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Comparison between continuous and microwave oxygen plasma post-treatment on organosilicon plasma deposited layers: Effects on structure and properties

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Abstract

The aim of this work is to characterize and understand the effects of oxygen plasma post-treatments on plasma polymerized hexamethyldisiloxane (ppHMDSO) layers, as these post-treatments on plasma polymerized layers are an alternative way to produce SiO_x ($x \approx 2$) films. Oxygen discharges on ppHMDSO films in continuous plasma (DC) and microwave multipolar plasma excited by distributed electron cyclotron resonance plasma (MW) are compared by studying their effects on the post-treated layer thickness, chemical composition, film structure and functional properties. Fourier Transform Infra-Red and X-ray Photoelectron Spectroscopies have been used to determine the film structure and composition of the initial ppHMDSO films and the post-treated layers. The oxygen post-treatment etches the end bonds and leads to a cross-linking of the polymer chains (formation of SiOC bonds). Oxidation process is strongly linked to the plasma type. A pre-existing model for the oxide growth has been applied, showing that the MW process is more effective than the DC. The main conclusion is that the structure of the resulting films is different for each process and that the oxygen diffusion coefficient is linked to the film structure. Higher oxygen diffusion is achieved in MW films, which are less dense than the films obtained by using the DC technique. It is also shown that the film properties (such as wettability, hardness and electrical and optical properties) are modified after the oxygen post-treatment. Finally, we briefly discuss on the most appropriate process to obtain these films according to the final application of the coatings.

Keywords: Plasma processing and deposition; Oxidation; Silicon oxide; XPS; FTIR; Spectroscopic ellipsometry; Hardness

1. Introduction

The production of SiO_2-like coatings has been studied for a long time as the applications of these materials cover many fields (for example optics [1], barrier for food packaging [2], interlayer dielectrics [3,4] or corrosion protection layers [5,6],...). In addition to chemical vapour deposition, several other processes are employed for the deposition of SiO_x films. Among these processes, plasma enhanced chemical vapour deposition (PE-CVD) has become one of the most attractive thin film deposition processes because of its ability to prepare coatings with good quality at low substrate temperature.

Mixtures of organosilicon precursors with oxygen are frequently used for SiO_x ($x \approx 2$) thin film plasma deposition [7] and the most widespread precursor is hexamethyldisiloxane (HMDSO) [8]. But, when using a polymer substrate, oxygen can etch organic species and then lead to the polymer deterioration and/or to an organic contaminated layer. An alternative way to produce SiO_x films on polymers is to post-treat a plasma polymerized organosilicon layer from pure organosilicon precursor with oxygen discharges [9,10]. This process is frequently described as an organic etching step which leads to SiO_x ($x \approx 2$) films.

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The aim of this work is to characterize and understand the effect of oxygen plasma post-treatments on plasma polymerized HMDSO (ppHMDSO) layers. The effects of oxygen discharges on ppHMDSO films in continuous plasma (DC) and in microwave (2.45 GHz) multipolar plasma excited by distributed electron cyclotron resonance (MMP-DECR, which will refer to as MW for simplicity) are compared by studying their effects on the post-treated layer thickness, chemical composition, film structure and functional properties. Finally, we discuss on the oxidation process and a definition of the most appropriate process for some specific applications is given.

2. Experimental details

$SiO_xC_yH_z$ films were deposited by PE-CVD using hexamethyldisiloxane (HMDSO) as liquid precursor. To evaporate the liquid monomer and in order to avoid any condensation, the HMDSO flask and supply line were heated. The plasma was generated in DC and MW reactors which have already been described in the literature [9,11]. The experimental conditions related to the present study are as follows:

–DC Intrinsic (100) silicon wafers pasted on glass slides were used as substrates and placed at a distance of 10 cm from the cathode. HMDSO was injected in the reactor at a pressure of about 5 Pa. The DC bias was kept on the Al cathode at −2000 V (100 W) referred to the grounded reactor walls. 150-nm-thick films were reached in 3 min. These films were post-treated by oxygen plasma. The pressure was about 15 Pa and the DC bias was −2000 V (100 W). The oxygen post-treatment lasted from 0.5 to 30 min.

–MW HMDSO pressure was about 0.1 Pa. The microwave power was kept at 400 W. Intrinsic (100) silicon wafers were used as substrates and placed in the diffusion plasma (in the middle of the discharge) with −30 V self bias using a Radio Frequency (RF) generator. 150-nm-thick ppHMDSO layers were reached after 2 min. These films were post-treated with oxygen plasma. The pressure was about 0.1 Pa, the microwave power was kept at 400 W and the self bias was −30 V. The oxygen post-treatment duration varied from 0.5 to 30 min.

In order to study whether the effects of the post-treatment on organosilicon coatings depend on the excitation source of the oxygen plasma, ppHMDSO films obtained in the DC reactor were post-treated in the MW reactor.

We will use a simplified notation when referring to the post-treated layers, so that the deposition and post-treatment techniques are more clearly shown. From now on, the post-treated layers will be referred to as follows:

–DC/DC ppHMDSO films deposited in the DC reactor and post-treated in DC oxygen plasma.

–MW/MW ppHMDSO films deposited in the MW reactor and post-treated in MW oxygen plasma.

–DC/MW ppHMDSO films deposited in the DC reactor and post-treated in MW oxygen plasma.

The chemical bonding states of the different films were characterized by Fourier Transform Infra-Red (FTIR) spectroscopy in the absorbance mode using a Bio-Rad (FTS60A) spectrometer. The resolution is 4 cm^{-1}.

The film thickness d was measured with profilometry and spectroscopic ellipsometry using a microspot beam (Sopra GES5) with an incident angle of 75.3° (silicon Brewster angle). The film thickness d, refractive index n_∞ and band gap energies E_g were calculated from ellipsometric data using the Forouhi Bloomer model [12].

Transmission electron microscopy (TEM) was used to observe the depth profile of the film structure. Cross-sections of the samples were prepared and thinned by Ar ion milling down to a thickness transparent to the electron beam of the TEM carried out with a 200 kV microscope. The TEM image contrast was carefully adjusted in order to compensate for the very low contrast found in the amorphous layers.

XPS analyses were performed in ESCALAB VG MK2 and PHI Model 550 systems with a base pressure of 10^{-8} Pa. Samples were placed in the system 12 h before analysis. XPS spectra were obtained in a survey spectrum mode to determine the film composition and in a multiplex repetitive scan mode to determine bonds types on the following binding energies: Si2p, C1s, O1s. Deconvolution process on Si2p peak is as follows: bond energies were fixed and the fit runs on peaks intensities and FWHM (with the condition FWHM <2 eV). Argon ion sputtering was used in order to perform depth profiles or to avoid surface contamination of the measurements. The sputtering rate is about 5 nm min^{-1}. Samples were excited with 1253.6 eV energy Mg K_α X-rays. The spectrometer was calibrated using standard procedure and binding energy calibration was based on C 1s at 284.6 eV.

Finally, surface energy measurements were carried out with a contact angle meter (DIGIDROP, GBX) using 3 different liquids (water, formamide, diiodomethane) and the hardness was measured using a NanoTest 550 (Micro Materials Ltd., UK) with a Berkovitch indenter.

3. Results

3.1. HMDSO plasma deposited layers

FTIR was used to investigate the chemical composition of both plasma polymerized films. Fig. 1 reports the normalised spectra according to their thicknesses. Table 1 summarizes the main absorption peaks range and their assignments found in the literature [9,10,13–15].

The same main peaks can be observed in Fig. 1 for DC and MW plasma polymerized HMDSO films. Omitting the region below 1000 cm^{-1}, which is really difficult to exploit, some differences appear in the spectra such as SiH, $SiCH_x$, or SiOSi composition. SiH intensity, between 2250 and 2100 cm^{-1}, is 5 times higher in the case of MW. These end bonds are frequently linked to the film density [10]: in order to reach denser films, a low concentration of end bonds is needed. Then, it seems that MW films are less dense than the DC ones. In the region between 3100 and 2800 cm^{-1}, it appears that methyl groups