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Etching yields of HfO_2 under Ar^+ and CF_X^+ (X = 1, 2, 3) ion beam irradiation

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1. Introduction

As high-k gate materials are being developed to replace SiO_2 in future generations of microelectronics devices, understanding their etching characteristics becomes vital for introducing the materials into the manufacturing process. Because some of high-k materials are quite inert to strong acids [1, 2], making it difficult to completely remove the high-k materials above the source and drain regions of the transistor. However, a systematic study of the etching of high-k materials for gate dielectrics application has not been reported, and in particular understanding of the surface reactions during the etching process is rather limited. The etching of high-k materials for gate dielectric application will probably become the most critical issue of integrating those materials into device fabrication. Thus, knowledge of the elementary surface reactions in plasma etching is essential for understanding etching reactions for high-k materials. The beam irradiation method is a useful tool in investigating the interaction of individual ion species or radicals with surfaces.

In the present work, we examined etching yield of HfO_2 resulting from irradiation of Ar^+ and CF_X^+ (X=1, 2, 3) ions which are contained in fluorocarbon plasma. By using fluorocarbon plasma, high selective SiO_2/Si etching processes have been developed in recent years, so that fluorocarbon plasma is a candidate for etching processes of high-k materials on Si.

2. Experimental

The low-energy mass-analyzed ion beam apparatus [3] is shown schematically in Fig. 1. The apparatus consists of an ion beam source and an ultra high vacuum (UHV) scattering chamber. Between the source and scattering chamber, there are three differentially pumping stages. Therefore, the scattering chamber was maintained at UHV condition during all experiments. As the ion beam, which was transported at 25 keV through an extraction electrode, contains impurity ions, a 90° mass-selecting electromagnet was used to select only the desired ions. After transported through the ion beam optics, they were decelerated to 200–2000 eV by deceleration electrodes and the ions irradiated on a substrate that was mounted on a manipulator with a Faraday cup. The flux of incident ions was measured by the Faraday cup at sample irradiation position. The etching depth, which results from irradiation of ions, was measured by an interferometry with a refractive index 1.987. Etching yields of ion irradiation were estimated from the incident ion flux and etching depth of the sample. The X-ray photoelectron spectroscopy (XPS) spectra were obtained for irradiated surface to determine the surface compositions.

Typical experimental conditions are listed in Table 1. The HfO_2 films used in this work were deposited by chemical vapor deposition.

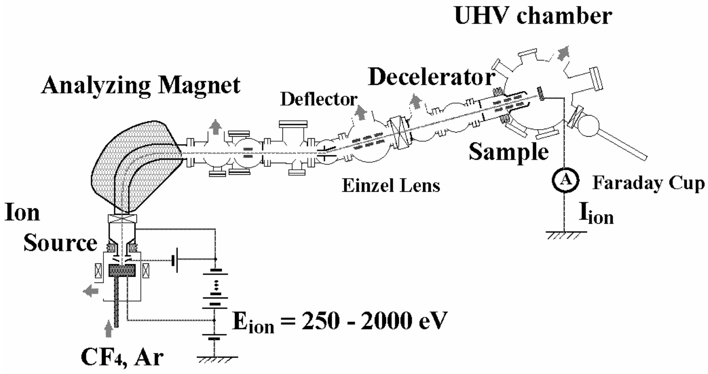

Fig.1 Schematic diagram of mass-analyzed low-energy ion-beam apparatus.

Ion species	Ar^+, CF_X^+ (X = 1, 2, 3)
Mass resolution	$M/\Delta M > 80$
Ion energy	200 ~ 2000 eV (ΔE < 20eV)
Ion current density	5 ~ 20 $\mu A/cm^2$
Ion dose	< 1×10^{17} ions /cm^2
Base pressure	< 7×10^{-8} Pa

Table 1 Typical experimental conditions.

3. Results and Discussion

Figure 2 shows the HfO_2 etching yield dependence on incident ion species at 1000 eV. The etching yield of CF_3^+ ion was larger than that of Ar^+ which only resulted from physical sputtering. This suggests that the etching yield of CF_3^+ was slightly enhanced by the chemical effects of incident ions. However, the etching yield decreased with decreasing fluorine atom content in incident CF_x^+ ion. This indicates that carbon atom contained in CF_x^+ ion behaves as suppressor for HfO_2 etching. Figure 3 shows the ion energy dependence of etching yield. Etching yields of Ar^+, CF_2^+ and CF_3^+ increased with increasing ion energy. The etching yield of CF_3^+ scaled linearly with the square root of ion energy with threshold energy. This indicates that the etching reaction is limited by the momentum transfer to the etched film in a collision cascade [4].

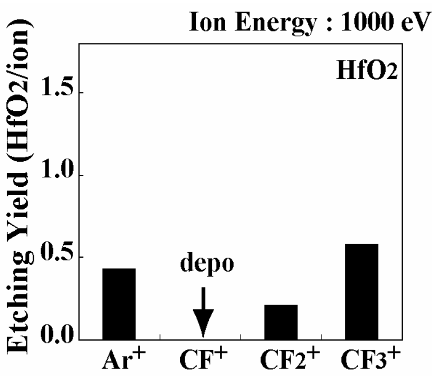

Fig.2 Etching yields of HfO_2 for Ar^+ and CF_X^+(X=1, 2, 3) ion with energy of 1000 eV.

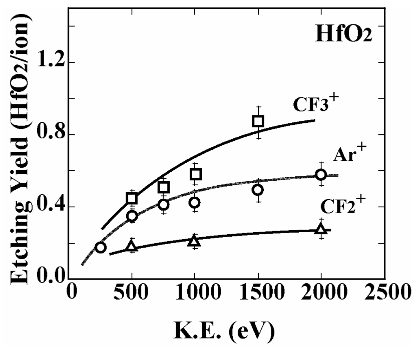

Fig.3 Etching yields of HfO_2 as a function of ion energy

In the case of CF^+ ion irradiation up to 2000 eV, a steady etching did not occur. Figure 4 shows the dose dependence of the thickness irradiated by CF^+ ion at 1000 eV. At about 3.5×10^{16} cm^{-2}, the thickness starts to increase by deposition. We analyzed the irradiated surface with ex-situ XPS to determine the surface composition (Fig.5). After irradiation with a dose of 0.5×10^{16} cm^{-2}, signals from carbon and fluorine were clearly observed. At an ion dose 1.0×10^{16} cm^{-2}, chemical shifts by bonding to neighboring fluorine atoms were observed in the C_{1s} signal. As the ion dose exceeded

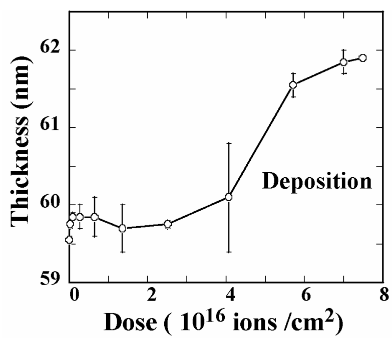

Fig.4 Change in thickness of irradiated HfO_2 film as a function of CF^+ ion dose with energy of 1000 eV.

1.0×16 cm^{-2}, the signal intensities for both Hf4f and O_{1s} decrease because of deposition of amorphous fluorinated carbon (*a*-C:F) film. Thus, the transition to the *a*-C:F deposition is caused by surface modification in which carbon accumulates on the surface at the early stage when CF^+ ion dose increases.

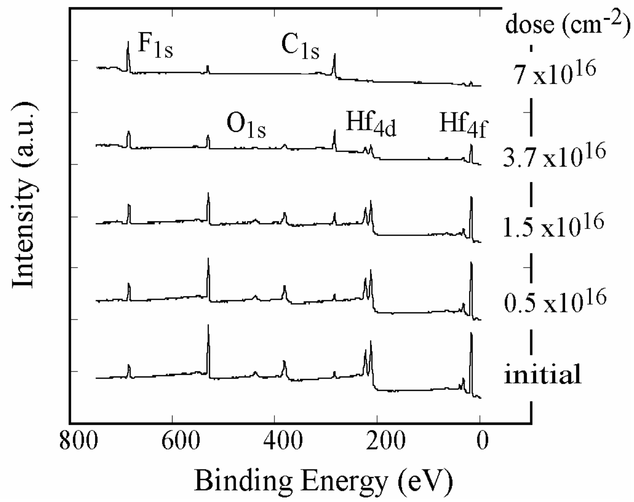

Fig.5 Series of XPS spectra of HfO_2 surfaces after each dose of CF^+ ion irradiation with energy of 1000 eV.

Next, we discuss the etching properties of HfO_2 with respect to Si either in Ar or fluorocarbon plasma from the aforementioned etching yields. We obtained the following: 1) The selectively of HfO_2 to Si using Ar plasma, in which etching is caused by physical sputtering, is about 0.9. 2) The etching rate in fluorocarbon plasma strongly depends on the composition of ionic species. However, if it is assumed that radicals contained in fluorocarbon plasma play no significant role in etching, the etching selectivity is higher than 1.

4. Conclusion

We have studied etching for HfO_2 by Ar^+, CF_X^+(X=1, 2, 3) ion with mass-analyzed ion beam. The etching yields for HfO_2 ion irradiation were determined as a function of incident ion energy in the range of 200-2000 eV. We show that the etching yields decreases with decreasing fluorine atom content in incident fluorocarbon ions, and scaled linearly with the square root with ion energy. We found that *a*-C:F film deposits on the HfO_2 surfaces under CF^+ ion irradiation.

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