21st International Symposium on Plasma Chemistry (ISPC 21)
Sunday 4 August – Friday 9 August 2013
Cairns Convention Centre, Queensland, Australia

Effects of hydrogen on plasma etching for silicon and silicon nitride

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Abstract: For more precise control of plasma etching processes, a better understanding of interaction of ions and radicals contained in plasmas with Si, SiO_2 and SiN surfaces is desirable. In this study, mass-analyzed ion beam experiments were employed to clarify hydrogen effects during plasmas etching process containing hydrogen such as HBr and hydrofulorocarbon. It has been shown that H^+ ion injection damages Si surfaces and also enhances oxygen radical diffusion in Si if oxygen radicals are simultaneously supplied. As to SiN etching by hydrofluorocarbon ions, it has been found that the presence of hydrogen in the $CHxFy^+$ ion beam increases the sputtering yield of SiN, which is consistent with the observation of SiN etching by hydrofluorocarbon plasmas.

Keywords: Plasma etching. Semiconductor devices. Ion beam.

1. Introduction

Hydrogen halide plasmas and hydrofluorocarbon plasmas are widely used for semiconductor gate etching processes and selective etching processes for silicon nitride (SiN). In such plasmas, there are various chemically reactive halogen ion species (such as Br^+, F^+ and $CxFy^+$). Etching properties by such ions have been widely studied to achieve high etching rates and anisotropy.

However, for more precise control of etching processes to be achieved, a better understanding of interaction of ions and radicals contained in these plasmas with surface materials is desirable. In general, hydrogen is considered to play relatively minor roles in gate etching processes. For example, the reason that HBr, rather than Br_2 is widely used for gate etching processes is that HBr is easier to handle and more readily available in the industry. Hydrogen may contribute to mitigating oxidation of the surface due to its reducing nature and therefore to controlling fine structures on the surface at nano scales. However, energetic hydrogen incident on the surface may damage its surface crystalline structures [1-2].

On the other hand, hydrogen in hydrofluorocarbon is known to play a major role in selectively etching SiN. It has been also known that hydrogen gas added to a fluorocarbon plasma in reactive ion etching (RIE) processes increases SiN etch rates, which suggests that hydrogen in hydrofluorocarbon plasmas plays a determining role for etching rates of SiN [3]. Although effectiveness of use of hydrogen for such etching processes has been known, the exact role of hydrogen for etching selectivity was not understood well prior to this study.

In this study, we have performed mass-analyzed ion beam experiments to clarify roles and effects of hydrogen in such processes.

2. Experimental

In this study, we used a mass-analyzed ion beam system, which can independently/simultaneously irradiate a sample surface with controlled ion or radical beam. A schematic diagram of the beam system used in this study is given in Fig. 1 [4-5]. The ion beam system consists of four parts. As shown in Fig. 1, our beam system has an ion beam source, an analyzing magnet, a beam line, and a reaction chamber in which a sample substrate can be placed. Firstly, ions are produced in the Free-man type ion source by arc discharge. The ions are extracted by a high voltage and accelerated to 25 keV, which sufficiently suppresses beam divergence arising from space charge. Ions of interest are selected based on their mass by the large analyzing magnet. The selected ions with high energy are then decelerated to desired energy by the deceleration electrode before reaching the sample substrate in the reaction chamber. In this system, the beam energy at the substrate surface can be varied from 0 to 2 keV.

The reaction chamber is always maintained in ultrahigh vacuum conditions with the pressure of about 10^{-10} Torr, which minimizes the effect of back ground gases on the sample surface. The manipulator, which the sample substrate may be set on, can be rotated against the ion beam line, which enables to select the incident beam angle. The reaction chamber is equipped with two charge-neutral radical sources; one based on a radio-frequency (RF) plasma and another for a supersonic molecular beam. These beams can be independently controlled and simultaneously injected into the sample surface. The reaction chamber is also equipped with

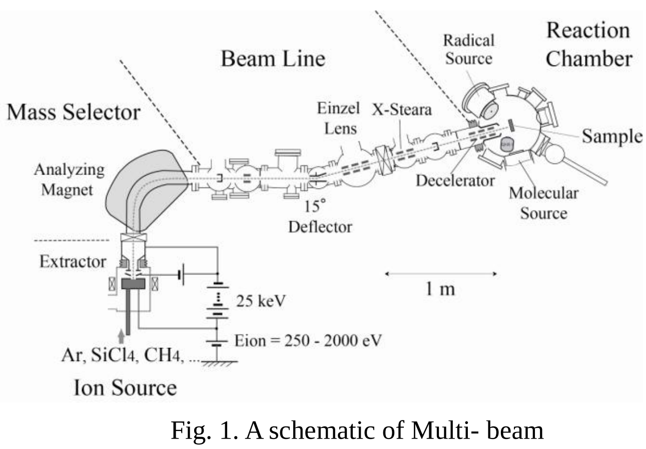

Fig. 1. A schematic of Multi- beam injection system

X-ray photoelectron spectroscopy (XPS) and a differentially pumped quadrupole mass spectrometer (QMS), which allows in situ surface analysis.

3. Experimental results

3.1 Analyses of Si surface damage by simultaneous irradiations of hydrogen ion and oxygen radical beam

In order to clarify the mechanism of formation of “Si recess”, which is serious damage of a Si substrate underneath a gate oxide observed during poly-Si gate etching by HBr/O_2 plasmas, experiments of simultaneous ion and oxygen radical beam injection were employed. Using the ion beam system, we first examined Si dislocation caused by 500 eV H^+ ion injections. In this study, the angle of incident ion beam was set to be normal to the substrate surface. Before use, its native oxide was removed by hydrofluoric acid treatment.

Figure 2 shows atomic compositions of dislocated Si atoms for a Si(100) substrate near the top surface after 500 eV H^+ beam exposure with different ion doses, obtained from high-resolution Rutherford backscattering spectroscopy (HRBS) measurements. The horizontal axis represents the depth measured from the top surface. The vertical axis represents the atomic composition. Each curve represents the ratio of the number of dislocated Si atoms that are not located at Si lattice sites to the number of all Si atoms in percentage form. In Fig. 2, for the sake of simplicity, the profile of Si atoms on the crystalline sites is not plotted. It is seen that the thickness of dislocated Si layer increases as the ion dose increases. It is also seen in Fig. 2 that the thickness of the dislocated Si layer by H^+ ions (1.0×10^{17} ions/cm^2) is nearly 40 nm. Although hydrogen atoms are not counted in HRBS measurement, the figure indicates that incident H^+ ions are expected to penetrate into a depth of around 40 nm or more.

Damage formation caused by H^+ ions with oblique angles has been also examined with the use of the ion beam system and MD simulations. The beam experiments and molecular dynamics simulations have shown that the depth of a Si damage layer caused by H^+ ion injections has weak dependence on the angle of incidence [6].

Furthermore H^+ ion beam at 500eV as well as atomic oxygen radical beams were also analyzed with HRBS. It has been found in Fig. 3 that oxidation of a Si surface exposed to oxygen radicals is significantly enhanced only if the surface is subject to both oxygen radical supply and energetic hydrogen ion bombardment simultaneously [7].

These results present an unequivocal evidence that ion assisted oxygen diffusion takes place with H^+ ion beam injection.

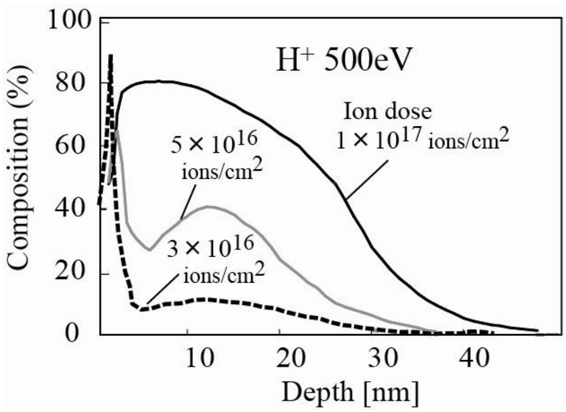

Fig. 2. A profiles of damaged Si layer caused by 500 eV H^+ ion injections

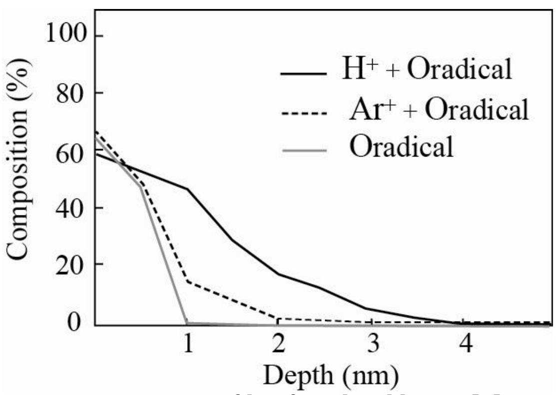

Fig. 3. A profile of oxidized layers [7]

3.2 Characteristics of SiN and SiO_2 Etching by CHxFy ions

To clarify the effects of hydrogen in SiN etching by hydrofluorocarbon such as CHF_3 and CH_2F_2, we measured SiN etching yields by CHF_2^+ ion injections and compared the results with those by CF_2^+ ion injections. We also performed similar measurements of SiO_2 etching yields. It is widely known that, when the incident energy of fluorocarbon ions is not sufficiently high, a fluorinated carbon layer is formed on the substrate surface and its deposition rate depends on the number x of fluorine atoms in the incident ion species CF_x^+ [8]. Surface characteristics of such fluorinated carbon layers were examined by XPS.

The ion dose (which is evaluated from the exposure time and ion current) used in this study is typically in the range of 1.0-2.0×10^{17} ions/cm^2. A substrate used in this study is a 1.5 cm×1.5 cm square wafer chip, on which either a 300 nm thick SiN film may be formed by chemical vapor deposition (CVD) or a SiO_2 film may be thermally grown. Change in thickness of the substrate is measured by optical interference.

Figure 4 shows etching yields of SiO_2, and SiN by CHF_2^+ and CF_2^+ ion injections. In the case of SiO_2, there is no deference between hydrofluorocarbon and fluorocarbon ions. However, the SiN etching yield by CHF_2 ions is higher than that by CF_2 ions. This is likely to be caused by reactions that form volatile species containing both hydrogen and nitrogen, such as HCN.

When fluorinated carbon-film deposition takes place, XPS analyses of the surfaces indicate that hydrogen of incident hydrofluorocarbon ions tends to scavenge fluorine of the deposited film, reducing its fluorine content.

These results indicate that controlling hydrogen in fluorocarbon plasmas is needed during SiN etching processes.

4. Conclusions

In this study, we have clarified hydrogen effects on plasma etching processes by mass selected ion-beam injection experiments with controlled fluxes and energies.

It has been found that energetic hydrogen ions in gate etching processes can damage Si crystalline structures of the surface region even when hydrogen ions enter vertical side walls at large angles of incidence. Incidence of energetic hydrogen ions are also found to enhance oxidation. As to SiN etching by hydrofluorocarbon plasmas, hydrogen is found to control the thickness and atomic compositions of fluorocarbon (CF) films deposited on the surface during plasma etching, which affects the etching yield of underlying material.

These experimental data are indispensable for an understanding of fundamental reactions between the surface and plasma and can contribute to the further development of plasma etching processes.

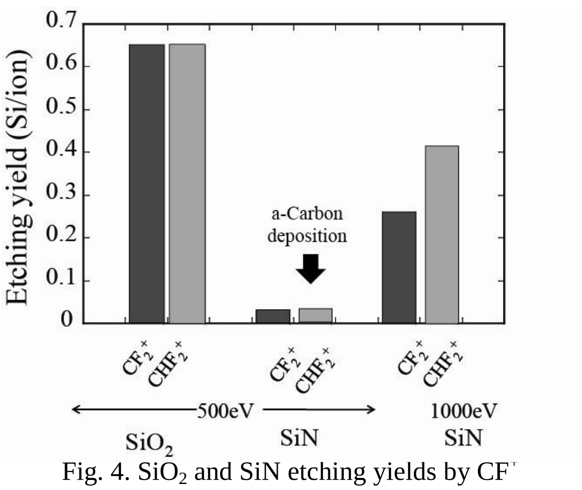

Fig. 4. SiO_2 and SiN etching yields by CF_2^+ and CHF_2^+ ions

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