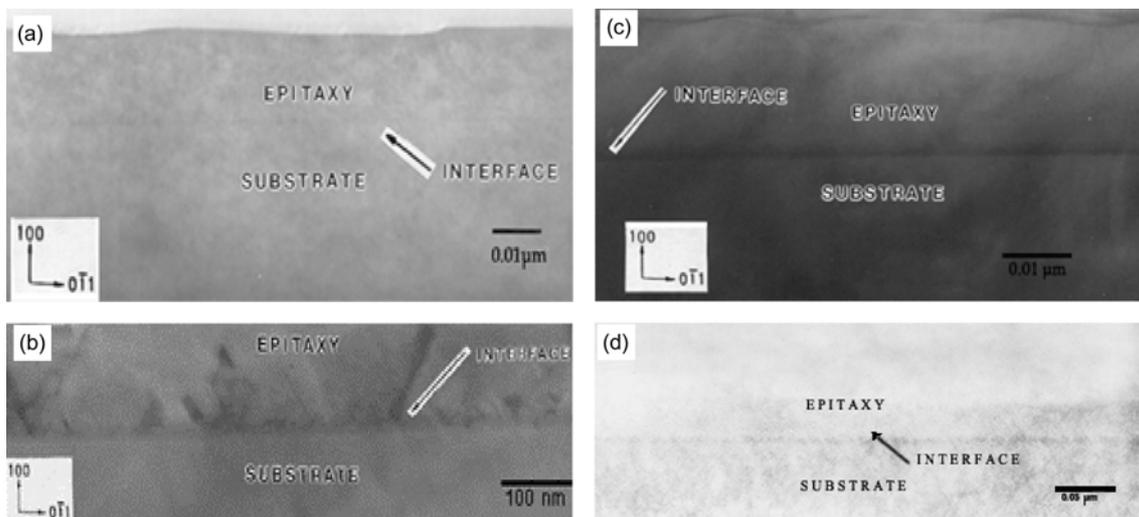


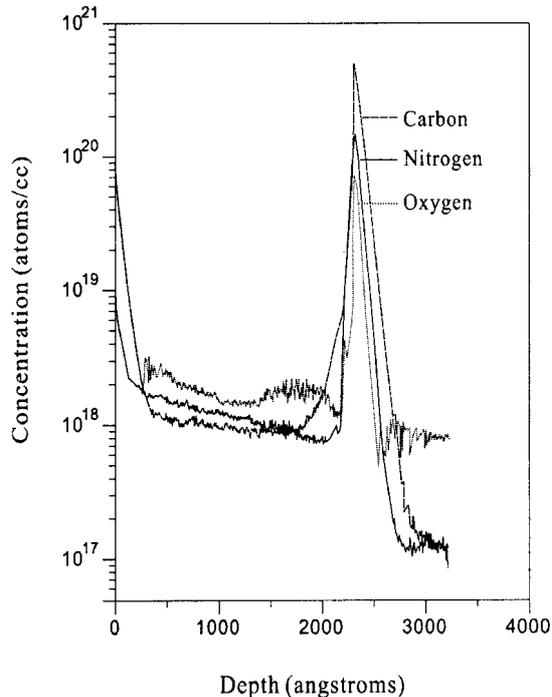
Fig. 1. XTEM micrographs of epitaxial films cleaned in-situ at 600°C : (a) Sample A, (b) Sample C, (c) Sample B and (d) Sample D.

Table 1. In-situ cleaning conditions

	Power	DC bias	Temperature	Time	Pressure
Sample A	300W	10V	600°C	5 min	1mTorr
Sample B	300W	0V	600°C	5 min	1mTorr
Sample C	300W	10V	600°C	5 min	8mTorr
Sample D	300W	10V	600°C	20 min	1mTorr
Sample E	300W	10V	RoomT	5 min	1mTorr
Sample F	750W	10V	RoomT	5 min	1mTorr
Sample G	300W	0V	RoomT	5 min	1mTorr
Sample H	300 W	10V	600°C	5 min	1mTorr
Sample I	300 W	10V	660°C	5 min	1mTorr

Table 2. SIMS data at the epilayer/substrate interface

	Oxygen (cm ⁻²)	Oxygen(cm ⁻³)	Carbon(cm ⁻²)	Carbon(cm ⁻³)
Sample A	4.8×10 ¹³	8×10 ¹⁹	4.5×10 ¹⁴	5×10 ²⁰
Sample B	8.1×10 ¹⁴	3.5×10 ²⁰	3.8×10 ¹³	3×10 ¹⁹
Sample C	1.0×10 ¹⁵	8×10 ²⁰	6.3×10 ¹⁴	7×10 ¹⁹
Sample D	5.9×10 ¹⁴	6×10 ²⁰	2.1×10 ¹³	2×10 ¹⁹
Sample E	7.8×10 ¹⁴	7×10 ²⁰	1.4×10 ¹³	1×10 ¹⁹
Sample F	3.0×10 ¹⁴	3×10 ²⁰	6.9×10 ¹²	6×10 ¹⁸
Sample G	8.5×10 ¹⁴	1×10 ²¹	8.0×10 ¹²	7×10 ¹⁸
Sample H	1.5×10 ¹⁵	8×10 ²⁰	1.7×10 ¹³	1×10 ¹⁹
Sample I	1.0×10 ¹⁴	3×10 ¹⁹	1.7×10 ¹⁴	7×10 ¹⁹
Sample J	1.4×10 ¹³	9×10 ¹⁹	6.7×10 ¹³	1.5×10 ¹⁹
Sample K	5.2×10 ¹⁴	2×10 ²⁰	-	-

**Fig. 2.** SIMS depth profiles of epitaxial film cleaned in-situ under standard conditions at 600°C (rinsed and blow-dried).

Samples E, F and G were in-situ cleaned at room temperature. Their SIMS data showed high (more than 3×10^{14} atom/cm²) interfacial oxygen concentrations. Their interfacial carbon concentration were 1.4×10^{13} , 6.9×10^{12} and 8.0×10^{12} atoms/cm², respectively (Table 2) and lower than the Samples which were in-situ cleaned at 600°C. In Samples E and F, defect-free epitaxial layers were deposited and in Sample G, a polycrystalline film was deposited. The structural qualities of the deposited film and the epilayer/substrate interface were not degraded by the presence of carbon. Very low temperature in-situ cleaning resulted in less interfacial carbon concentration than high temperature ($\geq 600^\circ\text{C}$) in-situ cleaning. The hydrogen gas we used in our reactor passed through the Nanochem purifier. The purifier reduced the levels of complex hydrocarbons to less than 1 ppb. It was shown that standard in-situ cleaning at 600°C generated carbons, in contrast to the sample which did not receive the in-situ cleaning.

Fig. 3(a) shows the dependence of interfacial oxygen and carbon concentration on the temperature of in-situ cleaning and deposition. The wafers were spin-dried after being dipped into HF aqueous solution. Processing at 660°C (Sample I) was more efficient in removing oxygen than processing at 600°C (Sample H). This showed a reverse tendency to carbon. Oxygen was greatly reduced by raising processing temperatures by 60°C. However, this effect should be the sum of

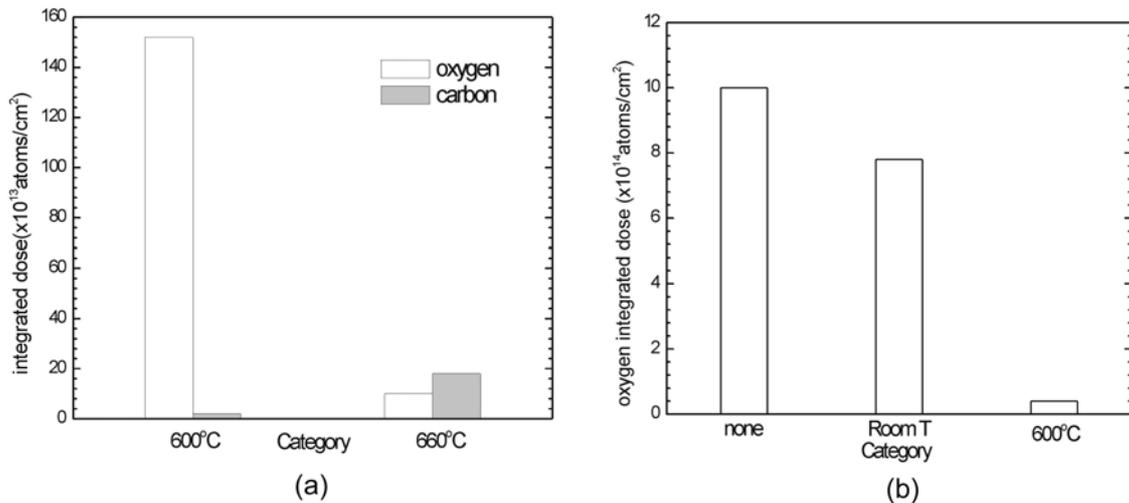


Fig. 3 (a) Effect of in-situ cleaning and deposition temperature (600°C, 660°C) on interfacial oxygen and carbon concentration and (b) effect of in-situ cleaning temperature (non, 25°C, 600°C) on interfacial oxygen concentration.

the hydrogen pre-bake effect and in-situ plasma cleaning effect. This means that Sample I not only received a higher temperature (660°C) in-situ cleaning, but also heated up to a higher temperature in hydrogen ambient. Fig. 3(b) shows the dependence of interfacial oxygen concentrations on the standard in-situ cleaning process. The in-situ cleaning temperature was set at 25°C (Sample E) and 600°C (Sample A) and deposition was performed. The wafer received an HF dipping, rinsed in DI water and blow-dried. The oxygen concentration decreased with increasing the cleaning temperature. Even room temperature in-situ cleaning, if it is optimized, reduced the interfacial oxygen concentration.

To investigate the origin of the surface contaminates, in

Sample L, a total of three layers were deposited. The wafer was dipped into HF aqueous solution and blow dried by nitrogen, before being loaded into the Load Lock Chamber. Standard in-situ cleaning was done at 600°C, followed by deposition at the same temperature for 60 minutes. The standard in-situ cleaning and deposition was repeated for the second layer. Then hydrogen was kept flowing for 5 minutes, without ECR plasma and the third layer was deposited. In the SIMS analysis, volumetric concentration at the highest point was used, because the widths of the peaks were higher than the resolution depth of the SIMS measurement.

Fig. 4 and Table 3 show the SIMS data for Sample L. The oxygen concentration of the first and second interface were

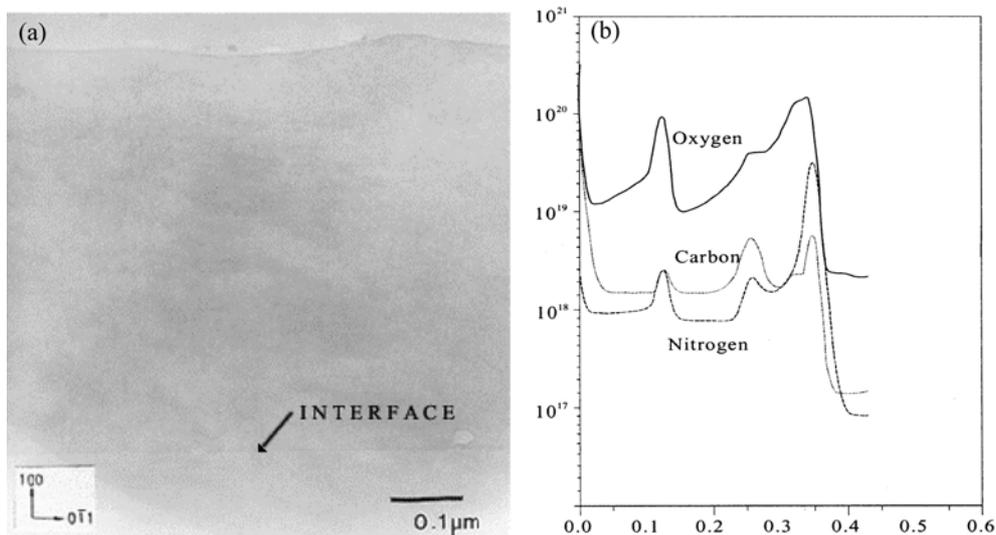


Fig. 4. (a) XTEM micrograph of epitaxial film, Sample L: interfaces, except the epi/substrate interface are not visible and (b) SIMS depth profiles of epitaxial film, cleaned in-situ under standard conditions at 600°C (blow-dried without rinsing). For second layer, cleaned in-situ under standard conditions at 600°C and for third layer, with hydrogen kept flowing for 5 minutes, without plasma enhancement (Fitting curve).

Table 3. SIMS data for Sample L

	Oxygen (cm ⁻²)	Oxygen (cm ⁻³)	Carbon (cm ⁻²)	Carbon (cm ⁻³)
Interface 1	6.1×10 ¹⁴	1.5×10 ²⁰	7.1×10 ¹³	3×10 ¹⁹
Interface 2	-	4×10 ¹⁹	2.7×10 ¹³	5×10 ¹⁸
Interface 3	2.5×10 ¹⁴	9×10 ¹⁹	1.1×10 ¹³	2.5×10 ¹⁸

1.5×10²⁰ atoms/cm³ and 4×10¹⁹ atoms/cm³, respectively. The significant difference in the oxygen concentrations between the two interfaces means that there was surface natural oxide from the beginning and this oxide could not be removed completely by in-situ wafer cleaning. In the third interface, the hydrogen kept flowing at 600°C for 5 minutes and oxygen accumulated on the surface (9×10¹⁹ atoms/cm³). This means that plasma enhancement is necessary to reduce the interfacial oxygen concentration. The house hydrogen gas was used, and was passed with a Nanochem purifier before being introduced into the chamber. This purifier reduces the level of water and oxygen to less than 1 ppb level. This means that less than 2-2.7×10¹³ atoms of oxygen were introduced within 5 minutes. But the oxygen peak indicates that, by calculation of its real density, 2.5×10¹⁴ oxygen atoms accumulated at the epilayer/substrate interface per square centimeter. Also in-situ plasma cleaning played a role in removing the oxygen species from the wafer surface. This analysis can be applied to carbon as well. By comparing the first and second interface, it is evident that considerable amounts of carbon were adsorbed onto the surface after the ex-situ cleaning. By comparing the second and third interfaces, it seems that the ECR plasma cleaning generated carbon in addition to carbon atoms which came from the hydrogen gas or from inside the reactor.

In the carbon removal process, etchant forms and will be adsorbed on the substrate for subsequent reaction. Product should be desorbed for etching to continue. The following reactions are considered and their free energy changes are calculated at room temperature, 600°C and 660°C (Table 3). In ECR hydrogen plasma, hydrogen gas (H₂ (g)) will be converted into more reactive H(g), at low temperatures (<600°C). A lower temperature is reported to be favored for carbon removal [14]; also, in our study very low temperature in-situ cleaning resulted in less interfacial carbon concentration than high temperature (more than 600°C) in-situ cleaning. There-

fore, desorption of reaction products will not be a rate-determining step in carbon removal processes. By approximate calculation, the number of molecules of a gas at rest that strike is given by [15].

$$v = 3.513 \times 10^{22} \frac{P_{mm}}{\sqrt{MT}} \text{cm}^{-2} \text{sec}^{-1}$$

and for hydrogen at 300°K and at a pressure of 1mTorr ($\cong 10^{-3}$ mmHg), $v=1.43 \times 10^{18} \text{ cm}^{-2} \text{sec}^{-1}$. The number of hydrogen molecules adsorbed on the wafer surface per second is $v \times p \times a \times s$ where p is the gas pressure in mmHg, a is the area of the wafer in cm² and s is the sticking probability ($\cong 10^{-5}$).

Therefore hydrogen flux = $1.43 \times 10^{18} \times 10^{-3} \times 10^{-5} \text{ cm}^{-2} \text{sec}^{-1} = 1.43 \times 10^{10} \text{ cm}^{-2} \text{sec}^{-1}$. If an ionization efficiency of 10⁻¹ is assumed, the adsorption flux of H(g) might be approximately $2.06 \times 10^9 \text{ cm}^{-2} \text{sec}^{-1}$. In the hydrogen flow of 10 sccm, 1.6×10^{22} molecules will be introduced into the chamber every second. Because the adsorption flux of hydrogen is very small compared to the amount of hydrogen introduced into the chamber, adsorption/reaction can be a rate-determining step. It is thought that the carbon removal mechanism at low temperature was related to the removal of the methyl group from the surface by H(g) [11,12]. It is known of the behavior of Si-CH₃ that, at above 577°C, only the presence of adsorbed carbon on the surface is verified [16] and at below 427°C, surface carbon will be present as CH₃(ad) and this can be removed by reactions Si-CH₃+3H(g)→CH₃SiH₃(g). In this situation, CH₃(ad)+H(g)→CH₄(g) will be another possible reaction, however, this reaction was not dominant because of its small reaction cross section [12]. By theoretical studies of the thermochemistry of molecules in the Si-C-H system, among the molecules in the series of H_mSi(CH₃)_n and H_mSiCH_n, H_mSi(CH₃)_n (m+n=4) had the lowest free formation energies [17] and CH₃SiH₃ is known to have a lower boiling point (-57°C) than that of (CH₃)₂SiH₂ and (CH₃)₃SiH.

From Table 4, since Reaction 1 can occur with a high driving force, in room temperature in-situ cleaning this reaction will be the dominant one. It is notable that even without plasma, reaction 2 will occur. In 5 minutes during in-situ cleaning, $300 \times 1.43 \times 10^{12} \cong 4 \times 10^{12}$ hydrogen species will adsorb on the surface (per square centimeter), and this order matches with our SIMS measurement and is smaller than the existing interfacial carbon concentration. Therefore, at low temperature (room temperature), Reactions 1 and 2 occur and adsorption of hydrogen molecules and ions seem to play an

Table 4. Free energy changes for carbon removal reactions (J/mole) [18,19]

Reactions	27°C	600°C	660°C
1. SiCH ₃ +3H(g)→CH ₃ SiH ₃ (g)	-895,325	-713,361	-669,859
2. SiCH ₃ +3/2H ₂ (g)→CH ₃ SiH ₃ (g)	-285,767	-195,444	-162,055
3. SiC (β)+4H(g)→Si(s)+CH ₄ (g)	-792,527	-618,536	-602,362
4. SiC (β)+2H ₂ (g)→Si(s)+CH ₄ (g)	20,217	72,020	74,710

important role. Reaction 2 may consist of the dissociation of H_2 (g) to H(g) and Reaction 1. In this case, Dissociation on the surface can be a rate-determining step. From the observation that room temperature in-situ cleaning was particularly more efficient than by flowing hydrogen, Reaction 1 dominates the carbon removal process. It is evident that the reactive H(g) played a major role; even the C=C bonds in organic layer on the silicon surface can be reduced to CH-(ad), CH_2 -(ad) and up to CH_3 (ad) and thus can be easily removed. At high temperature ($>600^\circ C$), although the carbon should be in the SiC form in equilibrium, most carbon will be in the silicon lattice in its meta-stable state. Reaction 3 can occur considering thermal equilibrium, meaning that carbon in meta-stable state can react more easily to form CH_4 (g). If we accept the observation that $600^\circ C$ was the more favored temperature than $660^\circ C$, atomic diffusion through silicon or desorption of CH_4 gas should not be a rate-determining step.

In Reaction 4 $\Delta G_{600^\circ C}=72.020J$ at equilibrium and $P_{CH_4} \cong 8.7 \times 10^{-17}$ (0.1 Mpa) $=6.5 \times 10^{-14}$ Torr at 1mTorr of hydrogen pressure. Reaction 4 does not occur and, thus, at high temperatures, carbon cannot be removed by just hydrogen pre-bake. It should be noted that the standard state in our thermodynamic data is defined as 0.1 MPa, which is 750 Torr. Unexpected carbon can be generated during in-situ cleaning because of SiC-coated filament. Reaction 3 may occur and increase the level of gaseous CH_4 in the atmosphere. These species may directly adsorb on the silicon surface, however, this action does not seem to occur significantly, because Reaction 2 is favored at lower temperature; However, the room temperature in-situ cleaning was efficient in our experiments. It is probable that carbon was generated during high temperature in-situ cleaning, because the sample which received a standard in-situ cleaning at $600^\circ C$ turned out to have higher interfacial carbon concentration than the sample which did not receive the in-situ cleaning. The carbon removal in the room temperature in-situ cleaning is thought to occur by volatilization through hydrogenation. Therefore, it is surmised that the carbon removal in our room temperature in-situ

cleaning process would be a chemical etching process [15].

The possible thermal etching reactions in hydrogen ambient at relatively low temperatures ($\leq 660^\circ C$) in our system are listed in Table. 5 and their free energies of reactions are presented. In Table 5, Reactions 4, 9 and some reactions which generate SiH(g) were excluded because in Si_nH_n species with an odd n are known to be thermodynamically unstable [20].

In considering free energy changes, Reactions 1, 3, 6 and 7 cannot occur. In Reaction 10, $\Delta G_{600^\circ C}=406,212$ J. At equilibrium, $P_{SiH_4}=1.0 \times 10^{-23}$ Torr (if $P_{H_2O}=10^{-18}$ Torr) and Reaction 10 will not proceed. In Reaction 8, $\Delta G_{600^\circ C}=346,296$ J. At equilibrium, $P_{SiH_2}P_{H_2O}^2 \cong 4.09 \times 10^{-29}$ Torr³. In our system, the base pressure is about 1×10^{-8} Torr and P_{H_2O} will be more than 10^{-19} Torr [24] and $P_{SiH_2(eq)}$ will be less than 4.09×10^{-11} Torr, and therefore Reaction 8 will not occur in our system. In Reaction 5, $\Delta G_{600^\circ C}=290,685$ J and at equilibrium, $P_{H_2O} \cong 7 \times 10^{-9} \cong 7 \times 10^{-12}$ Torr, and thus Reaction 5 will not proceed. In Reaction 11, $\Delta G_{600^\circ C}=319,433$ J and $P_{SiO(eq)} \cong 6.3 \times 10^{-10}$ Torr. In Reaction 2, $\Delta G_{600^\circ C}=305,059$ J and if it is assumed that $P_{H_2}=1$ mTorr and $P_{H_2O}=10^{-8}$ Torr, $P_{SiO(eq)} \cong 6.3 \times 10^{-10}$ Torr and this reaction may occur slightly. Reaction 11 occurs in the same system and thus Reaction 2 can be neglected. (Note: standard state P_o in our thermodynamic data is 0.1 MPa, which is 750 Torr). In our research, H_2 cleaning without plasma excitement does not noticeably reduce oxygen contamination and interface thickness according to the SIMS data and XTEM micrograph of Sample J and K. (Table 2, XTEM is not shown here) Both Samples were deposited at $660^\circ C$ and Sample F received in-situ hydrogen cleaning without plasma excitement, Sample K did not receive any in-situ cleaning. Reaction 11 occurred and SiO (g) was generated and desorbed at 660. Thomas *et al.* found that SiO (g) was desorbed at $700^\circ C$ [14]. Ishizaka *et al.* suggested that the thermal etching process be conducted in two steps when the oxide film is very thin [25]. Kobayashi added the SiO desorption step; however, SiO (g) is known as a very volatile material [26].

Table 5. Free energy change for oxygen removal reactions without plasma excitement (J/mole) [21-23]

Possible reactions	25°C	600°C	660°C
(1) $SiO_2(s) + 1/2H_2(g) \rightarrow SiH(g) + O_2(g)$	1,137,808	973,292	956,524
(2) $SiO_2(s) + H_2(g) \rightarrow SiO(g) + H_2O(g)$	439,213	317,173	305,059
(3) $SiO_2(s) + H_2(g) \rightarrow SiH_2(g) + O_2(g)$	999,024	764,364	738,836
(4) $SiO_2(s) + 3/2H_2(g) \rightarrow SiH_3(s) + O_2(g)$	-	-	-
(5) $SiO_2(s) + 2H_2(g) \rightarrow Si(s) + 2H_2O(g)$	337,936	294,545	290,685
(6) $SiO_2(s) + 2H_2(g) \rightarrow SiH_4(g) + O_2(g)$	851,927	803,927	798,752
(7) $SiO_2(s) + 5/2H_2(g) \rightarrow SiH(g) + 2H_2O(g)$	680,644	574,202	563,984
(8) $SiO_2(s) + 3H_2(g) \rightarrow SiH_2(g) + 2H_2O(g)$	541,920	365,384	346,296
(9) $SiO_2(s) + 7/2H_2(g) \rightarrow SiH_3(g) + 2H_2O(g)$	-	-	-
(10) $SiO_2(s) + 4H_2(g) \rightarrow SiH_4(g) + 2H_2O(g)$	394,763	404,152	406,212
(11) $SiO_2(s) + Si(s) \rightarrow 2SiO(g)$	540,940	339,801	319,433

Table 6. Free energy change for oxygen removal reactions with plasma excitement (J mole⁻¹) [21-23]

Possible reactions	25°C	600°C
(12) SiO ₂ (s) + H (g) → SiH (g) + O ₂ (g)	934530	800653
(13) SiO ₂ (s) + 2H (g) → SiO (g) + H ₂ O(g)	32657	-28105
(14) SiO ₂ (s) + 2H (g) → SiH ₂ (g) + O ₂ (g)	592468	419086
(15) SiO ₂ (s) + 4H (g) → Si (s) + 2H ₂ O(g)	-475176	-396011
(16) SiO ₂ (s) + 4H (g) → SiH ₄ (g) + O ₂ (g)	38815	112676
(17) SiO ₂ (s) + 5H (g) → SiH (g) + 2 H ₂ O(g)	-335746	-288993
(18) SiO ₂ (s) + 6H (g) → SiH ₂ (g) + 2 H ₂ O(g)	-677748	-670550
(19) SiO ₂ (s) + 8H (g) → SiH ₄ (g) + 2 H ₂ O(g)	-1231461	-976960

Surface native oxide has been known to be removed by hydrogen pre-bake at high temperatures. Kobayashi studied thermal cleaning at 760°C and 900°C without hydrogen flowing: the reaction product was identified as SiO [26]. Racanelli *et al.* revealed that hydrogen bake aided the removal of surface oxygen and that a higher temperature bake (795°C) was more efficient in their UHVCVD system [27]. Meyerson also used high temperature bakes to remove surface native oxide in a hydrogen ambient [28]. They all suggested that the dominant etching reaction should be: Si(cr)+SiO(s) → 2SiO(g). It can be assumed that other reduction reactions by hydrogen may occur and in addition to that, hydrogen may be necessary for the first reaction to proceed.

In ECR hydrogen plasma, dissociation, direct ionization and dissociation ionization of H₂ (g) will occur in the plasma chamber [29].

The dissociation reaction can be written as: H₂ (g)+e⁻→2H (g)+e⁻. Burke *et al.* found that in his ECR hydrogen cleaning experiments, the atomic hydrogen produced in the plasma was the dominant agent during the cleaning process in reducing the native oxide and the carbonated compounds [30]. In our system, it was assumed that SiO₂+nH (g) (n=1, 2, ...) occurred; their free energy changes are listed in Table 6. Reactions (15), (16), (17), (18) and (19) cannot be dominant reactions because these reactions are thermodynamically more favorable at lower temperature and do not match with our observation. In Reaction (14), ΔG_{600°C}=419086 J and at equilibrium, P_{SiH₂}P_{O₂}≅8.4×10⁻³⁴Torr² and this reaction cannot occur (it was assumed here that P_H=0.1 mTorr, by considering an ionization efficiency of 0.1). In Reaction (12), ΔG_{600°C}=800653 J and at equilibrium, P_{SiH}P_{O₂}≅9.3×10⁻⁵⁰Torr². Reaction (12) will not occur in our system. Therefore, Reaction (13): SiO₂(s)+2H(g)→SiO(g)+H₂O(g) will be a dominant reaction. Since ΔG_{600°C} = -28105 J and at equilibrium, P_{SiO}P_{H₂O}≅2.7×10⁻⁷Torr². If P_{H₂O}=10⁻⁸Torr, P_{SiO(eq)}=27 Torr by calculation, this reaction has a high enough driving force to proceed. Also, ΔG_{25°C}=32657 J and at equilibrium, P_{SiO}P_{H₂O}≅1.9×10⁻¹⁴Torr² and if P_{SiO}=P_{H₂O}, P_{SiO}P_{H₂O}≅1.4×10⁻⁷Torr and the reaction will proceed even at room temperature. The oxygen removal process with hydrogen plasma excitation will be reaction controlled or desorption controlled. By

Reaction (2), the SiO (g) and H₂O (g) are desorbed. The boiling point of SiO (g) is known to be lower than that of H₂O (g); SiO (g) is a volatile product. So it is possible that the removal process is dominated by desorption of water vapor. Sample A⁺ (It did not receive an in-situ plasma cleaning) was rinsed and blow-dried, then heated up to 600°C for subsequent epitaxial growth. Its interfacial oxygen concentration was measured to be 1.0×10¹⁵ atoms cm⁻². By comparing Samples A and E, the standard in-situ plasma cleaning at 600°C and at room temperature may be compared directly. Their SIMS data are shown in Table 2. Both samples were rinsed and blow-dried and heated up to 600°C for 7 min. By calculation, the room temperature in-situ cleaning reduced 1.0×10¹⁵-7.8×10¹⁴=2.2×10¹⁴ oxygen atoms cm⁻². The standard in-situ cleaning at 600°C reduced 1.0×10¹⁵-4.8×10¹³=9.5×10¹⁴ oxygen atoms cm⁻². Therefore, the in-situ plasma cleaning was more efficient at higher temperature in removing oxygen contaminants in our system. Room temperature in-situ cleaning removed 2.2×10¹⁴ oxygen atoms cm⁻² and in-situ cleaning at 600°C removed 9.5×10¹⁴ oxygen atoms cm⁻². Since the in-situ cleaning was performed for 300 s, oxygen removal rates were 6.7×10¹¹ atoms cm⁻²s⁻¹ at room temperature and 3.2×10¹² atoms cm⁻²s⁻¹ at 600°C. The kinetic expression can be written as: rate=A exp(-E/RT) and if it is assumed that E is not a function of temperature,

$$\ln = \frac{\text{rate at } T_2}{\text{rate at } T_1} = \frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

By substituting T₁=298 K and T₂=873 K and R=8.314 J deg⁻¹ mole⁻¹, E=5500 J mole⁻¹. The heat of evaporation of water is 41090 J mole⁻¹ at 100° [31]. If it is assumed that the activation energy of the desorption process is equal to the heat of evaporation of water vapor, the oxygen removal process with plasma excitation is shown to be reaction controlled.

4. CONCLUSIONS

The carbon removal reaction is thermodynamically favorable at low temperatures, and it was found that the removal was especially effective at room temperature. Oxygen was

removed by heating in hydrogen ambient and SiO(g) may be desorbed from the reactions. With plasma excitation, H₂ will change to more reactive H(g). In-situ hydrogen plasma cleaning in our experiments was more efficient at higher temperature in terms of oxygen removal. Thermodynamically, SiO₂(s)+2H(g)→SiO(g)+H₂O(g) is surmised to be the dominant reaction. Kinetically, the oxygen removal process with plasma excitation seems to be reaction controlled, rather than water vapor-desorption controlled.

ACKNOWLEDGMENT

This work was supported by grant No.2001-070-2 from the University Basic Research Program of the Ministry of Information and Communications.

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