

HF/CH₃H(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/CH₃OH(Alcohol) Vapor cleaning<HAVC> was developed in order to remove the oxide film on silicon substrate effectively, in which process CH₃OH was used as a solvent for HF replacing conventional H₂O. this technique was applied to form polycrystalline silicon (polysilicon) contacts with silicon substrate. The contact resistance was improved comparing with those of conventional HF/H₂O 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/H₂O wet and vapor cleaning method.

HF/CH₃OH (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.¹⁾ 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 N₂ gas, CH₃OH vapor, and the mixture of HF and CH₃OH vapor as shown in Fig.1. N₂ 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 n⁺(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 μm diameter were measured. SiH₄ and N₂ 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 Å/min. In order to make a comparison with HAVC, HF/H₂O 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),

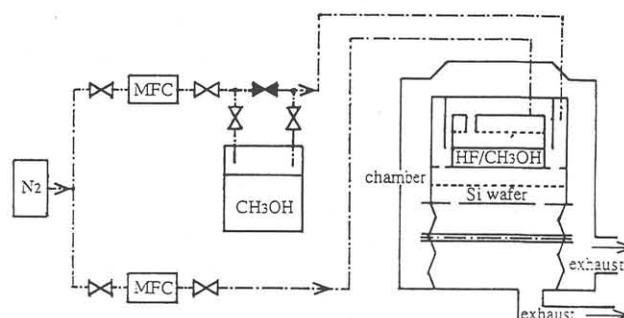


Fig.1 Schematic diagram of HF/CH₃OH vapor cleaning apparatus

Table 1 Cleaning conditions for native oxide on silicon substrate.

	Liquid Condition (vapor source) wt %	Etching Rate of Thermal Oxide nm/min.	Process Time sec.
HF/CH ₃ OH vapor.	HF : 38.5 CH ₃ OH : 61.5	0.8-3.5	60
HF/H ₂ O dip.	HF : 1-5	under 17	10-60
HF/H ₂ O vapor.	HF : 50 H ₂ O : 50	0.8-3.0	60

AFM SPI3600 (SEIKO Instruments) and FT-IR(ATR) ²⁾ 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 100.8eV corresponds to the signal from SiO_x (x :0.5-2). It is clearly seen that the peak intensity from SiO_x (x :0.5-2) of substrate surface after HAVC was weakest and chemical shift between binding energies of photoelectrons from Si and SiO_x was smallest by HAVC.

6 ϕ n⁺-Si(100)
take off angle : 15 $^{\circ}$

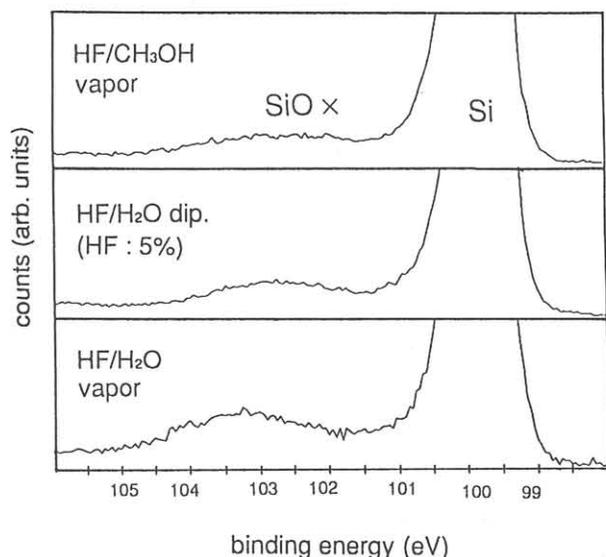


Fig.2 Si2p ESCA spectra. These samples were kept in air for 2.5 hour after cleaning. HF/H₂O dip. cleaning didn't include ultrapure water rinsing.

Native oxide growth on n⁺-Si(100) substrate after HAVC could be suppressed effectively.

Fig.3 shows FT-IR(ATR) spectra of silicon-hydrogen stretching vibrations on n-Si(100) surface after cleaning. 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.

Fig.4 shows SIMS profiles of sample deposited polysilicon films by LPCVD. We found that the amounts of oxygen, carbon and fluorine at the interface between the polysilicon layer and the silicon substrate after HAVC were reduced comparing with those of HF/H₂O (HF 1%) dip. cleaning with ultrapure water rinsing for 10 min.

Fig.5 shows the relationships between contact resistance and storage time of samples in clean air after cleaning. The contact resistances were improved by using HAVC in comparison with those of HF/H₂O (HF 1%) dip. cleaning with ultrapure water rinsing for 10 min. The degradation of contact resistance could not be seen even after HAVC followed by exposure of sample to clean air for 8 hours. Fig.6 shows the relationships between contact resistance and contact diameter of samples, which were cleaned by HAVC, and HF/H₂O dip. with ultrapure water rinsing. The storage time of cleaned samples in clean air was 4

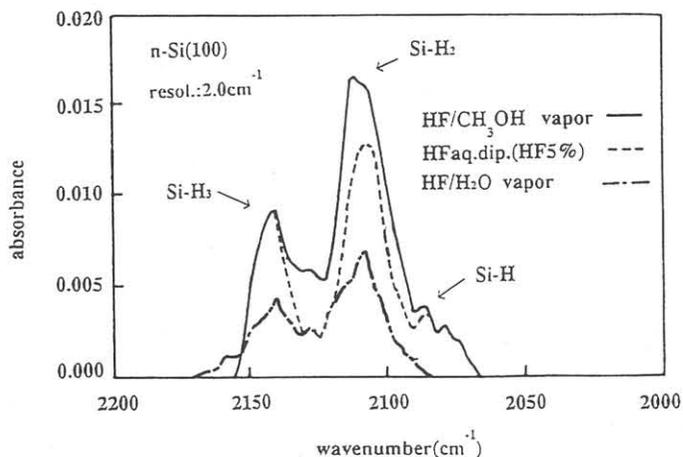


Fig.3 Internal reflection spectra of cleaned n-Si(100) surfaces. Si(100) surface after HAVC was dominantly terminated by Si-H₂. HF/H₂O dip. cleaning didn't include ultrapure water rinsing.

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.²⁾ 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.³⁾ Because the concentration of H₂O and O₂ during etching reaction is reduced 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.

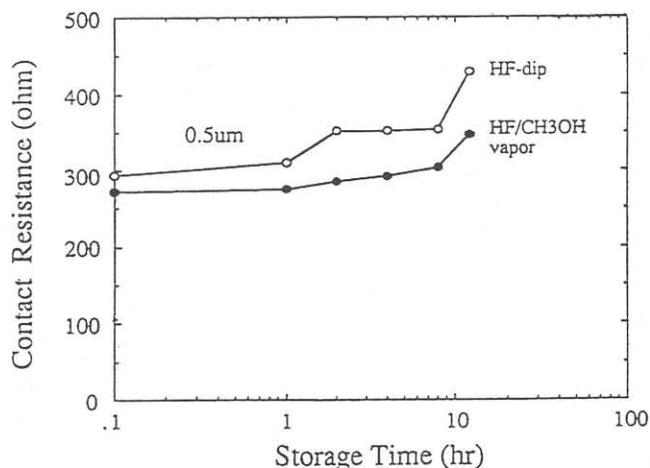


Fig.5 Relationships between contact resistance and storage time of samples in clean air after cleaning. These cleanings were followed by the deposition of poly-Si by LPCVD. The resistance of polySi-n⁺Si sub. contacts with 0.5 μ m diameter were measured.

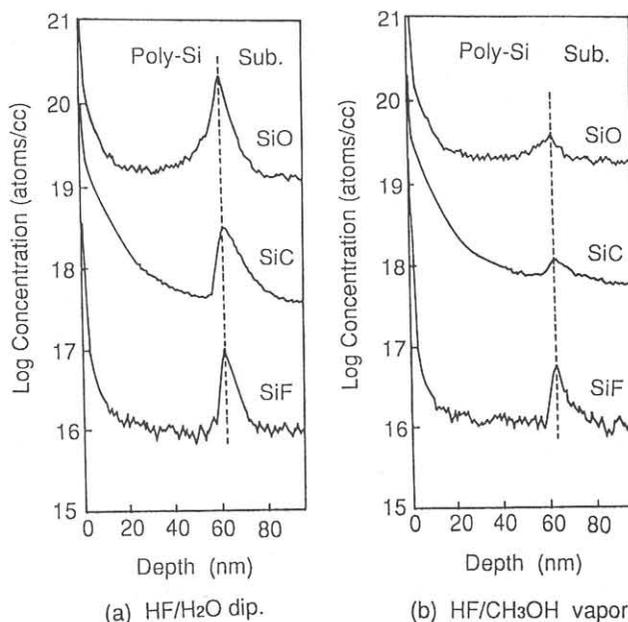


Fig.4 Depth profiles of deposited poly-Si films measured by SIMS after (a) HF/H₂O dip. with ultrapure water rinsing and (b) HF/CH₃OH vapor.

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

Reference

- 1) A. Izumi, T. Matsuka, T. Takeuchi and A. Yamano, in Extended Abstracts of the 1991 International Conference on Solid State Devices and Materials, p135, Yokohama, 1991.
- 2) K. Sawara, T. Yasaka, S. Miyazaki and M. Hirose, Jpn. J. Appl. Phys., **31**, 931 (1992)
- 3) T. Takahagi, A. Ishitani, H. Kuroda and Y. Nagasawa, J. Appl. Phys. **68**, 2187 (1990)
- 4) M. Morita, T. Ohmi, E. Hasegawa, M. Kawakami and K. Suma, Applied Physics Letters, **55**, 562 (1989)

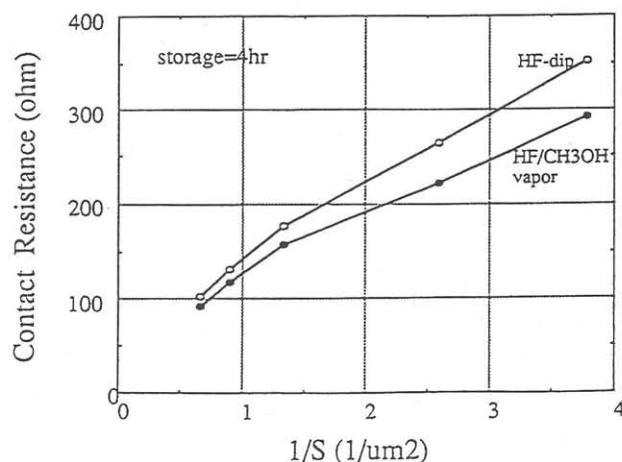


Fig.6 Relationships between the resistance of polysilicon / n⁺-Si substrate contacts and contact diameter. Sample wafers were cleaned by HAVC and HF/H₂O dip. with ultrapure water rinsing prior to the deposition of poly-Si by LPCVD.