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Effect of Rinsing and Drying on Silicon Surface Cleaning for Epitaxial Growth

Hyoun Woo Kim, Kwang-sik Kim, Woon-suk Hwang, and Rafael Reif*

School of Materials Science and Engineering, Inha University
253 Yonghyeon 3-dong, Nam-gu, Incheon 402-751, Korea
*Department of Electrical Engineering and Computer Science
Massachusetts Institute of Technology
Cambridge, MA 02139, USA

We investigated the effect of the rinsing and drying technique on the oxygen and carbon concentration on a silicon surface. Rinsing in deionized water increased the interfacial oxygen concentration and helped generate defects. Blow-drying was more efficient than spin-drying in reducing interfacial oxygen concentration. Exposure to the atmosphere was detrimental to obtaining high crystallinity in the epitaxial layer. We evaluated the effectiveness of the cleaning process by observing the grown epilayer and the epilayer/substrate interface.

Keywords : epitaxy, rinsing, oxygen, blow-drying, interface

1. INTRODUCTION

In the new ultra large-scale integration (ULSI) era, surface preparation techniques that avoid surface contamination and generate very clean wafer surfaces have become of critical importance. Surface impurities are especially detrimental if present on substrate surface and the bare silicon surface is highly reactive and susceptible to impurity adsorption. The potential sources of gases and vapors in a vacuum system can be found in the literature [1,2]. Before epitaxial growth, two precleaning methods have been widely used. The first method utilizes oxidizing chemical cleaning to form a hydrophilic carbon-free oxide, which should then be removed in situ to expose the bare silicon surface for subsequent epitaxial deposition [3]. The second method utilizes dipping in strong acid to generate a hydrophobic hydrogen-terminated surface and thus prevent the surface from being exposed to air and oxidation [4-6].

In this work, we have chosen the second method because our chemical vapor deposition (CVD) chamber is not exposed to atmosphere and because the protecting oxide may contaminate the chamber. We have used a low temperature cleaning process: obtaining a contamination-free, damage-free substrate with undestroyed hydrogen passivation is important. By employing an HF dipping technique to get rid of the residual natural oxide, the hydrogen atoms make for surface passivation and the fluorine atoms remain on the surface as a minor species. We perform a rinsing and a drying process right after the HF dipping; these are extremely critical steps because the clean surface can be recontaminated easily if not processed properly [7]. Rinsing in deionized (DI) water removes species that are weakly bound to the surface and can even etch the surface [8]. In this study, we evaluate the cleaning efficiency of rinsing and drying techniques. We also compare the cleaning efficiency of drying techniques, such as blow drying and spin drying. The effect of air-exposure time before loading into the chamber is investigated. The crystalline quality of epitaxial film and the epilayer/substrate interface is investigated using transmission electron microscopy (TEM). 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 established cleaning methods [9]. The amount of carbon and oxygen elements at the epilayer/substrate interface is evaluated by secondary ion mass spectroscopy (SIMS). The TEM images and SIMS data are compared.

2. EXPERIMENTAL PROCEDURE

We have used wafers of 4 inch, czochralski-grown, p-type <100> silicon with a 0.5−20 Ωcm resistivity. The wafers were cleaned in RCA solution and then dipped into the 10%-diluted HF solution for 20−30 sec. The HF solution used was a ULSI grade hydrofluoric acid and DI water was added to prepare the solution. Some wafers were rinsed with DI water for 3 min but the others were not. At the end of the

water-rinsing step, some wafers were dried by blowing nitrogen with a gun but the other wafers were spun-dried. The spin drying step was composed of a spin rinse at 1000 revolutions per minute (RPM) for 160 sec and a spin rinse at 2000 rpm for 240 sec. It is noteworthy that all the processes were performed inside the class 100 cleanroom and it took only 10 sec to load the wafer into the Load Lock Chamber after the wafer had been dried. The internal surfaces of the main chamber should be evenly coated with layers of water molecules which will become a predominant residual gas [6]. Therefore, during heating, some water molecules desorb and may adsorb onto the wafer surface. To reduce this phenomenon, the Load Lock Chamber was installed in our CVD system. The bake-out treatment was performed to remove some of the water molecules. The *ex situ* cleaned wafers were loaded into the Load Lock chamber which was then pumped down to about 1×10^{-7} Torr and the wafers were transferred to the CVD chamber in which the base pressure was about $1–2\times10^{-8}$ Torr. Subsequently, the wafers were heated up to 600°C or 660°C in hydrogen flow with a pressure of 1 mTorr and a flow rate of 20 standard cubic centimeters per minute (SCCM). It took about 7 min and 8 min, respectively, to heat the wafer from 25 to 600°C and 660°C. To remove effectively the carbon and oxygen species at lower temperatures, hydrogen plasma was used to clean the semiconductor surfaces. We used an electron cyclotron resonance (ECR) plasma, operated at 2.45 GHz S-band microwave frequency with 300 W of microwave power, 150 ampere/120 ampere of current for the top and bottom magnets, and 10 V of a DC bias. As an *in situ* cleaning gas, hydrogen was used with a flow rate of 20 sccm and a pressure of 1 mTorr, for 5 min. Depositions were done by flowing 10 sccm of SiH_4 gas without plasma, immediately after the *in situ* cleaning process. A TEM was used to investigate the epitaxial layer and the epilayer/substrate interface. The TEM used was a model of JEOL 200 CX with a LaB_6 filament and a line-to-line resolution of about 2.7Å. A SIMS was used to quantify the amount of oxygen and carbon elements at the interface. The SIMS used was a model of Perkin Elmer/PHI Model 6300. The Csion is used as the ion source for sputtering and the primary ion energy was 5 keV and the beam current was 200 nA. The SIMS data was plotted in a unit of concentration (atoms/cc) vs. depth and the area density of the carbon and oxygen was obtained by integrating the areas under the interfacial peaks in the SIMS depth profiles. The overall accuracy of the profiles was expected to be in the 15–20% range.

3. RESULTS AND DISCUSSION

In order to investigate the effect of rinsing on surface cleaning, we compared two samples cleaned with and without a rinsing step. We *in situ* cleaned both samples at 600°C and deposited the Si epitaxial films at the same temperature. Sample 2 was rinsed in DI water and then spun-dried, while sample 1 was spin-dried without rinsing. Fig. 1 shows the interfacial oxygen and carbon concentration based on the SIMS data, revealing that the sample without rinsing has a lower interfacial oxygen concentration and a higher interfacial carbon concentration. Since the lower oxygen interfacial concentration corresponds to the higher quality of the epitaxial film [10], we surmise that the rinsing step degrades film quality.

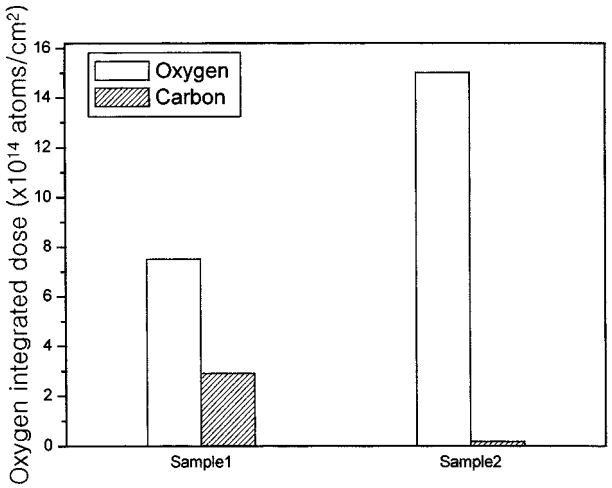

Fig. 1. Interfacial oxygen and carbon concentration based on SIMS data. Sample 2 is rinsed in DI water and then spin-dried, while sample 1 is spin-dried without rinsing. Both samples are *in-situ* cleaned at 600°C.

In another set of experiments, we *in situ* cleaned both samples at 660°C and deposited the Si epitaxial films at the same temperature. Sample 3 was rinsed in DI water and then spin-dried, while sample 4 was spun-dried without rinsing. Fig. 2 shows the interfacial oxygen and carbon concentration based on the SIMS data, revealing that the sample without rinsing has a lower interfacial oxygen concentration and a higher interfacial carbon concentration.

In order to investigate the effect of the drying technique, we compared two samples: one using blow drying and one spin drying. We *in situ* cleaned both samples at 600°C and deposited the Si epitaxial films at the same temperature. Sample 5 was blow-dried without rinsing in DI water and sample 1 was spin-dried without rinsing. Table 2 shows the interfacial oxygen and carbon concentration based on the SIMS data, revealing that the blow-dried sample has a lower interfacial oxygen concentration than the spin-dried sample. Since the lower oxygen interfacial concentration corresponds to the higher quality of the epitaxial film, we surmise that the blow drying is a more efficient technique in lowering the interfacial oxygen concentration and improving film quality. The spin drying process consists of the spin-rinsing step and the spin-drying step. Compared to the blow drying tech-

Table 1. Summary of cleaning conditions

	rinsing	drying	In-situ cleaning	Deposition	Characteristics
Sample 1	-	spin	Done at 600°C	600°C	
Sample 2	rinse	spin	Done at 600°C	600°C	
Sample 3	rinse	spin	Done at 660°C	660°C	
Sample 4	-	spin	Done at 660°C	660°C	
Sample 5	-	blow	Done at 600°C	600°C	
Sample 6	rinse	blow	-	600°C	
Sample 7	-	blow	-	600°C	
Sample 8	-	blow	-	660°C	
Sample 9	-	-	-	660°C	
Sample10	-	-	-	660°C	Long exposure to air

Table 2. SIMS data at the epilayer/substrate interface

	Oxygen (cm^{-2})	Oxygen (cm^{-3})	Carbon (cm^{-2})	Carbon (cm^{-3})
Sample 1	7.5×10^{14}	6.0×10^{20}	2.9×10^{14}	4.0×10^{20}
Sample 2	1.5×10^{15}	8.0×10^{20}	1.7×10^{13}	1.0×10^{19}
Sample 3	1.8×10^{14}	5.0×10^{19}	9.6×10^{14}	2.5×10^{20}
Sample 4	1.0×10^{14}	3.0×10^{19}	1.7×10^{14}	7.0×10^{19}
Sample 5	6.1×10^{14}	1.0×10^{20}	9.1×10^{13}	3.0×10^{19}
Sample 6	1.0×10^{15}	7.0×10^{20}	1.1×10^{14}	1.0×10^{20}
Sample 7	-	-	-	-
Sample 8	1.4×10^{13}	9.0×10^{18}	6.7×10^{13}	1.0×10^{19}
Sample 9	5.2×10^{14}	2.0×10^{20}	9.0×10^{13}	3.0×10^{19}
Sample 10	1.8×10^{15}	2.0×10^{21}	1.4×10^{13}	1.0×10^{19}

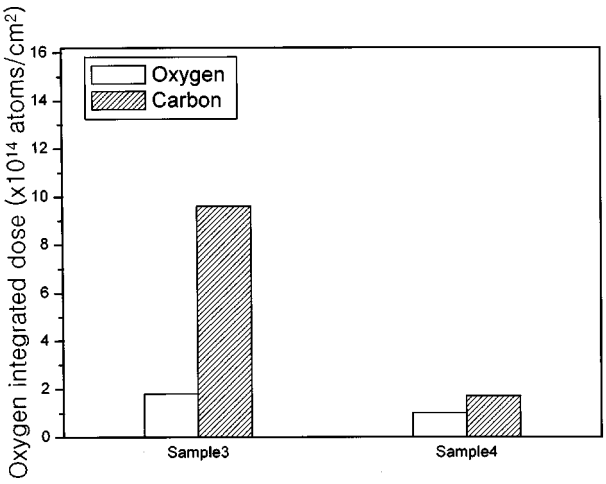

Fig. 2. Interfacial oxygen and carbon concentration based on SIMS data. Sample 3 is rinsed in DI water and then spun-dried, while sample 4 is spun-dried without rinsing. Both samples are *in situ* cleaned at 660°C.

nique, the spin drying process has an additional rinsing step of 160 min. In the spin drying process, rinsing water at high pressure may help to grow the surface native oxide and the oxide may not be removed completely by *in situ* cleaning.

In another set of experiments, we compared two samples cleaned with and without a rinsing step. To reveal the effect of the drying technique precisely, they are blow-dried and we do not perform an *in situ* cleaning prior to epitaxial deposition at 600°C. Sample 6 is rinsed in DI water, while sample 7 is not. Fig. 3(a) shows a typical XTEM micrograph of sample 6, revealing that stacking faults and dislocations are nucleated in the epilayer/substrate interfaces and the thickness of the interface ranges from 100 to 150Å. The SIMS analysis indicates that the interfacial oxygen concentration is 1×10^{15} atoms cm^{-2} and the interfacial carbon concentration is about 1.1×10^{14} atoms cm^{-2}. Since there was no ion bombardment and mechanical damage in Sample 6 due to *in situ* cleaning, we surmise that the generation of defects results from the surface oxygen. Further study is necessary to reveal the detailed mechanism of the generation of oxygen-induced defects. Fig. 3(b) shows a typical XTEM micrograph of Sample 7, revealing that the epitaxial layer deposited on the substrate is almost defect-free and the thickness of the interface is about 50Å. The structural quality of the epilayer/substrate interface in sample 7 is higher than that of sample 6. We surmise that in sample 6, additional water rinsing helps to grow the natural oxide on the silicon surface. In addition, the natural oxide could not be removed due to the absence of the *in situ* cleaning process.

To certify the effect of the blow drying method precisely, we removed the *in situ* cleaning step and deposited the silicon epitaxial layer at 660°C. Fig. 4(a) shows an XTEM

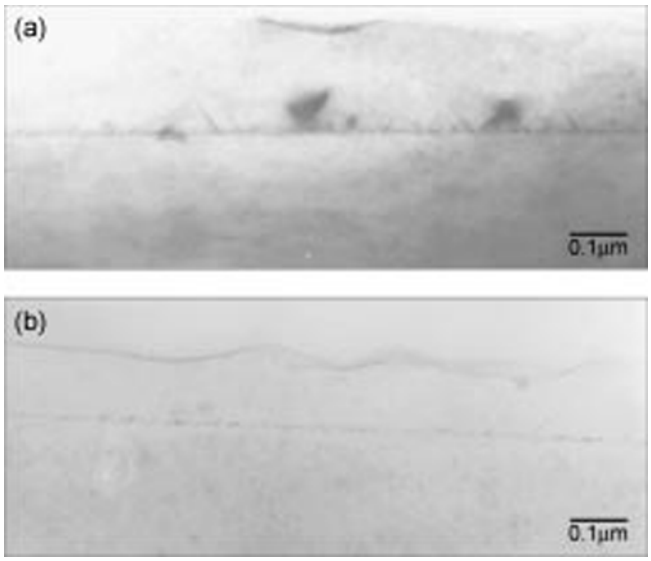

Fig. 3. Comparison of two samples cleaned with and without a rinsing step. They are blow-dried and do not experience an *in-situ* cleaning prior to epitaxial deposition at 600°C. (a) XTEM micrographs of sample 6 rinsed in DI water. (b) XTEM micrographs of sample 7, without rinsing. The structural quality of the epilayer/ substrate interface in the Sample without rinsing is higher than that of the Sample with rinsing.

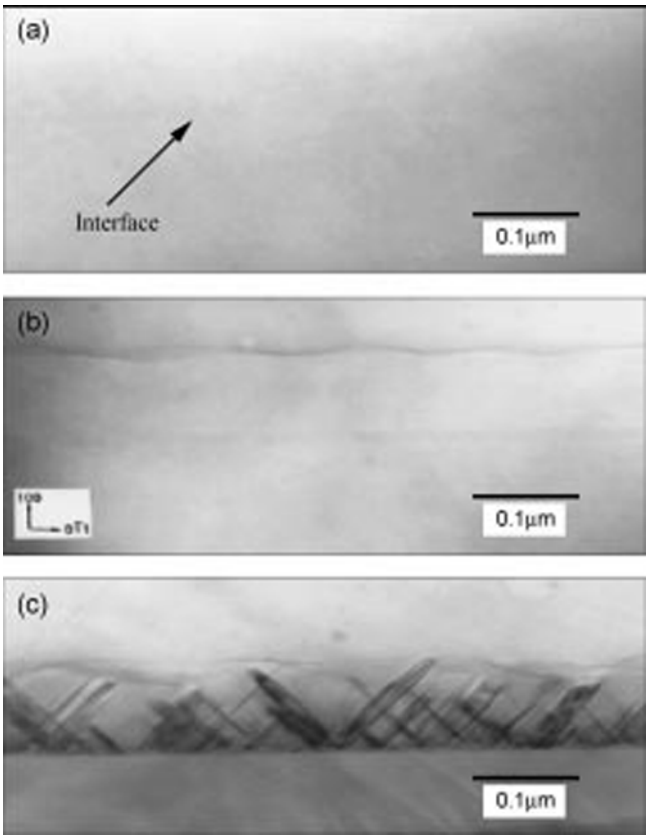

Fig. 4. (a) XTEM micrograph of the epitaxial film (Sample 8), which is blow-dried without water rinsing. (b) XTEM micrograph of the epitaxial film (Sample 9), in which the rinsing and blow drying steps are removed. (c) XTEM micrograph of the epitaxial film (Sample 10), in which the rinsing and blow drying steps are removed and the wafer is kept for several hours in a cleanroom before loading into the load lock chamber.

micrograph of the epitaxial film (Sample 8), which is blow-dried without water rinsing. The XTEM image indicates a defect-free epitaxial layer with an almost invisible interface. The SIMS data reveal that the oxygen concentration in the epitaxial film is about 1-2×10^{18} atoms cm^{-3} and the interfacial oxygen concentration at the highest point of the SIMS profile is 9×10^{18} atoms cm^{-3}. The integrated dose of oxygen at the interface is 1.4×10^{13} atoms cm^{-2}. Fig. 4(b) shows an XTEM micrograph of the epitaxial film (Sample 9), in which the rinsing and blow drying steps are removed. The XTEM image reveals that defect-free epitaxial layer is deposited and the thickness of the epilayer/interface is about 100-110Å. The interfacial oxygen concentration calculated from the SIMS data is 5.2×10^{14} atoms cm^{-2}, revealing that the interfacial oxygen concentration of the untreated sample is higher than that of the blow-dried sample. Since the interfacial oxygen induces the defects and the thickness of the epilayer/substrate interface is closely related to the interface defects, we conclude that the SIMS data agree with the XTEM image. We suppose that air-exposure time affect the crystalline quality of the epitaxial film and interface because exposing the wafer to atmosphere helps to grow the native oxide. Fig. 4(c) shows an XTEM micrograph of the epitaxial film (Sample 10), in which the rinsing and blow drying steps are removed and the wafer is kept for several hours in a cleanroom before loading into the load lock chamber. The XTEM image reveals that there are major differences in the structural quality of the epitaxial layer as a result of keeping the wafer in the cleanroom environment for long periods. The SIMS data indicate that the interfacial oxygen concentration is 1.8×10^{15} atoms cm^{-2}. We surmise that very high oxygen density on the substrate surface may induce stacking faults in the epitaxial film.

4. CONCLUSIONS

We investigated the effect of the rinsing and drying technique on the crystallinity of epilayer and epilayer/substrate interface and on the oxygen and carbon concentration on the silicon surface. Rinsing in deionized water increased interfacial oxygen concentration thus helping to generate defects. Blow-drying by nitrogen turns out to be efficient in reducing interfacial oxygen concentration and the thickness of epilayer/substrate interface. Exposure to atmosphere was detrimental to obtaining a high crystallinity in the epitaxial layer. We evaluate the quality of the epitaxial

layer by observing the grown epilayer and the epilayer/substrate interface.

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