Extended Abstracts of the 21st Conference on Solid State Devices and Materials, Tokyo, 1989, pp. 413-416

Reduction of Interface States of MOS Structure Using Photo-CVD SiO_2 Film by F_2 Treatment

Masakazu NAKAMURA, Masanori OKUYAMA, Yoshihiro HAMAKAWA

Department of Electrical Engineering,
Faculty of Engineering Science,
Osaka University, Toyonaka, Osaka 560, Japan

A new process, F_2 treatment, for the reduction of the Si-SiO_2 interface state density has been developed. 5% F_2 gas diluted in He was introduced into the CVD chamber at 20Pa for 5 minutes just before deposition of SiO_2 film. The minimum value of the interface state density is about $5x10^9 cm^{-2} eV^{-1}$ at the Si mid gap for the film deposited at 180°C. IR-ATR measurement shows that Si-H bond at the interface decreases by F_2 treatment at the substrate temperature lower than 200°C.

1. Introduction

Recently, considerable attention has been gathered on the low-temperature process for the production of ULSI devices. The fabrication of damage-free MOS structure is a key technology for the semiconductor devices. We have made a series of systematic studies about SiO_2 film growth by photo-CVD using vacuum ultraviolet (VUV) light.[1-3] The good quality SiO_2 films having very low interface state density have been obtained by this photo-CVD, but less interface state density is needed to improve device performance of the integrated devices. The Si substrates should be clean just before the deposition in order to obtain the good interface. Heating of Si substrates in high vacuum at high temperature is conventionally used to make the surface clean, but this process needs high temperature more than 800°C. Therefore, chemical process for surface cleaning is desirable instead of the high temperature treatment. Fluorine (F_2) gas is expected to remove contaminants on the Si substrate, however, is stable under circumstances without water or hydroxyl and so suppresses contaminants produced from the chamber wall. Therefore, we introduced F_2 gas for the cleaning before the deposition and tried to improve the interfacial property. In this paper, we present the method to reduce the interface state density and characterization of the interface using infrared reflection.

2. Film growth and electrical property

n-Si(100) wafer of 0.4Ωcm was used to make a MOS structure. The wafer was cleaned up by conventional organic solvent and the mixture of sulfuric and nitric acids to remove organic and metallic contaminants. Thin oxide on the wafer was etched off by 25% HF diluted with pure water, and the wafer was rinsed in ultrapure water. It was confirmed from Auger electron spectroscopy measurement that the obtained Si surface treated by the HF has no carbon, oxygen nor fluorine signal. So the wafer surface is considered to be clean enough before setting into the CVD chamber.

The apparatus for the photo-CVD was almost the same as the previous report.[2] A D_2 lamp (Hamamatsu Photonics L1835) was used as an excitation light source and set on the top of the chamber. Si_2H_6 and O_2 were used as source gases. The chamber was evacuated to $1x10^{-3}$Pa by a turbo-molecular pump before the deposition. The 5% F_2 gas diluted with He was blown against the Si wafer for 5 min. at 20Pa just before the film deposition. F_2 has absorption band in the wavelength region between 200 and 300nm. A Xe short arc lamp has strong radiation in this UV light region, and so was horizontally directed to the space just above the substrate from outside of the chamber during the F_2 treatment. Then, the chamber was evacuated again down to $1x10^{-3}$Pa. SiO_2 films were deposited at 25-300^oC. The deposition rate was 12nm/min in the deposition at room temperature and 15nm/min at 180^oC. The refractive indices of the films deposited at 100-280^oC were about 1.45. These values had no change by the F_2 treatment. Al dot electrodes were evaporated on the deposited SiO_2 film for the MOS diodes. The interface state density, N_{ss}, was measured by DLTS method.

Figure 1 shows the substrate temperature dependence of the minimum N_{ss} near the Si mid gap for the films without the F_2 treatment, with the F_2 treatment and with the F_2 treatment under the UV irradiation. The N_{ss} for the film deposited at 140^oC without the F_2 treatment and that with the F_2 treatment without the UV irradiation are more than $10^{11}cm^{-2}eV^{-1}$. The N_{ss} was remarkably reduced by the F_2 treatment and more reduced by the F_2 treatment under the irradiation of UV light. The minimum N_{ss} is about $5x10^9cm^{-2}$ eV^{-1} and is the lowest in the Si-SiO_2 interfaces made of the CVD SiO_2 films. In the low temperature region less than 240^oC, the F_2 treatment is effective to reduce the N_{ss}, but this reduction effect decreases with

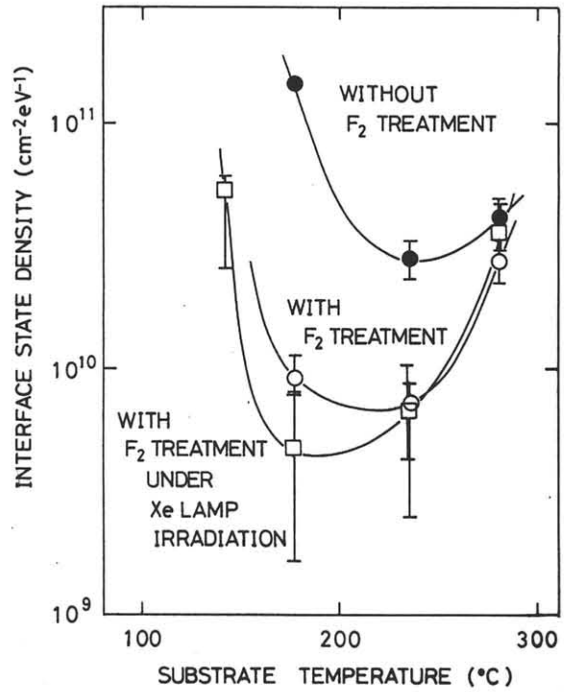

Fig.1 Substrate temperature dependence of the minimum interface state density near the Si mid gap for the films without the F_2 treatment, with the F_2 treatment and with the F_2 treatment under UV irradiation.

the increase of the substrate temperature and disappears at 280^oC. It is considered from these results that the reduction effect is related to the amount of adsorbed species such as F_2 or H_2O on Si. This reduction saturates when the treatment time was more than 1 minute. The SiO_2 thickness measured by ellipsometory, changed little by exposing to the same atmosphere for 1 hour.

3. Characterization by Infrared Spectroscopy

3-1 Infrared transmission spectroscopy

Figure 2 shows the infrared transmittance spectra of the films deposited on semi-insulating Si wafers at 180^oC with and without the F_2 treatment. No difference can be found between these two spectra. The absorption peaks of Si-F bondings are not found, because total amount of the residual fluorines is quite small even if it was as large as the number of interface silicon

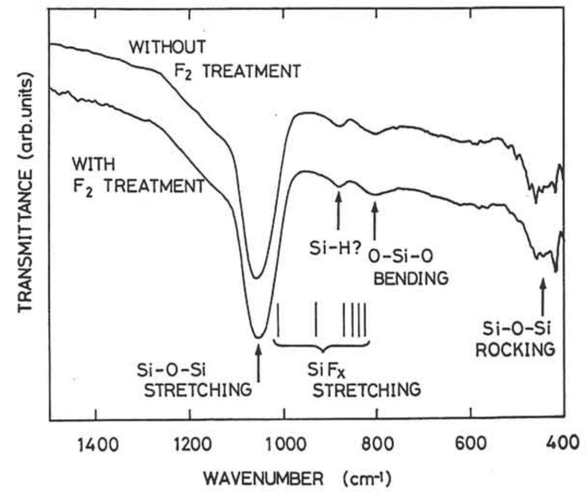

Fig.2. Infrared transmittance spectra of the films deposited at 180°C with and without the F_2 treatment.

atoms. The residual fluorine estimated by X-ray photoelectron spectroscopy (XPS) are corresponding to almost a monolayer on the Si surface. But ,its binding energy is higher than that of SiF- or SiF_2- like species.[4]

3-2 IR-ATR spectroscopy

Infrared attenuated total reflection (IR-ATR), in other words multiple internal reflection (MIR), was used considerably for studies on Si surfaces.[5-7] IR-ATR gives detailed information of number, position and direction of atomic bonds of adsorbates on surface Si. Si substrate used for IR-ATR was Si (111) wafer of 1.0mm thick, 3.0cm long and 1.0cm wide with 45° bevels at each of the short sides, and its resistivity was more than 1000Ωcm. The infrared radiation is normally incident on the bevel and is internally reflected 29 times by the surface. The Si wafer is transparent in wavenumber region from $1500cm^{-1}$ to $4000cm^{-1}$ and incident angle is larger than the critical angle when SiO_2 film is deposited on the substrate or not. IR spectra were measured by a fourier transformation spectrometer (Japan spectroscopic Co., Ltd. FT/IR-3).

Figure 3 shows IR-ATR spectra of Si-H stretching vibrations for chemically oxidized Si and HF etched Si. Short vertical lines are the calculated frequencies of various vibrational modes reported by Burrows.[5] M, M', D and T correspond to coupled monohydride, isolated monohydride, isolated dihydride and isolated trihydride, respectively. ATR spectra for the oxidized Si have little absorption peaks of the Si-H bonds over the Si surface. After removal of thin oxide by fluoric acid, the Si-H peaks appeared. A sharp peak at 2085 cm^{-1} is considered to be highly polarized normal to the surface because it is observed in the p-polarized spectra, but not in the s-polarized. Burrows showed also the existence of dihydride which can not be observed in Fig. 3, and suggests that the surface is microscopically rough. In our case, the surface of the substrate seems to be rather "flat" because of little dihydride that can exist only on defects or steps.

Figure 4 shows IR-ATR spectra of Si-H stretching vibrations for the Si-SiO_2 inter-

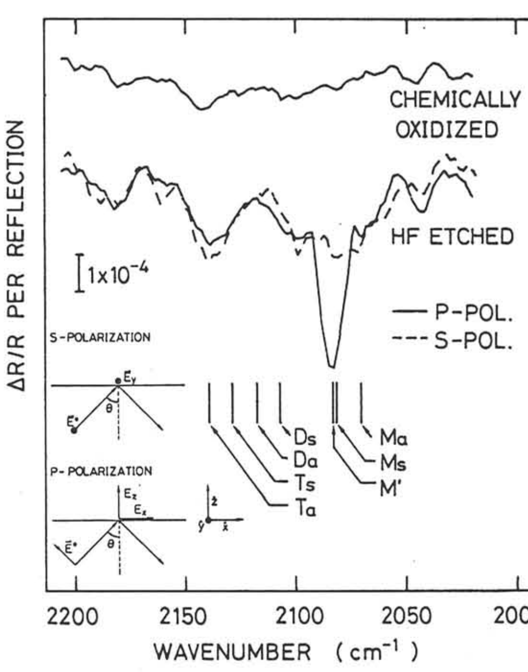

Fig.3. IR-ATR spectra of silicon-hydrogen stretching vibrations for the chemically oxidized silicon and HF etched silicon.

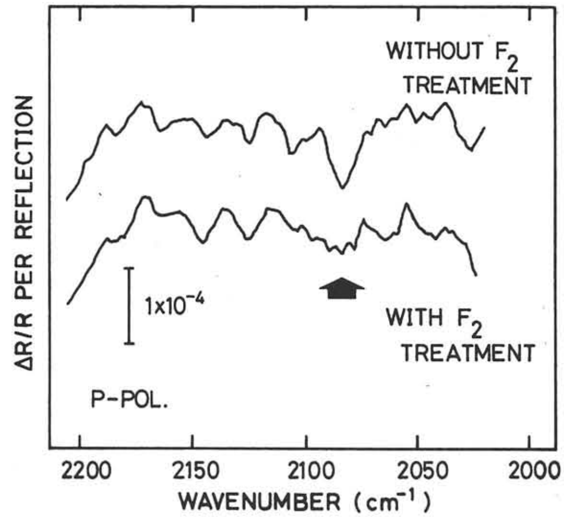

Fig.4. IR-ATR spectra of silicon-hydrogen stretching vibrations for Si-SiO_2 interface prepared without the F_2 treatment and with the F_2 treatment at Ts=160^{o}C.

face prepared with and without the F_2 treatment. Many absorptions indicate that a small quantity of hydrogen bonded to the surface Si, still remains at the Si-SiO_2 interface. The spectrum for the sample without the F_2 treatment has a peak pointed by an arrow. This peak is considered to be monohydride at the interface, but disappears in the spectrum for that with the F_2 treatment. Many kinds of absorption peaks in 2050-2300cm^{-1} are categorized into four regions. The absorption in 2200-2300cm^{-1}, which is not shown in Fig. 4, is hydrogen in amorphous SiO_2 layer. The absorption in 2050-2100cm^{-1} is considered to be the monohydride, and 2100-2160cm^{-1} to be the dihydride and trihydride. The absorption in 2160-2200cm^{-1} is estimated to be Si-H bonded to one or two oxygen.[7] Every hydride signal except that in 2160-2200cm^{-1} decreases with increase of the substrate temperature, Ts. Only the signals in 2050-2100cm^{-1} decreased by the F_2 treatment and the difference between those with and without the treatment, decreases with increase of Ts. From these results, it is considered that the decrease of the hydrogen is closely related to the decrease of the interface state density, but this is inconsistent to the fact that the hydrogen passivation reduces the interface states. Therefore, it is considered that the F_2 treatment forms a large number of tight Si-O bonds, but not weak and impure bonds at the interface.

4.Summary

The interface state density, N_{ss}, of Si-SiO_2 structure made from SiO_2 film deposited by photo-CVD, has been reduced by the F_2 treatment and its minimum value is about $5x10^9 cm^{-2}$ eV^{-1}. The N_{ss} reduction by the F_2 treatment becomes ineffective with the increase of the substrate temperature and is not observed above 240^{o}C. IR-ATR has been measured to characterize atomic bonds on the Si surface and the Si-SiO_2 interface. Silicon monohydrides decrease by the F_2 treatment and are considered to be closely related to the N_{ss} reduction.

Acknowledgment

The authors express our sincere thanks to Dr. K.Inoue, Mr. R.Nagayoshi and Mr. C.Sada for their useful discussion and technical assistance, and Prof. H.Tsubomura and Dr. H.Kobayashi for XPS measurement.

References

1) M. Okuyama, Y. Toyoda and Y. Hamakawa; Jpn. J. Appl. Phys. **23** (1984) L97.
2) K. Inoue, M. Michimori, M. Okuyama and Y. Hamakawa; Jpn. J. Appl. Phys. **26** (1987) 805.
3) K. Inoue, M. Okuyama and Y. Hamakawa; Jpn. J. Appl. Phys. **27** (1988) L2152.
4) B. R. Weinberger, G. G. Peterson, T. C. Eschrich and H. A. Krasinski; J. Appl. Phys. **60** (1986) 3232.
5) V. A. Burrows, Y. J. Chabal, G. S. Higashi , K. Raghavachari and S. B. Christman; Appl. Phys. Lett. **53** (1988) 998.
6) T. Takahagi, I. Nagai, A. Ishitani, H. Kuroda and Y. Nagasawa; J. Appl. Phys. **64** (1988) 3516
7) Y. J. Chabal; Phys. Rev. B**29** (1984) 3677.