Chemical composition of C_4F_8 plasma polymerized film in the Bosch process

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Abstract: In the Bosch process, polymerized film deposited by C_4F_8 plasma is used for sidewall protection. The relationship between deposition rate and chemical composition of the polymerized film was investigated by varying gas flow rate. High CF_2 bond fraction was found at low flow rate (50sccm), and C-CF_X bond fraction increased at higher flow rate (800sccm); at both flow rates, the deposition rate has local maxima. At the higher flow rate, the films developed increased resistance against F radicals.
Keywords: Bosch process, DRIE, Plasma, C_4F_8, polymerized film, XPS

1. Introduction

Silicon-deep-reactive-ion-etching (Si-DRIE) processes have been developed as a processing technology for bulk silicon by applying dry etching technology cultivated in semiconductor manufacturing [1]. Among these, the processing method developed by Robert Bosch GmbH [2], which alternately switches the deposition of sidewall protection film and the etching of silicon, is called the Bosch process (Fig.1), and is known for its ability to achieve high aspect ratio processing with high etch rate.

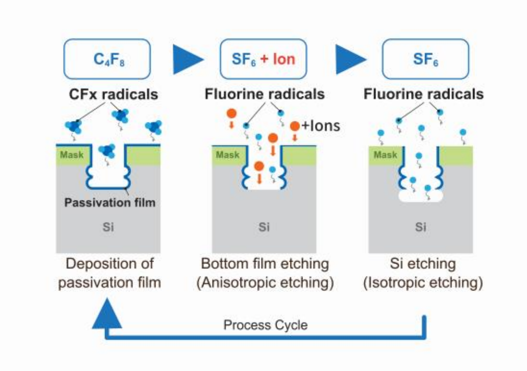

Fig.1 The principles of Bosch Process

Fluorocarbon plasmas containing C_4F_8 were originally used for oxide film etching in the semiconductor manufacturing process, and a lot of research has been done in this area. Since oxide film etching is an ion-assisted etching-based process, the plasma is structured to be generated close to the substrate, such as in a capacitively-coupled-plasma (CCP) or planar type inductively-coupled plasma ICP. Addition of Ar or O_2 suppresses the growth/over-degradation of radicals in the gas phase. [3].

On the other hand, the Bosch process uses a cylindrical semi-remote ICP, where the distance between the plasma and the substrate is far apart. Therefore, the type and rate of radicals in the deposition process of the Bosch process will also differ from the SiO_2 etchers that have been well studied.

Here, a down-flow cylindrical ICP with a long gas residence time, which is commonly applied in the Bosch process, is used. The polymerized film composition, deposition rate and F radical resistance were obtained with respect to C_4F_8 flow rate to investigate the polymerized films used as sidewall protection in the Bosch process.

2. Experimental

An ICP etcher RIE-800iPBC (Samco) for the Bosch process was used as the generator of C_4F_8 plasma. (Fig. 2). This ICP etcher is a cylinder type with an inner diameter of φ220 mm. The distance from the ICP coil to the stage where the substrate is placed, is variable between 350 and 450 mm. The ICP coil is capable of applying 13.56 MHz RF up to 5 kW. The stage can accommodate 200 mm wafers, wafers are chucked by a Johnsen-Rahbek type electrostatic-chuck (ESC), and cooling is provided by a helium heat exchanger. The temperature can be set from -10 to +20°C. The power supplies for the lower electrode consist of 13.56 MHz 1 kW and 400 kHz 300 W sources, which can output high-frequency wave superimposed on pulse wave in addition to continuous wave.

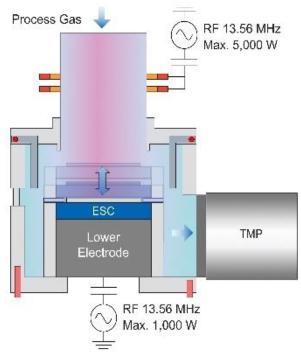

Fig. 2. ICP reactor for Bosch-process (RIE-800iPBC Samco)

Turbo molecular pump has a pumping capacity of 2200 L/min. The pressure in the reaction chamber is measured by Baratron capacitance manometers and the value is fed back to the control gate valve (CGV) for control. The pressure and ICP power for the deposition step were fixed at 4 Pa and 1600 W, respectively.

Thickness of the polymerized film was measured with a reflectance spectrometer FE-3000 (Otsuka Electronics) The x-ray photoelectron spectroscopy (XPS JPS-9010MX (JEOL)) was used for chemical composition analysis of the polymerized film.

The resistance of C_4F_8 plasma polymerized film to F radicals was determined from the amount of change in the polymerized film thickness when C_4F_8 and SF_6 were alternately discharged and the etching time during deposition was varied.

3. Results and discussion

When the ICP power and pressure are fixed and the flow rate of C_4F_8 gas is varied, the deposition rate shows a curve with two peaks in Fig. 3. One of the peaks is formed at a deposition rate of 430 nm/min at a flow rate of 50 sccm. Another peak is formed at a deposition rate of 400 nm/min at a flow rate of 800 sccm. These two deposition rate peaks can be attributed to two different polymerized film formation mechanisms.

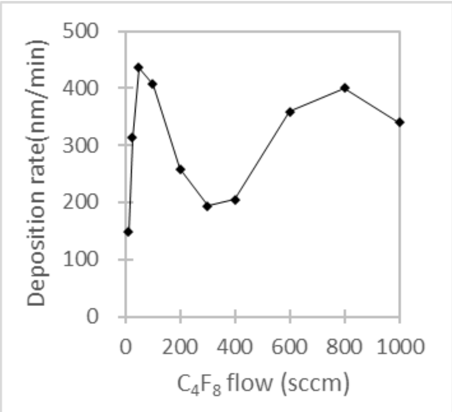

Fig. 3. Deposition rate as a function of C_4F_8 flow rate, measured in Bosch-ICP reactor.

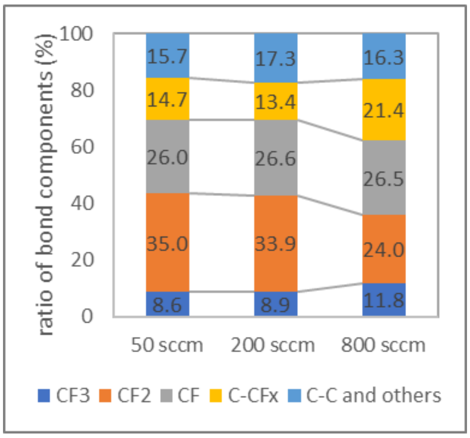

Fig. 4. XPS spectra of C_4F_8 polymer films on the Silicon surface at C_4F_8 flow rates are 50, 200, 800sccm

The chemical composition of the polymerized film was measured by XPS as shown in Fig. 4, indicating that the composition changes significantly at 800 sccm compared to 50 sccm and 200 sccm. The composition fraction of the polymerized films at 50 sccm and 200 sccm show that CF_2 bonds account for a larger component, more than 33%. On the other hand, at 800 sccm, CF, CF_2, and C-CF_X bonds are found to be present in almost equal proportions at 26%, 24%, and 21%, respectively. This predicts that the seed radicals that produce the polymerized film are different in the 800sccm region and in the region from 50sccm to 200sccm.

In the Bosch process, the role of the C_4F_8 plasma polymerized film is to protect the silicon sidewalls from etching by F radicals generated by SF_6 plasma. Since the C_4F_8 plasma-polymerized film itself is etched by F radicals, the F radical resistance of the polymerized film has a significant impact on the processed profile during the Bosch process.

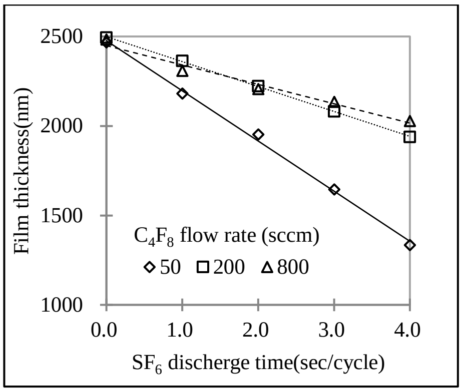

Fig. 5. Film thickness as a function of SF_6 discharge time after Bosch process with the Film etch step excluded.

In order to evaluate the etch resistance of the polymerized film, we performed Bosch process excluding the Film etch step. In the Bosch process without the Film etch step, the amount of polymerized film deposited per cycle exceeds the amount of polymerized film etched, so the polymerized film can be deposited on the silicon wafer.

Figure 5 shows the thickness of the polymerized film as a function of silicon etch step time; this indicates that the polymerized film at 800sccm is the most resistant to F radicals. The resistance of the polymerized film decreases as the flow rate decreases, and at 50 sccm, the resistance is less than half that at 800 sccm.

4. Conclusions

In this study, we were able to confirm what kind of C_4F_8 plasma polymerized film is deposited in the Bosch process discharge range. In order to achieve the ideal Bosch process, it is important to know the characteristics of the C_4F_8 plasma and its polymerized film before creating the process. Investigating what kind of film is needed for each processing requirement is a future task.

5. References

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