Effect of Kr Gas Dilution on O Atom Density in Surface Wave Excited Kr/O₂ Plasma for Low -Temperature and Damage-free Plasma Oxidation Processes

Y. Kubota, K. Yamakawa and M. Hori

Department of Electrical Engineering and Computer Science, Nagoya University Address:Furo-cho, Chikusa-ku, Nagoya, 464-8603, JAPAN Phone:+81-52-789-4420 FAX:+81-52-789-3462 E-mail:h046409m@mbox.nagoya-u.ac.jp

1. Introduction

Oxygen-based plasmas have been intensively used for the low temperature oxidation of the gate dielectric materials in ULSIs and LCD devices. It has been reported that the SiO₂ film of high quality was successfully formed at a low temperature by a high Kr gas dilution (about 97%) to O_2 gas plasma¹. From the viewpoint of developing the low temperature oxidation processes used for the gate dielectric film in the advanced ULSI devices, a quantitative study on the behavior of O atoms in the high dilution Kr/O2 surface wave excited plasma (SWP) has been strongly required ^{2, 3}. Recently, our group has developed a compact measurement system of absolute densities of hydrogen, nitrogen and oxygen atoms in the plasma using the vacuum ultraviolet absorption spectroscopy (VUVAS) with a micro discharge hollow cathode lamp (MHCL)⁴.

In this study, we have measured for the first time the absolute O atom density in the Kr/O_2 SWP using the VUVAS technique employing the MHCL. Moreover, the production mechanism of O atoms has been discussed. On the basis of measured results of ionic species and their energy distributions using quadrupole mass spectroscopy (QMS), we have clarified the low-temperature plasma oxidation mechanism for the damage-free gate dielectric film formation from viewpoint of gas phase reactions.

2. Experiment

The plasma chamber was 35 cm in diameter and 45 cm in height, which is a production level apparatus. The slot antenna was set on the quartz window on the flat top of the chamber. Microwave of 2.45 GHz was applied to the slot antenna to produce the SWP. The absolute densities of O atom and metastable Kr* species were measured by the absorption spectroscopy.

Furthermore, ionic species and their energy distributions were measured by QMS. The mass spectrometer (Hiden EQP500) was positioned at the wall of chamber.

3. Results and discussion

Figure 1 shows the absolute O atom density in the Kr/O_2 SWP as a function of Kr flow rate ratio at a pressure of 90 Pa, a microwave power of 1kW and a total flow rate of 100 sccm. When the Kr flow rate ratios were varied from 90 % to 97 %, the absolute O atom density was changed from 6×10^{14} to 3×10^{13} cm⁻³. As a production process of O atom, the electronic collision dissociation of O_2 was evaluated. The electron density and electron temperature were measured by the single probe method as shown in Figure 2. The electron density and electron temperature were changed from 5×10^{10} to 3×10^{12} cm⁻³ and from 0.8 to 1.4 eV, respectively when the Kr dilution ratio was increased from 0 to 99%.

At the Kr high dilution, it is considered that the O atom was produced by the collision of metastable Kr* species with O2 molecules. We measured firstly the absolute Kr* density in the SWP plasma as shown in Figure 3. The O atom generation rate by the electron- O_2 collision and the Kr*-O2 collision was estimated by the electron density, the Kr* density and the dissociation rate constant evaluated. Figure 4 shows the O atom generation rate by electron-O2 and Kr*-O2 collisions. The dominant production of O atom was found to be due to the electron- O_2 collision dissociation. Figure 5 shows the O_2^+ was the main ion in the Kr/O2 SWP and had a drastic increase with a high Kr dilution. It is noteworthy that any intensity of Kr⁺ except for in the pure Kr plasma was not detectable due to the effect of charge exchange from Kr⁺ to O_2^+ . Figure 6 shows the O_2^+ ion energy distribution as a function of Kr flow rate ratio. Each intensity was normalized by the sum of all intensities. Although the ion energy of O_2^+ increased with the Kr flow rate ratios, the ion bombardment of low energies less than 7eV will be very effective for the formation of damage less and highly densified oxidation films at a low temperature in the Kr/O₂ SWP.

4. Conclusions

The qualitative behaviors of the absolute densities of O, Kr^* and O_2^+ ions in the Kr/O_2 SWP plasma were clarified for the first time and it was found that the dominant production of O atoms was due to electron-O₂ collision even in a high dilution of Kr. The high quality SiO₂ gate dielectric film will be formed with a large amount of O atoms above 10^{13} cm⁻³ and low energy O_2^+ ions with low energies less than 7eV above 10^{12} cm⁻³.

5. References

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Fig. 1 Absolute O atom density in the surface wave excited Kr/O_2 plasma as a function of Kr flow rate.



Fig. 2 Electron density and electron temperature as a Function of Kr flow rate ratio.



Fig. 3 Absolute Kr* (${}^{3}P_{2}$) density as a function of Kr flow rate ratio.



Fig. 4 O atom generation rate as a function of Kr flow rate ratio .



Fig. 5 Intensity of the quadrupole mass spectroscopy as a function of Kr flow rate ratio.



Fig. 6 O_2^+ ion energy distribution as a function of Kr flow rate ratio.