Plasma Chemical Kinetics of Silicon Dioxide Etching with
Fluorocarbon Compounds

by

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ABSTRACT

Plasma chemical kinetics of oxide etching with fluorocarbon compounds were studied in this work. Surface kinetics and gas phase kinetics of oxide etching were studied in inductively-coupled and capacitively-coupled plasmas. The first part of this work is a study of the surface kinetics of silicon dioxide etching and fluorocarbon deposition in inductively-coupled fluorocarbon plasmas. Surface reaction kinetics were studied by measuring etching and deposition rates with quartz crystal microbalance (QCM) as a function of ion bombardment energy, ion-to-neutral flux ratio, ion-impinging angle, and surface temperature. The characterization of surface kinetics is essential for the feature profile evolution modeling of silicon dioxide etching in inductively-coupled fluorocarbon plasmas to understand various concerns in oxide etching: RIE (ractive ion etching) lag, inverse RIE lag, etch stop, trench, bowing and so on. Fluorocarbon deposition is known to be responsible for some of the concerns above. C_2HF_5, C_2F_6, $C_2H_4F_2$ and C_4F_8 were used in this study. Two different fluorocarbon deposition mechanisms are justified in this work – neutral deposition and ion-enhanced deposition. The low-energy ions are believed to enhance the deposition rates by creating active sites and flurorcarbon neutrals deposit on the active sites with higher sticking probability. A surface kinetic model is suggested to explain the ion-enhanced mechanism and shows good agreement with experimental data. The deposition rate is sensitive to surface temperature and decreases as temperature is increased. Angular dependence of oxide etching has been studied and it indicates when flurorcarbon deposition is severe, etching yields decrease significantly as the incident angle increases and deposit fluorocarbon at a high incident angle above 60°.

The second part of this work is environmentally motivated and the goal is to reduce the emission of perfluorocompounds (PFC) such as CF_4, C_2F_6, NF_3, and SF_6. PFCs are global warming gases largely emitted from semiconductor industry, and they have very long lifetime of up to 50,000 years in the atmosphere (CF). A plasma cleaning process after oxide deposition is studied in this work, because it is known to be the largest PFC emission source in semiconductor industry. Using a capacitively-coupled plasma enhanced chemical vapor deposition (PECVD) reactor, oxide was deposited in tetraethyorthosilicate (TEOS)/O_2 and etched with various hydrogen and/or oxygen containing fluorocarbon compounds. The kinetic study shows linear correlation between silicon dioxide etching rate and atom fluorine density in the gas phase. Low activation energy of about 0.05 eV was measured at 30°C - 100°C and about 0.16 eV of activation energy measured at 200° - 400°C. The activation energy measurements indicate that ion-enhanced etching is the dominant mechanism below 100°C, and ion flux and energy are limited. However above 200°C atomic F spontaneous chemical etching is dominant and atomic

fluorine concentration is the only limiting factor for the oxide etching rate. This result indicates that high atomic fluorine density should be maintained to achieve the high oxide etching rate in the chamber cleaning condition which runs at about 400° C. A combined etching rate model was developed and fit experimental data satisfactorily. Effluent analysis with GC (gas chromatography)/ MS (mass spectroscopy) shows that a significant amount of CF_4 and C_2F_6 is made in the chamber cleaning process due to recombination reaction of carbon and fluorine for all fluorocarbon compounds. This indicates that carbon-containing compounds may not be good candidates as alternative chemicals for PFC.

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