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Analysis of the impact of different additives during etch processes of dense and porous low-*k* with OES and QMS

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ABSTRACT

The focus of this paper is the impact of CF_4 based plasma etch processes with the additives argon and C_4F_8 on material properties and geometrical parameters of etched trenches using dense and porous SiCOH. Argon and C_4F_8 were added to change the radical to ion composition and to shift the carbon to fluorine ratio, respectively. With several techniques, FTIR, spectral ellipsometry and contact angle measurements, modifications in the structure of the materials and their surface conditions were analyzed. To understand the influences of the additives on the plasma conditions, optical emission spectroscopy (OES) and quadrupole mass spectrometry (QMS) were used to estimate the composition of the plasma *in situ*.

For the additive argon, a slightly enhanced etch rate and an increased refractive index due to serious plasma damage for porous SiCOH was observed. At higher Ar flow rates peaks of $Si_2O_4H_x$ clusters in the QMS spectra and increased CO and O lines, measured with OES, indicate a higher sputter yield on the SiCOH network. SEM cross-sections show, that argon has no effect on the sidewall geometry of etched trenches. A higher CH/CN line in the OES spectra indicates an enhanced sputter effect of the SiCN films in via bottoms.

For C_4F_8 addition results of spectral ellipsometry show a decreased etch rate and refractive index. Using FTIR the formation of a polymer film on the surface was observed. Higher C_2 lines in the OES spectra are indications of enhanced polymerization efficiency. Finally, the addition of C_4F_8 decreases the etch rate in the trench sidewalls and therewith assumedly the sidewall damage.

1. Introduction

In the last years the low-*k* material SiCOH replaces SiO_2 nearly complete as interlevel dielectric to fabricate ULSI devices with high performance, low cross talk noise and low power dissipation. Commonly used SiCOH materials consist of a $SiO_{4/2}$ matrix with 10–15% incorporated hydrophobic CH_3 groups in an $O{\equiv}Si{-}CH_3$ structure. These groups decrease the density and polarizability and avoid moisture absorption, with the result of a lower *k*-value in comparison to SiO_2. To reach values lower than 3.0 artificial pores in the SiCOH films are needed. Typical porous SiCOH materials have a porosity of 30–50% with an average pore size of 2–2.5 nm [1].

The trench and via patterning of dense and porous SiCOH films with reactive ion etching (RIE) results in various challenges, especially for further scaling of the interconnect dimensions. During these processes SiCOH materials are damaged, with the result of a serious increase in their *k*-values. The damage causes are penetration of in diffusing active radicals, radiation and ion bombardment [1,2], in which the combination of radiation and radicals as well as the ion bombardment were identified as strongest mechanisms [2]. The consequences are an increased hydrophilic behavior due to the loss of CH_3 groups and a degradation of the film morphology [2]. These effects are mostly important on the sidewalls of trenches and vias and results in an increasing of the line to line and the interlevel capacitance.

Fluorocarbon based etch plasmas provide beside the etch reaction a plasma enhanced deposition of a polymer film, which has a $-(CF_2)_n-$ structure. This film offers a possibility to protect the sidewalls against damaging ions and radicals. The etch process can be shifted sensitively between etch and polymerization mechanism by varying the carbon to fluorine ratio $R_{C/F}$. A higher fluorine content enhances the etch reaction whereas a carbon rich chemistry increases the polymerization efficiency [3]. The additives H_2 and O_2 are able to form HF and CO_x compounds and have therewith an influence on the fluorine and carbon content, respectively.

The dependence of etch process results on process parameters is very complex. For the understanding it is necessary, to estimate the chemical composition of the plasma. OES and QMS are

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common methods to measure ion, molecule and fragment concentrations of possible species during the etch process *in situ* [4,5].

2. Experimental

In this work the alteration of the etch reaction using the additives Ar and C_4F_8 were aspired. With the argon addition a change of the ion to radical ratio can be achieved because argon is an inert material and not able to form reactive radicals. In the literature was reported, that argon may enhance the production of CF and CF_2 radicals, which act as a precursor for the formation of polymer films [4]. A C_4F_8 addition offers the possibility, to control carbon to fluorine atomic ratio $R_{C/F}$ directly with the CF_4 and C_4F_8 fluxes, shown in Eq. F1.

$$R_{C/F} = \frac{F_{CF_4} + 4F_{C_4F_8}}{4F_{CF_4} + 8F_{C_4F_8}}, \quad \frac{1}{4} \leqslant R_{C/F} \leqslant \frac{1}{2} \tag{F1}$$

All etch processes were performed in an Oxford Plasmalab system 100. The ICP power was adjusted to 1000 W and bias power to 60 W. The pressure in the etch chamber was 7 mTorr and the CF_4 flow was predefined with 12 sccm. The flow rates of the additives argon and C_4F_8 were variegated from 2 to 8 sccm.

The OES spectra were collected with an USB 4000 fiber optic spectrometer in combination with a 74-UV silica collimating lens. The spectra were measured from 180 to 890 nm in steps of 0.2 nm. For the QMS spectra an UTI 100C quadrupole mass spectrometer were used. It was connected to the plasma chamber using a standard KF-40 flange. Atoms and molecules in the reactor rest gas

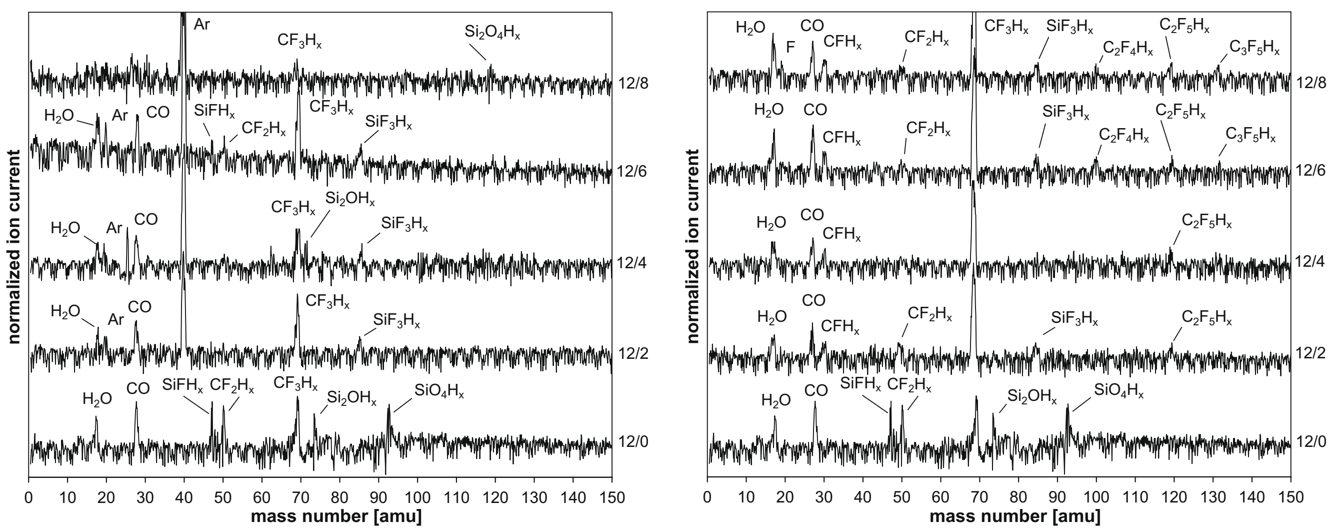

Fig. 1. QMS spectra measured during etch processes (left) with Ar addition and (right) with C_4F_8 addition.

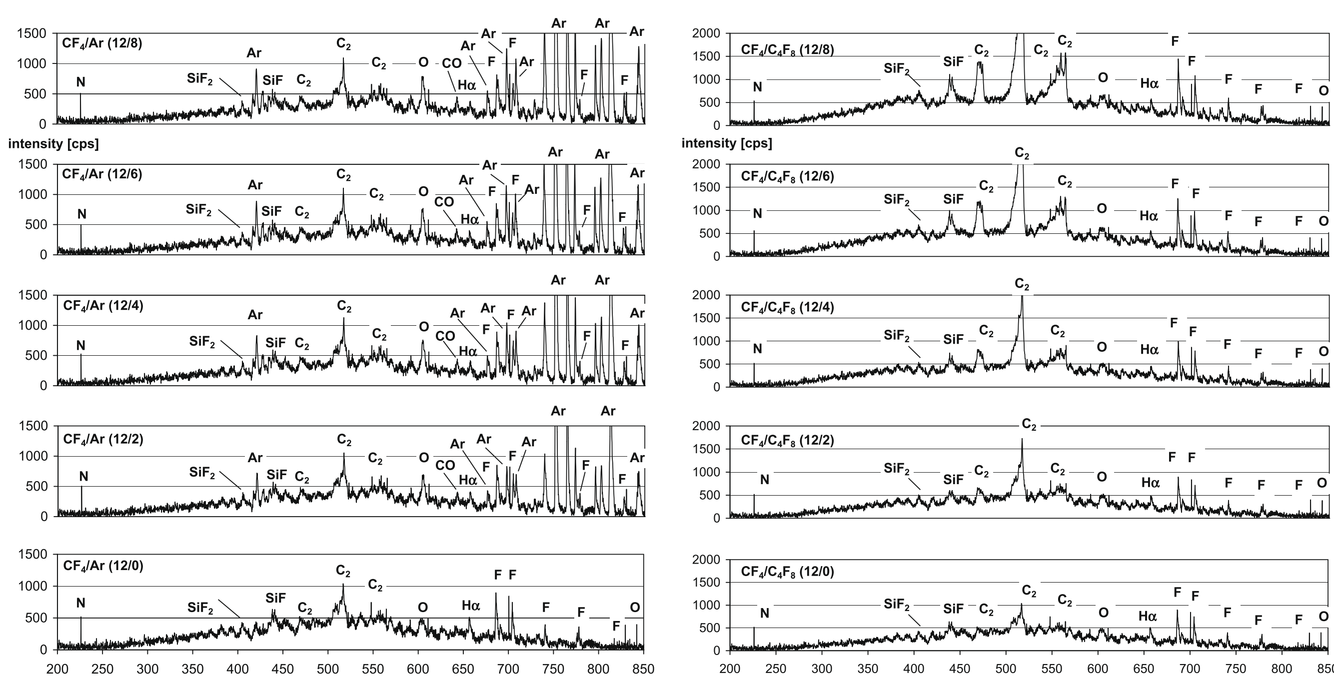

Fig. 2. OES spectra measured during etch processes (left) with Ar addition and (right) with C_4F_8 addition.