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High selectivity (SiN/SiO_2) etching using an organic solution containing anhydrous HF

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ABSTRACT

An etching process with high selectivity for SiN relative to SiO_2 at a low temperature is required for an etching process in LSI process. We achieved SiN film etching with high selectivity using an organic solvent (ethylene glycol dimethyl ether) containing anhydrous hydrogen fluoride. Selectivity as high as 15 was obtained at 80 °C. It was found that anhydrous HF effectively induces high selectivity for SiN relative to SiO_2. SiN film etching with high selectivity performed at low temperature for a single wafer process can be readily applied to future node technology devices.

1. Introduction

Silicon nitride (SiN) films are essential for future large-scale integrated (LSI) circuits and microelectronic mechanical systems (MEMS). They have many applications in semiconductor processes, e.g., as gate spacers, polishing stopper for chemical mechanical polishing (CMP), antireflective films, and hard masks. Etching of SiN films on semiconductor wafers is a key process for microelectronics manufacturing.

Achieving high etching selectivity for SiN films relative to SiO_2 films is a serious issue for next generation devices and beyond. A SiN film deposited by low-pressure chemical vapor deposition, the film known as an LP-SiN film is used as a CMP stopper for the high-density plasma (HDP) CVD SiO_2 layer during shallow trench isolation (STI) process as shown in Fig. 1. After CMP of the SiO_2 layer, the LP-SiN film needs to be removed without etching the HDP-SiO_2 film of STI. Thus, an LP-SiN film etching process with high selectivity that does not etch the SiO_2 layer is required.

It is well known that SiN is selectively etched using hot H_3PO_4 in a wet process [1]. However, this requires a high temperature of ~130–180 °C and a special equipment that can withstand high temperature and strong acid. On the other hand, recently, wet etching by a single wafer process has been widely used for quick process control and effective LSI manufacturing. However, it is difficult to control the single wafer processes at temperatures higher than 100 °C. In addition, diffusion of phosphorus atmosphere from H_3PO_4 into the clean room causes atmospheric contamination. Therefore, temperatures lower than 100 °C are required for the single wafer process.

SiN films can also be etched with an aqueous HF solution, but it does not have sufficient etching selectivity for SiN relative to SiO_2. The SiN etching rate is about 0.1 times lower than the SiO_2 etching rate. To improve the selectivity, SiN etching processes using an organic solvent containing aqueous HF were reported [2,3]. But these processes are not adequate to selectively etch the SiN film on SiO_2 as shown in Fig. 1. Therefore, a new etching process that exhibits higher selectivity at temperatures lower than 80 °C is required for LSI production.

In this study, in order to achieve high selectivity, we investigate the etching properties and etching reaction of organic solvents containing hydrogen fluoride. SiN etching with a selectivity greater than 10 at a temperature lower than 100 °C can be achieved using an organic solvent containing anhydrous hydrogen fluoride.

2. Experiment

SiN films (200 nm) were deposited by LP-CVD on bare silicon substrates. Such LP-SiN films are known to be harder than the SiN

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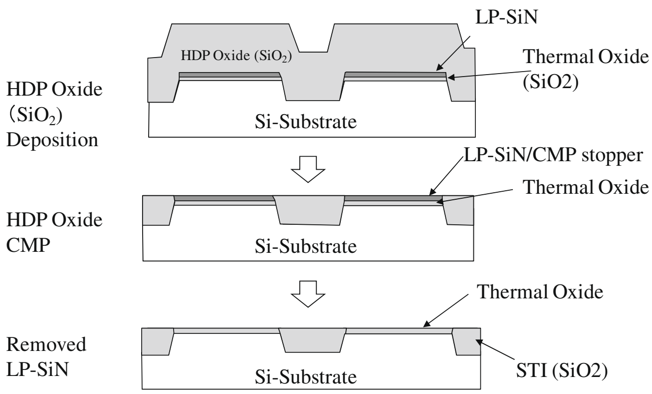

Fig. 1. Typical process flow for shallow trench isolation (STI) formation.

films formed by other methods such as plasma CVD. SiO_2 films (100 nm) were prepared by thermal oxide growth (wet oxidation at 1050 °C) on bare silicon wafers as samples for etching measurements.

The etching solutions were prepared by mixing anhydrous HF or 50% HF (50 mass% HF + 50 mass% H_2O) with the organic solvents. We investigated the relation between the relative dielectric constant of the organic solvent and the selectivity of solvent containing aqueous HF at room temperature. Ethylene glycol dimethyl ether (EGDE), ethylene glycol, and isopropyl alcohol (IPA) were used as organic solvents. SiN and SiO_2 films (size: 1×1 cm^2) cut from a 200 nm wafer were immersed into the solvent (0.2 L) in a plastic beaker. The beaker was submerged in a water or oil bath to control the etching temperature. The film thickness was measured with a nanospec using an optical range of 400–800 nm in wavelength. The film etching rate was calculated using the difference in the thickness of the film before and after etching.

3. Results and discussion

3.1. Influence of H_2O concentration in the solution on the etching selectivity

Fig. 2 shows the dependence of the etching rates of SiO_2 and SiN films on the H_2O concentration. The etching rates of both SiN and SiO_2 films increase with an increasing H_2O concentration in the solutions. The selectivity increases with a decreasing H_2O concentration. This result indicates that suppression of the water concentration of

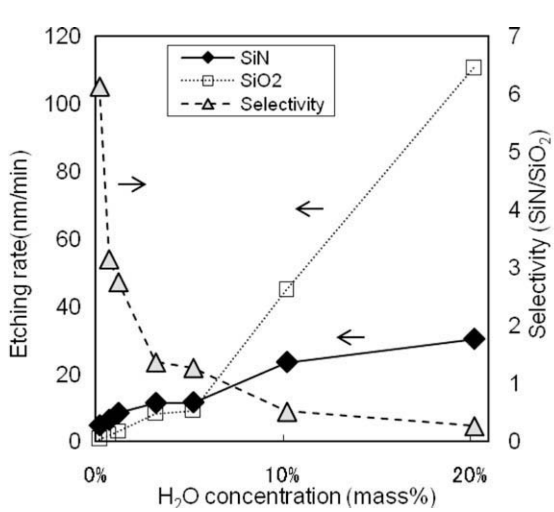

Fig. 2. Dependence of SiO_2 and SiN etching rates and selectivity on H_2O concentration (mass%) in EGDE containing 20 mass% AHF at 60 °C.

water in the solution is useful to achieve high selectivity. We attempted the etching of SiN and SiO_2 films in an organic solvent using anhydrous HF (AHF) solution.

Table 1 shows the etching rates of SiN and SiO_2 films and selectivity (ratio of the etching rate for SiN to that for SiO_2) for various aqueous and organic solutions (solvents). EGDE containing AHF (25%) at 50 °C shows the highest selectivity of 2.5 in Table 1. Thus, it is found that EGDE containing AHF is useful to achieve both high selectivity and an adequate etching rate.

3.2. Dependence of the etching selectivity on the AHF concentration in EGDE

We investigated the etching properties of EGDE containing AHF, which has the highest selectivity of 2.5, as shown in Table 1. Fig. 3 shows the dependence of SiN and SiO_2 etching rates on AHF concentration (10–29%) in EGDE. The etching rates of both SiN and SiO_2 films increase with increasing AHF concentration in EGDE. The increase in the SiO_2 etching rate is greater than that in the SiN etching rate. As a result, the selectivity decreases with AHF concentration. This tendency was observed at all temperatures. It is difficult to achieve high selectivity with high AHF concentration. At 30 °C, the highest selectivity (5) is reached for EGDE containing 10 mass%.

It is thought that selectivity increases with decreasing AHF concentration, because the ratio of HF which has a high dielectric constant (~80) is reduced. Therefore, it is important to investigate the relationship between the dielectric constant of solutions and selectivity.

Fig. 4 shows the relationship between the dielectric constant of the organic solvent and the selectivity of SiN relative to SiO_2 in (a) the organic solvents containing 25 mass% AHF and (b) the organic solvents containing 25 mass% HF and 25 mass% H_2O. The result indicates that the selectivity of the solvents containing only AHF is higher than those containing aqueous HF for each organic solvent. Solutions with a small dielectric constant have higher selectivities than those with a large dielectric constant. Therefore, the results support that the selectivity mainly depends on the dielectric constant of the etching solution.

3.3. Dependence of etching rate on temperature for EGDE containing AHF

The dependence of SiO_2 and SiN etching rates on the solution temperature is shown in Fig. 5. The selectivity increases with increasing temperature, because the increase in the SiN etching rate is faster than the SiO_2 etching rate. Table 2 shows the apparent activation energy for SiN etching and SiO_2 etching in EGDE containing AHF 10–25 mass% in the temperature range 23–80 °C. The apparent activation energy for SiN etching and SiO_2 etching were calculated from the Arrhenius plot. The both apparent activation energies increase with increasing AHF concentration. The apparent activation energy for SiN etching is higher than that for SiO_2 etching in each AHF concentration. The ratio of the energy for SiN etching to that for SiO_2 increases with a decreasing AHF concentration. Therefore, the selectivity is significantly improved by increasing temperature in low AHF concentration.

To obtain higher selectivity, the AHF concentration in EGDE and the solution temperature were optimized. We achieved a high selectivity of 15, and a SiN etching rate of about 5 nm/min with an AHF concentration of 10 mass% and an etching temperature of 80 °C as shown in Fig. 5.

3.4. Etching reaction

The etching mechanism of SiO_2 using dHF has been reported [4–6]. It was confirmed that system of HF containing solutions,