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Efficiency of reducing and oxidizing ash plasmas in preventing metallic barrier diffusion into porous SiOCH

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ABSTRACT

This work focuses on the efficiency of reducing and oxidizing plasma chemistries in preventing metallic barrier diffusion into porous dielectric materials (SiOCH with a *k* value close to 2.2, porosity content around 40%). The ash processes have been performed on SiOCH coated blanket and patterned wafers in either reactive ion etching (RIE) or downstream (DS) reactors. The Rutherford backscattering spectroscopy technique (RBS) has shown that titanium based compounds diffuse into the blanket porous SiOCH without treatment during a typical TiN barrier deposition process by chemical vapor deposition (CVD). The metallic barrier diffusion is strongly limited on blanket wafers when the porous SiOCH has been previously modified (partially or fully) by ash plasmas (RIE-O_2, RIE-NH_3, DS-H_2/N_2 and DS-O_2/N_2) while the metallic barrier diffusion occurs with no modifying ash plasmas (DS-H_2/He). We have shown that ellipsometric porosimetry (EP) measurements clearly point out that no complete pore sealing is achieved with all the investigated ash plasmas. Energy-filtering transmission electron microscopy experiments (EFTEM) performed on single damascene structures have revealed significant titanium diffusion into the porous dielectric lines for DS-H_2/He and RIE-O_2 and sidewalls modification of the porous SiOCH lines (lower C/O ratio) for all the ash plasmas. The *RC* product (resistance × capacitance) have been extracted from the single damascene structures and the evolution of *RC* product will be discussed in terms of lines modification (titanium diffusion and porous SiOCH modification).

1. Introduction

For 45 nm technology node and beyond of the CMOS technology, the interconnections require the integration of low-*k* dielectric materials, such as SiOCH films, with effective *k* values between 2.5 and 2.9 [1]. To reach this goal, porosity is introduced into the materials leading to an increased sensitivity of the material to etch and ash plasmas.

In a previous article, we have shown that porous materials are altered during fluorocarbon (FC) plasma exposures leading to a film degradation that directly scales with the degree of porosity in the material [2].

After exposures to oxidizing downstream (DS) plasmas (DS-O_2, DS-N_2/O_2) porous SiOCH are fully modified (hydrophobic and total carbon depletion). We have also shown that such porous materials are partially altered after exposures to capacitive discharge (RIE-NH_3 and RIE-O_2) and to DS-N_2/H_2 leading to the formation of a hydrophobic and dense top layer ($SiO_xN_yH_z$ after RIE-NH_3 and DS-N_2/H_2 plasmas exposure and SiO_xH_y RIE-O_2 plasma exposure) [3]. In all cases, *k* values are higher than that this of the pristine material, which is mainly attributed to moisture uptake [3].

Another main issue that has to be considered today is the metallic barrier diffusion through the pores which can lead to an increase of the *k* value. Indeed the continuous reduction in dimensions leads to the development of new metallic diffusion barrier layer depositions for copper/low-*k* dielectrics interconnects. Thus chemical vapor deposition (CVD) and atomic layer deposition (ALD) become more attractive alternatives than current physical vapor deposition (PVD) because they enable the deposition of very thin conformal metallic layer [4,5]. But the CVD or ALD deposition techniques on such materials bring in serious issue since one of the key issues is the risk of precursor diffusion through the pores [6]. It has been reported that the effects of the diffusion of organo-metallic precursors into the pores leads to an increase of the effective *k* value and higher leakage current between metal lines [7].

Therefore, the porosity of such materials leads to serious integration issues which are: (i) their sensitivity to etch and ash

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plasma exposures [2,3], (ii) the risk of metallic precursor diffusion through the pores during conformal barrier deposition by CVD or ALD [6,7].

To reduce the precursor diffusion, sealing the pores on the sidewalls of the damascene structure is one of the emerging solutions. To achieve a pore sealing, different ways have been proposed in the literature such as the deposition of a thin dense layer [6,8] and the modification and densification of the sidewalls surface by plasma treatments [9–12]. Other techniques such as UV treatment [13] have also been investigated.

This article will focus on the capabilities of different ash plasmas in sealing the porous SiOCH surface. We will study the impact of the surface modification induced by reducing and oxidizing plasmas (DS and RIE mode) on metallic precursor diffusion into the porous SiOCH. Experiments will be performed on blanket porous films and patterned wafers. Single damascene structures will be used to determine the real impact of the modified layer on the *RC* product.

2. Experimental

Plasma experiments have been performed either in a magnetically enhanced reactive ion etcher (MERIE) eMAX™ from applied materials using O_2 and NH_3 or in a photoresist Novellus PEP Iridia™ microwave stripper using oxidizing and reducing chemistries H_2/He (3:1), H_2/N_2 (3:1) and O_2/N_2 (3:1) [3].

The eMAX™ reactor generates capacitively coupled plasmas. The wafer sits on an electrode powered with a RF generator operating at 13.56 MHz in a power range between 100 and 2000 W. The reactor is surrounded by four electromagnets producing a rotating magnetic field (0.5 Hz, 0–200 Gauss) leading to an increase in plasma density. In this study, the reactor has only been operated in a mode without magnetic field (RIE mode). The pressure in the chamber is set at 75 mTorr by a motorized throttle valve and the power is set at 200 W. Wafers are clamped using an electrostatic chuck and the wafer temperature is kept constant at 15 °C by a helium backside temperature regulation. Before each experiment, a cleaning process (O_2 plasma) using a blanket silicon wafer and a conditioning process are performed in order to generate reproducible chamber conditions from wafer to wafer.

The Novellus PEP Iridia™ photoresist stripper features downstream (DS) microwave plasma (2450 MHz) and a RF biased platen (13.56 MHz). The substrate temperature is controlled by infrared lamp heating. For this study, the substrate temperature is set at 270 °C and the downstream mode has only been used (DS mode). Before each run of plasma, a conditioning process on a blanket resist wafer is performed in order to generate reproducible chamber conditions from wafer to wafer. Pump/purge steps are included into recipes to avoid any possible air contamination.

With a standard KrF 248 nm photoresist, the ash efficiency is estimated at 150 nm min^{-1} for RIE-NH_3, DS-H_2/He and DS-H_2/N_2. For oxidizing plasmas, the ash rate is 300 nm min^{-1} for RIE-O_2 and one order of magnitude higher (>1 μm min^{-1}) for DS-O_2/N_2. For the experiments presented in the next sections, all process durations are performed with a step time adapted to remove at least 150 nm of post etch remaining resist. Therefore, the process time is set at 60 s for reducing plasmas, whereas the time is set at 30 s for all oxidizing chemistries.

In this study, we have used 200 mm diameter silicon wafers coated with 300 nm thick spin-on porous MSQ from JSR (LKD-5109™) with a dielectric constant k close to 2.2 (porosity content around 40%). The porous SiOCH film consists of a siloxane network terminated by methyl groups. The modifications induced by the different ash plasmas investigated in this work have been presented in a previous paper [3].

To characterize the diffusion of metallic precursor, a 10 nm thick TiN barrier has been deposited on the porous SiOCH material by chemical vapor deposition (CVD) and physical vapor deposition (PVD) after exposure to the different ash plasmas. The CVD process consists of a pyrolysis of tetra dimethylamino titanium (TDMAT) at 380 °C coupled with a plasma treatment performed in a 200 mm CVD chamber. The PVD process uses a titanium target with a mixture of Ar/N_2 at a temperature of 100 °C. Both depositions are performed in 200 mm chambers. To determine the capabilities of the different ash plasmas to prevent metal barrier diffusion into the porous SiOCH, Rutherford backscattering spectroscopy technique (RBS) measurements have been performed with an incident 2 MeV He^+ beam. The backscattered He atoms were analyzed either in normal incidence (for DS samples) or at 75° (for RIE samples).

The pore sealing efficiency of the different plasmas has been estimated by ellipsometric porosimetry (EP) using a SOPRA ellipsometer. This technique, which allows the measurement of open porosity, consists of a rotating polarizer spectroscopic ellipsometer coupled with a vacuum chamber which is operated at a pressure ranging from 10^{-3} Torr to the saturation vapor pressure (P_s) of the adsorptive. The solvent used is methanol (P_s = 115 Torr at room temperature, refractive index at 633 nm n_{met} = 1.329). Ellipsometric spectra were recorded simultaneously between 1.55 and 4.13 eV with a CCD detector. The angle of incidence was set at 60.15°. Thickness and refractive index of the dielectric layers were calculated from the ellipsometric data as a function of the relative pressure ($P_{rel} = P/P_s$, with P the chamber pressure) using a Cauchy law in adjunction with a Lorentz oscillator to take into account the absorption band in the ultraviolet region. On the basis of the Lorentz–Lorenz effective medium approximation, the fraction of solvent adsorbed in the pores is calculated at each relative pressure. When the saturated pressure is reached, this fraction corresponds to the open porosity of the sample [14].

Complementary experiments have also been performed on single damascene structures (one level of metal) in order to evaluate the impact of the different ash plasmas on sidewall modifications and metal barrier diffusion into the dielectric lines. The single damascene structures have been achieved using a single hard mask strategy (100 nm thick SiC hard mask). The porous SiOCH film has been deposited on a 30 nm thick SiC etch stop layer. After photolithography and etching steps in fluorocarbon-based plasmas, wafers have been stripped using three different ash plasmas: (a) RIE-NH_3, (b) RIE-O_2 and (c) DS-He/H_2. It should be noted that DS-O_2/N_2 ash chemistry could not be studied since the porous SiOCH dielectric lines are completely etched away during this ashing step. Conventional metallization including TiN barrier deposition by CVD, copper seed and copper electrochemical deposition have then been carried out on the patterned dielectric trenches. The wafers were finally polished and passivated for electrical testings. The process flow as well as the final stack is represented in Fig. 1.

After the etch and ash steps of the patterned structures, the pore sealing of the trench sidewalls has been determined by ellipsometric porosimetry. In the case of patterned structures, ellispometric porosimetry cannot directly quantify the open porosity but can discriminate samples into which solvent can diffuse or not by a change of ellipsometric angle. After metallization, cross-section specimens of the patterned structures were prepared using a focused ion beam (FIB). These samples were then analyzed by energy-filtering transmission electron microscopy (EFTEM) using a JEOL 2010FEF omega filter (S)TEM. The TEM was operated at 200 kV with a 15 mrad objective aperture and a 20 eV energy selecting slit for EFTEM imaging. EFTEM images were acquired on a 1024 by 1024 pixel CCD camera binned by 4 with an exposure time of 30 s. Titanium diffusion profiles are extracted to compare the pore sealing effectiveness of the different treatments. The