

Effects of the oxygen fraction and substrate bias power on the electrical and optical properties of silicon oxide films by plasma enhanced chemical vapour deposition using TMOS/O₂ gas

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Abstract

Thin oxide films are deposited from tetramethoxysilane in an inductively coupled oxygen glow discharge supplied with radio frequency power. The chemical bonding states of deposited films are analysed by Fourier transform infrared spectroscopy. The deposition rate and optical properties are determined from spectroscopic ellipsometry. Capacitance–voltage measurements are performed in MOS capacitors to obtain the electrical properties of the deposited films. With these tools, the effects of the substrate bias power and the oxygen mole fraction in the gas on the properties of the film are investigated. The refractive index first decreases with an increase in the oxygen mole fraction, and then increases again, showing a behaviour opposite to that of the deposition rate. The deposition rate increases with increasing substrate bias power and then saturates, while the refractive index increases slightly with an increase in the substrate bias power. The fixed oxide charge density decreases with increasing oxygen fraction and with increasing substrate bias power, while the interface trap density increases with increasing oxygen fraction and with increasing substrate bias power.

1. Introduction

Silicon dioxide is one of the most widely used thin films, as interlayer dielectric, in integrated circuits and microelectronics devices. When the substrate materials have poor heat resistance, it is necessary to deposit silicon oxide at low temperature. Plasma enhanced chemical vapour deposition (PECVD) allows deposition of good quality films at low substrate temperature. The merits of a PECVD process, such as film quality, deposition rate and deposition uniformity, are closely connected to the species transport and reactions in plasma as well as to the reactions on the wafer surfaces [1].

Although silane is widely used as a silicon precursor, deposition from organosilicon sources such as TMOS (tetramethoxysilane: Si(OCH₃)₄) [2], TEOS (tetraethoxysilane) [3], TMS (tetramethylsilane) [4], HMDS (hexamethyldisilazane) [5] and HMDSO (hexamethyldisiloxane) [6] with an oxidizer such as oxygen is much better because it results

in conformal thin films. PECVD of silicon dioxide from organosilicon sources and oxygen plasma has been extensively investigated [1–11]. The primary issues have been regarding how process conditions such as silicon precursor dilution, pressure and power govern film deposition and composition.

In PECVD, the plasma is used as an aid to chemically decompose the vapour precursor and as a source of active species involved in the film growth. The activation energy for deposition delivered to the substrate is controlled by the electric field at the surface of the growing film. It has been suggested that low-temperature deposition by PECVD can become practical when combined with ion bombardment during the film growth by applying an electrical bias to the substrate [7]. Energy provided by ion bombardment may induce changes in the film density and composition similar to those that may occur at high deposition temperature. Film density and hardness increase as sputtering removes the weakly bonded material. One can control the energetic growth conditions of a PECVD film.

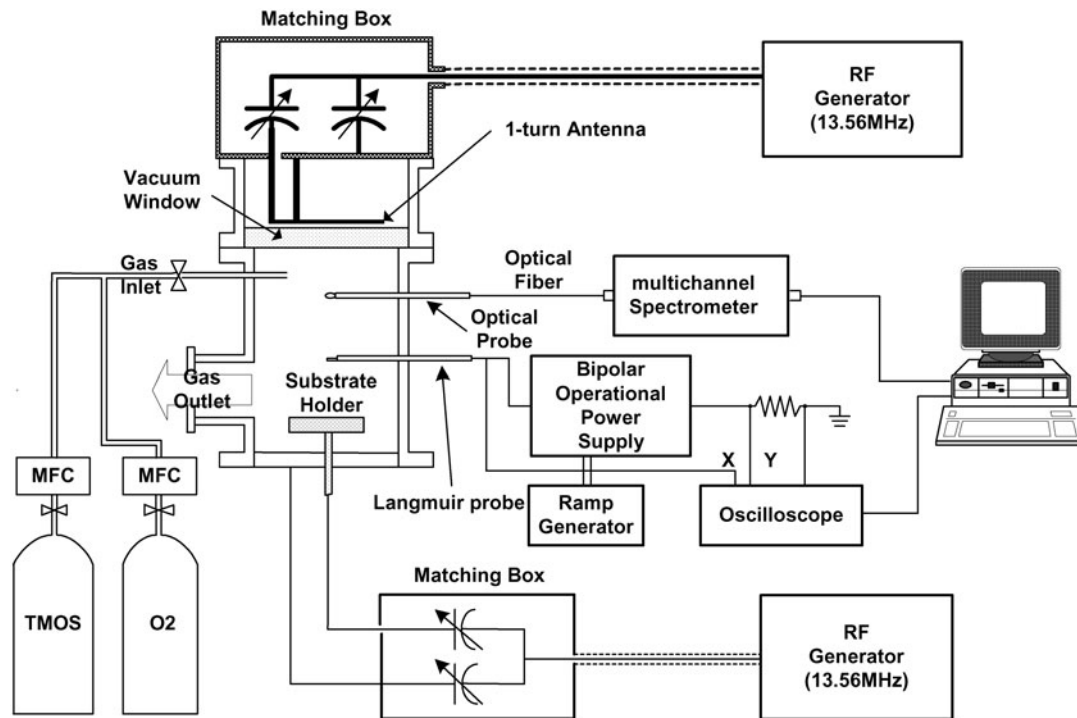


Figure 1. Schematic diagram of the ICP PECVD system with plasma diagnostics.

In a previous paper [12], we investigated the effects of parameters such as the r.f. power of inductive coupling, substrate bias power, oxygen partial pressure and total pressure on the deposition rate and on the chemical bonding states of SiO₂ thin films deposited from TMOS/O₂ in an inductively coupled RF plasma. The plasma was also characterized using Langmuir probe measurements and optical emission spectroscopy. The correlation between the film properties and the plasma characteristics was explained to some extent. In this study, we extend our treatment to the optical and electrical properties of the deposited films since the many applications of this film are determined on the basis of the optical and electrical properties. The film's optical properties are characterized by refractive index measurements using ellipsometry. The characterization of the SiO₂ layers is also performed by *ex situ* Fourier transform infrared spectroscopy (FTIR). The electrical properties of the silicon dioxide film and SiO₂/Si interface are investigated using capacitance–voltage (*C–V*) measurements. Specifically, the aim of this paper is to study the effects of the oxygen mole fraction in the gas and substrate bias power on the electrical and optical properties of the deposited film. The variation of the refractive index is discussed in relation to the deposition rate and the FTIR spectra.

2. Experiment

The PECVD reactor utilizes an inductively coupled plasma source operating at 13.56 MHz to sustain low-pressure (1–50 mTorr) high-density plasmas. The inductively coupled plasma yields a high degree of ionization and significant decomposition of the precursor. Oxygen gas flow and TMOS, regulated by mass flow controllers (AFC 50), are introduced downstream from the plasma, about 10 cm above the substrate.

Films are deposited on p-type Si (100) substrate at room temperature.

The schematic diagram of this system is shown in figure 1. The plasma chamber consists of a stainless-steel cylinder with 28 cm diameter and 34 cm length. A tempered glass plate, 1.9-cm thick and with a 27-cm diameter mounted on one end separates the planar one-turn induction coil from the plasma. The induction coil is made of copper (with water-cooling) and connected to an L-type capacitive matching network and an r.f. power generator (ENI OEM-12). To control the ion bombardment energy, the electrode on which the substrate is placed can be independently driven by a capacitively coupled r.f. source. Hence independent control of the ion/radical fluxes (through the ICP power) and the ion bombardment energy (through the substrate bias power) is possible.

The partial pressure of the organosilicon compound and that of the oxygen gas were controlled by mass flow controllers. The parameter R is defined as the ratio of the partial pressure of the oxygen gas to the total pressure $R = p_{O_2}/p_{total}$, which is the oxygen mole fraction. The total pressure is fixed at 10 mTorr.

Deposition studies were carried out as functions of the substrate bias r.f. power (P_s) and the O₂ mole fraction (R). The chemical bonding states of deposited films were analysed using FTIR (BIO RAD Excalibur). The deposition rate was determined from the ratio of the film thickness to the deposition time. The thickness of the deposited SiO₂ layer is measured using an ellipsometer (Gaertner Scientific L117). The refractive index of the film is determined by modelling the *ex situ* experimental spectroscopic ellipsometric curve in the 1.5–5 eV range. Hereafter, only its value at 632 nm will be reported. High frequency *C–V* measurements are performed using a probe connected to a computer controlled capacitance meter (Keithley 590).

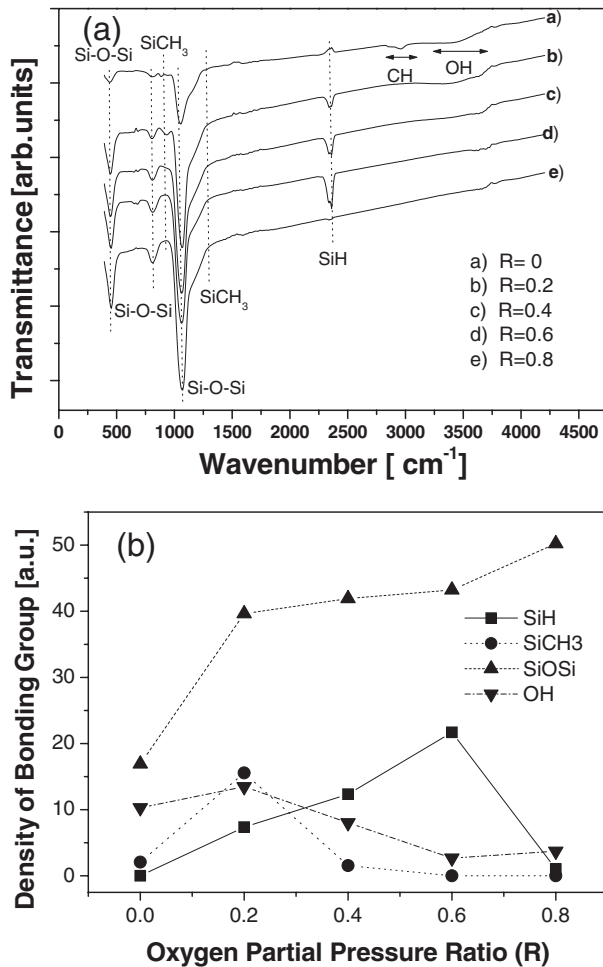


Figure 2. (a) FTIR transmission spectra for films deposited at various oxygen mole fractions, R , where $P_p = 400$ W, $P_s = 30$ W, $p = 1.3$ Pa. (b) Density of bonding group plotted against R .

3. Results and discussion

Figure 2(a) shows FTIR spectra of films deposited at various values of R . The ICP power and substrate bias power are fixed at 400 W and 30 W, respectively. The spectra were obtained from films with the same thickness (200 nm). The spectra exhibit absorption peaks corresponding to Si–O–Si stretching at 1062 cm^{-1} , Si–O–Si deformation at 796 cm^{-1} and Si–O–Si stretching at 440 cm^{-1} . The absorption at 2250 cm^{-1} is assigned to Si–H stretching vibrations [13]. This peak is maximal at $R = 0.6$. When $R = 0$ or 0.2 , strong absorption bands at $870\text{--}760\text{ cm}^{-1}$ and a small band at $1280\text{--}1250\text{ cm}^{-1}$, which are related to the rocking and bending vibrations of SiCH_3 , are clearly observed. The $R = 0$ case has a CH absorption band at $2800\text{--}3100\text{ cm}^{-1}$. Figure 2(b) shows the estimated densities of the bonding groups shown in figure 2(a) as a function of R . Note that the estimated values are obtained by measuring the depth of the absorption peaks from the neighbouring baseline and have arbitrary units. Here, Si–O–Si bonding indicates the Si–O–Si stretching bond at 1062 cm^{-1} , SiOH bonding indicates a broad band between 3300 and 3700 cm^{-1} and SiCH_3 indicates the rocking bond at $870\text{--}760\text{ cm}^{-1}$. The density of the Si–O–Si bonding group increases with increasing R .

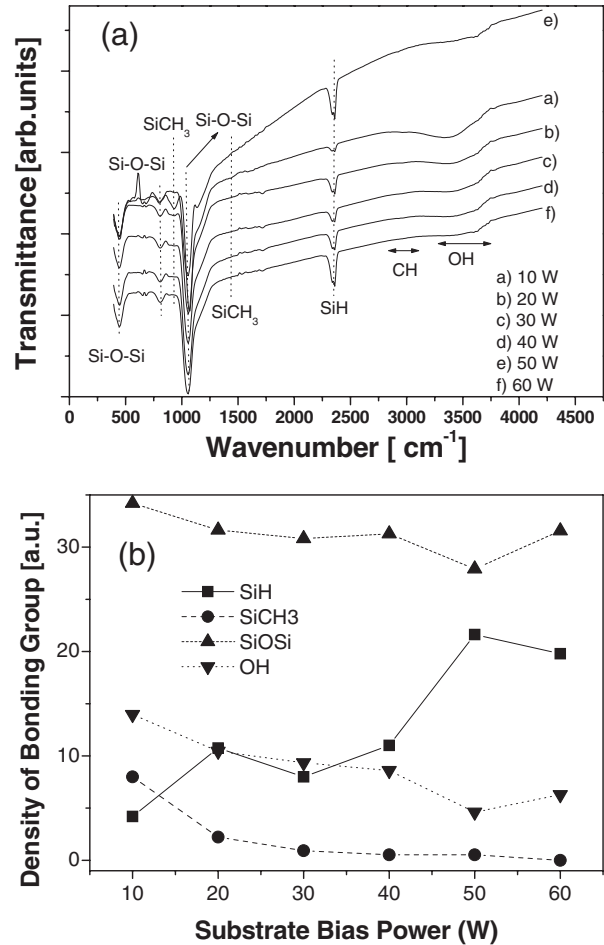


Figure 3. (a) FTIR transmission spectra for films deposited at various substrate bias powers where $P_p = 400$ W, $R = 0.4$, $p = 1.3$ Pa. (b) Density of bonding group plotted against substrate bias power.

Figure 3(a) shows IR spectra of films deposited at various values of substrate bias power. The ICP power and oxygen mole fraction are fixed at 400 W and 0.4 W, respectively. Figure 3(b) shows the estimated densities of the bonding groups as a function of the substrate bias power. One of the effects of increasing the substrate bias power is the net decrease of the entire SiOH integrated absorbance between 3300 and 3700 cm^{-1} . The SiCH_3 peaks decrease on increasing the substrate bias power, while the SiH peak is maximal at $P_s = 50$ W.

The mechanism of deposition from organosilicon precursors such as TMOS has been explained in several ways. One view is that the formation of the Si–O–Si bond is based on dehydration condensation from the silanol group [2]. Another view is that TMOS molecules are almost completely broken into small radicals [7, 8] and the Si–O–Si network is formed from the surface reactions of these fragments. The deposition occurs through ion assisted and oxygen atom initiated pathways [14]. The deposition rate depends on the sum of oxygen atom induced and oxygen ion assisted pathways.

In figure 4, the dependence of the deposition rate on oxygen mole fraction R is shown. The ICP power substrate bias power and pressure are kept constant at 400 W, 30 W

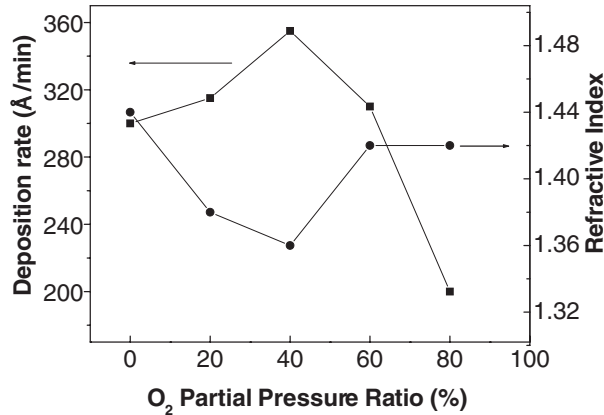


Figure 4. Deposition rate and index of refraction as a function of oxygen mole fraction, R , where $P_p = 400$ W, $P_s = 30$ W, $p_{\text{total}} = 1.3$ Pa.

and 1.3 Pa, respectively. Starting from the TMOS-only case ($R = 0$), the deposition rate increases with the addition of oxygen, which promotes gas-phase decomposition of the TMOS molecules and formation of intermediate precursors. The plot shows that the deposition rate reaches its maximum at $R = 0.4$. This is caused by a balance between the amount of atomic oxygen needed to convert the TMOS in the film and the amount of TMOS supplying the material for the film growth. For high O₂ mole fraction, the deposition rate is limited by the availability of TMOS, while for low O₂ mole fraction, the surface is covered with the fragments of TMOS and the deposition rate is limited by the availability of O atoms. This is due to the depletion of TMOS with increasing oxygen mole fraction in the gas. A similar trend is found in the case of TEOS [3], but this behaviour is in contrast to the case of HMDSO, where the deposition rate depends linearly on the HMDSO concentration [15]. Note that the deposition rate is lower than that obtained in microwave plasma reactors [16].

As can be seen in figure 4, the refractive index lies between 1.36 and 1.44. These values are quite low with respect to that of thermal SiO₂ ($n \approx 1.456$). The refractive index first decreases with an increase in the oxygen mole fraction, and then increases again. The variation of the refractive index with the oxygen fraction is the reverse of the variation of the deposition rate. As the oxygen mole fraction decreases from 1 in the gas, films successively evolve from good to porous SiO₂ and finally to organic SiO_xC_yH_z films. Although oxygen atoms are assumed to play a role in the dissociation of the TMOS molecules, they are also responsible for the elimination of C and H atoms from the growing films [17]. For lower oxygen fraction in the gas, the refractive index increases due to incorporation of carbon species [18, 19]. We can attribute the decrease of the refractive index to the incorporation of more oxygen. It was previously shown in different PECVD reactors that the refractive index decreased with increasing oxygen concentration at a fixed flow rate of precursor molecules [4, 10, 20]. The high refractive index could be attributed to the densification of the film and/or to the presence of Si–H bonds [21]. Low values of the refractive index are also likely to be related to a higher fraction of voids in these films [18]. The increasing of the void fraction might be a consequence of the increasing growth rate. These results

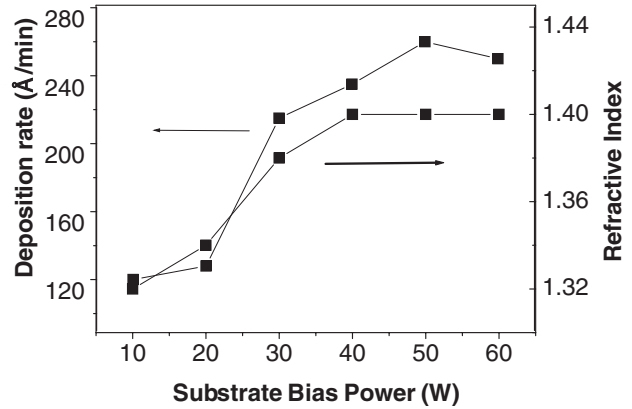


Figure 5. Deposition rate and index of refraction as a function of substrate bias power, where $P_p = 400$ W, $R = 0.4$, $p_{\text{total}} = 1.3$ Pa.

indicate that good quality films are deposited at low deposition rate. However, a quantitative analysis should be performed in order to discover whether the increase in the deposition rate is due to a decrease in film density or whether it is purely due to an increase in mass due to the availability of constituent materials (which was discussed above).

Figure 5 shows the deposition rate as a function of substrate bias power. The deposition rate increases with increasing substrate bias power up to 50 W and then saturates. As was discussed in the previous paper [12], this phenomenon seems to be related to the variation of electron density and electron temperature with substrate bias power. With increasing substrate bias power, the electron density increases and then saturates, while the electron temperature continues to increase. It has been established that electrons play an important role in TEOS fragmentation [22]. In other views, the surface bombardment of ions activates the surface adsorption sites, leading to an increase of net adsorption rate [21]. A substrate bias power larger than 60 W results in capacitive discharge near the substrate and changes the plasma properties. Generally, larger substrate bias facilitates the etching of the deposited film.

Figure 5 also shows the refractive index as a function of the substrate bias power. The refractive index increases slightly with the substrate bias power. The energetic ions are also responsible for the observed improvement of oxide film properties since they can induce local bond rearrangement resulting in dense stable films with low stress [23]. In figure 3, we observe that as the substrate bias power increases the Si–OH infrared absorption decreases. The OH elimination is achieved due to the temperature increase of the substrate at higher substrate power. PECVD films always contain precursor fragments such as hydrogen, carbon or a hydrocarbon group. It is possible to minimize their concentration by raising the substrate temperature or by increasing the degree of ion bombardment during deposition. Since the void and SiOH fraction in the films can be reduced by increasing ion bombardment energy, ion flux at low ion energies (25–50 eV) is particularly useful for increasing the refractive index.

Figure 6 shows the C – V curves of the silicon oxide films deposited at different O₂ mole fractions (R). The C – V curves are shifted towards negative voltage. A negative flat-band voltage (V_{fb}) indicates the presence of positive charges in

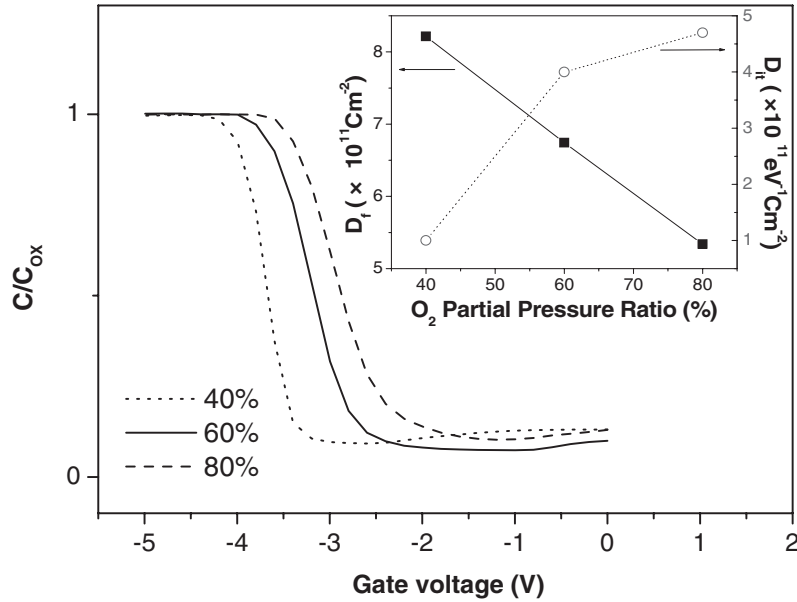


Figure 6. C - V curves of the films deposited at different oxygen mole fractions, R , where $P_p = 500 \text{ W}$, $P_s = 30 \text{ W}$, $R = 0.4$, $p_{total} = 1.3 \text{ Pa}$. The inset shows the variations of the interface trap density (D_{it}) and fixed oxide charge density (D_f) with R .

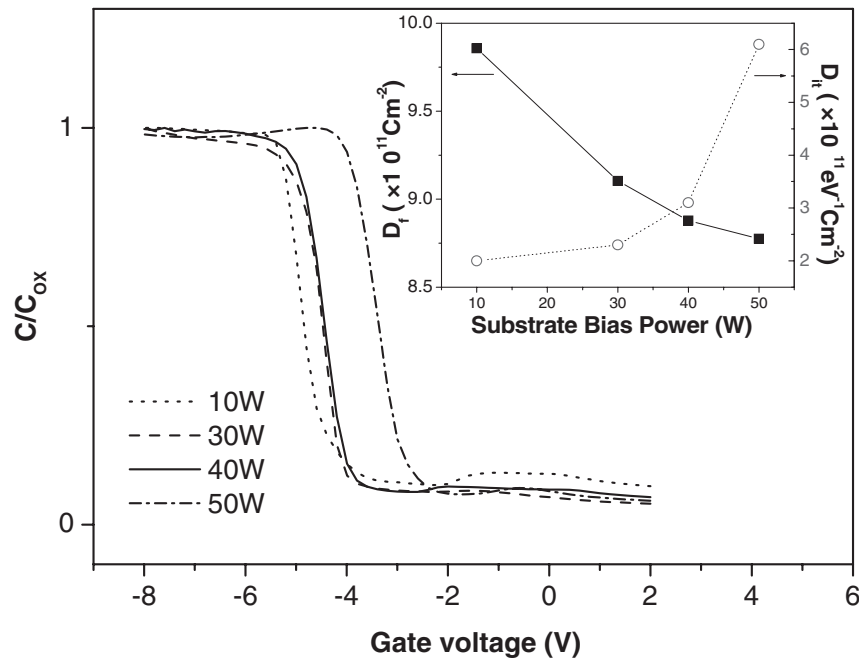


Figure 7. C - V curves of the films deposited at different r.f. bias powers, where $P_p = 500 \text{ W}$, $R = 0.4$, $p_{total} = 1.3 \text{ Pa}$. The inset shows the variations of the interface trap density (D_{it}) and fixed oxide charge density (D_f) with the r.f. bias power.

the oxide. These positive charges are defects which are usually holes trapped at the oxygen vacancies [24]. The V_{fb} becomes more negative with decreasing oxygen fraction in the gas because decreasing oxygen mole fraction increases oxygen vacancy defects. Interface trap density (D_{it}) and fixed oxide charge density (D_f) were calculated by fitting the C - V curves with a theoretical curve. The theoretical curve is obtained by a numerical integration of semiconductor depletion capacitance presented in [25]. The model assumes constant D_{it} through the Si energy gap and this assumption is sufficient for the scope of the present study. As shown in the inset of figure 6,

D_f decreases with increasing oxygen fraction. The trend is expected since the fraction of sub-stoichiometric silicon oxide should decrease with increasing oxygen fraction in the gas. The interface trap density increases with increasing oxygen fraction. Excess oxygen or impurities (carbon or OH) might also act as trap sites in the oxide films [26]. The general tendency presented here is in agreement with the TEOS/ O_2 case [24] but in contrast to the O_2 /(HMDS + He) case [5].

Figure 7 shows the C - V curves of the silicon oxide films deposited at different substrate bias powers. D_{it} increases with increasing substrate bias power. An increase of the

oxygen ion bombardment rate would deteriorate the interface property. As shown in the inset, D_f decreases with increasing substrate bias power. Defects and/or contaminants, which are loosely bound, are effectively removed by increasing the ion bombardment energy. However, the increased ion bombardment energy causes damage at the interface and increases D_{it} .

4. Conclusion

Plasma enhanced chemical vapour deposition of silicon dioxide thin films using tetramethoxysilane and oxygen gas was investigated in an inductively coupled RF discharge. The optical and electrical characteristics of the deposited films have been studied with varying process parameters. The process parameters, such as oxygen mole fraction in the gas and substrate bias power, had profound effects on the deposition rate and the film properties. The refractive index first decreased with an increase in the oxygen mole fraction, and then increased again, showing behaviour opposite to the deposition rate. For a lower oxygen fraction in the gas, the refractive index increased due to the incorporation of carbon species. We can attribute the decrease of the refractive index to the incorporation of more oxygen. The high refractive index could be attributed to the densification of the film and/or to the presence of Si–H bonds. The deposition rate increased with increasing substrate bias power up to 50 W and then saturated, while the refractive index increased slightly with the substrate bias power. As the substrate bias power increased, the void and SiOH fraction in the films reduced due to the increase of ion bombardment energy. The fixed oxide charge density decreased with increasing oxygen fraction and with increasing substrate bias power, while the interface trap density increased with increasing oxygen fraction and with increasing substrate bias power.

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