Etch Rate of Oxide Grown on Silicon Implanted with Different Ion Implantation Conditions prior to Oxidation

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Abstract—The experimental studies for the etch properties of the oxide grown on silicon substrate, which is in diluted hydrogen fluoride (HF) solution, are presented. Using different ion implantation dosages, dopants and energies, silicon substrate was implanted. The wet etching in diluted HF solution is used as a mean of wafer cleaning at various steps of VLSI processing. It is shown that the wet etch rate of oxide grown on various implanted silicon substrates is a strong function of ion implantation dopants, dosages and energies. This phenomenon has never been reported before. This paper shows that the difference of wet etch rate of oxide by ion implantation conditions is attributed to the kinds and volumes of dopants which was diffused out into SiO₂ from implanted silicon during thermal oxidation.

Index Terms—dopant, dosage, ion implantation, energy, dilute HF solution

I. INTRODUCTION

Silicon surface cleaning has recently attracted a lot of attention. Studies have shown that the selection of chemicals, concentration of chemicals, impurity and water rinse can all affect the surface quality of silicon wafer after cleaning. Not only complete stripping of the oxide is essential, but precise control of the etching process is also important as it can affect the silicon surface quality and remaining oxide thickness.

It is widely known that the wet etch rate of ion implanted oxide in dilute HF is dependent on its dosage and energy [1]. This is attributed to the breakage of Si-O bonding [1]. This paper presents the wet etching characteristics of thin oxide grown on silicon implanted with various ion implantation conditions, which has been never been dealt with before. This study shows that wet etch rate of oxide in dilute HF is sensitively influenced by ion implantation conditions before oxidation.

II. EXPERIMENTAL

P-type, <100> oriented silicon wafer was fabricated as following sequences. After 10min. in SC① (RCA cleaning: NH₄OH + H₂O₂ + H₂O, 50 °C) and 60seconds cleaning in 1:99HF, ion implantation was carried out into blanket silicon wafers with different dopants (P⁺, B⁺), dosages (1E12, 1E13, 1E14, 1E15 cm⁻²) and energies (20KeV, 50KeV, 100KeV) as variables. Following ion implantation, wet oxidation targeting 100 Å was carried out in conventional furnace at 850°C. We evaluated the wet etch rate of oxide grown on silicon implanted with various implant conditions. Wet etch test was done in 1:99 HF solution for 30seconds. The HF chemicals is changed every 7 lots and consumed with process. So, for the reliability of data, each test was performed 7 times in series with the same condition and the etch rate data were averaged. The wet etch rate of thermal oxide without ion implantation was used as the base for normalization. Its etch rate was 15 Å per 30seconds. The thickness of oxide was measured by ellipsometry thin film measurement system before and after etch. We made a comparative study of dopant concentration in SiO₂ by ion implantation conditions after oxidation to analyze the difference of etch rate by different ion implantation dopants, dosages and energies.

III. RESULTS AND DISCUSSION

In case of P⁺ ion implantation into silicon before oxidation, the wet etch rate of oxide in dilute HF solution is risen as the implantation dosage increases and the energy decreases. Especially, wet etch rate of oxide showed a sharp increase with the decrease of energy in high dose implanted (over 1E15 cm⁻²) wafer (Refer Fig. 1). On the other hand, the wet etch rate of oxide grown on silicon implanted with B⁺ ion is higher in the lower dosage and higher energy (Refer Fig. 2).

Dopants (boron, phosphorus) implanted into silicon are diffused out into SiO₂ from implanted silicon during thermal oxidation (Refer Fig. 3). Fig. 3 is SIMS profiles of dopant concentration showing out-diffusion of dopants after oxidation. As the implantation dosage increases and the energy decreases, more dopants remain in silicon surface causing more diffused out into SiO₂ during oxidation. Refer Fig. 4 showing the concentration of borons diffused out into SiO₂ in which borons were implanted with various dosages and energies before oxidation.

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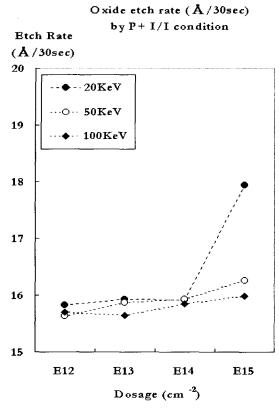
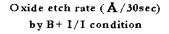


Fig. 1 The wet etch rate of oxide grown on silicon implanted with P + with the increase of dosage and energy.



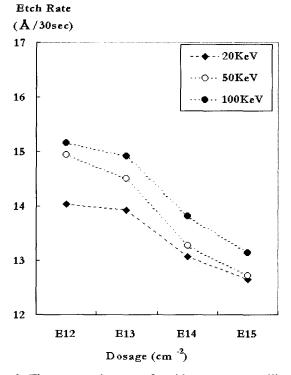
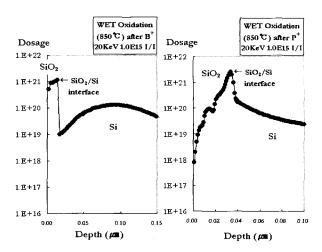


Fig. 2 The wet etch rate of oxide grown on silicon implanted with B + with the increase of dosage and energy.



* The unit of dosage : atom/cm3

Fig. 3 SIMS profiles of boron and phosphorus after oxidation. They are implanted into blanket silicon before oxidation. The profiles show that a large number of dopants are diffused out into SiO₂ during oxidation.

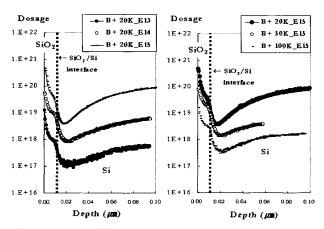


Fig. 4 SIMS profiles of boron by different ion implantation dosages and energies. With increase of dosage (a) and decrease of energy (b), more borons are diffused out into SiO₂ during oxidation.

As known, after B and P are diffused out into SiO_2 , they replace Si in SiO_2 resulting in generating B_2O_3 and P_2O_5 respectively by high thermal energy of oxidation [2-4]. The wet etch rate of SiO_2 diffused with less borons and more phosphoruses became higher [2]. We found the same phenomenon in wet etch rate of BPSG (boron & phosphorous doped silicate glass) which is SiO_2 doped with boron and phosphorus [3]. Doping boron and phosphorus into SiO_2 under high thermal energy makes BPSG as following [2], [4].

$$SiO_2 + B_2O_3 + P_2O_5 \xrightarrow{\text{high Temp.}} BPSG$$
 (1)

Etch rate of BPSG is proportional to the volume of phosphorus doped into SiO₂. Instead, as more borons are doped within SiO₂, the oxide wet etch rate remarkably decreases (Refer Fig. 5).

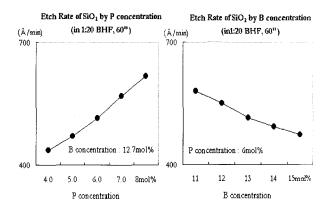


Fig. 5 The wet etch rate of BPSG (boron & phosphorus doped silicate glass) with the increase of phosphorus and boron concentration within SiO₂.

Boron causes a reduced wet etch rate ratio (W.E.E.R.) compared with thermal oxide film [6]. B₂O₃ is a modifying oxide which increases the durability of the glass from chemical attack [2]. As more borons are outdiffused into SiO₂ more B₂O₃ are made and etch rate in HF becomes lower [6]. Instead, P₂O₅ etch rate increases approximately logarithmically with weight percent phosphorous [3], [5-6]. Phosphorous displays a high wet etch rate ratio (W.E.E.R.) compared with thermal oxide film [6].

IV. CONCLUSION

In this paper, we investigated the wet etch rate in dilute HF solution for oxide grown on silicon implanted with various conditions; ion implantation dopant, dosage and energy. It is shown that the wet etch rate of oxide grown on silicon implanted with P^+ rises with increase of implantation dosage and decrease of energy. But, it is vice versa in case of B^+ . The implanted dopants into silicon are diffused out into SiO_2 during oxidation, which is believed responsible for this dependence of wet etch rate on implantation conditions. In conditions of higher ion implantation dosage and lower implantation energy, more dopants are diffused out into SiO_2 during oxidation.

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