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Influence of plasma pulsing on the deposition kinetics and film structure in low pressure oxygen/hexamethyldisiloxane radiofrequency plasmas

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Abstract

The deposition rate and structure of films deposited in an oxygen/hexamethyldisiloxane 85:15 low pressure radiofrequency plasma are investigated as a function of the pulse parameters. The variations of the deposition rate with the plasma-off and plasma-on times are compared to a model involving characteristic rise and decay times for the deposition, which are found to be equal to 2 and 80 ms, respectively. Such a long decay time suggests the presence of long lifetime species, which act as precursors to the film growth. These latter allow to reduce the average applied power without significantly reducing the deposition rate. On the other hand, the structure and the properties of the deposited film can be controlled and varied from SiO_2-like to $SiO_xC_yH_z$ organic film by tuning the pulse parameters. Pulsed plasmas are shown to be very attractive in order to deposit graded composition layers without changing the oxygen to organosilicon flow rate ratio.

Keywords: PECVD; Pulsed plasma; Hexamethyldisiloxane; Silicon oxide; Optical properties

1. Introduction

SiO_2-like and $SiO_xC_yH_z$ thin films deposited by plasma enhanced chemical vapor deposition in hexamethyldisiloxane (HMDSO)/oxygen mixtures are used in many applications such as optics [1,2], gas barriers [3–5], membranes [6], biomaterial film [7] or corrosion protection layers [8]. It was extensively shown that the carbon content in the deposited films could be changed by varying the oxygen to HMDSO flow rate ratio: inorganic transparent and hard SiO_2-like films are deposited in oxygen-rich plasmas whereas softer and UV-absorbent $SiO_xC_yH_z$ plasma polymers are obtained in organosilicon-rich plasmas [9]. Hence, the gas flow rate ratio is a commonly used parameter to control the structure and the properties of the deposited film.

In this context, plasma pulsing opens up promising perspectives for the control of particle and film growth kinetics. Pulse modulation of the power input may induce an alteration of the discharge chemistry [10,11], which can lead to changes in composition and properties of the deposited films. In the case of microwave HMDSO/O_2 plasmas, Georg et al. have recently shown that pulsed plasma were efficient to improve the quality and reduce the roughness of the films [12]. Pulsed plasma can also be used to decrease the ion to neutral flux ratio on the substrate in order to reduce the compressive stress in the SiO_2-like deposited film, as shown by C. Charles and Boswell in low pressure helicon SiH_4/O_2 plasmas [13].

In this work, we investigate the effects of a pulse modulation on films deposited in a low pressure radiofrequency (rf) inductively coupled plasma. This study focuses especially on the evolution of the deposition rate and the composition of the deposited films for different pulse parameters. The aim is both to gain insight into the deposition kinetics and to investigate the influence of pulse parameters on the structure of the deposited films.

2. Experimental details

The pulsed experiments were carried out in a helicon reactor, described previously in detail [14]. In brief, it was composed of

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a source, a Pyrex tube surrounded by a helicon antenna, and a diffusion chamber, where the silicon substrate (*p*-type Si(100) wafers with a 5–15 Ω cm resistivity) was located. The base pressure of the reactor was less than 2×10^{-4} Pa. Oxygen was introduced at the top of the source, whereas HMDSO was injected via a gas ring located in the diffusion chamber, 6 cm above the substrate. The organosilicon flow rate was controlled by a heated pressure-based mass flow controller. Experiments were performed in O_2/HMDSO 85 : 15 mixture at a total gas flow rate fixed at 16 sccm, which corresponds to a pressure of 0.33 Pa before plasma ignition and a resident time of 330 ms. Two Helmoltz-type coils surrounding the helicon antenna were generating a static magnetic field inside the source. A current of 1 A was running in the two coils in the same direction, which yielded a magnetic field of about 60 G over the source. As 300 W is applied, a dense plasma is created by inductive coupling in the source. Due to the low pressure, this plasma diffuses into the deposition chamber, so that a plasma exists in the diffusion chamber where typical values of the electron density and temperature are 10^9 cm^3 and 3 eV.

In pulsed mode, a radio-frequency (13.56 MHz) 300 W power was 100% rectangular-wave modulated. The rise and falling times for the wave modulation, around 10 μs, are negligible compared to the plasma-on and the plasma-off times used in this study. A first set of films was deposited with a constant plasma-on time (T_{on}) of 5 ms and a plasma-off time (T_{off}) varied from 1 to 95 ms. A second set of films was deposited with a plasma-on time (T_{on}) varied from 1 to 50 ms and a constant plasma-off time (T_{off}) of 50 ms. A last set of films was deposited by varying the pulse frequency from 10 Hz to 1 kHz at a constant duty cycle ($DC=T_{on}/(T_{on}+T_{off})$) of 0.25. For sake of comparison, films were also deposited in continuous mode at 300 and 75 W rf powers.

The film refractive index and thickness were determined using an in situ spectroscopic phase modulated UV–visible (1.5–5 eV) ellipsometer (Jobin Yvon UVISEL) mounted on the diffusion chamber. The films were described by the Cauchy formalism with absorption. The infrared absorption spectra (400–4000 cm^{-1}) of the deposited films were recorded ex situ using a Nicolet 20 SXC spectrometer equipped with a HgCdTe (MCT) detector. The resolution was 4 cm^{-1} and 300 scans were recorded and averaged. All the experimental infrared spectra exhibit a sloping baseline due to optical interference fringes, which has been removed. The normalized absorbance spectra are obtained by converting this corrected transmission spectra in absorbance spectra and dividing the result by the film thickness [15].

3. Results

3.1. Deposition rate

3.1.1. Influence of the plasma-off time

To determine the characteristic rise and decay times of the deposition kinetics, we first measured the deposition rate of films obtained for $T_{on}=5$ ms and T_{off} varied from 1 to 95 ms. The corresponding deposition rates are plotted as a function of T_{off} in Fig. 1. As T_{off} is increased from 0 (continuous mode) to 95 ms, the deposition rate only decreases from 14 to 8 nm min^{-1} while the fraction of the plasma-on time in a period, e.g. the duty cycle ($DC=T_{on}/(T_{on}+T_{off})$), is divided by 20. Hence, it can be concluded that the deposition efficiently proceeds during the post-discharge. To account for this phenomenon, a simple model consists in assuming a constant deposition rate, denoted R_{on}, during the plasma-on time and an exponential decay of the deposition rate during the post-discharge. This latter, denoted R_{off}, can be written as:

$$R_{off}(t) = R_{on}\exp\left(-\frac{t-T_{on}}{\tau_{off}}\right) \quad (1)$$

where t is the time referenced to the beginning of the plasma-on time and τ_{off} is the characteristic decay time for the deposition rate during the post-discharge.

In this first simple model, R_{on} is assumed to be equal to the deposition rate in continuous mode, R_c. Then, the mean deposition rate R over one period ($T=T_{on}+T_{off}$) is given by the following relation:

$$\begin{aligned} R &= \frac{1}{T}\left[\int_0^{T_{on}} R_c \cdot dt + \int_{T_{on}}^{T_{on}+T_{off}} R_c \cdot \exp(-(t-T_{on})/\tau_{off})dt\right] \\ &= \frac{T_{on}}{T}R_c + \frac{\tau_{off}}{T}R_c(1-\exp(-T_{off}/\tau_{off})) \end{aligned} \quad (2)$$

τ_{off} is deduced from the best fit between the measured and predicted deposition rates. The best fit, shown by the dashed line in Fig. 1, corresponds to a decay time constant of 60 ms. A very good agreement is observed for $T_{off}>50$ ms, but for shorter plasma-off times, the predicted values are greater than the measured one. This discrepancy might mean the hypothesis of a constant deposition rate during the plasma-on time, equal to the value measured in continuous plasma, is not correct.

3.1.2. Influence of the plasma-on time

To further investigate the deposition kinetics during T_{on}, a second set of films was deposited at $T_{off}=50$ ms and plasma-on times varied from 1 to 50 ms. T_{off} was fixed at 50 ms in order to

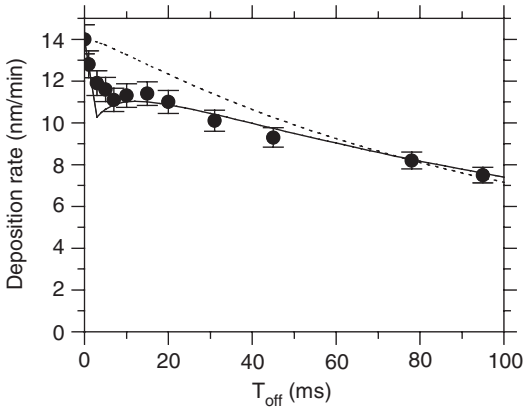

Fig. 1. Deposition rate in O_2/HMDSO 85 : 15 pulsed plasma with $T_{on}=5$ ms as a function of T_{off}: measured values (●) and values predicted by the first (dashed line) and the second model (continuous line).