S5-2

Negative Ion Surface Reactions in Plasmas and Its application to Silicon Processes
プラズマ中における酸素および塩素負イオンの表面反応と半導体プロセスへの応用

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For one application of negative ions in plasma, silicon oxidation at low temperature and silicon etching were studied by employing negative oxygen ions as well as halogen negative ions. In the downstream region of a microwave and RF surface-wave plasmas, the silicon oxidation and etching were examined under DC and RF bias. The oxidation depth showed a strong dependence on RF bias, and thus it was concluded that the oxidation was due to the negative ions. The oxidation depth by negative ion became as high as more than two times of that by positive ion. Film quality was analyzed by XPS, showing less suboxide compared with positive ion oxidation.

1. Introduction

A low temperature and low damage silicon oxidation technique[1] is highly required in various ULSI processes. In particular for trench isolation of a memory cell to realize further integrations, the oxidation should be ion-assisted for directionality but with low damage. In addition, a low damage etching is also highly required, and it becomes more important as the cell size shrinks. For this purpose, a new method of negative ion assisted silicon oxidation and etching have been proposed employing a microwave O_2 and halogen plasmas.[2,3]

The objective of this work is to study silicon oxidation and etching by negative ions under the RF bias. For a practical application of this method, the oxidation and etching should be proceeded under the RF bias, because the DC bias becomes ineffective as the oxide film is grown. In this work, the silicon oxidation and etching were investigated under a transformer coupled RF bias. This device enables us to irradiate the negative ions as well as the positive ones onto silicon surface. In particular the major role of negative ions in oxidation and etching was examined under the conditions. In particular, an innovative method to produce a negative ion rich plasmas is proposed by employing RF surface-wave with a very high dielectric constant discharge tube.

2. Experimental Apparatus

The two types of apparatus were employed in the experiment. The one employed in this work is schematically shown in Fig.1. The surface-wave plasmas of O_2 and SF_6 were produced in a discharge tube of 15 mm in inner diameter with the thickness of 2 mm and the length of 330 mm as shown in Fig.1. The two discharge tube materials were employed; the one is a ceramic of TiCa-TiMg composite, K-140, which is commercially available from KYOCERA Co. and another is quartz. The permittivity values of these tube materials are, respectively, 140 and 3.8. To the one end of the tube, the mesh electrode of 60 mm in width is wound, and it is energized by the 13.56 MHz RF power. The process gases of O_2 and SF_6 were introduced from the one end of the tube and another end of the tube was connected with the process chamber of the stainless steel.

The optical emission line measurements were carried out from the both lateral and axial view to diagnose plasmas thus produced. The surface-wave propagation was also examined from the phase shift observed between the two dipole antennas. One of the dipole antennas was fixed at the upstream and another one was axially moved, and the phase difference obtained between these two was measured as a function of the

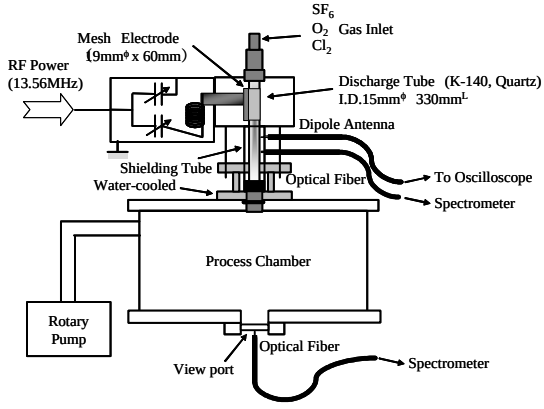

Fig.1. Experimental apparatus of RF surface-wave.

axial distance.

Another experimental apparatus is a microwave plasma with a dielectric disc plate. The plasma was produced in a 6 inch stainless-steel chamber and the downstream plasma was mainly considered because this region the negative ion was highly populated. The plasma parameters were measured using a Pt Langmuir probe. Silicon oxidation was made on a stage which was biased by the DC voltage as well as the RF bias to irradiate both negative and positive ions. The RF bias voltage was applied to the stage with a transformer, and the secondary of the transformer was biased by DC voltage at the same time. The oxidation experiment was also performed at the substrate temperature of 400 ^{o}C.

The oxide film quality thus produced was analyzed by X ray photoelectron spectroscopy (XPS). The oxide film thickness was measured by the XPS.

3. Experimental Results and Discussions

In Fig.2, typical examples of the optical emission line measurements are shown, where the relative intensities of the six fluorine atomic lines are plotted against the axial distance Z for the K-140. The intensity in the ordinate is normalized by the maximum value obtained at Z=8 cm for each line. The axial decay rate of the line intensities is very fast in the K-140 discharge tube and its rate was 5 times larger than that in the quartz. In particular, a sudden decrease at Z=13 cm may be due to the surface-wave ending, providing a high density after-glow. This is because the permittivity of K-140 is very high as 140 and the group velocity of the surface-wave is low. In these after-glow region, Langmuir probe measurements were made. In Fig.3, the saturation current ratio of positive to the negative is plotted as well as the positive ion saturation current. The saturation current ratio in the K-140 becomes quite low with keeping the high value of the positive ion saturation current, indicating the rich negative ions populated in this region.

A typical result of silicon oxidation in the microwave plasma is shown in Fig.4, where the oxidation depth obtained at Z=15 cm by XPS measurements is plotted against the DC bias V_{dc} and the RF bias V_{pp} of the frequency 1.1 MHz. It is seen that the oxidation depth is very critical to both the V_{dc} and V_{pp}. In particular, in positively biased conditions the depth becomes higher.

XPS measurements showed that the SiO_2 peak observed with the positive ion oxidation film is shifted and widened, demonstrating that the film quality is improved by the negative ion irradiations with less suboxide. The fact that the film quality is improved by the negative ion irradiation may be explained as the following. The mass analysis of the ion species using a quadrupole mass analyzer showed that the dominant negative ion was O^- and its density was almost one order of magnitude higher than that of O_2^-, while the dominant positive ion was O_2^+.[4] The dominant negative ion O^- is very atomically similar to the oxygen radical with a high chemical reactivity and this may be the origin of the high quality oxidation.

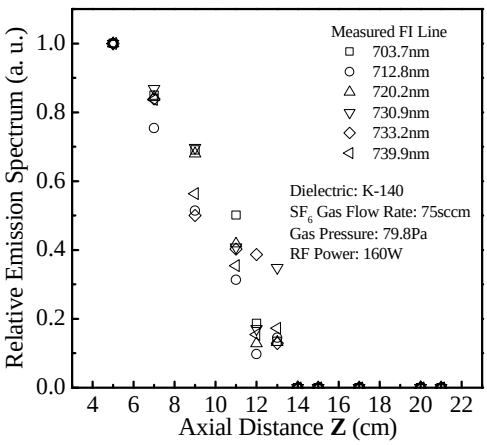

Fig.2. Emission line intensity of FI.

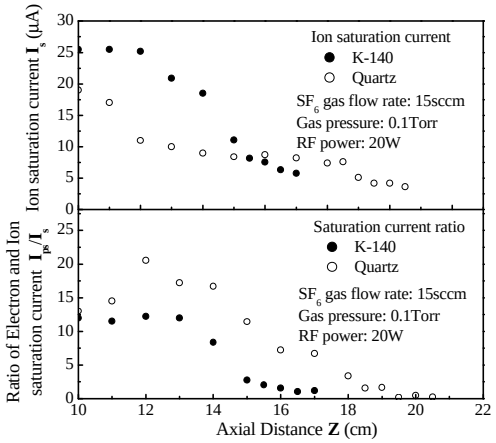

Fig.3. Ion saturation current and saturation current ratio.

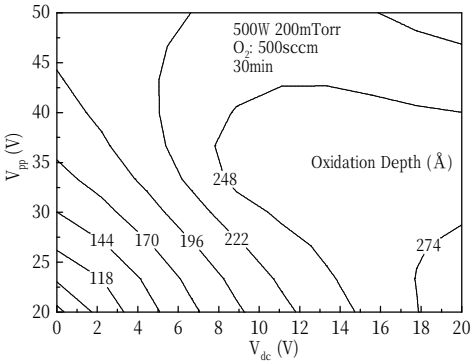

Fig.4. Oxidation depth contour for V_{dc} and V_{pp}.

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