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Through-Oxide Cleaning of Silicon Surface by Photo-Excited Radicals

Rinshi Sugino, Yasuo Nara, Tatsuya Yamazaki, Satoru Watanabe, and Takashi Ito

FUJITSU LABORATORIES LTD., Atsugi

10-1, Morinosato-Wakamiya, Atsugi, Kanagawa, Japan 243-01

Chlorine radicals excited by ultraviolet light can be used to clean silicon surfaces through native oxide. Surface flatness was improved over that obtained with conventional HF treatment by using a wet solution of NH_4OH and HNO_3 that formed a 1.1nm oxide layer on the silicon surface. Silicon substrate etching was initiated without a delay. Atomic absorption spectrophotometry after photo-excited cleaning showed that contamination by metals such as Na, Mg, Ca, Fe, and Cr was reduced. The metal-oxide-semiconductor's carrier generation lifetime was increased to 2.5ms following photo-excited cleaning, compared with the 1.6ms obtained with wet solution treatment only.

1. Introduction

Removing contaminants from silicon surfaces are very important for VLSI/ULSI production, especially to obtain high purity epitaxial films and high quality MOS gate dielectrics because the contaminants such as hydrocarbons, heavy metals and alkaline metals impede crystal growth and/or form recombination centers in the silicon crystal.

Conventionally, contaminants are removed by immersing silicon wafers in wet chemical solutions.[1,2] In this case, however, there are some problems which should be solved for VLSI/ULSI production; purification of reactive solutions, cleaning of sharp trenches, drying, treatment of exhausted solutions, and so on.

Chlorine radicals generated by ultraviolet (UV) light irradiation to Cl_2 gas etch a silicon substrate.[3,4] Contaminants are removed as a result of volatile chloride compounds which are formed from contaminant atoms and chlorine radicals.

The authors previously demonstrated photo-excited (UV light) cleaning by etching a silicon substrate slightly, and have shown the effectiveness of this method in the increased dielectric breakdown field when combined with wet chemical cleaning.[5] In this experiment, however, surfaces following photo-excited cleaning were sometimes rough, and reproducibility and controllability were not good enough. It was thought that these were caused by a thin nonuniform layer formed during HF and H_2O treatment to etch native oxide just before photo-excited cleaning.

In order to solve these problems, a new cleaning method that intentionally grows a uniform oxide layer by wet chemical treatments and then removes contaminants with photo-excited chlorine radicals is proposed.

2. Experiments

A microwave-excited mercury lamp was used as a UV light source. The light intensity at the substrate position was $22mW/cm^2$ measured by UV power meter (USIO UVD 254-p) having maximum sensitivity at 254 nm. A 4-inch silicon wafer was set in a quartz holder and heated from the back by infrared heaters. The cleaning temperature was monitored by a

thermocouple sensor located in the vicinity of the sample.

The silicon wafers used in the experiments were phosphorus doped n-type with the resistivity in the range from 10 to 20 ohm-cm and (100) oriented surface. For growing a thin uniform oxide layer on a silicon substrate, a process using NH_4OH-H_2O_2 and HNO_3 treatment was adopted. After this wet treatment, a 1.1 nm thick native oxide was formed on the silicon surface, which was measured by ellipsometry. Just after the wet treatment, the wafer was set in the cleaning chamber. 99.999% purity Cl_2 gas was used. The etching pressure was fixed at 2.7kPa. After photo-excited cleaning, TEM image observation using the conventional two step replica method was used to evaluate surface morphology. Contaminants concentration on the silicon surface was measured by the flameless atomic absorption spectrophotometry after the wafer oxidized in dry oxygen. C-t measurements were also performed for the MOS structure to evaluate the carrier generation life time.

3. Results and Discussion

Figure 1 shows the dependence of the silicon etching rate on various wet treatments before photo-excited cleaning of silicon. The surface morphologies after etching differed, indicating that silicon etching by photo-excited chlorine radicals was affected by the quality and thickness of the thin oxides formed by the wet treatments.

Figure 2 shows typical replica TEM photographs before and after photo-excited cleaning. The surface morphology is compared for treatments with HF and that with NH_4OH-H_2O_2 and HNO_3. Etching depths were 0.3 microns for both samples. The surface morphology was greatly improved by using NH_4OH-H_2O_2 and HNO_3 treatment. It is thought that the improvement of the surface morphology was caused by the better structural homogeneity of the oxide layer after wet treatment compared with after HF treatment. The silicon surfaces after HF and H_2O treatment are thought to be characterized by Si-H and Si-CH_x groups,[6] which cause surface roughness after dry etching.

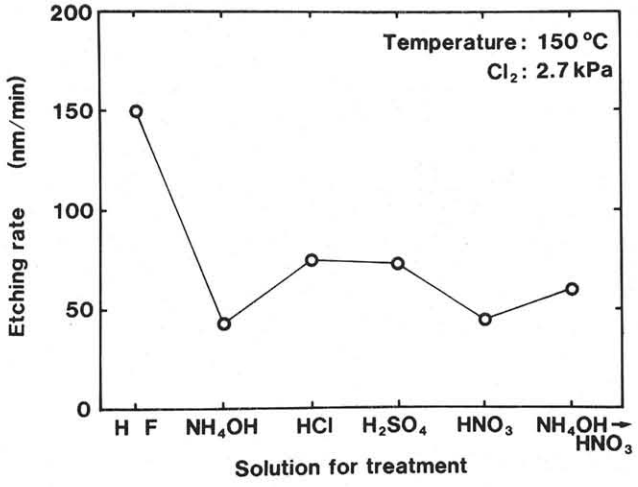


Fig. 1. Influences of various wet treatments before photo-excited cleaning of silicon.

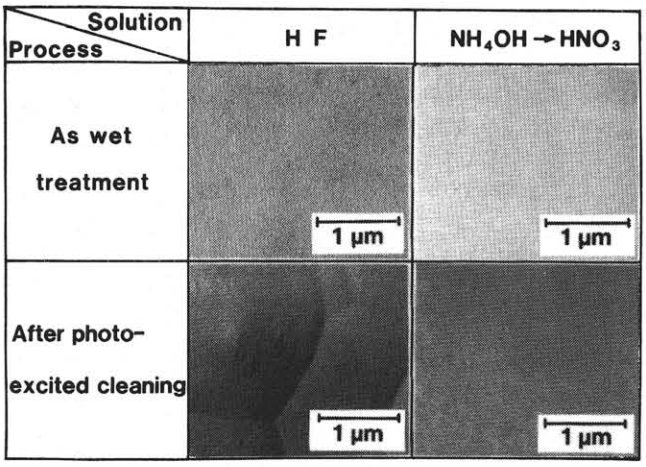


Fig. 2. Replica TEM images before and after photo-excited cleaning.

Figure 3 shows the etching depth dependence on the UV irradiation time at 150°C. Despite the 1.1nm oxide layer on the substrate surface, there was no delay at the beginning of etching. An initial delay in the etching of silicon surfaces with native oxide was reported in the case of using an argon-

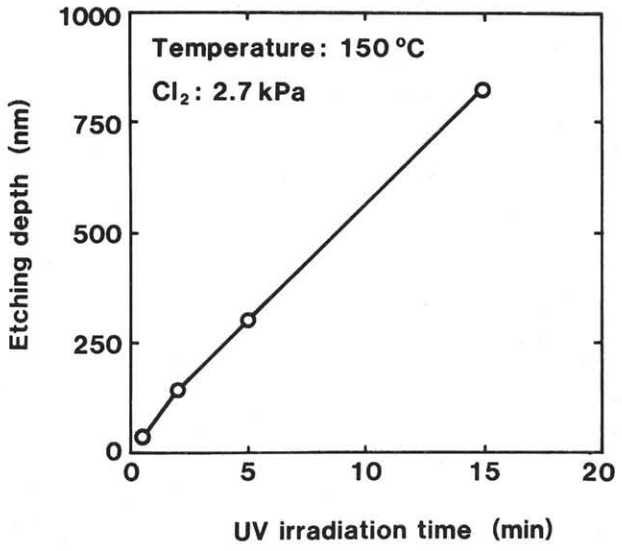
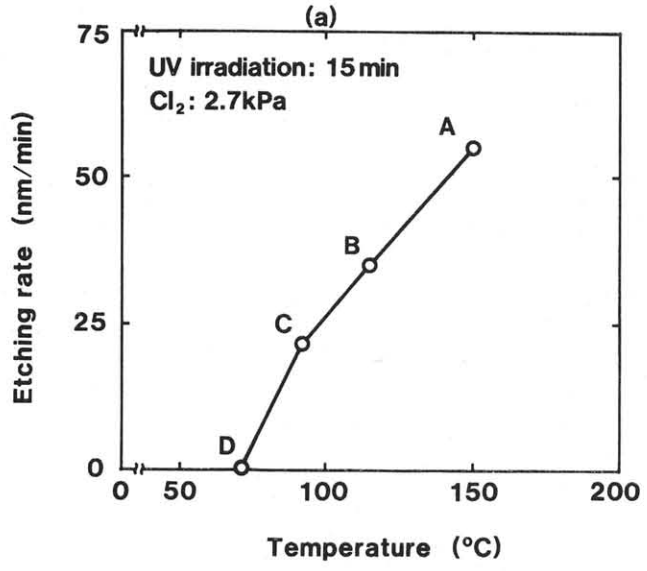


Fig. 3. Etching depth dependence on UV irradiation time.



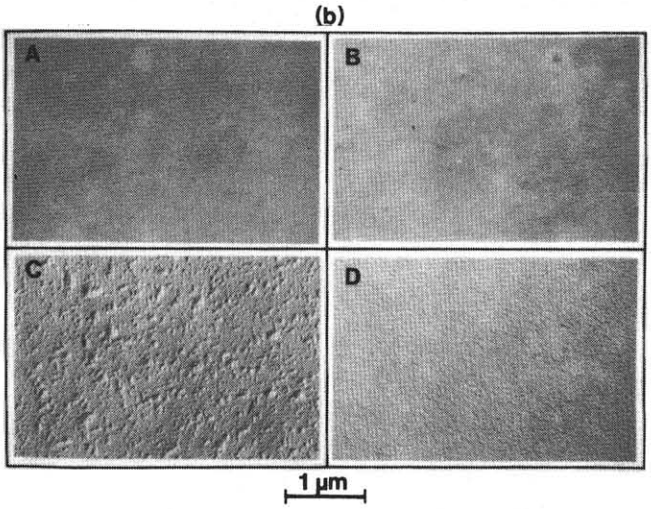


Fig. 4. (a) Cleaning temperature dependence on etching rate. (b) The replica TEM image for each case.

ion laser and Cl_2 system.[7] It was thought to be due to the increased surface temperature caused by the high-power laser beam, rather than due to a photochemical reaction. Photo-excited chlorine radicals probably diffused through the thin oxide in a very short time and reacted with silicon atoms, producing volatile species such as $SiCl_2$ and/or $SiCl_4$.

Figure 4 (a) shows the cleaning temperature dependence of the silicon etching rate for a 1.1nm native oxide layer. The etching rate increased linearly with substrate temperature between 90 and 150°C. The replica TEM image as etched in each case is shown in Fig. 4 (b). Judging from surface morphologies, the temperature suitable to photo-excited cleaning should be higher than 150°C.

Figure 5 shows the concentration of contamination atoms measured by flameless atomic absorption specrophotometry for HF vapor phase decomposition of a 50nm oxide layer thermally grown after photo-excited cleaning. Concentrations of Na, Mg, Ca, Fe, and Cr contaminants after photo-excited cleaning were lower than those for wet cleaning, indicating that dry cleaning with photo-generated chlorine radicals remove contaminants otherwise not completely removed by conventional wet cleaning.

MOS structures with 20nm gate oxides and Al gate electrodes were fabricated after photo-excited cleaning. The C-t was measured to evaluate the carrier generation lifetime. Figure 6 shows the relation between the carrier generation lifetime measured at 50°C and the photo-excited etching depth. The carrier generation lifetime was increased to 2.5ms for an etching depth of 50nm, compared to 1.6ms after wet cleaning. This improvement

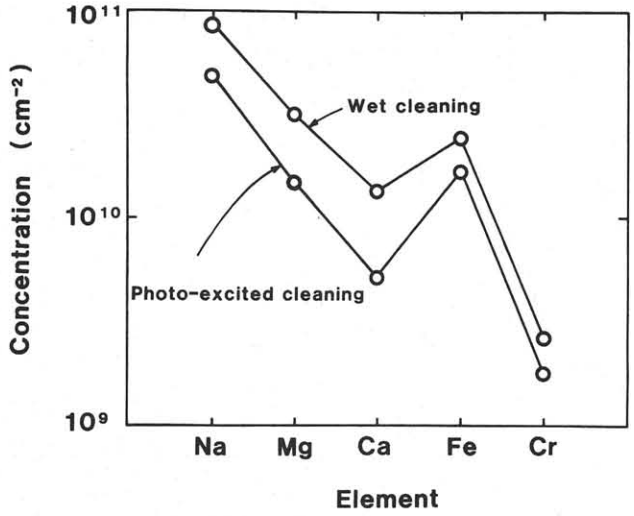


Fig. 5. Comparision of contaminant levels between photo-excited cleaning and wet cleaning.

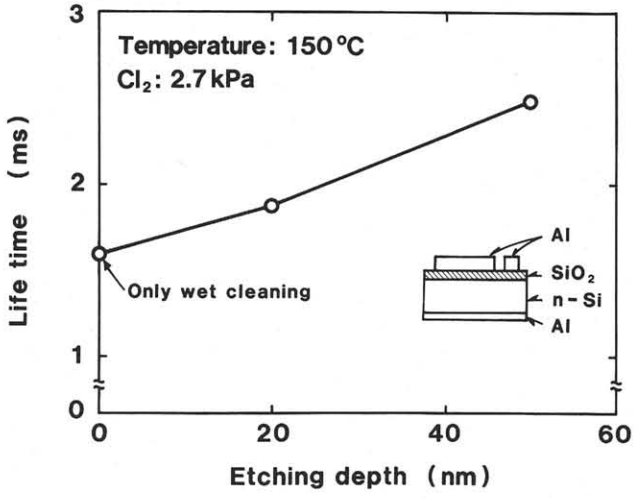


Fig. 6. Dependence of carrier lifetime on etching depth measured at 50°C.

was apparently due to the removal of surface defects and contaminants from the silicon surface simultaneously with the etching of the silicon substrate.

4. Conclusion

Silicon substrates with native oxide can be cleaned by photo-excited chlorine radicals. The etching of silicon with the native oxide was initiated without a delay. This process enables us to obtain flat surface reproducibly after cleaning. This was apparently made possible by the increased uniformity of the oxide layer formed by a wet treatment, as opposed to an HF treatment, before etching. Contaminant concentrations were below levels for conventional wet cleaning. The carrier generation lifetime was also confirmed for wafers receiving photo-excited cleaning. The results of these experiments show that photo-excited cleaning through native oxide is a potentially important technology in the fabrication of high performance VLSI devices.

Acknowledgments

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