HF/CH<sub>3</sub>OH(Alcohol) Vapor Cleaning <HAVC> and Its Application to Polycrystalline Silicon/Silicon Contact Formation

A.Izumi, T.Matsuka, K.Miya, T.Takeuchi, A.Yamano
Development Department 2, Dainippon Screen Mfg. Co. Ltd.
322, Furukawa-cho, Hazukashi Fushimi-ku, Kyoto 612, Japan
J.Tsuchimoto, H.Itoh and H.Abe
LSI Laboratory, Mitsubishi Electric Corporation
4-1 Mizuhara, Itami, Hyogo 664, Japan

HF/CH<sub>3</sub>OH(Alcohol) Vapor cleaning <HAVC> was developed in order to remove the oxide film on silicon substrate effectively, in which process CH<sub>3</sub>OH was used as a solvent for HF replacing conventional H<sub>2</sub>O. This technique was applied to form polycrystalline silicon (polysilicon) contacts with silicon substrate. The contact resistance was improved comparing with those of conventional HF/H<sub>2</sub>O wet cleaning method, and good control of interface quality between polysilicon and silicon substrate were obtained by using HAVC. HAVC was also effective to reduce the contaminations of carbon, fluorine and native oxide, to form atomically flatter silicon surface.

1. Introduction

ULSI fabrication pursue more stringent requirements on the cleanliness of silicon wafers. The performance of semiconductor devices can be altered by the presence of native oxide during device fabrication. On the basis of this standpoint, it is necessary to suppress native oxide growth, to keep particle free and to remove any other contaminations. However, these goals are difficult to realize for conventional HF/H<sub>2</sub>O wet and vapor cleaning method.

HF/CH<sub>3</sub>OH (Alcohol) vapor cleaning <HAVC> was developed in order to remove the oxide film on silicon substrate effectively, and particle generation was suppressed and the etching selectivity was improved. In this study HAVC technique was applied to form polycrystalline silicon (polysilicon) contacts with silicon substrate. Good control of polysilicon/silicon substrate interface led to improve the contact resistance, and to reduce contaminations.

2. Experimental

The single wafer type equipment for HAVC consists of the vapor process chamber, and the supply system of N<sub>2</sub> gas, CH<sub>3</sub>OH vapor, and the mixture of HF and CH<sub>3</sub>OH as shown in Fig. 1. N<sub>2</sub> carrier gas go through each source liquid tank, and the mixed vapor is introduced into the etching chamber. This equipment also consists of the UV cleaning chamber with a low pressure mercury lamp and wafer auto-handling mechanism. The vapor cleaning condition was at 22 degree C and under the atmospheric pressure.

The sample wafers used were 10-15 ohm-cm n-type, p-type and p<sup>+</sup>(As doped P type) (100) oriented single crystal silicon, 6 inches in diameter. Sample wafers were irradiated with UV-ray in clean air for organics removal. And then the native oxides on silicon substrate were removed by HAVC. This cleaning was followed by the deposition of polysilicon by LPCVD, which was used to form contacts with silicon substrate. 100nm polysilicon was deposited on silicon substrate implanted with As (50 kev, 4E15/cm²) and the resistance of contacts between 0.5 and 1.2 um diameter were measured. SiH<sub>4</sub> and N<sub>2</sub> gas were used for polysilicon deposition and the flow rate were both 200 sccm. The pressure was 0.3 Torr. The deposition temperature was at 550 degree C. The deposition rate was 20 A/min. In order to make a comparison with HAVC, HF/H<sub>2</sub>O wet and vapor etching was also examined. Table 1 shows these cleaning conditions for silicon substrate. The surface condition after cleaning were analyzed by ESCA 5500MT (Perkin Elmer), SIMS 6600 (Perkin Elmer).

Fig.1 Schematic diagram of HF/CH<sub>3</sub>OH vapor cleaning apparatus
Table 1 Cleaning conditions for native oxide on silicon substrate.

<table>
<thead>
<tr>
<th>Liquid Condition (vapor source)</th>
<th>Etching Rate of Thermal Oxide</th>
<th>Process Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF/CH₃OH vapor</td>
<td>HF: 38.5</td>
<td>0.8-3.5</td>
</tr>
<tr>
<td></td>
<td>CH₃OH : 81.5</td>
<td>60</td>
</tr>
<tr>
<td>HF/H₂O dip.</td>
<td>HF: 1-5</td>
<td>under 17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10-60</td>
</tr>
<tr>
<td>HF/H₂O vapor</td>
<td>HF: 50</td>
<td>0.8-3.0</td>
</tr>
<tr>
<td></td>
<td>H₂O: 50</td>
<td>60</td>
</tr>
</tbody>
</table>

AFM SPI3600 (SEIKO Instruments) and FT-IR(4ATR) FT-200 (HORIBA), respectively.

3. Results and Discussion

Fig. 2 shows Si2p ESCA spectra of n⁺-Si(100) substrate after HAVC, HF/H₂O dip. without ultrapure water rinse and HF/H₂O vapor cleaning, respectively. The storage time of cleaned samples in clean air was 2.5 hour prior to ESCA measurement. In the Si2p ESCA spectra, the peak at binding energy of near 99.8 eV corresponds to the signal from Si substrate, and those higher than about 100.8 eV corresponds to the signal from SiOₓ (x : 0.5-2). It is clearly seen that the peak intensity from SiOₓ (x : 0.5-2) of substrate surface after HAVC was weakest and chemical shift between binding energies of photoelectrons from Si and SiOₓ was smallest by HAVC.

6" n⁺-Si(100) take off angle : 15°

Fig. 2 Si2p ESCA spectra. These samples were kept in air for 2.5 hour after cleaning. HF/H₂O dip. cleaning didn’t include ultrapure water rinsing.

Fig. 3 Internal reflection spectra of cleaned n-Si(100) surfaces. Si(100) surface after HAVC was dominantly terminated by Si-H₂. The absorbance of Si-H₂ vibration after HAVC was stronger than those of HF/H₂O dip. without ultrapure water rinse, and HF/H₂O vapor cleaning. The amount of hydrogen on silicon surface increased more than those of HF/H₂O dip. and HF/H₂O vapor cleaning. This data shows the possibility of atomically flatter silicon surface after HAVC than HF/H₂O dip. and HF/H₂O vapor treated silicon surfaces. This results is consistent with the one of AFM measurement. From AFM measurement, it was also found that silicon surface after HAVC was atomically flatter than those of HF/H₂O dip. and HF/H₂O vapor cleaning.
hours prior to the deposition of poly-Si by LPCVD. The difference of contact resistance between samples by HAVC and HF/H2O dip. cleaning increased with the decrease of contact diameter. The results mentioned above show that good control of interface quality between polysilicon and silicon substrate were obtained by HAVC.

The reduction of contaminations including native oxide on silicon substrate after HAVC can be explained as follows. Si-H2 hydrogen termination and atomically flatter Si(100) surface lead to the suppression of adsorbed contaminations and native oxide formation. The atomically flatter silicon surface after HAVC, which was evaluated by FT-IR(ATR) and AFM, is not readily oxidized, because the amount of reactive surface point is reduced. Silicon surface after HAVC is covered with reductive atmosphere by means of physically adsorbed alcohol, which is easily oxidized. Those physically adsorbed alcohol can be desorbed from silicon surface by heating or reduced pressure during next process. Coexistence of H2O and O2 promote the oxidation of silicon surface. Because the concentration of H2O and O2 in the HF/CH3OH system, the reoxidation of bare silicon surface after HAVC is suppressed.

4. Conclusion

The contact resistance of polysilicon contacts with silicon substrate was improved by using HAVC in comparison with those of conventional HF/H2O dip. cleaning. The degradation of contact resistance could not be seen even after HAVC followed by exposure of sample to clean air for 8 hours. Contaminations such as oxygen, carbon and fluorine at the interface between the polysilicon layer and the silicon substrate were reduced.

Fig.4 Depth profiles of deposited poly-Si films measured by SIMS after (a) HF/H2O dip. with ultrapure water rinsing and (b) HF/CH3OH vapor.

HAVC was also effective to form atomically flatter silicon surface comparing with HF/H2O dip. and HF/H2O vapor cleaning.

Reference