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The effect of TEOS plasma parameters on the silicon dioxide deposition mechanisms

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ABSTRACT

In this study, the effects of tetraethyl orthosilicate (TEOS) plasma parameters on the silicon dioxide deposition mechanisms are studied. The films are deposited by the organometallic based plasma enhanced chemical vapour deposition method. The plasma generator is capacitively coupled radio frequency power source. The plasma is the mixture of organometallic TEOS vapour, oxygen and argon. The effects of the TEOS/O_2 pressure ratio (0.05–1.5), the applied power (100–400 W) and the argon gas percentage into the plasma (0–20) on the quality of the film are investigated. The film properties such as structure and chemical composition, surface topography are analysed by Fourier transform infrared spectroscopy and atomic force microscopy. In addition, the relation between the mechanism of deposition phenomenon and the process parameters is studied. It is found that in the deposition process the oxidation and the electron impact mechanisms determine the film characteristics as they can be controlled by adjusting the TEOS/O_2 pressure ratio, applied power and argon gas percentage.

1. Introduction

The silicon dioxide (SiO_2) films with specific electrical, optical and mechanical properties are employed in several different applications. These films can be used as passivation, insulation [1], waveguides [2], sensors [3], anti-reflection coating [4] and corrosion protection layers [5] in the integrated circuits, microelectronic and optoelectronic devices. Also they can be used in solar cells [1], food packaging and gas barriers [6]. This film is extensively produced by TEOS based on plasma enhanced chemical vapour deposition (TEOS-PECVD) system. This system is able to produce high quality SiO_2 films with high deposition rate, good conformality at low temperature. Furthermore, its high controllability allows depositing a wide range of SiO_2 like films (from polymer like to pure SiO_2) with desired specification [2–8].

To deposit SiO_2 film by TEOS-PECVD, often an oxidant gas such as oxygen, ozone or N_2O is used. Many researchers reported that adding an oxidant gas to TEOS plasma, the film is deposited with higher quality especially with less impurity, less surface roughness, better conformality and step coverage [8–10].

Generally the low temperature deposited SiO_2 films by TEOS-PECVD are porous and contain carbon and hydrogen impurities which in many applications have negative effects on the quality of the film. Hence in a large number of studies, the effects of various parameters on the chemical composition and structure of the PECVD grown SiO_2 films are investigated. On the other hand, the correlation of the parameters and the deposition mechanisms are not studied extensively.

In this work, PECVD system is used to deposit SiO_2 films using TEOS as a silicon source and oxygen as an oxidant gas. We evaluated the effects of PECVD parameters on the film properties and their relation to the mechanisms of the deposition phenomenon.

2. Experimental

SiO_2 films are deposited on glass substrates by a 34 MHz capacitively coupled radio frequency (RF) PECVD system. The substrates are placed on the powered electrode with a self DC-bias voltage. This electrode is equipped with water cooling and electrical heating to control the temperature of the substrate during the process. The deposition temperature is around 100 °C. The distance between the gas feed shower and the substrate is 3 cm. Plasma is a mixture of organometallic TEOS vapour, oxygen and argon. The flux of liquid TEOS (Merck-99%) is controlled via a liquid needle valve and transformed to the gas phase using a vaporizer. Its vapour flow is controlled by a needle valve and then enters to the chamber through a shower near the substrate. By adjusting the oxygen, argon and TEOS flow, the working pressure is maintained approximately 0.2 Torr. Also, the deposition processes are performed in 15 min.

In the present study, the effects of the TEOS/O_2 pressure ratio (R) in the range of 0.05–1.5, applied RF power in the range of 100 to 400 W, and argon percentage in the plasma of gas mixture (Ar%) in the range of 0–20 on the film characteristics are investigated.

To monitor the plasma process, the optical emission spectroscopy (OES: Oceanoptic-HR4000) is used. Chemical bonding states of the film are studied through the Fourier transform infrared spectra of the scraped film (FTIR: Bruker-Tensor27). Also the surface topography and the film

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microstructure are analysed, using atomic force microscopy (AFM: Nanosurf Easyscan2). Then the thickness of the deposited films is measured by surface profilometer (Dektak 8000). All the experiments at least have been done three times. Therefore, the results obtained by taking the average of analysed data, and finally the errors were determined by calculating the mean deviation.

3. Results and discussion

3.1. Plasma diagnostic and dissociation mechanisms

The OES spectrum of pure TEOS plasma and a typical OES spectrum of the O_2–TEOS plasma (R: 0.1, Ar%: 10, power: 300 W) are shown in Fig. 1a and b, respectively. The main observed transition lines are given in Table 1 [10–12]. The OES of pure TEOS plasma has only a clear atomic emission of excited H_α at $\lambda = 486.1$ nm with some low intensity molecular emission of CH, CO, C_2 and H_2. However, the OES of pure oxygen plasma has several transition lines related to the oxygen atom or ions, with $\lambda = 844.6$ nm and $\lambda = 777.4$ nm, as the most intensiveness. These transitions arise from the decay of various excited states of oxygen atoms. These excited states can be generated due to both energetic electron impact excitation of oxygen atoms and energetic electron impact dissociation of O_2 molecules. In addition, there are two small transition lines at 524 nm and 559 nm corresponding to O_2^+ ion. Looking at the pure TEOS spectrum, it can be deduced that the H_α excitation line is a proof of the TEOS molecule dissociation.

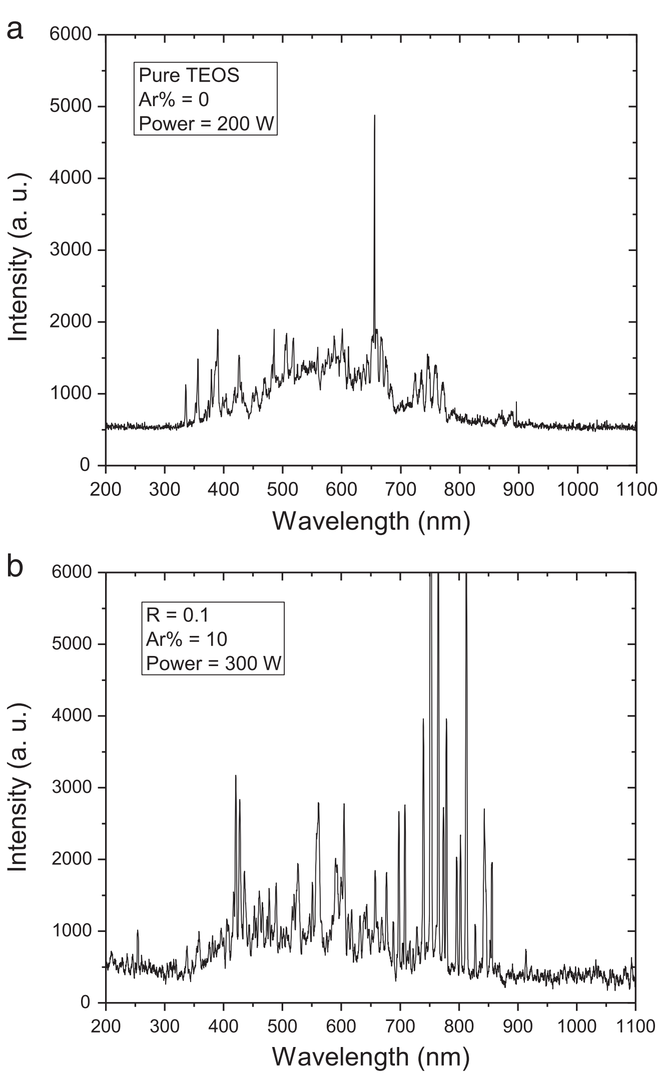

Fig. 1. The OES spectrum of (a) pure TEOS plasma and (b) a typical OES spectrum of the O_2–TEOS plasma (R: 0.1, power: 300 W, Ar%: 0).

Table 1
Main transition lines observed in optical emission spectra.

Wavelength (nm)	Species	Transition line
656.0	H	H_α: $H(n = 3) \rightarrow H(n = 2)$
486.1		H_β: $H(n = 4) \rightarrow H(n = 2)$
777.4	O	$3p^5P \rightarrow 3s^5S$
844.6		$3p^3P \rightarrow 3s^3S$
431.4	CH	$A^2 - X^2\Pi$
388.9		$B^2\Delta - X^2\Pi$
451.1	CO	$B^1\sum - A^1\Pi(0,0)$
483.5		$B^1\sum - A^1\Pi(0,1)$
519.8	CO	$B^1\sum - A^1\Pi(0,2)$
580–650	H_2	Fulcher α : $H_2(d^3\Pi - a^3\sum_g^+)$
559, 525	O_2^+	–
512.9	C_2	$A^3\Pi_R{-}X'^3\Pi_u(1,1)$
516.5		$A^3\Pi_R{-}X'^3\Pi_u(0,0)$
720–760	H_2	Fulcher α : $H_2(d^3\Pi_u - a^3\sum_g^+)$
811.5	Ar	$3s^23p^5(^2P^\circ_{3/2})4s–3s^23p^5(^2P^\circ_{3/2})4p$
427.7	Ar^+	$3s^23p^4(^1D)4s–3s^23p^4(^1D)4p$

In order to investigate the effects of the parameters on the plasma, the OES spectra of O_2–Ar–TEOS plasma at various R, power and Ar% are studied and are given in Table 2.

Related to the study of the dissociation process of TEOS molecules in the TEOS–O_2 discharge, Stout and Kushner [13] presented a Monte-Carlo simulation of SiO_2 film in plasma chemical vapour deposition (CVD) system. They reported that there are two mechanisms for TEOS molecule dissociation, oxidation and electron impact mechanisms. Some authors reported that when the oxygen concentration is high, the oxidation mechanism is the dominant process for the dissociation of TEOS molecules. In addition, other literature reported that increasing of atomic oxygen in the TEOS plasma gives rise to the decrease of the impurity contents in the film, suggesting oxygen plays a dominant role in the TEOS decomposition [14–16]. On the other hand, in an X-ray photoelectron spectroscopy (XPS) and mass spectroscopic study, Fracassi et al. [10] concluded that the TEOS decomposition is primarily due to the electron impact dissociation while oxygen dose does not play important role. In reality, in TEOS–O_2 discharge in plasma CVD systems, unlike non-plasma processes in thermal CVD systems, TEOS can be dissociated both by electron impact and oxidation mechanisms to form a close to pure SiO_2 film. So TEOS molecules are transferred to several types of fragments as below: [13]

$$Si(OC_2H_5)_n(OH)_{4-n} + e \rightarrow Si(OC_2H_5)_{n-1}(OH)_{4-n+1} + C_2H_4 + e \quad n = 1-4, \tag{1}$$

$$Si(OC_2H_5)_n(OH)_{4-n} + O \rightarrow Si(OC_2H_5)_{n-1}(OH)_{4-n+1} + C_2H_4O + e \quad n = 1-4. \tag{2}$$

These TEOS fragments, consisting of alkyl groups, are adsorbed to the substrate but not to the alkyl-saturated surface. Therefore, the deposition rate is improved by the removal of the alkyl groups. Finally, Si–O–Si network is formed on the substrate by the reaction of these fragments with each other while other by-products are exhausted. However, excited oxygen atoms and ions help the removal of the ligands from the adsorbed fragments on the surface and improve the formation of the Si–O–Si band. The rate for these two processes is proportional to the product of the concentrations as described by Eq. (3), for electron impact dissociation (R_e^{TEOS}) and Eq. (4) for oxidation process (R_O^{TEOS}).

$$R_e^{TEOS} \propto n_e \times n_{TEOS}, \tag{3}$$

$$R_O^{TEOS} \propto n_O \times n_{TEOS}, \tag{4}$$