Cleaning of Silicon Surfaces by NF₃ Added Hydrogen and Water Vapor Plasma Downstream Treatment

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Native oxide was removed from silicon surfaces by NF₃ added hydrogen and water vapor plasma downstream treatment. It took 45 sec to remove native oxide. FT-IR ATR measurement revealed the roughness after the downstream treatment was the same as that by 2% HF wet cleaning. Silicon epitaxial layer was grown on the surface cleaned by the downstream treatment. Even process temperature was as low as 100°C, this downstream treatment had the same effect as in-situ hydrogen annealing.

1. INTRODUCTION

As device size shrinks, native oxide will more affect reliability of gate oxide and contact resistance. It is required, therefore, to remove native oxide from silicon surfaces prior to thin film growths. However, it is getting more difficult to clean silicon surfaces with finer patterns by conventional wet treatment because of viscosity. Hence, damageless dry cleaning process for silicon surfaces has been needed. We have reported that native oxide was removed from silicon surfaces by NF₃ added hydrogen and water vapor plasma downstream treatment without leaving damage on the silicon surface. However, since the equipment was small, only small size specimens could be treated and it took 7 min to remove native oxide from silicon surfaces. In the present study, using a larger size chamber with higher power, we surveyed the applicability of the downstream treatment as a precleaning in massproduction. Also we used this downstream treatment as a precleaning for silicon epitaxial film growth.

2. EXPERIMENTAL

Figure 1 shows the schematic diagram of the plasma downstream chamber. The plasma was generated by microwave (2.45 GHz, 300 W). Hydrogen (180sccm) was introduced into the plasma. Water vapor (20sccm) was added to hydrogen to increase the concentration of atomic hydrogen in the plasma downstream. The plasma and its downstream were contained in quartz vessel, tube and bell jar because, at present, the effect of the added water vapor was observed only with quartz wall. NF₃ (100sccm) was injected into the downstream of the hydrogen and water vapor plasma. The injector was placed 300 mm away from the plasma so that fluorine atoms were not generated due to high energy particles from the plasma. Wafers used were p-type Si(111) 100 Ωcm for FT-IR ATR measurement and Si(100) 10 Ωcm for silicon epitaxial growth. Native oxide formed in H₂SO₄/H₂O₂ solution on the silicon wafers was removed by the downstream treatment (at 25°C, 0.5 Toor) followed by heating in nitrogen without electrical discharge at 80°C.

Silicon surfaces after the downstream treatment was surveyed by Fourier transformation infrared attenuated total reflection (FT-IR ATR) measurement. We measured the increase in the number of particles during the downstream treatment.

Silicon epitaxial layer was grown on the surface cleaned by the downstream treatment. Stacking faults in the epitaxial layer were observed with an optical microscope. Silicon epitaxial layers were also grown on the surfaces prepared by conventional hydrogen annealing and HF wet cleaning and compared with the downstream treatment.

3. RESULTS AND DISCUSSION

3.1 FT-IR ATR MEASUREMENT

Figure 2 shows the FT-IR ATR signal of the silicon surface after the downstream treatment for 45 sec followed by heating for 1 min (solid line). Removal of native oxide was confirmed from the finding that no peak was observed from 2150 to 2250 cm⁻¹, which corresponds to silicon-hydrogen bonds with oxygen atoms in their backbones. The formation of absorption peaks from 2050 to 2200 cm⁻¹ indicates that a hydrogen terminated surface was obtained after native oxide removal. As compared with the surface treated by 2% HF wet cleaning (dotted line), the areas under the peaks from 2050 to 2200 cm⁻¹ for both treatments are almost equal. Hence, the roughness of the silicon surface after the downstream treatment is considered to be the same.
as that by 2% HF wet cleaning.

### 3.2. PARTICLE GENERATION DURING THE DOWNSTREAM TREATMENT

Table 1 shows the number of particles on the silicon wafers before and after the downstream treatment. In this experiment, silicon wafers were exposed to the plasma downstream for 10 min. The numbers of the particles increased during the downstream treatment were 16 and 20 for each wafer. We have reported that the quartz chamber was not etched during the downstream treatment and its surface was clear after 30 hours of the treatment because NF3 was not introduced into the plasma, but into the plasma downstream. This effect was considered to minimize the particle generation during the downstream treatment.

### 3.3. EPITAXIAL FILM GROWTH

Figure 3 shows the experimental procedure of silicon epitaxial growth. Prior to the epitaxial growth, native oxide on the silicon surfaces were removed by the downstream treatment, hydrogen annealing and 2% HF wet cleaning. Only the hydrogen annealing was conducted in the same chamber as that for the epitaxial growth. Silicon epitaxial layer was grown for 5000 Å on each surface. In Fig. 4, the optical microscope photographs of the surfaces after the film growths were shown. Stacking faults were typically appeared in the epitaxial layer prepared by 2% HF wet cleaning (Fig. 4(c)). When the silicon surface was prepared by the downstream treatment, stacking faults were not observed at the interface (Fig. 4(a)). The surface cleaning by this downstream treatment was as effective as that by in-situ hydrogen annealing (Fig. 4(b)). From Fig. 2, the roughnesses of the surface after the downstream treatment and 2% HF wet cleaning were appeared to be equal. However, stacking faults appeared only in the epitaxial layer prepared by the HF wet cleaning. This seemed to be because native oxide formed again on the silicon surface during water rinsing after the HF dip. From the downstream chamber to the epitaxial growth chamber, the silicon wafer was transferred in the air for about 5 min. XPS measurement revealed native oxide was not observed on the silicon surface cleaned by the downstream treatment after the wafer was exposed to the air for that period of time.

### 6. CONCLUSIONS

We designed the larger scale chamber for NF3 added hydrogen and water vapor downstream treatment with higher

![Fig. 1. Plasma downstream chamber.](image)

![Table I. Numbers of particles before and after the downstream treatment.](image)
microwave power and examined its applicability to mass-production as a precleaning. Native oxide was removed by the downstream treatment for 45 sec. From FT-IR ATR measurement, the surface roughness after the native oxide removal was the same as that by 2% HF wet cleaning. We used this downstream treatment as the precleaning for the silicon epitaxial growth. The silicon epitaxial layer without stacking faults was obtained on the silicon surface cleaned by this downstream treatment. Even the temperature during the process was as low as 100°C and the wafer was transferred in the air from the downstream chamber to the epitaxial growth chamber, the same effect as the in-situ hydrogen annealing was obtained.

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REFERENCES


Fig. 3. Experimental procedure for epitaxial film growth.

Fig. 4. Optical microscope photographs after silicon epitaxial film growth: (a) is obtained by the downstream treatment, (b) is obtained by hydrogen annealing and (c) is obtained by 2% HF wet cleaning as pre-treatments.

(a) 100μm  
(b) 100μm  
(c) 100μm