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In Situ Analysis of Plasma-Induced Modification on Porous SiOCH Films

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1. Introduction

There have still needed to assess the plasma induced damage on the porous SiOCH (p-SiOCH) films as materials for insulator of interconnects layer of ultra large scale integrated circuits (ULSI). Plasma processes were utilized in various applications such as plasma etching, plasma-enhanced chemical vapor deposition, plasma assisted surface treatments and so on. However, chemical reactions in and/or after the plasma processes are so complicated because of various reactive species such as electrons, ions, neutrals and photons irradiated simultaneously. Thus we need to evaluate individual and synergistic effects occurred on the reactions. For this purpose, we have proposed the method used the pallet for plasma process evaluation (PAPE) and clarified separately those effects [1].

Moreover, in clarification of the damage on the p-SiOCH materials, air exposure after plasma processes was considered to be influenced their structural properties but the mechanism had not evidenced by the researchers. So we prepared the experimental setup for in situ analysis, and carried out the experiments for evaluating in situ during and just after the plasma processing [2]. However, the mechanism of damage creation on the p-SiOCH has not been clarified comprehensively.

Previously, while carbon content of p-SiOCH was lost, its dielectric property became worse so that the dielectric constants increased significantly. Many researchers concluded that end-on methyl group was abstracted by reactions and was resulted to form considerable damages on the films. Compared with oxidative plasmas, a use of reductive plasmas has improved reduction of the damages. There were fewer studies on modification of the Si-O-Si skeleton in the film. However, the Si-O-Si properties affected to the various film's properties such as dielectric constants, mechanical strength, and so on [3-6].

In this study, we focused on structural changes on Si-O-Si skeleton in the p-SiOCH films during the pure hydrogen plasma and on proceeding air exposure after the plasma processes.

2. Experiments

Figure 1 shows schematics of our experimental setup. Plasma reactor had capacitively-coupled parallel-plate electrodes. One was excited 100 MHz power for generating plasmas and the other was grounded. Samples were electrical-static chucked on the grounded electrode and cooled at 20ºC. Hydrogen gas was introduced and chamber pressure was maintained at 2.0 Pa. Typically a 100MHz power of 450 W was supplied.

Samples were p-SiOCH film with thickness of 75 or 150 nm and the dielectric constants of 2.3. Figure 2 shows schematically drown diagram for the evaluation of individual and synergistic effects of ions, neutrals, and photons by according with the method used PAPE. Normally all parti-

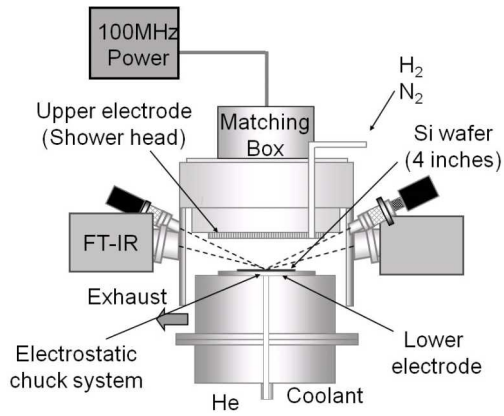

Figure 1 Schematic of our experimental setup.

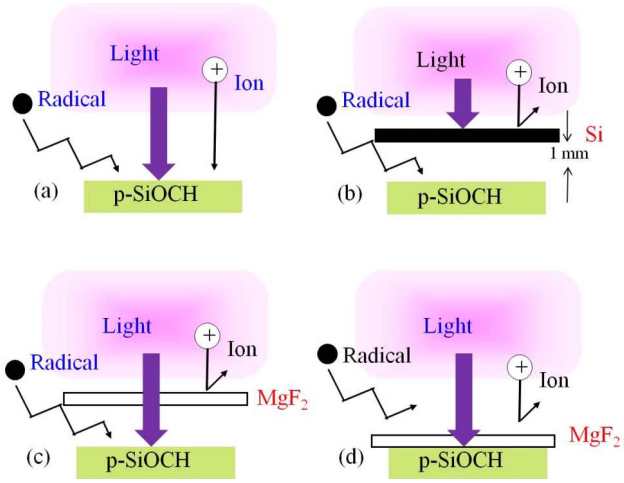

Figure 2 Schematic diagram of the evaluation method of individual and synergistic effects of ions, neutrals, and photons by according with the pallets for evaluation of plasma processes (PAPE).

cles generated in plasmas will irradiate on the surface. By covering plates on the surface, the ions can be excluded on the evaluations. Likewise with placing of transparent window on the surface, photons can irradiate. For neutrals, we set the windows or plates with a gap on the surface so that the neutrals can diffuse inside the gap to react on it. Moreover to evaluate the effect of the interaction with vacuum ultraviolet lights (VUV), we used a MgF_2 window as transparent materials.

3. Results and discussion

Figure 3 shows infrared spectra of p-SiOCH films during pure hydrogen plasma exposure. In Fig. 3a, illumination of plasma emissions with wavelength above 115 nm was indicated to change. Oppositely in Fig. 3b exposure of atomic hydrogen as main long-lived neutral was not influenced to change in the modification. This can be interpreted by that bonds such as Si-C(3.9eV), C-H(4.2eV) or Si-O(4.6eV) are having large bond energies compared with that of atomic hydrogen (2.3eV). Notably simultaneous exposures of lights and radicals as shown in Fig. 3c were brought significant changes in the Si-O-Si structures. During plasma processing for 180s, the absorption peak located at about 1060 cm^{-1} arisen from the Si-O transverse optical (TO) mode shifted to higher wavenumber. This shift was reflected by corresponding with that tetrahedrally substituted methyl group for Si atoms was removed and linked bridging O by forming Si-O-Si network. This cross-linking was accelerated by air exposure due to hydration. However with ion bombardments, we detected clearly difference in infrared spectra for the Si-O-Si structure as shown in Fig. 3d. Namely some higher wavernumber shift as previously mentioned was not observed. A little change at air exposure occurred. This indicated that the modifications resulted by exposure of various species from plasmas were essentially different in mechanical. So only the in situ real time measurements can reveal to realistic reactions occurred on the surface.

4. Conclusions

We evaluated plasma-induced modification of Si-O-Si skeleton on the porous SiOCH films during plasma process and at air-exposure by in-situ infrared spectroscopic measurements. The individual and synergistic effects of ions, radicals, and light were elucidated by using the PAPE technique. By analyzing the results, the mechanism of damages created were clarified in detail the effects of primary modification during plasma of bond-scission and air exposure of Si-O cross-linking following hydration.

Acknowledgements

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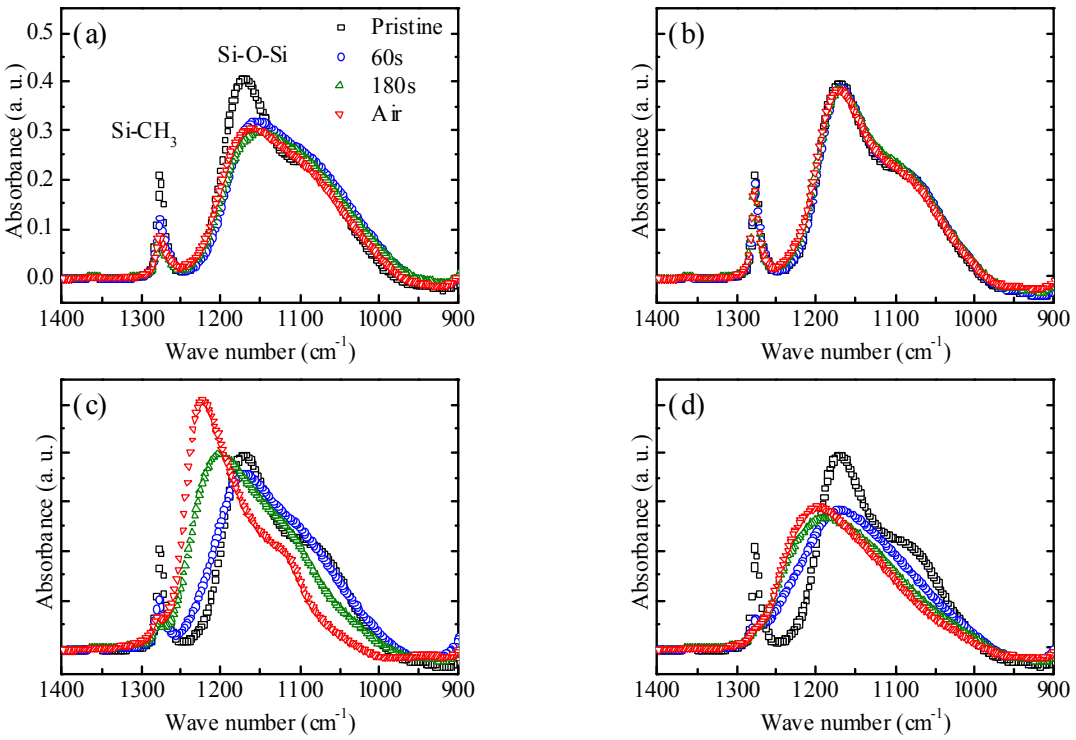

Figure 3 IRRAS spectra of p-SiOCH films during H_2 plasma exposure and after air exposure in 1400-800 cm^{-1} region at different conditions: (a) light, (b) radical, (c) light + radical, and (d) light + radical + ion.