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Quantification of processing damage in porous low dielectric constant films

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Abstract

A method for evaluation of degree of hydrophilization of low-k films occurred as a result of technological processing damage is reported. The evaluation is based on analysis of adsorption isotherms of water vapors. It is shown that the degree of hydrophilization is a qualitative measure of plasma damage that correlates with the carbon depletion measured by TOF-SIMS. The presented method gives also a unique possibility to calculate water contact angle of internal surface of low-k films that cannot be measured by other methods.
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1. Introduction

One of the most critical challenges during the integration of porous low dielectric constant (low-k) materials in ULSI technology is their degradation during different technological processes such as plasma etching, resist stripping, cleaning, and chemical mechanical polishing (CMP). Removal of carbon-containing hydrophobic groups by oxygen or hydrogen radicals and subsequent adsorption of water and other polar molecules having high polarizability significantly increases the effective dielectric constant of low-k films [1]. The degree and depth of such kind of damage increases with pore size and degree of their interconnectivity. Therefore, ultra low-k materials with $k < 2.6$, which have relatively large porosity and pore size, suffer much stronger than microporous materials [2,3].

The depth and profile of the carbon depletion can be evaluated using various analytical techniques such as X-ray Photoelectron Spectroscopy (XPS), Time-of-Flight Secondary Ions Mass spectroscopy (TOF-SIMS), Energy Filtered Transmission Electron Microscope (EFTEM) [1] or by means of a so called HF-immersion test [4]. In the first cases, it is assumed that the carbon concentration is directly responsible for the hydrophilic properties that finally define the effective dielectric constant of the film via the concentration of the adsorbed moisture. The idea of HF dip test is based on higher etch rate of damaged low-k dielectrics, which contains less carbon with respect to the pristine film. This test more directly reflects the film's hydrophilic properties but the complex mechanism of HF interaction with SiO_2 makes it difficult to be applied for a direct estimation of the depth of damage: the etch rate and the calculated depth of damage strongly depends on HF concentration [4]. In addition, most of these methods are destructive and the obtained information is not directly correlated with damage having largest impact in to the dielectric constant.

This paper demonstrates a novel method for direct measurement of hydrophilic properties of low-k material, internal surface energy, and depth of technological damage in low-k films.

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2. Results and discussion

The idea of this method is similar to Ellipsometric Porosimetry (EP) that is widely used for evaluation of porous low-k materials [5,6]. A porosimetry tool with a special water source has been used in these experiments. The water vapor pressure is varied from 10^{-3} to saturated ones (≈ 20 Torr at room temperature). The amount of the adsorbed water (C_{wat}) is calculated from the change of refractive indices occurred during the water adsorption by using Lorenz–Lorentz equation [5]:

$$C_{wat}\ (\%) = 100 \cdot \frac{V_{water}}{V_{film}}$$
$$= 100$$
$$\cdot \left[\left(\frac{n^2 - 1}{n^2 + 2} \right) - \left(\frac{n_{min}^2 - 1}{n_{min}^2 + 2} \right) \right] \Big/ \left(\frac{n_{wat}^2 - 1}{n_{wat}^2 + 2} \right) \quad (1)$$

where V_{water} and V_{film} are volumes of adsorbed water and film, respectively. n is refractive index of the film after water adsorption, n_{min} and n_{wat} are refractive indices of the film with empty pores (in vacuum) and liquid water, respectively.

Pristine low-k materials are hydrophobic and the amount of the adsorbed moisture at 100% of humidity does not exceed a few percents in film volume (Fig. 1). It is interesting to note that the low-k material X with improved mechanical properties is more hydrophilic than the others. The reason is, probably, that the improvement of mechanical properties needs an increase of degree of cross-linkage that in turns requires a decrease of concentration of hydrophobic groups like CH_3.

Fig. 2 demonstrates results of evaluation of ultra low-k spin-on glass (SOG) films that were exposed in fluorine containing etch plasmas. One can see that the plasma-etched low-k dielectrics become more hydrophilic and the degree of hydrophilicity reflects the degree of plasma damage. The most hydrophilic surface is obtained for low-k films exposed in oxygen-containing plasma (CF_4/O_2). The amount of the adsorbed water in this film at $P/P_0 = 1$ is
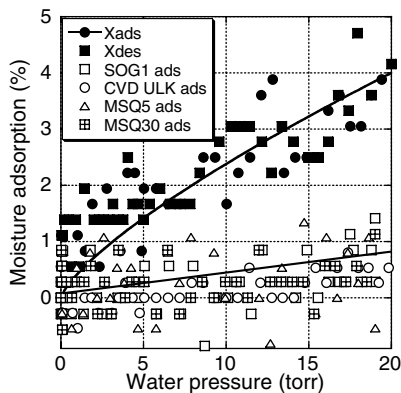

Fig. 1. Adsorption isotherms in typical low-k materials. The film with improved mechanical properties (X) is more hydrophilic in comparison with others.
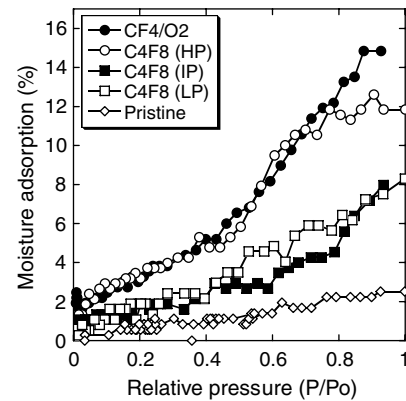

Fig. 2. Adsorption isotherms of water vapors showing the change of hydrophilicity after plasma etching. HP, IP, and LP stand for plasma etch at high, intermediate and low power, respectively. More detailed description of plasma etch conditions can be found in [7].

equal to 15% of the films volume. The open porosity of this film, measured by toluene adsorption, was equal to 30%; therefore, half of the pores are filled by water. Oxygen-free highly polymerizing C_4F_8-based plasma is more promising for integration because of low degree of plasma damage and possibility of *in situ* sealing during the etching [7]. However, even in this case both the sealing efficiency and degree of plasma damage depends on plasma power and only low power condition gives a clear advantage in comparison with CF_4/O_2 plasma.

2.1. Internal contact angle

The amount of adsorbed water in pristine low-k materials reflects the concentration of active centrums such as surface hydroxyl groups. Pristine low-k materials are hydrophobic and contain a limited number of such centrums and only completely isolated water clusters form during the adsorption. Technological damage increases the number of active centrums and starting from a certain concentration, the adsorbed water is able to form continuous surface layer. As soon as it becomes possible, the bulk condensation of water occurs [8]. Therefore, the amount of water condensed in the pores depends on wettability of internal surfaces. Adsorption/desorption isotherms measured in the wide range of water vapor pressures from zero to saturated one should allow characterization of hydrophilic properties that normally are quantified through the contact angle. This type of analysis is based on the following simple ideas.

Determination of pore size in adsorption porosimetry (EP is one of them) is based on the Kelvin equation that correlates the critical pressure (P) when happens condensation, with pore radius.

$$\ln \left(\frac{P}{P_0} \right) = -\cos \theta \cdot \frac{\gamma V_L}{RT} \cdot \left(\frac{2}{r} \right) \quad (2)$$

where γ and V_L are surface tension and molar volume of the liquid adsorptive, respectively. θ is the contact angle