Repairing oxygen plasma-damaged on low dielectric constant MSQ (methylsilsesquioxane) films with anneal

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Abstract Low dielectric MSQ (methylsilsesquioxane) films are obtained by spin-coating deposition on the p-Si (100) wafer. MSQ could be synthesized by one-step processing. Fourier transform infrared spectrometer (FTIR) was used to identify the network structure and cage structure of Si–O–Si bonds. C-V characteristic was used to calculate the dielectric constant. I-V characteristic was used to determine the leakage current density and the breakdown electric field. The results indicate that oxygen plasma exposure damaged the MSQ films by removing the carbon content on the surface of the films. Oxygen plasma exposure on MSQ films form the Si–OH bonds which induce to the increase of the hydrophilicity. The increase of the hydrophilicity on the surface of MSQ films increases the dielectric constant and leakage current density of MSQ films. Both the dielectric constants and leakage current density of MSQ films decreased with anneal at 350°C for 1.5 h in nitrogen ambient.

1 Introduction

According to the international technology roadmap for semiconductors (ITRS), dimensions of devices in ULSI (Ultra Large Scale Integration) circuits continue to shrink. These leads to increase the RC (Resistance-capacitance) delay. This RC delay can be solved by using high conductivity metal for interconnects and by using low-k materials as dielectric [1–3]. In order to reduce the dielectric constant of a film, we can introduce pores and reduce the polarization of chemical bonds. Dielectric materials presently under investigation are MSQ, HSQ (hydrogensilsesquioxane), SiCOH, porous silica and silicon-carbon and fluorinated carbon [4–6]. Methylsilsesquioxane (MSQ) is one of the promising candidates with a highly porous and three-dimensional network structure. MSQ has been used as low-k dielectric materials in electrical devices for many years [7, 8]. They are generally prepared by sol–gel method. The precursors are CH_3SiX_3, where X is generally CL, OCH_3 (methyltrimethoxysilane (MTMS)), or OC_2H_5 (methyltriethoxysilane (MTES)) [9, 10].

MSQ displays exceptional properties to polar solvents and has a water contact angle larger than 150° [11]. The so-called "superhydrophbic" material has been received many attentions by researcher recently [12]. A variety of deposition techniques have been reported to fabricate porous low-k materials. Sol–gel process is a very potential method because pore volume and pore size can be controlled at the chemical solution stage.

Plasma treatment is widely used for photoresist stripping, which is an indispensable step. Photoresist removal is commonly implemented with oxygen plasma treatment or by wet chemical stripping [13]. Many studies show that the dielectric constant of low-k materials can be increased after oxygen plasma treatments [14–16].

In this work, the MSQ was obtained by one-step processing. The structural and electrical properties of the spin-coated MSQ film which was exposed to oxygen plasma for 5 min are studied. The destroy can recover through anneal at 350°C in nitrogen ambient.

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Fourier transform infrared spectroscopy (FTIR) was used to identify the structural composition. C-V and I-V measurements were used to determine the dielectric constant, the break-down electric field, leakage current, respectively.

2 Experimental details

The overall experiment procedure for the synthesis of low-k organic silicon thin films is given in Fig. 1, and the detail in each step is described below.

The low-k organic silicon thin films were prepared by the hydrolysis-condensation reaction. First, 10 mL MTMS, 3 mL EtOH, and 0.02 mL deionized water were mixed for 10 min at room temperature (20°C), after which 0.1 mL HCL as catalyst was added to the solution to promote hydrolysis and early stage condensation reactions. Let the ph = 2, using the ph test paper. To make them react completely, the solution was stirred for 20 min at room temperature. After 20 min, the sol was spun on p-type Si (100) wafer at 2300 rmp for 20 s. The spun-on films were baked on a hot plate at 400^0 C for 1 min.
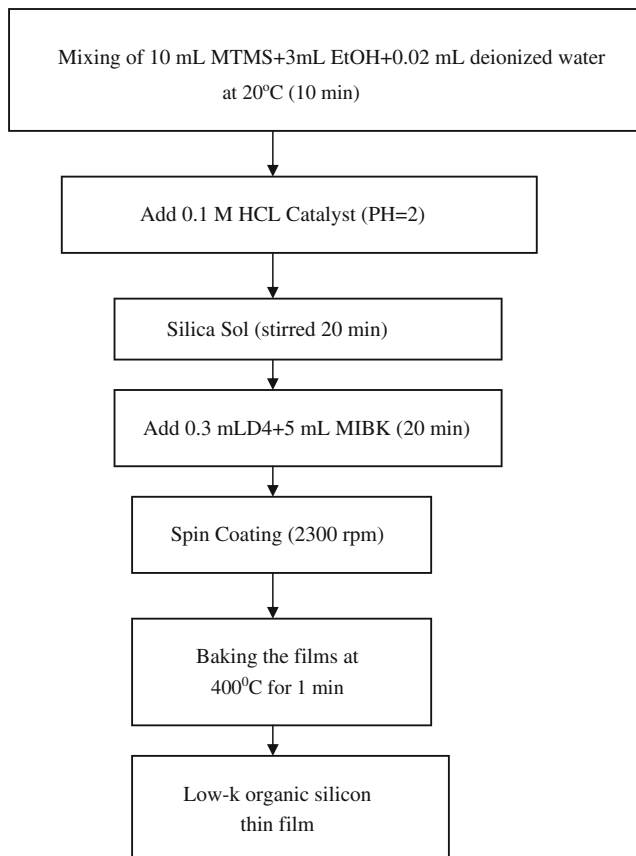
The oxygen plasma treatments were carried out in ECR-CVD (electron cyclotron resonance plasma-chemical vapor deposition) chamber. O_2 gas flow rate was 5 sccm and the substrate temperature was kept at 100°C. The r.f. (2.45 GHz) power was 300 w and the I_1 was 140 A and the I_2 was 110 A. The chamber pressure was maintained at 3 Torr. The treatment time was 5 min and followed by furnace anneal at 350°C for 1.5 h in nitrogen ambient. The thickness of film was measured by ET 350 profilometer. The film's chemical bonding and structure were characterized by FTIR spectroscopy using a JASCO 600 Plus with 4 cm^{-1} resolution. The dielectric constant (k) was extracted from the capacitance–voltage (C–V) characteristics which measured at 1 MHz frequency by HP4294A. The current–voltage (I–V) characteristic was measured by Keithley6517A. The C–V characteristics and the current–voltage (I–V) measurements were performed on MIS structures fabricated as Aluminum/MSQ/p-Si. The current–voltage (I–V) characteristics of these MIS structures were also measured to evaluate the leakage current

3 Results and discussion

Figure 2 shows the FTIR spectra of these thin films Fig. 2 (a) is the infrared absorption spectrum of the film with no oxygen plasma treatment and annealed at 300°C for 1.5 h, which reveals the Si–CH$_3$ bending mode at ~1274 cm^{-1}, and Si–H stretching mode in the range of ~2300 cm^{-1}. The shoulder peak is at ~1105 cm^{-1} (Si–O cage structure) and around 1024 cm^{-1} (network Si–O bond structure) absorption peak [17, 18]. Figure 2 (c) is the infrared absorption spectrum of MSQ film which was exposed on oxygen
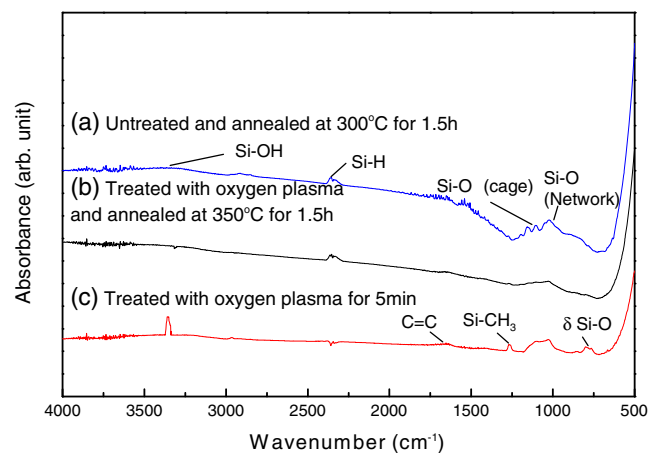

Fig. 1 Overall experiment procedure

Fig. 2 FTIR spectra of the films (**a**) untreated and annealed at 300°C for 1.5 h in nitrogen ambient; (**b**) treated with oxygen plasma for 5 min and annealed at 350°C for 1.5 h in nitrogen ambient; (**c**) treated with oxygen plasma for 5 min

plasma. The intensities of Si–H and Si–CH$_3$ peaks are decreased after oxygen plasma treatment. A broad peak at 3350 cm^{-1} which is characteristic of water absorption appeared. The Si–O peak shifts from 1016 cm^{-1} to 1041 cm^{-1}, as shown in Fig.2 (b–c). The results showed that during oxygen plasma treatment, oxygen radicals reacted with the functional groups of MSQ films and broke Si–CH$_3$ and Si–H bonds. This caused the MSQ films to generate dangling bonds. The dangling bonds can easily react with hydroxide ions in the environment and form Si–OH bonds. The contribution of the highly polarized Si–OH components will increase the k value of the films. Furthermore, the orientation polarization Si–OH bonds in the MSQ films lead to moisture uptake, which is responsible for the increase of k value and leakage current density [14]. On the other hand, part of these dangling bonds form Si–O bonds.

Figure 2 (b) is the infrared absorption spectrum of annealed at 350°C for 1.5 h in nitrogen ambient after oxygen plasma treatment. The intensity of Si–OH peak was decreased greatly. This can be explained on the basis of the following reaction.

$$Si - OH + OH - Si = Si - O - Si + H_2O$$
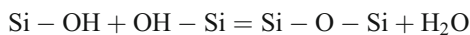
The Si–O peaks at 1068 cm^{-1} (network structure) increases, and the peak at 1108 cm^{-1} (cage structure) decreases. This result indicates that the bonding structure of the MSQ films changed from cage structure to a network structure.

The dielectric constant was calculated using the standard expression k=Cd/ε$_0$A, where C is the capacitance, d is the thickness of the film, ε$_0$ is the permittivity (8.854×10^{-12} fm^{-1}), and A is the electrode area. The thickness of these films was conducted by ET350 profilometer. They were estimated as 280 nm, 282 nm, and 290 nm, respectively. Figure 3 shows the dielectric constants (relative permittivity) which were measured at 1 MHz of these films. The dielectric constant of

(b) annealed at 350°C for 1.5 h in nitrogen ambient after oxygen plasma treatment film decreased from 2.8 to 2.6. The reason is that the structure transformation inside films. The Si–OH bonds were broken and formed the Si–O bonds [19].

Figure 4 shows the leakage current density of these films. The leakage current increased one order of magnitude after oxygen plasma exposure. They decreased after annealed at 350°C for 1.5 h. in nitrogen ambient. The density of the annealed film would increase because Si–OH (the water uptake) bonds were removed. Some surface open porous of the annealed film would be sealed because the network structure of Si–O increased after annealed.

NH$_3$ plasma post-treatment leads to a denser modified top layer which is the most efficient for surface pore sealing effect [20]. The extent of oxygen plasma-induced damage has been studied using a modulus mapping technique. The effective modulus of the near-surface region of a plasma-treated low-k film is significantly higher than that measured on the same type of low-k film without treatment [21]. The different plasma treatments can reduce rough surface and change thickness of films. The densities of the layers can be changed, which will lead to changes the k-values [22]. H2/He reactive plasma clean treatment (RPC) successfully prevented Cu from diffusing into low-k polymer after annealing at 200°C for 1000 h. The method is proven to be effective for characterizing and improving pore-sealing and barrier performance for Cu/porous ultra low-k interconnect [23]. The CHF$_3$ plasma treatment on the SiCOH film lead to a reduction in the flat-band voltage V_{FB} shift and leakage current of the Cu/SiCOH/Si structure, a decrease in surface roughness, and a deterioration of the hydrophobic property [24]. Porous low-k film damage is induced by plasma etching radicals [25]. Air-plasma exposure increases the defect concentrations by breaking silicon–hydrogen bonds.
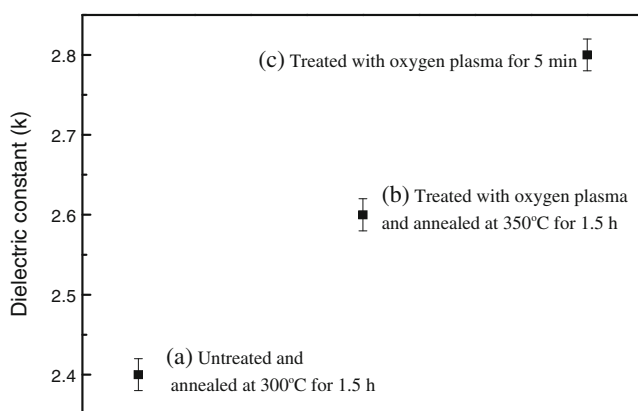
Fig. 3 Dielectric constants of these films (a) untreated and annealed at 300°C for 1.5 h in nitrogen ambient; (b) treated with oxygen plasma treatment for 5 min and annealed at 350°C for 1.5 h in nitrogen ambient; (c) treated with oxygen plasma for 5 min
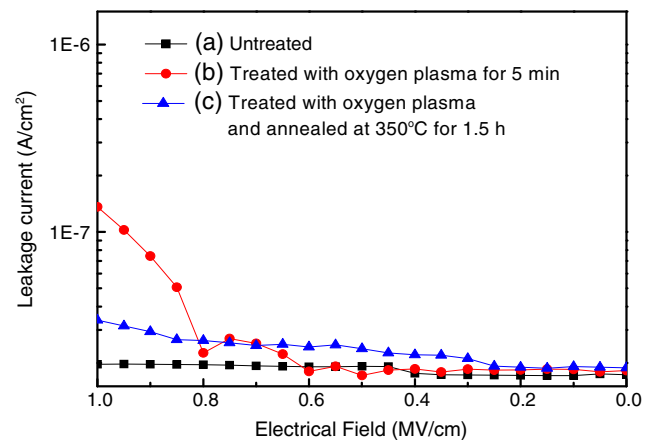
Fig. 4 Leakage current densities of these films (a) untreated and annealed at 300°C for 1.5 h in nitrogen ambient; (b) treated with oxygen plasma for 5 min; (c) treated with oxygen plasma treatment for 5 min and annealed at 350°C for 1.5 h in nitrogen ambient

Nitrogen-plasma exposure as well as free-radical exposure has only a small influence on the bond breaking. Ultraviolet curing can improve the chemical-damage resistance of the dielectric [26].

4 Conclusions

In this study, the MSQ films are prone to damage when exposure to oxygen plasma. As we know, it is an unavoidable step using the oxygen plasma ashing in VLSI fabrication process. The Si–OH bonds appeared after oxygen plasma treatment. The high polarity bonds can adsorb water molecules, which lead to increase the leakage current and dielectric constant. But after annealing at 350°C for 1.5 h in nitrogen ambient, the leakage current density decreased and dielectric constant decreased. The reason is that the Si–OH structure decreased and Si–O (network structure) increased within the annealed films. The structure of MSQ films changed from cage structure to a network structure.

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