Extended Abstracts of the 2007 International Conference on Solid State Devices and Materials, Tsukuba, 2007, pp. 326-327

P-1-2

Si Oxidation Mechanism in Ar/O_2 Surface Wave Plasma

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1. Introduction

In silicon semiconductor technologies, the high quality oxidation films become very important for ULSI devices due to the shrinking of sizes in integrated circuits. The conventional thermal Si oxidation has many problems, such as dopant diffusion, defect formation, etc. Thermally induced problem lead to the serious degradation of the device performance.[1] Therefore, the plasma oxidation process has attracted very much attention to realize the low temperature processes and has been investigated for synthesizing high quality Si oxidation films at lower temperature.[2,3] It was reported that Kr/O_2 plasmas have a potential for realizing the high Si oxidation rate and synthesize the high quality Si oxidation films.[4] However, the Ar/O_2 surface wave plasma (SWP) has been frequently used for synthesizing the Si oxidation films in industry. In order to investigate the optimum condition of the plasma oxidation process, it is important to obtain the quantitative information of the behaviors of activated species in the Ar/O_2 SWP. Therefore, we investigated systematically the behaviors of the species, such as the O atoms in the ground ($^3P_2$) and excited states ($^1D_2$), ionic species, and electrons in the Ar/O_2 SWP. From these results, we have estimated fluxes of the activated species on the Si surface and discussed the effects of the species in the plasma on the plasma oxidation of Si wafer.

2. Experimental Setup

The production level SWP reactor for 8 inch Si wafer oxidation process was used for investigating the Si oxidation mechanism in the Ar/O_2 SWP, as shown in Fig. 1. Microwave (2.45GHz) was applied to the quartz window on the flat top of chamber to produce the SWP. The absolute densities of O ($^3P_2$) and O ($^1D_2$) atoms were measured by using the vacuum ultraviolet laser absorption spectroscopy (VUVLAS). The relative density of ionic species, the ion current and electrons were measured by using quardrupole mass spectroscopy (QMS) and a Langmuir probe, respectively. These measurements were carried out at 73mm below the quartz window.

3. Results and Discussions

The absolute densities of O($^3P_2$) and O($^1D_2$) atoms in the Ar/O_2 SWP were measured as a function of O_2 flow rate ratio by using VUVLAS. For the first time, the quantitative information about the behaviors of O($^3P_2$) and O($^1D_2$) atoms in the Ar/O_2 SWP were obtained in this study. A pressure and a microwave power density were fixed at 133.3Pa and 1.2W/cm^2, respectively. The absolute density of O($^3P_2$) atom slightly decreased from 2.9 to 1.4×10^{12}cm^{-3} with decreasing the O_2 flow rate ratio. On the other hand, the absolute density of O($^1D_2$) atom increased from 4.3×10^{10} to 1.8×10^{12}cm^{-3} with decreasing the O_2 flow rate ratio from 40 to 1% and then the density decreased to 1.0×10^{12}cm^{-3}. Figures 3(a) and (b) shows the relative densities of ionic species and the ion current density measured by using the QMS and a Langmuir probe. In the Ar/O_2 SWP, the charge transfer effect ($Ar^+ + O_2 \rightarrow Ar + O_2^+$) occurred efficiently. Therefore, as shown in Fig. 3(a), Ar^+ ion was detected only in the pure Ar discharge. On the other hand, the O_2^+ and O^+ ions increased drastically with an increase in O_2 flow rate ratio from 0 to 0.2%, and then decreased markedly up to the detection limit. This result indicates that the O_2^+ ion is dominant ionic species in the Ar/O_2 SWP. If the ion density corresponds to the electron density measured by the probe measurement shown in Fig.4, it is supposed that the density is estimated to be around 10^{11}cm^{-3} in the low O_2 flow rate ratio. On the other hand, the ion current was very low in the O_2 flow rate ratio from 5 to 40%, as shown in Fig. 3(b). However, in the low O_2 flow rate ratio, the ion current increased drastically with decreasing the O_2 flow rate ratio. Therefore, the effects of the O_2^+ ion on the Si oxidation could not be neglected in the low O_2 flow rate ratio.

Figure 5 shows the Si oxidation thickness synthesized in Ar/O_2 SWP as a function of O_2 flow rate ratio. The Si oxidation processes were carried out at a fixed temperature and processing time. The Si oxidation rate increased with decreasing the O_2 flow rate ratio and was a maximum at the O_2 flow rate ratio of 1%. The behavior was similar to that of O($^1D_2$) atom.

From quantitative measurement results of activated species in plasma gas phase, the fluxes of activated species incident on the substrate were estimated as a function of Si oxidation thickness synthesized in the Ar/O_2 SWP, as shown in Fig.6. The Si oxidation thicknesses increased linearly with the processing time for relatively small oxidation time. Each flux of species in the SWP was plotted as a function of the Si oxidation thickness synthesized in the process condition. As shown in Fig. 6, the behavior of O($^1D_2$) atom flux had good correlated with that of Si oxidation thickness, while that of O($^3P_2$) atom flux had negatively and weakly correlated. These data indicated that the $O(^1D_2)$ atom is a dominant species for synthesizing the Si oxidation film in the Ar/O_2 SWP and the growth of Si oxidation are limited by the supply of the $O(^1D_2)$ atom incident on the Si substrate. On the other hand, the effect of O_2^+ ion was saturated with increasing the Si oxidation thickness synthesized by the Ar/O_2 SWP. This means that the bombardment of O_2^+ ion affects only the top surface of Si substrate surface and enhances the oxidizing reaction near the top Si surface.

4. Conclusions

We have investigated the mechanism of Si oxidation in the Ar/O_2 SWP on the basis of the plasma diagnostics. From these results, at the initial stage of Si oxidation process, the oxidizing reaction due to the $O(^1D_2)$ atom adsorbed to Si surface can be enhanced by the activation of Si surface due to the O_2^+ ion bombardments. However, with increasing the Si oxidation thickness, the effect of ion bombardment on the Si oxidation decreased and the growth of Si oxidation films will be limited by the supply of $O(^1D_2)$ atom incident on the Si substrate.

References

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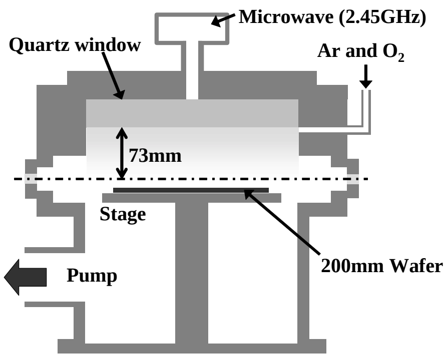

Fig.1 Schematic diagram of SWP reactor for the plasma oxidation process with the Ar diluted O_2 SWP.

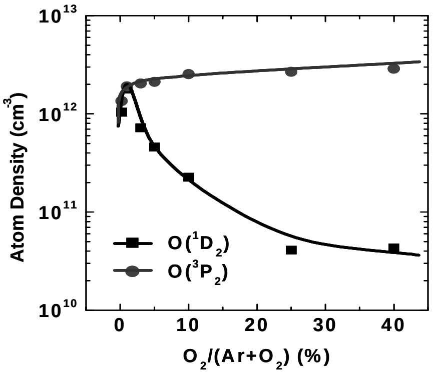

Fig.2 Absolute densities of $O(^3P_2)$ and $O(^1D_2)$ atoms as a function of O_2 flow rate ratio.

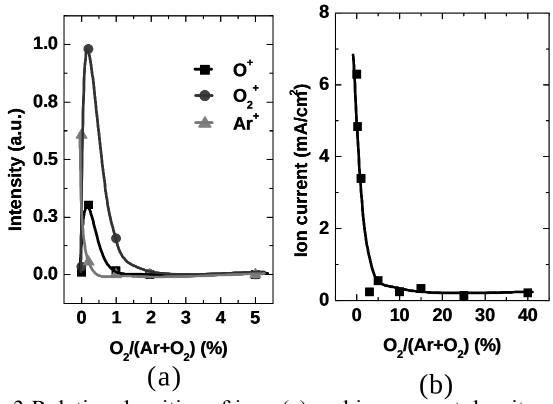

Fig. 3 Relative densities of ions (a) and ion current density as a function of O_2 flow rate ratio.

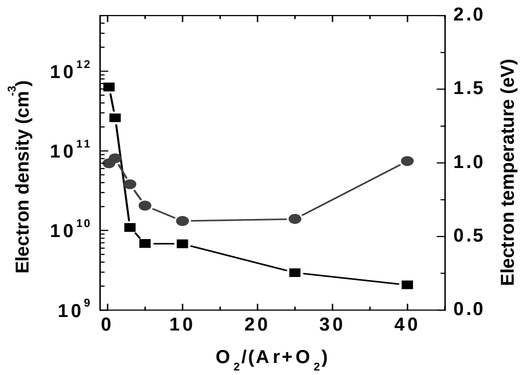

Fig. 4 Electron density and temperature as a function of O_2 flow rate ratio.

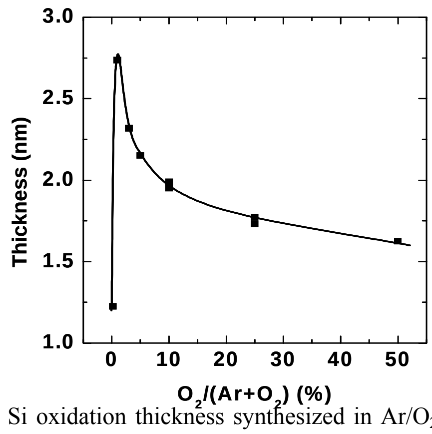

Fig. 5 Si oxidation thickness synthesized in Ar/O_2 SWP as a function of O_2 flow rate ratio.

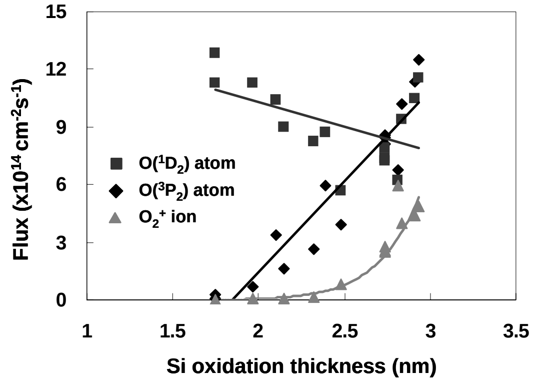

Fig. 6 Fluxes of species in the plasma gas phase as a function of Si oxidation rate in the Ar/O_2 SWP.