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RF power effect on TEOS/O_2 PECVD of silicon oxide thin films

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Abstract

The effect of the RF power at two excitation frequencies (13.56 and 27.12 MHz), on the growth rate and on the chemical composition of the deposited SiO_2 films from TEOS/O_2 discharges is investigated. The increase of RF power was found to significantly enhance the film growth rate up to an optimum and after that a slight decrease was observed, whereas for the same power level, the film growth rate at 27.12 MHz was always higher compared to 13.56 MHz. On the other hand, both hydroxyl groups and carbon content decreased with the increase of the discharge power while the increase of frequency was found to leave almost unaffected the number of hydroxyl groups and to reduce the Si-O bonded carbon.
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Keywords: PECVD; Silicon oxide; TEOS; Radio frequency; Infrared spectroscopy

1. Introduction

Silicon dioxide is one of the most widely used thin film coatings due to its exceptional electrical, chemical and mechanical properties. Plasma enhanced chemical vapor deposition (PECVD) is suitable for growing silicon oxide at low temperatures which is surely an advantage as there is an increasing number of applications with low temperature requirements [1–4]. The structure and consequently the applicability of the films, depends on specific process parameters and may vary from silicone ($SiO_xC_yH_z$) to SiO_2-like [5]. However, in some specific applications, like in semiconductor device fabrication and in protective layers of metals, a complete removal of C and H from the SiO_2 films is required. Among the process parameters the increase of RF power was found to be of specific importance as being able to alter both the film growth rate and its stoichiometry [6–12]. Nevertheless, the studies found so far in literature contain controversial results concerning both the RF power effect on the film growth rate and the carbon content of the films. The origin of these controversies is certainly due to the lack of exact and direct measurements of the power actually consumed in the discharge and not in the matching network and stray resistances.

In this direction, the present work reports on the investigation of the true effect of RF power in TEOS/O_2 discharges on the film growth rate and the chemical composition of $SiO_xC_yH_z$ films. The exact power consumed in the discharge was determined by applying an accurate method based on voltage and current waveform measurements at the RF electrode. The effect of power was studied at low temperatures (373 K) and for two different excitation frequencies: The conventional frequency of 13.56 MHz and the frequency of 27.12 MHz.

2. Experimental

The film depositions on silicon (100) wafers were performed in a capacitively coupled high vacuum (HV) parallel plate reactor having a base vacuum of 10^{-7} mbar. The upper electrode (22 cm in diameter) is connected to the RF power generator via a pi type matching network while the bottom grounded electrode (19.1 cm in diameter) works as substrate holder and is heated to 373 K. The distance between the two electrodes was set at 20 mm. Two different excitation frequencies (13.56 and 27.12 MHz) were used for the experiments. The chamber pressure was constant at 0.4

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mbar using a downstream throttle valve controller, while the flow rate was independently adjusted using mass flow and liquid flow controllers, respectively. Liquid TEOS is heated up to 70 °C and then transported together with a O_2/He gas mixture in the reactor through a showerhead.

The deposition rate was measured in-situ using Laser Reflectance Interferometry and the film thickness was kept at 2 μm in all cases. The real power consumed in the discharge and the discharge impedance were determined by using Fourier Transform voltage and current waveform measurements on the RF electrode as described in detail in Ref. [13]. The chemical composition and the stability of the films were examined by Fourier Transform Infrared Spectroscopy using a Nicolet 740 FTIR spectrometer with a MCT-B detector and a KBr beam splitter.

3. Results and discussion

Different sets of electrical measurements were performed at each frequency and the results concerning the real power dissipated in the discharge as a function of the applied voltage are shown in Fig. 1. The increase of the applied voltage at both 13.56 and 27.12 MHz leads to an enhancement of the power consumption. In the case of 13.56 MHz the increase of power consumption is steeper for amplitudes higher than 160 V. In addition, the increase of frequency for the same voltage (vertical arrow, Fig. 1) results in a much higher power consumption, whereas a significant drop of the voltage is required for operating the discharge at the same power level (horizontal line, Fig. 1). These results are indicative of the enhancement of electron density with excitation frequency [14].

Moreover, the change of the electrical properties caused by the variation of the electron density will certainly affect the production of radicals through electron–molecule collisions, which in turn are responsible for the film growth.

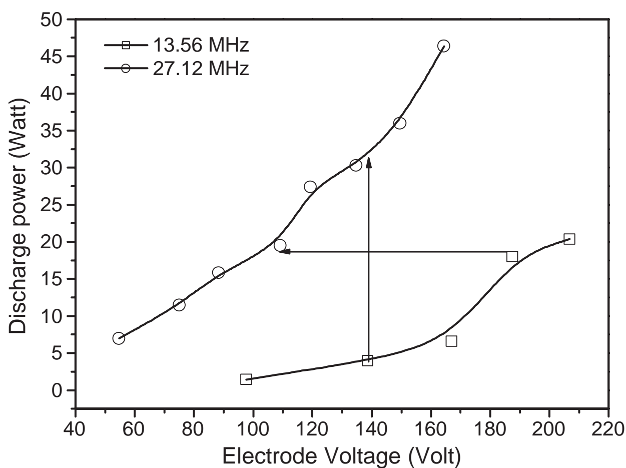

Fig. 1. Discharge power as a function of electrode voltage amplitude at two excitation frequencies in 51% TEOS/O_2 discharges at the pressure of 0.4 mbar. Lines are guides for the eye.

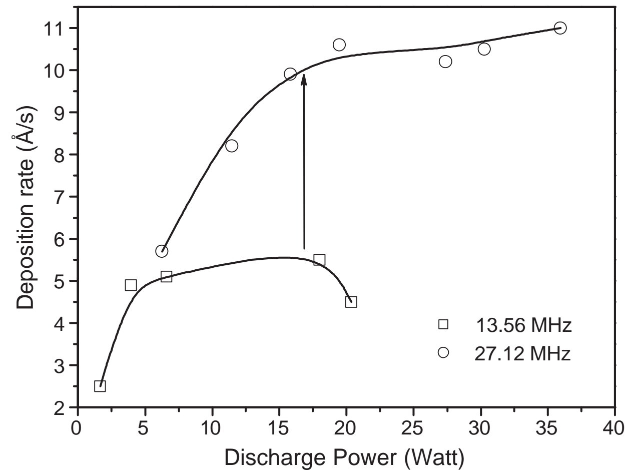

Fig. 2. Deposition rate as a function of the dissipated power in 51% TEOS/O_2 discharges at two excitation frequencies at the pressure of 0.4 mbar. Lines are guides for the eye.

Thus, Fig. 2 shows the effect of RF power on the deposition rate of $SiO_xC_yH_z$. The increase of the power at both 13.56 and 27.12 MHz leads to an enhancement of the film growth rate up to a certain value and after that a slight drop or an almost constant film growth rate is observed. It is worth noticing that the saturation of the deposition rate takes place at about the same RF power (~20 W) for both frequencies. In addition, the deposition rate at 27.12 MHz is almost double compared to 13.56 MHz and for the same power (vertical arrow, Fig. 3).

The dependence of the film growth rate on both the RF power and the frequency can provide some indirect information about the changes in the gas phase chemistry affected by these two parameters. Firstly, the increase of frequency and the consequent increase of the electron density leads to an enhancement of the electron impact dissociation of TEOS towards free radicals and consequently of the film growth rate. On the other hand, the initial very fast increase of the film growth rate at both 13.56 and

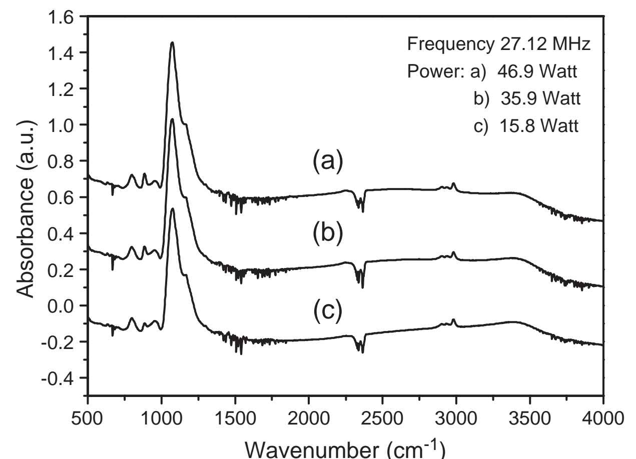

Fig. 3. Normalized FTIR spectra for three different values of power dissipated in the discharge.

27.12 MHz with RF power can be attributed to the enhanced dissociation of TEOS either via electron impact or through TEOS oxidation in the gas phase by reactive oxygen atoms [6]. On the other hand, the saturation of the film growth rate with further increase of power may be either due to TEOS depletion or from changes in TEOS dissociation paths towards the production of species that are not particularly favorable for the film growth.

Furthermore, the modification of the growth rate is certainly associated with changes in the deposited film composition. To investigate these effects, depositions on Si (100) substrates were performed and the films have been characterized by applying FTIR absorption spectroscopy. Fig. 3 presents the infrared spectra in the 500 ± 4000 cm^{-1} range for films deposited at different discharge power levels at the frequency of 27.12 MHz. The spectra exhibit the two characteristic peaks of SiO_2 modes near 800 and 1070 cm^{-1} and absorption bands at 960 and 3450 cm^{-1} assigned to O-H vibration of associated SiOH and water, respectively [9]. In addition, carbon bonding in different forms in the film is identified from Si-C, Si-O-C and C-H stretches located at 880, 1165 and 2970 cm^{-1}, respectively.

In order to investigate the effect of the consumed power on the chemical composition of the films and more precisely on the quantity of –OH groups and different *A*–C (*A*=Si, O and H) groups, FTIR spectra were analyzed to the corresponding peaks. Then, the ratio of the area of the Si-C peaks versus the area of the Si-O-Si peak and the area of the OH peak versus the area of the Si-O-Si have been calculated and the results are presented in Fig. 4. In the left axis is shown the variation of OH peak (3400 cm^{-1}) relative to Si-O-Si peak (1070 cm^{-1}) and it is clear that the increase of power decreases the –OH content of the films. This is consistent with most studies dealing with the effect of power on the composition of the films [6–12] and also with the extended fragmentation of TEOS molecules by either electron-impact or reactions with O-atoms.

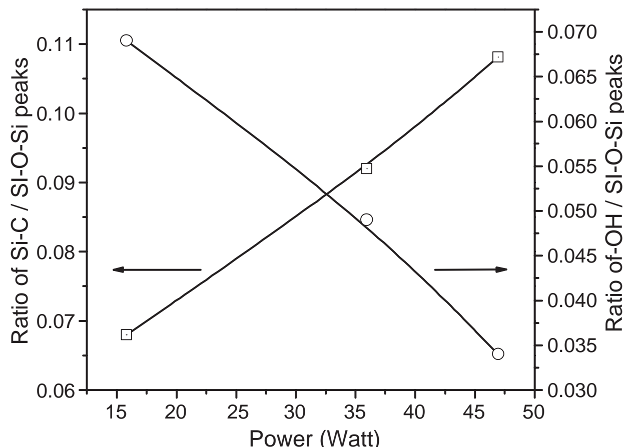

Fig. 4. The ratio of OH/Si-O-Si areas (left axis) and the ratio of Si-C/Si-O-Si areas versus power dissipated in the discharge.

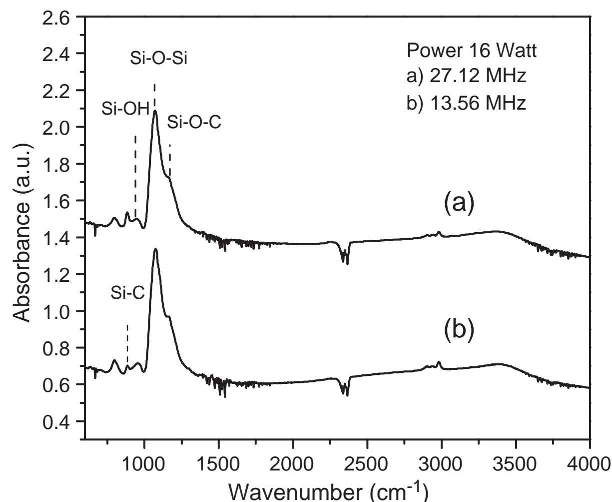

Fig. 5. Normalized FTIR spectra for 13.56 and 27.12 MHz and constant power dissipation of 16 W.

Concerning the carbon content, the increase of power increases the Si-C peak (880 cm^{-1}) relative to the O-Si-O in the RF power range from 15.8 to 46.9 W. This increase can be due to the effect of either secondary gas phase reactions or surface reactions because Si and C are not directly bonded in the TEOS molecule and therefore is a result of reactive transformation. As already shown the increase of power dissipation favors the dissociation of TEOS and enhances the probability of fragments to contribute to secondary gas phase reactions and to form precursors with Si-C bonds.

Finally, Fig. 5 presents FTIR spectra of the materials deposited at the two frequencies using the same RF power (16 W). Despite the much higher deposition rate at 27.12 MHz, the increase of frequency slightly decreases the hydroxyl groups in the film as well as the carbon in the Si-O-C form. This leads to the conclusion that the dissociation of TEOS through enhanced electron-impact must be pursued in order to deposit SiO_2-like thin films at high growth rates and with low content of –OH groups. On the other hand, the Si-C bonding as in the case of RF power, increases with frequency probably as a consequence of the extended dissociation of TEOS in the gas phase. However, the important point is that a combination of frequencies higher than 13.56 MHz and high discharge power dissipation can lead to fast growth of SiO_2-like thin films with very low –OH content at low substrate temperatures. Complete removal of –OH groups is expected if lower fractions of $TEOS/O_2$ are applied.

4. Conclusions

An investigation of the RF power and frequency effect on the film growth rate and the chemical composition of $SiO_xC_yH_z$ thin films, deposited through $TEOS/O_2$ discharges, was performed.

The RF power dissipated in the discharge increases significantly with frequency for the same applied voltage, whereas a significant drop of the applied voltage is required in order to maintain the same power consumption. Both these results indicate an enhancement of the electron density with frequency as reflected also on the deposition rate. The film growth rate is favored by the increase of frequency in general while it also increases with power up to a certain value and then saturates.

Concerning the chemical composition of the films it was found that the increase of power and excitation frequency favor the removal of both associated and isolated hydroxyl groups in the deposited films. Moreover, the Si-C content increases with both frequency and power, indicating that Si-C bonding in the films is due to the enhanced dissociation TEOS in the gas phase. Finally, the combination of high frequency and power seems to be a promising technique for depositing SiO_2-like films at high growth rates and low substrate temperatures.

Acknowledgments

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