

Effect of In-situ Plasma Cleaning on the Crystalline Quality of Silicon Homoepitaxial Films

Kwang-sik Kim and Hyoun-woo Kim

School of Material Science and Engineering, Inha University
253 Yonghyun-2-dong, Nam-ku, Incheon 402-751, Korea

Low temperature processing, which includes in-situ cleaning and epitaxial deposition, is not only important for future silicon ULSI (Ultra Large Scale Integration) technology but also for silicon based heterostructures. Low temperature processing cannot volatilize or dissolve the surface contaminants by heating the substrate, as was accomplished in the traditional high temperature epitaxial growth. In this study, electron cyclotron resonance (ECR) hydrogen plasma was used and films were deposited thermally at a low temperature. The epitaxial films, which were deposited in our chemical vapor deposition systems, immediately after the in-situ cleaning processes were characterized by cross-sectional transmission electron microscopy, etc. The role of a hydrogen ion in the in-situ cleaning was clarified by investigating the cleaning efficiencies for a variety of conditions. Process variables such as cleaning temperature and d.c. bias were investigated, and the d.c. bias turned out to play a crucial role in low-temperature in-situ cleaning processes. Also, the effect of the in-situ cleaning temperature on the cleaning efficiency was investigated and discussed.

Keywords : chemical vapor deposition, hydrogen, plasma processing and deposition, transmission electron microscopy

1. INTRODUCTION

As device dimensions are reduced into the sub-micron regime in pursuit of higher integration density and better circuit performance, low temperature epitaxy has been a major issue in microelectronics technology and will be more critical in the future. The reduction in temperature may suppress dopant diffusion so that abrupt transition regions can be obtained. It is crucial to minimize the thermal heating during in-situ cleaning to reduce autodoping and broadening of the dopant profile. A low-temperature cleaning technique not only reduces the thermal heating during the cleaning process, but also may be able to lower the subsequent deposition temperature by effectively cleaning the silicon wafer surface before depositing the epitaxial layer.

For low-temperature in-situ cleaning, numerous methods such as Ar ion sputtering [1], Ar/hydrogen ion sputtering [2], and hydrogen plasma cleaning [3] have been tried and investigated. In-situ Ar or He electron cyclotron resonance plasma sputtering was applied in our system [4]. However, many defects were generated in the epilayer/substrate interfaces, where the substrates were submitted to ECR argon plasma bombardment prior to growth. Hydrogen is the lightest element and is reported to react chemically with oxygen or carbon, so severe substrate damage during ion bombardment may be reduced,

while keeping the substrate surface clean. Hydrogen plasma exposure may be based on the ion etching effect [5,6] and the hydrogen passivation effect at low temperatures [7]. This issue is particularly important for our low-temperature epitaxial growth, because once the stacking faults were generated, defect-free epitaxial film could not be obtained. The ECR plasma system was selected because it has some advantages compared to conventional radio frequency (r.f.) plasma systems. The electron cyclotron resonance (ECR) plasma system, which operates at a microwave frequency of 2.45 GHz, is able to deliver a higher density of low energy ions to the wafer, because both ionization (about 10% of the gas is ionized in our system) and the saturated ion current are much higher than in the r.f. plasma system. Particularly, the ECR plasma can be operated with low energy (without sacrificing cleaning efficiency), and ion flux and ion energy can be controlled easily. Possible substrate damage may be reduced because of reduced plasma exposure time and less contamination may be expected due to electrodeless discharge [8]. ECR is compatible with ultra-high vacuum (UHV) chemical vapor deposition (CVD) systems. Epitaxial layers could not be deposited due to the excessive damage on the substrate surface. Therefore, it is surmised that the ECR technique may reduce the ion energy. However, once damage was introduced to the substrate, it could not be annealed at temperatures of

600°C or below.

Internal reflection measurements showed the presence of Si-H bonds on the HF-treated silicon surface at about a monolayer density [9,10]. Hprebake is a simple and reliable method for removing contaminants like oxygen and carbon from the silicon surface [11], but a very high temperature, more than 1000°C, is required. In an attempt to lower the prebake temperature, hydrogen plasma exposure has been tried [12]. Kishimoto *et al.* [13] studied the temperature dependence of the hydrogen plasma cleaning process by in-situ RHEED monitoring of the cleaned surface. They concluded that the cleaning efficiency was inversely proportional to the cleaning temperature. In our experiments, the temperature dependence of cleaning efficiency was studied by depositing epitaxial layers on the in-situ cleaned surfaces and by observing the structural qualities of those films.

2. EXPERIMENTAL PROCEDURE

A multichamber single-wafer CVD reactor, located in a class 100 clean room was used. The reactor was composed of four chambers: Load Lock, Analysis, CVD and ECR chambers.

Substrates were 4 inch, czochralski-grown, p-type<100> silicon with 0.5–20 Ωcm resistivity. The wafer was RCA cleaned and HF dipped for 20 to 30 s in 10:1 aqueous solutions. It was then rinsed in deionized (DI) water and dried by a blowing nitrogen gun inside the stations. All the processes were performed inside the class 100 clean room and it took approximately 10 s 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 analysis chamber by opening the gate valve between the chambers. Before the gate valve was opened, hydrogen gas was introduced and kept flowing through the CVD chamber to avoid cross contamination. A magnetically coupled rod with a pincher held a wafer and it was transferred linearly to the CVD chamber, where it was unloaded to the heater stage. After the wafers were loaded onto the heater stage, the CVD chamber was pumped down and ultimately $1\text{--}2 \times 10^{-8}$ Torr could be attained. It took about 7 min to heat the wafer to 600°C, with the flow of the hydrogen gas. In-situ predeposition wafer cleaning was done by using ECR hydrogen plasma at room temperature. The flow rate was kept at 20 sccm (standard cubic centimeters per minute) and the in-situ cleaning was carried out for 5 min. The window magnet was centered on the top flange of the ECR chamber and the bottom magnet was centered on the lower flange. Their currents were set to 150 A and 120 A, respectively. Deposition was performed by flowing 10 sccm SiH₄ without carrier gases, immediately after the plasma was extinguished. The wafer was then heated up to 600°C in a hydrogen flow rate of 20 sccm. It took about 7 min to heat it

from 25°C to 600°C, which was a well-characterized deposition temperature in our system. When the in-situ cleaning was done at 250°C, it took about 4.5 min to heat it. When the in-situ cleaning was done at 600°C, the loaded wafer was heated to 600°C and then in-situ cleaning was performed. A heater stage was installed to the side of the CVD chamber and the wafer was seated vertically in front of a resistive/radiant heater, which was made of SiC (silicon carbide)-coated graphite. Pure silane and house hydrogen were used for our experiments and these gases were passed through the Nanochem purifiers [14].

Electron cyclotron resonance (ECR) plasma is produced through the interaction between electrons which move with cyclotron motion due to a magnetic field and plasma waves induced by microwaves. The particle charging and dynamics of charged particles in ECR plasma have been studied experimentally by using a laser light scattering method [15]. Rutherford backscattering spectroscopy (RBS) was used to measure the crystalline quality of the epitaxial film which was determined by the ratio of the channeling yield of the film to the random yield (χ_{min}). Cross-sectional transmission electron microscopy (XTEM) was used to observe the epitaxial layer and the epilayer/substrate interface. Plain-view transmission electron microscopy (PTM) was used to check the epitaxial quality and crystal direction of the deposited films. Epitaxial film thickness was measured in-situ by the emission Fourier transform infrared spectroscopy (E/FTIR) technique. The E/FTIR were reported elsewhere in detail [16]. A non-contact, non-destructive, real-time, and in-situ epi-film thickness monitoring tool was demonstrated to be useful for observing real time growth rates.

3. RESULTS AND DISCUSSION

The XTEM micrographs were used to observe the images of the substrate and epitaxial layer and their interfaces. The in-situ cleaning condition was optimized by the structural characterization of the deposited films. The in-situ cleaning process was optimized and the process was evaluated. Samples A and A⁺ were RCA cleaned and dipped for 20–30 s into 10:1 DI water: HF solutions, to remove the surface natural oxide. The wafers were rinsed in DI water for about 3 min, and were dried by blowing nitrogen. Sample A received the standard (optimized) in-situ cleaning, while Sample A⁺ did not. The standard condition corresponded to the microwave power of 300 W, magnet currents of 150 A and 120 A for the top and bottom magnets, respectively. A positive 10 V d.c. bias was applied: the positive ions were repelled rather than the hydrogen ion energy being reduced. The cleaning was performed by a flowing 20 sccm of Hat 1 mTorr, at 600°C, for 5 min. Deposition was done by introducing 10 sccm of SiH₄ at 1 mTorr and at 600°C, immediately after the plasma was extinguished (Sample A).

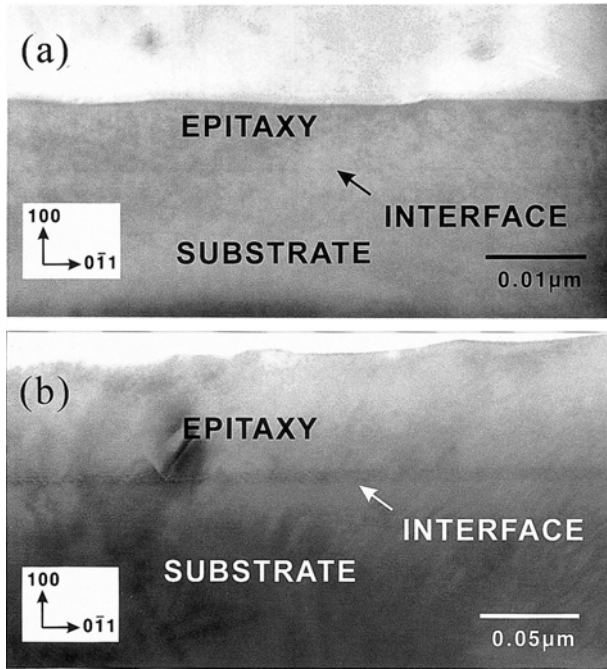


Fig. 1. (a) HRXTEM micrograph of an epitaxial film, cleaned in-situ with standard conditions at 600°C. (b) XTEM micrograph of an epitaxial film, without in-situ cleaning (rinsed and blow dried).

Fig. 1(a) shows the high-resolution cross-sectional transmission electron microscopy (HRXTEM) micrograph of a sample of Sample A. A defect-free epitaxial layer and almost invisible epilayer/substrate interface were observed. Fig. 1(b) shows the micrograph of Sample A⁺. Stacking faults were initiated in the epilayer/substrate interface. The thickness of the epilayer/substrate interface was about 100 to 150 Å. The interfacial oxygen concentration of Sample A⁺ was much higher than that of Sample A.

Therefore, the standard in-situ cleaning was effective in removing surface natural oxide, which was present on the wafer surface after ex-situ cleaning. Since Sample A⁺ did not receive an in-situ cleaning, the surface contaminants, surface oxygen, must have caused the stacking faults.

In RBS channeling experiments, the χ_{\min} of Sample A and Sample A⁺ was about 3% and 7%, respectively. Therefore, the structural quality of the epitaxial layer in Sample A was comparable to that of the substrate. Also in RBS channeling experiments, a detector with a high glancing angle (about 75°) was used to maximize the sensitivity in detecting heavy metal elements. For Sample A, no trace of such elements were found by this technique. This result is compared to an ECR Ar (argon) plasma cleaned sample [17] in our system, in which a considerable amount of heavy elements (Ar, Mo, Ta) was found in the epilayer/substrate interfaces.

The substrate was either floated or d.c. biased in our experiments. $V_p - V_f$ is the difference between the plasma potential and the floating potential, and $e(V_p - V_f) - e(V_{d.c.})$ thus repre-

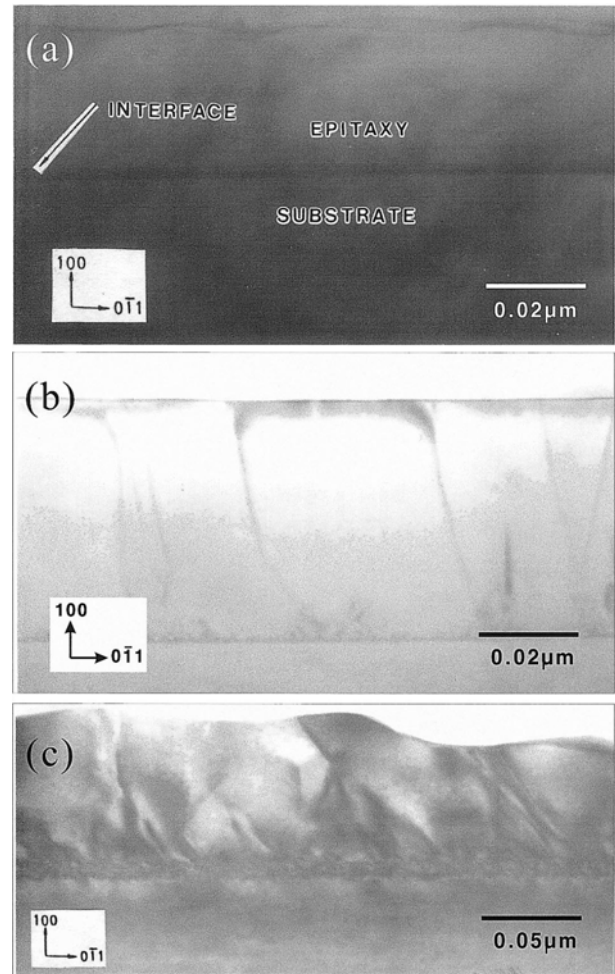


Fig. 2. XTEM micrographs of epitaxial films, cleaned in-situ at 600°C with the d.c. bias set at (a) 0 V, (b) 30 V and (c) -50 V.

sents the ion energy in the presence of the substrate d.c. bias [18].

Figs. 2(a)-(c) are XTEM micrographs of Samples B, C and D and in these cases 0 V, 30 V (floated) and -50 V of d.c. bias was applied, respectively. The other process variables were the same. When increasing the hydrogen ion energy by the amount of 10 eV from the standard condition, the substrate was floated and the interface became clear and thick (about 30 Å) enough to be observed, while the defect-free epitaxial layer was deposited (Sample A). It is interesting to observe that the surface of the 0V cleaned epitaxial layer is a slightly curved compared to the +10 V cleaned one, in which case the surface of the epitaxial film is quite smooth. Interfacial oxygen concentrations were measured by SIMS. Interfacial impurity concentration was represented by its areal density, instead of volume concentration at a particular interface. SIMS data tell us that Sample B has a higher oxygen concentration than Sample A in the epilayer/substrate interface (Table 2).

Table 1. Summary of in-situ cleaning conditions in our experiments

	Power(W)	D.c. bias (V)	Cleaning temperature (°C)	Pressure (mTorr)
Sample A	300	10	600	1
Sample B	300	0	600	1
Sample C	300	30	600	1
Sample D	300	-50	600	1
Sample E	300	10	280	1
Sample F	300	10	480	1
Sample G	300	10	RoomT	1

Table 2. SIMS and RBS data

	Oxygen (cm ⁻²)	Oxygen (cm ⁻³)	χ_{\min}
Sample A ⁺	1.0×10^{15}	7×10^{20}	7%
Sample A	4.8×10^{13}	8×10^{19}	3%
Sample B	8.1×10^{14}	3×10^{20}	5%
Sample G	7.8×10^{14}	7×10^{20}	5%

An oxygen species may be present at the epilayer/substrate interface of Sample B. As the epitaxial layer grows to some thickness, the silicon around the second phase coalesces and forms some surface structures. This may happen without generating dislocations or stacking faults if the sizes and quantities of the second phases are small. Hydrogen ion bombardment may have generated damage to the substrate, and the hydrogen ion energy is transferred to the silicon substrate, rather than used in removing the oxygen.

Fig. 2(b) is a XTEM micrograph of Sample C and in this case, +30 V of d.c. bias was applied in its in-situ plasma cleaning and the other process variables were the same as the standard condition. The film was an epitaxial layer with a smooth surface, but it had a considerable amount of stacking faults which were initiated from the interface. Threading dislocations were generated in the epilayer/substrate interface and they existed throughout the film. It was surmised that oxygen or other contaminants could not be removed easily from the surface, because the ion bombardment energy was reduced by supplying a positive 30 V of d.c. bias. In Sample D, where 50 V of d.c. bias was applied to the substrate, the ion energy was increased by 60 eV with respect to the standard condition (Sample A). About a 300 Å thick layer of substrate was highly damaged and the substrate below this region was observed to be highly stressed (Fig. 2(c)). Dark/bright contrasted regions were observed in the substrate, and high densities of stacking faults and dislocations were present in the film. This observation can be related to the hydrogen ion bombardment, which was energized by applying a negative substrate d.c. bias.

Current 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 and hydrogen atoms are easily desorbed and hydrogen passivation will be lost [19]. Oxygen removal is affected by hydrogen passivation. In this case, the sticking coefficient of the hydrogen radicals decreases at higher temperatures and may take longer to clean the surface at the higher temperatures. But this observation does not necessarily apply to our system because although in-situ wafer cleaning can be performed at room temperature, the temperature should be raised to at least 600°C in our depositions for actual epitaxial growth to be initiated. It took at least 7 min to heat the wafer from room temperature to 600°C in our system and hydrogen passivation may be lost during this process. It was shown by SIMS that some oxygen may have stuck onto the silicon surface when hydrogen was kept flowing at 600°C. But this oxygen contamination may be reduced at higher temperatures because of oxygen desorption phenomena. It can be assumed that oxygen desorbs at high temperatures. Also, oxygen removal is feasible only for weakly adsorbed oxygen [20], since the surface reaction between reactive species and passivation oxide films proceeds very slowly at temperatures less than 800°C [21]. Even for a sub-monolayer coverage of oxygen on silicon, the desorption temperature of the oxide, such as SiO₂, was reported to be about 700°C [22]. If the oxide layer is sufficiently thick from the beginning, or the cleaning temperature is so low that the desorption process becomes a rate-determining step, the rate of oxygen removal and thus the cleaning efficiency will increase with increasing temperature.

In addition, experiments (using Samples E, F) were performed to investigate the effect of cleaning temperatures between 25°C and 550°C on cleaning efficiency in terms of structural analysis. In-situ cleaning was performed with a microwave power of 300 W and a d.c. bias of +10 V, for both samples. Fig. 3(a) is the XTEM micrograph of Sample

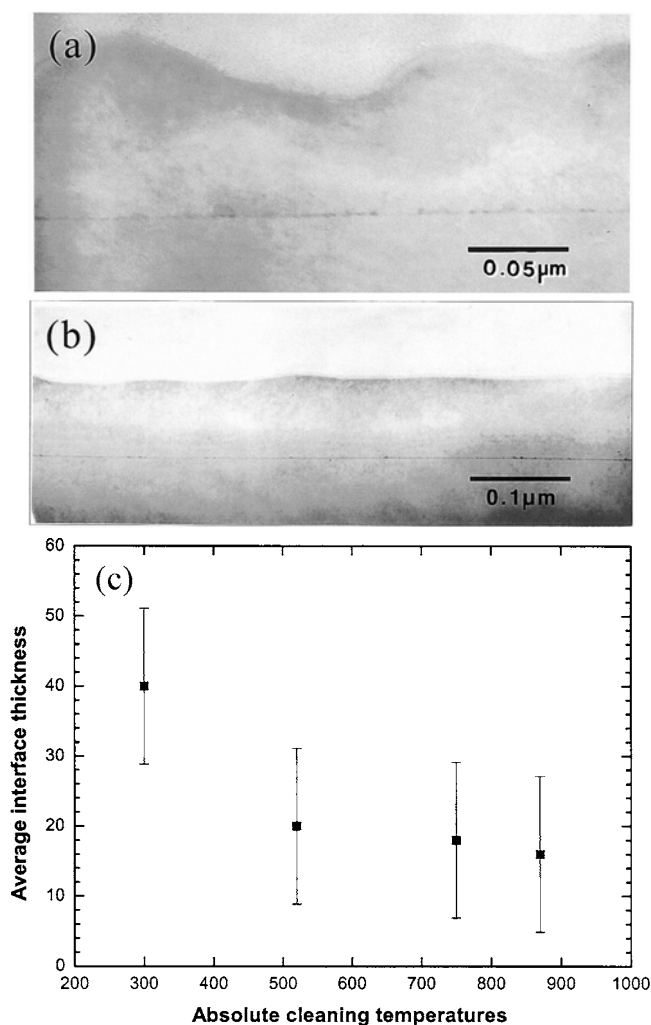


Fig. 3. XTEM micrograph of an epitaxial film, cleaned in-situ with standard conditions at (a) 280°C and (b) 480°C. (c) Average thickness (Å) of the epilayer/substrate interface as a function of cleaning temperature (°K).

E, in-situ cleaning was done at 280°C and the wafer was heated up during hydrogen flow for about 4.5 min. Deposition was performed at 600°C. The XTEM micrograph of Sample H shows that an almost defect-free epitaxial layer was deposited. The thickness of the epilayer/substrate interface was about 20 Å. The purpose of this experiment was to reduce the hydrogen exposure time and at the same time to lower the cleaning temperature as much as possible.

Fig. 3(b) is the XTEM micrograph of Sample F. In-situ cleaning was carried out at 480°C. The plasma was turned off after 5 min and silane was introduced immediately at the same temperature. The deposition temperature was adjusted to 600°C afterwards. Although hydrogen passivation may have begun to be lost at low temperatures of about 400°C [23], if we accept the report that the hydrogen desorption temperature is between 510 and 520°C [24], some hydrogen

species may stay at 480°C, so they prevent oxygen species from being adsorbed on the silicon surface. From the micrograph, a defect-free epitaxial layer was grown and the epilayer/substrate interface was thin (less than 20 Å). However, the interface clearly existed and was not invisible. There should be some remaining oxide or surface contaminants, probably due to low initial deposition temperature. Samples A, E, F and G are compared, to see the effect of the cleaning temperature on the cleaning efficiency. The thickness of epilayer/substrate interface was plotted as a function of cleaning temperature (Fig. 3(c)). Averaged values were used for the interface thicknesses and possible measurement error was considered. The interface thicknesses for Samples A, E, F and G were in the range of between 10 and 50 Å, and showed a slight decrease as cleaning temperature increased from 25°C to 600°C. It is shown that the structural qualities of epitaxial layers are not affected by the in-situ cleaning temperature significantly, as long as standard conditions hold [25].

In-situ ECR plasma cleaning may proceed by physical sputtering, chemical reaction (etching) or ion-assisted mechanisms. Excessive hydrogen ion bombardment produced a highly damaged silicon surface [26] and in our experiments, applying -50 V of d.c. bias during in-situ cleaning damaged the substrate. A positive bias was needed to reduce the hydrogen ion energy [27]. In our experiments, reducing the hydrogen ion energy by supplying a positive d.c. bias resulted in growing a defect-free silicon epitaxial layer. It is surmised that hydrogen ions played a major role in surface cleaning because the cleaning efficiency was affected significantly by varying a substrate d.c. bias. It was also observed that in-situ cleaning at higher hydrogen pressure generated many defects in the epitaxial layer and a defect-free epitaxial film was deposited with the in-situ cleaning at pressures of 1 mTorr or less. At this low pressure, the probability of collisions with other particles are lower and the impinging ions may not have lost their kinetic energy. Therefore, the ECR hydrogen plasma cleaning is more like an ion-assisted or physical sputtering process, rather than a pure chemical etching process.

4. CONCLUSIONS

The standard condition with in-situ hydrogen plasma cleaning at 600°C was optimized. In-situ cleaning time was optimized to be 5 minutes, and longer cleaning did not improve its efficiency. A substrate DC bias proved to play a major role in obtaining a damage-free, chemically clean interface. Low hydrogen gas pressure (~1 mTorr) was required to obtain a damage-free interface. The ECR hydrogen plasma cleaning was similar to an ion-assisted or physical sputtering process, because hydrogen ions turned out to play a crucial role in the in-situ cleaning process. By assuming the collision-cascade model, the threshold energy for physical sputtering was calculated. Ion-assisted etching proved to be the domi-

nant process, rather than physical sputtering, in wafer surface cleaning by the ECR hydrogen plasma technique. The interfacial oxygen concentration was reduced by adjusting the hydrogen ion energy with a substrate d.c. bias. In our analysis, hydrogen gas density, represented by microwave power and gas pressure, did not affect the film quality significantly, in the range from 300 W (1 mTorr) to 750 W (8 mTorr), compared to d.c. bias and cleaning temperature (both high gas pressure and high microwave power correspond to high gas density, and vice versa). Lower pressure is needed to turn the in-situ cleaning process into the physical sputtering regime. A defect-free epitaxial film was deposited with the in-situ cleaning at pressures of 1 mTorr or less. The structural qualities of epitaxial layers are not affected by the in-situ cleaning temperature significantly, as long as standard conditions hold. The ECR plasma cleaning generated carbon in addition to carbon atoms which came from the hydrogen gas or from inside the reactor.

ACKNOWLEDGMENT

This work was supported by grant No.2001-1-30100-018-3 (R02-2001-00843) from the Basic Research Program of the Korea Science & Engineering Foundation.

REFERENCES

1. R. Reif, *J. Vac. Sci. Tech. A* **2**, 429 (1984).
2. T. R. Yew and R. Reif, *J. Appl. Phys.* **68**, 4681 (1990).
3. I. Suemune, Y. Kunitsugu, Y. Tanaka, Y. Tanka, Y. Kan and M. Yamanishi, *Appl. Phys. Lett.* **53**, 2173 (1988).
4. Z. Ye, Y. Liu, Z. Zhou and R. Reif, *J. Electron. Mater.* **22**, 247 (1993).
5. H. W. Kim and Z.H. Zhou, *Thin Solid Films* **302**, 169 (1997).
6. M. Delfino, S. Salimian, K. Hocul, A. Ellingboe and W. Tsai, *J. Appl. Phys.* **71**, 1007 (1992).
7. B. S. Meyerson, *Proc. IEEE*. **80**, 1592 (1992).
8. W. H. Greene, *J. Vac. Sci. Tech. B* **9**, 366 (1991).
9. E. Yablonovitch, D. L. Allara, C. C. Chang, T. Gmitter and T. B. Bright, *Phys. Rev. Lett.* **57**, 249 (1986).
10. V. A. Burrows, Y. J. Chanbal, G. S. Higashi, K. Raghavachari and S. B. Christman, *Appl. Phys. Lett.* **53**, 998 (1988).
11. T. Y. Hsieh, K. H. Jung and D. L. Kwong, *J. Electrochem. Soc.* **138**, 1188 (1991).
12. R. E. Thomas, M. J. Mantini, R. A. Ruddler, D. P. Malta, S. V. Hattangady and R. J. Markunas, *J. Vac. Sci. Tech. A* **10**, 817 (1992).
13. A. Kishimoto, I. Suemune, K. Kamaoka, T. Kouji, Y. Honda and M. Yamanishi, *Jpn. J. Appl. Phys.* **29**, 2273 (1990).
14. T. O. Sedgwick, *Appl. Phys. Lett.* **58**, 2689 (1989).
15. G. S. Selwyn, *Jpn. J. Appl. Phys.* **32**, 3068 (1993).
16. Z. H. Zhou, F. Z. Yu and R. Reif, *J. Vac. Sci. Tech. B* **9**, 374 (1991).
17. Z. H. Zhou, *M. S. Thesis*, p. 59, MIT, USA (1991).
18. H. W. Kim and R. Reif, *Thin Solid Films* **298**, 192 (1996).
19. A. Kishimoto, I. Suemune, K. Kamaoka, T. Kouji, Y. Honka and M. Yamanishi, *Jpn. J. Appl. Phys.* **29**, 2273 (1990).
20. D. Kiniski, R. Qian, A. Lahajan, S. Thomas, P. Munguia, J. Fretwell, S. Banerjee and A. Tasch, *Mater. Res. Soc. Symp. Proc.* **315**, 223 (1993).
21. H. Yamada, *J. Appl. Phys.* **65**, 776 (1989).
22. J. R. Engstrom, D. J. Bonser, M. M. Nelson and T. Engel, *Surf. Sci.* **256**, 317 (1991).
23. S. S. Iyer, M. Arienzo and E. de Fresart, *Appl. Phys. Lett.* **57**, 895 (1990).
24. S. H. Wolff, S. Wagner, J. C. Bean, R. Hull and J. M. Gibson, *Appl. Phys. Lett.* **55**, 2017 (1989).
25. H. W. Kim, Z. H. Zhou and R. Reif, *Thin Solid Films* **302**, 169 (1997).
26. Z. Zhou, E. Aygil, R. Gottscho, Y. Chabel and R. Reif, *J. Electrochem. Soc.* **140**, 3316 (1993).
27. J. Ramm, E. Beck and A. Zuger, *Mater. Res. Soc. Symp. Proc.* **220**, 15 (1991).