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On the relationships between plasma chemistry, etching kinetics and etching residues in CF_4+C_4F_8+Ar and CF_4+CH_2F_2+Ar plasmas with various CF_4/C_4F_8 and CF_4/CH_2F_2 mixing ratios

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ABSTRACT

In this work, we investigated how the CF_4/C_4F_8 and CF_4/CH_2F_2 mixing ratios in CF_4+C_4F_8+Ar and CF_4+CH_2F_2+Ar inductively coupled plasmas influence plasma parameters, densities and fluxes of plasma active species and etching characteristics (process kinetics, etching rates and selectivities, etching residues) for both Si and SiO_2. For this purpose, we employed surface diagnostics by x-ray photoelectron spectroscopy (XPS), plasma diagnostics by Langmuir probes and 0-dimensional plasma model. It was found that the substitution of CF_4 for CH_2F_2 causes the stronger decreases in both F atom flux and ion energy flux compared with the effect of C_4F_8. Accordingly, the CF_4+CH_2F_2+Ar mixture provides the deeper fall of both Si and SiO_2 etching rates, leaves the higher amount of the fluorocarbon polymer on the etched surface (especially in the case of Si) and results in a bit higher SiO_2/Si etching selectivity. It was shown also that, in both gas systems, the etching process appears in the steady-state regime. The mechanisms influencing the etching/polymerization balance were discussed based on the correlation between Si and SiO_2 etching rates with fluxes of plasma active species.

1. Introduction

Fluorocarbon (FC) gases with a general formula of $C_xH_yF_z$ are widely used in the microelectronic industry for dry patterning of silicon wafers and dielectric (SiO_2, Si_3N_4) thin films [1,2]. Among these, the CF_4 is characterized by the highest F/C ratio and provides the domination of etching over the surface polymerization process under the typical reactive ion etching conditions [3,4]. Being used for the etching process, the CF_4 is frequently combined with Ar or O_2 in forms of binary CF_4 + Ar or CF_4 + O_2 gas mixtures with the aims of accelerating the physical etching pathway, increasing the F atoms yield and suppressing polymerization on the surfaces which are in a contact with plasma [4,5]. The more polymerizing fluorocarbons (C_4F_6, C_4F_8, CHF_3 and CH_2F_2) are normally used for the etching processes which require as much as possible SiO_2/Si etching selectivity. The nearest example is the etching of contact holes through the SiO_2 insulating films to poly- or mono-crystalline silicon under layers where one should obtain the submicron dimensions together with the high aspect ratio. From Refs. [3–7], it can be understood that the higher SiO_2/Si etching selectivity may be obtained when both Si and SiO_2 etching rates are sufficiently influenced by the solid-state diffusion of etchant species through the FC polymer film. In this case, the thickness of the FC polymer film on SiO_2 appears to be lower (due to the destruction of polymer in the reactions with surface oxygen atoms [6,7]), and the SiO_2 etching rate exceeds that for Si. At the same time, together with increasing SiO_2/Si etching selectivity, the decrease in absolute Si and SiO_2 etching rates as well as an increase in etching residues take place [5–7]. These facts also make difficulties for etching process optimization.

Though the etching mechanisms for Si and SiO_2 in various fluorocarbon-based gas systems have been explored with enough details [2–5], there are several issues which need additional attention. First, the most of existing studies have the experimental nature and discuss both etching and polymerization effects only through the relationships between input process conditions (pressure, input power and bias power), measured etching rates and FC polymer film characteristics (thickness, composition and permittivity for F atoms). Therefore, the detailed data on the heterogeneous stages of the etching process in most of cases are not

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matched with the changes in gas-phase characteristics such as internal plasma parameters, kinetics and densities of plasma active species. In such situation, any accurate and reasonable results (see, for example, Refs. [8–10]) do not provide the understanding of the whole process pathway, seem to be valid for the given reactor only and thus, have the limited value for the etching process optimization. And secondly, one can expect that the reasonable balance between SiO_2/Si etching selectivity, absolute etching rates and etching residues may be achieved by the use of two FC gases in one gas mixture. In such gas system, the less polymerizing component (for example, CF_4) provides the effective generation of etchant species while the more polymerizing component creates the favorable conditions for obtaining high SiO_2/Si etching selectivity. Accordingly, the mixing ratio between these two components directly influences the etching/polymerization balance and thus, allows one to adjust the output process characteristics. Though some binary (CF_4 + other FC gas) mixtures have been studied for the dry etching applications [11–13], the corresponding works were focused rather on technological aspects than on the analysis of plasma chemistry. At the same time, it is quite clear that the mixing of CF_4 with other $C_xH_yF_z$ ($x > 1$ or $y > 0$) gas mandatory results in more complicated reaction scheme, changes plasma parameters as well as influences the formation/decay kinetics and fluxes for all types of plasma active species. Therefore, an understanding of plasma chemistry in the gas systems with two fluorocarbon components as well as the comparative studies of such systems are the important tasks for the correct determination of etching mechanisms, optimal choice of gas chemistry for the given etching process and thus, for the future progress in the dry etching technology.

In our previous work [14], we carried out the phenomenological (without the surface analysis) study regarding to the influence of CF_4/C_4F_8 mixing ratio in CF_4+C_4F_8+Ar gas mixture on plasma parameters, active species kinetics and etching rates for Si, SiO_2 and photoresist. It was found that the substitution of CF_4 for C_4F_8 decreases both Si and SiO_2 etching rates (by 2.5 and 2 times respectively), but increases by ~ 30% the SiO_2/Si etching selectivity. The correlations between the changes in etching rates and internal plasma parameters allowed one to attribute the obtained effects to the decreasing F atom flux and increasing flux of polymerizing radicals. However, this wok did not answer the question about the etching residues. Also, in Ref. [15] we have performed the similar study concerning the effect of CF_4/CH_2F_2 mixing ratio on the etching characteristics of SiC in CF_4 + CH_2F_2 + N_2 +Ar inductively coupled plasma. From this work, it can be understood that an increase in CH_2F_2 fraction in a feed gas from 0 to 25% maintains the near-to-constant SiO_2 etching rate as well as increases the SiO_2/Si etching selectivity by ~1.6 times. Unfortunately, the results of mentioned works cannot be compared and analyzed directly because of the different both input process conditions and the non-FC mixture components. Therefore, the choice of an optimal additive FC gas in the CF_4-based gas mixture requires additional investigations. The goal of current work was to compare how the CF_4/C_4F_8 and CF_4/CH_2F_2 mixing ratios in CF_4+C_4F_8+Ar and CF_4+CH_2F_2+Ar inductively coupled plasmas under one and the same operating conditions influence kinetics of plasma active species, their densities and fluxes as well as the etching characteristics (process kinetics, etching rates and selectivities, etching residues) for both Si and SiO_2. The Si and SiO_2 were chosen as the test materials because of both rich etching experience and well-defined etching mechanisms in the fluorocarbon-based plasmas. In order to get the more detailed information compared with Refs. [14] and [15], we employed the analysis of etched surfaces by x-ray photoelectron spectroscopy (XPS) as well as performed the combined analysis of bulk and heterogeneous chemistries aimed at establishing the relationships between the changes in the gas-phase plasma parameters and etching characteristics. In the last field, the main attention was focused on the determination of the gas-phase-related factors (in fact, the flux-to-flux ratios) which directly characterize the amount of deposited polymer and thus, allow one to control the etching/polymerization balance and the SiO_2/Si etching selectivity through the choice of the appropriate additive gas.

2. Experimental and modeling details

2.1. Experimental conditions and techniques

Both etching and plasma diagnostics experiments were performed in planar inductively coupled plasma (ICP) reactor described in our previous works [16,17]. The reactor had a cylindrical ($r = 15$ cm) chamber made from the anodized aluminum. The 5-turns copper coil was connected to the 13.56 MHz power supply and located above the 10 mm thick-horizontal quartz window on the top side of the chamber. A distance (l) between the window and the bottom electrode used as a substrate holder was 12.8 cm. The bottom electrode was connected to 12.56 MHz power supply to maintain a negative dc bias voltage (U_{dc}). The etched samples (the fragments of oxidized or non-oxidized Si (111) wafers with the size of about 2 × 2 cm^2) were placed in the center of the bottom electrode. The temperature of the bottom electrode was stabilized at 17 °C using the water-flow cooling system. The etched depths were measured using a surface profiler (Alpha-step 500, Tencor). For this purpose, we developed the line striping of the PR (AZ1512, positive) with the line width/spacing ratio of 2 μm/2 μm. The initial thickness of the PR layer was about 1.5 μm.

The experiments were performed at fixed total gas flow rate (q = 60 sccm), gas pressure (p = 10 mTorr), bias power (W_{dc} = 150 W) and input power (W = 800 W). The last value corresponds to the input power density $W' = W/\pi r^2 l$ of 0.8 W/cm^3. The initial compositions of CF_4+C_4F_8+Ar and CF_4+CH_2F_2+Ar gas mixtures were set by adjusting the flow rates of the corresponding gases. Particularly, the Ar flow rate q_{Ar} was fixed at 20 sccm, so that the fraction of Ar in the feed gas $y_{Ar} = q_{Ar}/q$ was always 33%. The fluorocarbon gases were mixed at various ratios within $q_{CF_4} + q_{C_4F_8}$ or $q_{CF_4} + q_{CH_2F_2} = 40$ sccm while the maximum flow rate for C_4F_8 or CH_2F_2 did not exceed 15 sccm. Accordingly, the maximum fractions of C_4F_8 or CH_2F_2 in the corresponding gas mixtures reached 25%.

Plasma parameters were examined by double Langmuir probe (LP) (DLP2000, Plasmart Inc.). The probes were installed through a hole on the sidewall of the reactor chamber at 5.7 cm above the bottom electrode and centered in a radial direction. The output data were the electron temperature (T_e), ion current density (J_+) and floating potential (U_f). The treatment of $I - V$ curves was based on the Johnson & Malter's double probes theory [18]. In order to obtain the total positive ion density (n_+) from the measured J_+, we used the Allen-Boyd-Reynolds (ABR) approximation $J_+ \approx 0.61 e n_+ \upsilon$ [19], where υ is the ion Bohm velocity without accounting for negative ions. Earlier, it was shown that such an approach works adequately even for more electronegative plasmas [16,20]. In order to exclude the influence of the FC polymer film on the LP results, we conducted a set of preliminary experiments, where the $I - V$ curves were recorded continuously at fixed-feed gas composition and operating parameters. Even for the gas systems with the maximum fraction of the high polymerizing fluorocarbon component (42% CF_4 + 25% C_4F_8 + 33% Ar or 42% CF_4 + 25% CH_2F_2+ 33%Ar), the differences between the results of such measurements did not exceed the standard experimental error for a period of at least 10 min after the plasma was turned on. Also, throughout the main