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Investigation of oxide layer removal mechanism using reactive gases

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ABSTRACT

In a CMOS technology, the removal of silicon oxide and nitride layer is one of the critical steps as it represents a possible source of high contact resistance and a decrease of gate oxide reliability. In high aspect ratio (HAR), it is very difficult to remove SiO_2 with wet etching. In the present study, the effect of the gases such as plasma dry etching of ammonia (NH_3) and nitrogen trifluoride (NF_3) on the SiO_2 and Si_3N_4 substrates were analyzed and the etch rate was measured. The measurement of the SiO_2 and Si_3N_4 thickness was measured by Ellipsometer. Various factors such as chamber pressure, electrode power and NH_3/NF_3 gas ratio were affected by the combination and dissociation of NH_4F molecules. The existence of the by-product was analyzed by using a contact angle analyzer and scanning electron microscope, respectively. In this study we have found that, the removal efficiency was mainly dependent on the reaction mechanism and the effect of the by-product.

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1. Introduction

SiO_2 and Si_3N_4 are widely used in micro fabrication processes as a dielectric and mask material. As pattern size continues to decrease, lithography process required accuracy between layers. It is become harder to make contact hole and trenches into dielectric layers. Commonly, SiO_2 is the widely used dielectric material and Si_3N_4 has been used as a passivation layer [1]. In CMOS technology, removal of these films is a critical step as it makes a possible source of high contact resistance and a decrease of gate oxide reliability [2,3]. Possible over etch in the nitride processing may result in damages of a thin oxide and an underlying Si substrate through imperfections of the oxide [3]. The ability to achieve selective etching of SiO_2 and Si_3N_4 is becoming an increasingly important requirement. Silicon nitride is used as a passivation layer that protects circuits from mechanical and chemical attack, or as an etch stop layer, enabling the fabrication of certain damascene and self-aligned contact (SAC) structures. Selective SiO_2 and Si_3N_4 etching have been demonstrated in several systems [4–9].

High aspect ratio (HAR) silicon trench etch is a key process to remove the silicon oxide on the pattern. During the etching process, a chemical reaction between the chemical etchants and the surface layer has been occurred. It is very important to control the various factors affecting the chemical reaction because the etch rate and the surface quality has been changed depending upon this reaction. In general, hydrogen fluoride is used as a chemical for silicon oxide removal [10]. In the SiO_2 etching process, a wet process using an HF solution like BOE was employed. The etching rate of wet process was reached several μm/min. But, the usage of chemical solution and DI water rinse process, caused distortion and contamination in patterns [11]. As the decrease in minimum feature size, the removal of the silicon oxide on the pattern becomes difficult, however after the drying process, the etch pattern was collapsed by capillary force of water. Research of dry etching is being carried out to solve these problems. Dry etching is capable of reproducing anisotropic walls and the characteristics are highly reproducible [12].

In this study, the fundamental theory of SiO_2 etching of plasma activated NF_3/NH_3 gas was investigated. Plasma dry etching of ammonia (NH_3) and nitrogen trifluoride (NF_3) mixtures were employed in the detailed studies. From this process, we could generate ammonium hexafluorosilicate $(NH_4)_2SiF_6$ as a by-product, which is deposited on the surface and it interrupts the further etching reaction [13–14]. To investigate this problem, the etching of SiO_2 using NH_3/NF_3 reactive gas was analyzed and the etch rate was calculated as a function of NF_3 ratio, electrode power and pressure, respectively. From this study we could conclude that the

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removal efficiency mainly depends on the reaction mechanism and the effect of the by-product.

2. Materials and methods

A schematic representation of the dry etching reaction chamber is shown in Fig. 1. The NH_3/NF_3 mixture was excited using pulsed RF plasma (27.12 MHz pulse 3 kW). Helium gas was used as a carrier gas. The temperature was maintained at 35 °C throughout the experiment. The power of plasma was varied from 80 to 160 W, the chamber pressure from 3.75 to 5 Torr, gas ratio of NH_3/NF_3 from 0.14 to 7.82, and process time from 60 to 180 s, respectively. Thermally grown SiO_2 (10000 Å) and low pressure chemical vapor deposition (LPCVD) Si_3N_4 (1000 Å) were used as a material for the experiments. The size of the sample 20×20 mm was cleaned with dilute SC-1 [NH_4OH (25%):H_2O_2 (38%):DIW = 1:2:50] solution at 60 °C for 10 min before proceeding the dry etching, and then it was loaded into the reaction chamber. After dry etching was over, the annealing process was performed to remove the by-product. The measurement of the SiO_2 and Si_3N_4 thickness was measured by Ellipsometer (M-2000V, J.A. Woollam, USA). The existence of the by-products was analyzed by using a contact angle analyzer (Phoenix, SEO, Korea) and SEM (FE-SEM, MIRA3, TESCAN, Czech), respectively.

3. Results and discussion

Fig. 2 shows the schematic of the SiO_2 with substrate before proceeding to the etch rate, it was exposed to the plasma NH_3/NF_3 gas treatment. During the process by-product such as $(NH_4)_2SiF_6$ was produced in the chamber, which is deposited on the surface and it was evaporated under the high temperature at 180 °C for 1 min. In this paper, we defined fume as white solid by-product that is easily remove by high temperature treatment or DI water rinse. After the SiO_2 were etched without annealing, to find out the chemical composition of the fume, composition of fume was analyzed using Fourier transform infrared spectroscopy (FT-IR). Fig. 3 shows the ATR-FTIR spectrum of etched SiO_2 surface and $(NH_4)_2SiF_6$ powder. Fumes are formed on the SiO_2 surface which can be confirmed N–H, NH_4^+ and SiF_6^{2-} peak. These peaks are representative of $(NH_4)_2SiF_6$ powder composition. This observation suggested that $(NH_4)_2SiF_6$ created after NH_3/NF_3 dry etching process.

The etch rate of SiO_2 and Si_3N_4 was measured as a function of the process time as shown in Fig. 4. The substrates were introduced into the chamber using Helium as a carrier gas with a flow rate of 600 sccm. The etch amount of SiO_2 increased gradually with increase of process time. However, the etch rate decreased with an increase in process time. On the other hand, the etch rate of Si_3N_4 was increased. The results confirm that, the selectivity of SiO_2 and Si_3N_4 was decreased with increase in process time. The maximum selectivity was obtained around 9.3 at 90 s shown in Fig. 5. After excess 90 s., the etch rate of Si_3N_4 was increased compared with SiO_2.

Fig. 6 shows the etching behavior of SiO_2 in NH_3/NF_3 mixture of varying ratio. The overall chemical reaction of SiO_2 etching involved is normally understood as [15,16]:

$$SiO_2 + 4HF + 2NH_4F \rightarrow (NH_4)_2SiF_6 + 2H_2O \tag{1}$$

The reactions show that mechanism of SiO_2 etching in buffered HF (BHF). However, a plasma active NF_3/NH_3 etching process consists of two steps. Plasma converts NF_3 and NH3 to NH_4F and $NH_4F{\cdot}HF$ (Eq. (2)). These products condense on the SiO_2 surface and react with the SiO_2 to form solid by-product ($(NH_4)_2SiF_6$) (Eq. (3)) [16]:

$$3NH_3 + NF_3 \rightarrow NH_4F + NH_4F \cdot HF + N_2 \tag{2}$$

$$SiO_2 + 6NH_4F \rightarrow (NH_4)_2SiF_6 + H_2O + 4NH_3 \tag{3}$$

The NH_4F produced for contributing to the SiO_2 etching. At less than 2 (NH_3/NF_3 ratio) level, the etch rate of SiO_2 increases drastically with increasing NH_3/NF_3 ratio. At greater than 2 (NH_3/NF_3 ratio) level, the etch rate of SiO_2 gradually decreases with increasing NH_3/NF_3. On the other hand, the etch rate of Si_3N_4 (40 Å/min) was relatively diminished in above the same condition. The maximum etch rate of SiO_2 was 310 Å/min.

In order to investigate the effect of recombination and dissociation of etch rate, we altered the chamber pressure and electrode power, respectively. Fig. 7 shows the etch rate of SiO_2 as a function of pressure and power. The etch rate was decreased at increasing power. The etch rate of SiO_2 was obtained in the range of 330–240 Å/min at the pressure of (3.75–5 Torr) and the power of (80–160 W), respectively. At high RF power, the more decomposable gas was produced. However, no reaction gas was observed during the etching. Similarly, the etch rate was decreased as increasing the chamber pressure.

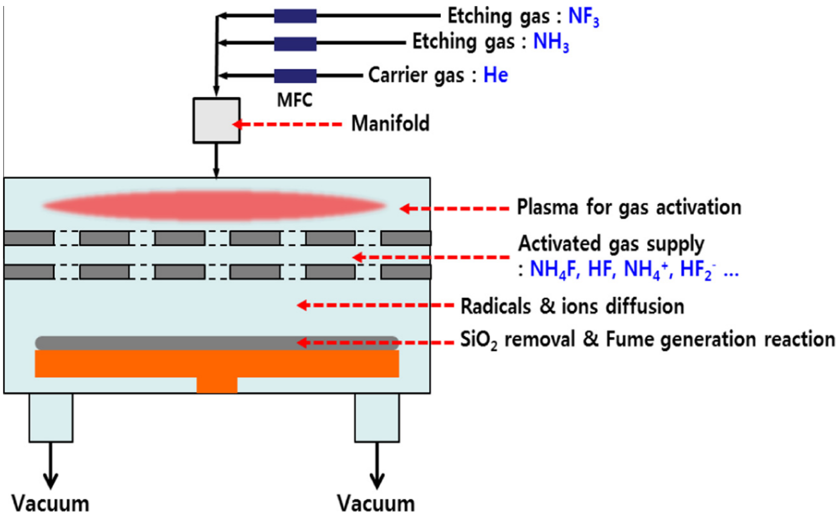
Etching gas : NF_3
Etching gas : NH_3
Carrier gas : He
MFC
Manifold
Plasma for gas activation
Activated gas supply
: NH_4F, HF, NH_4^+, HF_2^- ...
Radicals & ions diffusion
SiO_2 removal & Fume generation reaction
Vacuum
Vacuum

Fig. 1. Schematic of the dry etching reaction chamber.

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