PROPERTIES OF SILICON DIOXIDE FILM DEPOSITED BY PECVD AT LOW TEMPERATURE/PRESSURE

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Abstract

In this paper we report results on synthesis of thin films of silicon dioxide (SiO_2) using conventional plasma enhanced chemical vapor deposition (PECVD) at low temperature/pressure with silane (SiH_4) and nitrous oxide (N_2O) as precursor gases. The ellipsometer and stress measurement system were used to test the thickness and refractive index uniformity of the SiO_2 film fabricated. The effects of radio frequency (RF) power chamber pressure and N_2O/SiH_4 flow ratio on the properties of SiO_2 film were studied. The results show that the refractive index of SiO_2 film is mainly determined by N_2O/SiH_4 flow ratio .Moreover, the formation of SiO_2 thin films is confirmed by Fourier transform infrared (FTIR) spectroscopy. The thickness and refractive indices of the films measured by ellipsometry C-V measurement show that the electrical properties are directly related to process parameters and Si/SiO_2 interface. The MIS structures were also fabricated from optimized SiO_2 layer to study C-V measurement and to estimate interface, oxide and effective border traps density. The deposited SiO_2 films have good uniformity, compact structure, high deposition rate, low deposition temperature and controllable stress, which can be widely, used in semiconductor devices.
Keywords: Thin Films; Silicon Dioxide; Plasma Enhanced Chemical Vapor Deposition (PECVD); Fourier transform infrared (FTIR) spectra; UV-Visible Spectroscopy; Ellipsometry.

Introduction

Silicon dioxide thin films are widely used in semiconductor device technology as gate insulators, for passivation and as intermetallic dielectric layers. These films are

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either thermally grown through the oxidation of silicon or deposited by thermal or plasma-enhanced

Chemical Vapor Deposition (PECVD). The advantage of PECVD is that low deposition temperatures can be used, avoiding defect formation in the underlying silicon substrate, dopant diffusion and degradation of the metal layers.

However, PECVD-prepared silicon dioxide films are usually affected by a high impurity concentration (hydrogen and nitrogen, H_2O, Si–OH groups), and are characterized by a high porosity compared with those deposited at higher temperature [1]. To improve the quality of the deposited layers, PECVD processes can be optimized by varying some deposition (i.e. temperature, total and partial pressures, plasma power and frequency, etc.) and post-deposition (temperature and environment of the annealing process) parameters [2–4].

In this work, we present some results on the chemical and structural properties of SiO_2 thin films prepared by PECVD from silane (SiH_4) and N_2O precursors. We have mainly investigated the influence of the N_2O/SiH_4 flow ratio by using Rutherford backscattering spectrometry (RBS), ellipsometry and infrared (IR) spectroscopy. The idea was to show that a variation of the N_2O/SiH_4 flow ratio can influence not only, as expected, the composition of the deposited layers, but also their structure.

Experimental

The deposition processes were achieved in the FHR-PECVD 100 system. The structure of the system is illustrated in Fig.1. The system was equipped with both high-frequency (13.56 MHz) and low-frequency (300 kHz) powers for stress controlling but in our experiments only high-frequency power was used.
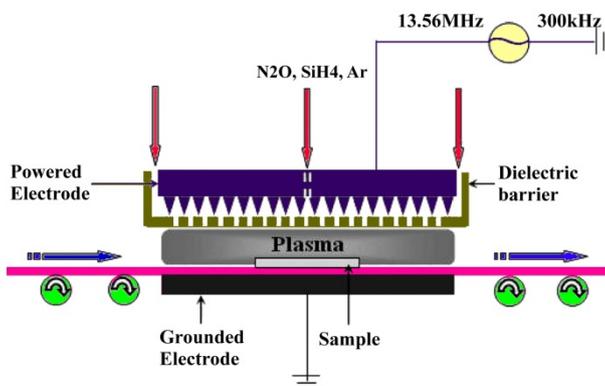

Fig.1. Schematic set up of PECVD system

The base pressure for predisposition was 1×10^{-3} Pa and the process pressure was adjusted by a throttle valve. In order to obtain the exact temperature on the substrate in process mode, the thermocouple was placed on the substrate and the temperatures both on the heater and the substrate were obtained as shown in Fig.2. The chamber pressure was set to be 40 Pa. The oxidation thickness and refractive index of the SiO_2 films were measured by an ellipsometer Auto EL-AV. The stress of the film was obtained by the stress measurement system FLX-2320-S.
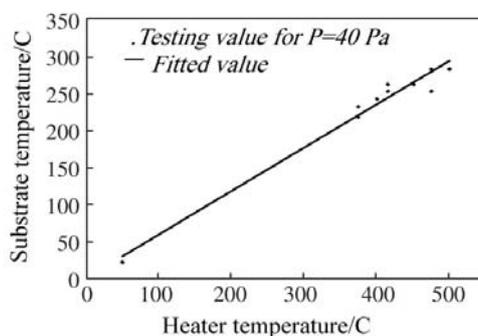
Fig.2. Temperature on the substrate and the heater

Fourier transform infrared (FTIR) spectra of the films were recorded by using FTIR spectrophotometer (JASCO, Japan). Bonded oxygen content (CO) was calculated from stretching mode of infra red (IR) absorption peak using the method proposed by Iftiquar [5]. The thickness of films is measured by using ellipsometery and was further confirmed by UV-Visible spectroscopy applying the method proposed by Swanepoel [6]. All samples were annealed at 450°C in ambient environment for 15 min and allowed to cool to the room temperature. After the substrate was loaded in the reaction chamber, it was baked for 20 min in the argon atmosphere to ensure the temperature

uniformity. The substrate temperature was fixed at 260 ℃ (the heater temperature was

450℃) and the side wall of the chamber was heated up to 50 ℃ in order to prevent SiO_2

from depositing on the sidewall. SiH_4 (25% in volume, diluted by helium) and N_2O were used as the precursor gases. The N_2O flow was set to be 200 cm^3/min and kept constant, and the N_2O/SiH_4 flow ratio was regulated by adjusting SiH_4 flow. The metal-insulator-semiconductor (MIS) structures were fabricated for capacitance-voltage (C-V) measurements and for interface characterization. The C-V measurements were achieved with the inductance, capacitance, and resistance (LCR) meter by varying voltage from 3 to 3 V at 1 MHz frequency. The operating variables were high frequency RF power, chamber pressure and N_2O/SiH_4 flow ratio. For safety reason, the chamber and the gasoline must be flushed with argon more than 5 circles before getting the substrate out.

Results

Deposition of SiO$_2$ film

The plot of deposition rate as a function of chamber pressure is shown in Fig.3 at various units of radio-frequency (RF) power. The SiH_4 flow was set to be the same for all samples, i.e. 55 cm^3/min and was held constant. It is shown that with the increase of

chamber pressure, the deposition rate first increased quickly and then the increase gradually slowed down. The higher the chamber pressure, the lower the change rate of the deposition rate.

This behavior may be explained considering that as the chamber pressure was increased, the concentration of the reactive gas rose, which accelerated the reaction process and the deposition rate. However, at higher chamber pressures, the ion collision was increased, and the energy reduced, which led to the slow increase of deposition rate.

Moreover, the deposition rate was increased with the increase of the RF power from 15 to 150 W. It was the increased energy of the electrons produced by higher RF power that increased the dissociation of the reactant gases and thus the deposition rate.
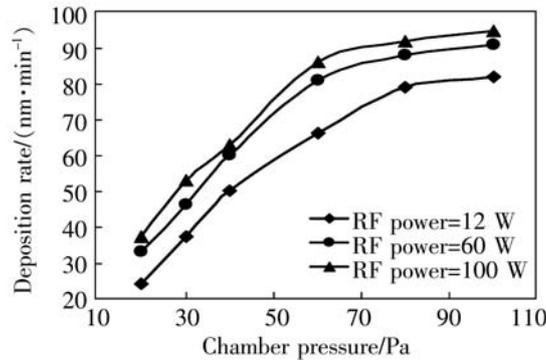

Fig.3. Variation of deposition rate of SiO$_2$ film with chamber pressure and RF power

The deposition rate showed a maximum decrease trend as SiH$_4$ flow increased, as illustrated in Fig.4. In this part, the RF power was set to be 60 W, and the chamber pressure was 100 Pa. It could be seen that the deposition rate was closely correlated with the N$_2$O/SiH$_4$ flow ratio, which could be explained by the reaction theory, as shown in Eq. (1) [5].

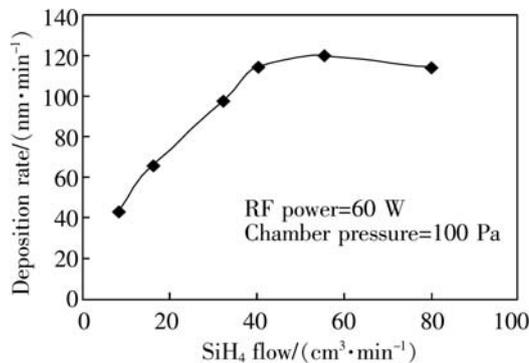$$SiH_4 + 2N_2O \rightarrow SiO_2 + 2N_2 + H_2 \tag{1}$$

Fig.4. Deposition rate of SiO$_2$ film as a function of SiH$_4$ flow

At first, by increasing the SiH_4 flow, the number of Si based radicals was increased in the plasma with the increase of deposition rate. When the SiH_4 flow was 55 cm^3/min, the deposition rate reached the maximum value of 120 nm/min. approximately

the N_2O/SiH_4 flow ratio was 14:1, much higher than the theoretical value of 2:1.

This phenomenon could be attributed to the low dissolution rate of N_2O. Furthermore, when SiH_4 flow was higher than 55 cm^3/min, white SiO_2 powder, which was a kind of byproduct, was deposited on the chamber wall and observed in the pumping line after deposition process. Then the deposition rate began to decrease because precursors were consumed to form these particles.

FTIR spectroscopic analysis
        The FTIR spectrum of SiO_2 films deposited at various oxygen partial pressures (PO_2) by PECVD are shown in Fig. 5.
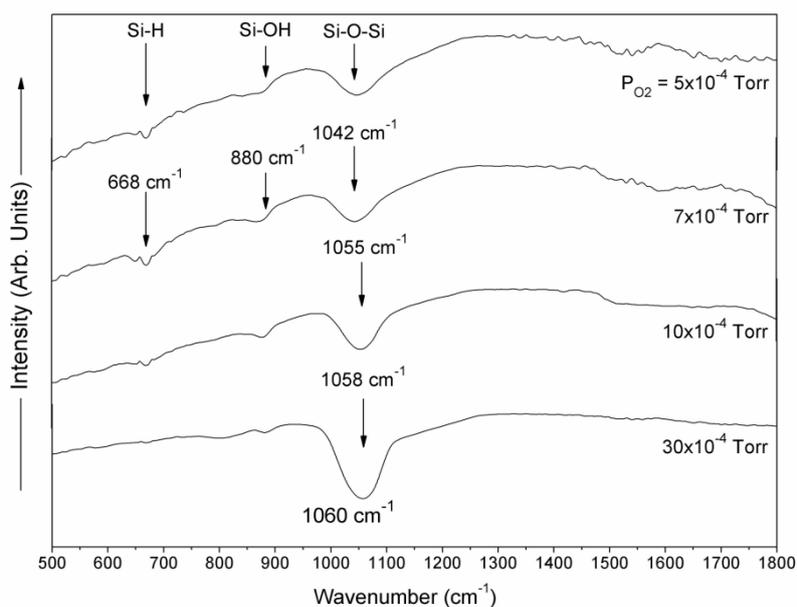

Fig. 5. FTIR transmission spectra of the series of samples deposited at different oxygen partial pressures. The spectra are arbitrarily shifted vertically for clarity

Taking into account the FTIR spectra for the films deposited at various oxygen partial pressures, observations are as follows:
- All films have major absorption bands at ~ 668 cm^{-1} due to Si-O-Si bending vibrational mode [7], at ~ 880 cm^{-1} due to bending vibrational mode of Si-OH bonded species [8], and at ~ 1042 cm^{-1} due to anisometric stretching vibrational mode of Si-O-Si [9].

- It can be clearly noticed that with increasing oxygen partial pressure, the intensity of absorption of band ~ 1042 cm^{-1} increases and it shifts towards higher wave number. The increase in intensity absorption of band indicates increase in oxygen content in the films with increase in oxygen partial pressure in SiH_4 and H_2 plasma, whereas the shifting of absorption of band towards higher wave number indicates the formation of stoichiometric SiO_2 [10].
- The presence of only one broad peak in Fig. 1 indicates that there is no hydrogen bonding present in the deposited films. This implies that H_2O concentration in the film is very low. The relative peak intensity of Si-O bending to O-H bending further supports conjecture.
- Furthermore, appearance of weak absorption peak at ~ 880 cm^{-1} in the FTIR spectra may be due to silanol which is formed due to unreacted silane, oxygen, and hydrogen in the plasma [9].

Therefore, the FTIR spectroscopic analysis clearly indicates the formation of SiO_2 films using the silane and oxygen mixture by using PE-CVD technique.

Ellipsometry analysis

Fig. 6 shows the variation of static refractive index (n_0) and deposition rate (r_d) for SiO_2 films deposited by PECVD as a function of oxygen partial pressure (P_{O2}).
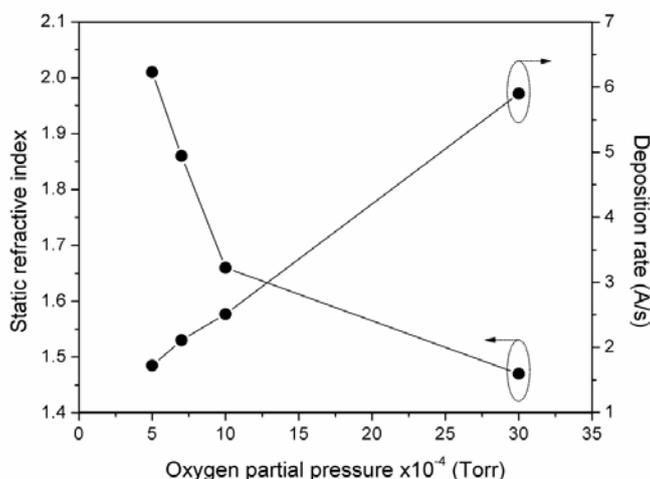

Fig. 6. Variation of static refractive index and deposition rate as a function of oxygen partial pressure for SiO2 thin films deposited by PECVD

As seen from the figure, the deposition rate of SiO2 films increases from 1.72 A^o/s to 5.90 A^o/s as oxygen partial pressure increases from 5×10^{-4} to 30×10^{-4} Torr. It was reasonable to expect the increase in deposition rate with increase in oxygen partial pressure. With increasing P_{O2} the density of O_2 in the deposition chamber increases. The O_2 is highly reactive with silane. Thus, at the fixed deposition pressure and the plasma excitation power employed, the density of reactive precursors responsible for the growth of SiO_2 increases with increase in P_{O2}. As a result the deposition rate increases with increase in oxygen partial pressure. The abrupt increase in deposition rate for the SiO_2 film deposited at $P_{O2} = 30 \times 10^{-4}$ Torr further supports this inference.

Also, as seen from the same figure, the static refractive index for SiO_2 films decreases from 2.01 to 1.47 as the oxygen partial pressure was increased from 5×10^{-4} to 30×10^{-4} Torr. It is interesting to note that the value of static refractive index for ultra-thin SiO_2 film having thickness of 88 Å (1.47) is same as that of bulk SiO_2. This result indicates that the dense SiO_2 films exhibiting very similar optical characteristics that of bulk SiO_2 can be obtained from PECVD technique using silane and oxygen mixture.

Capacitance-Voltage (C-V) measurements

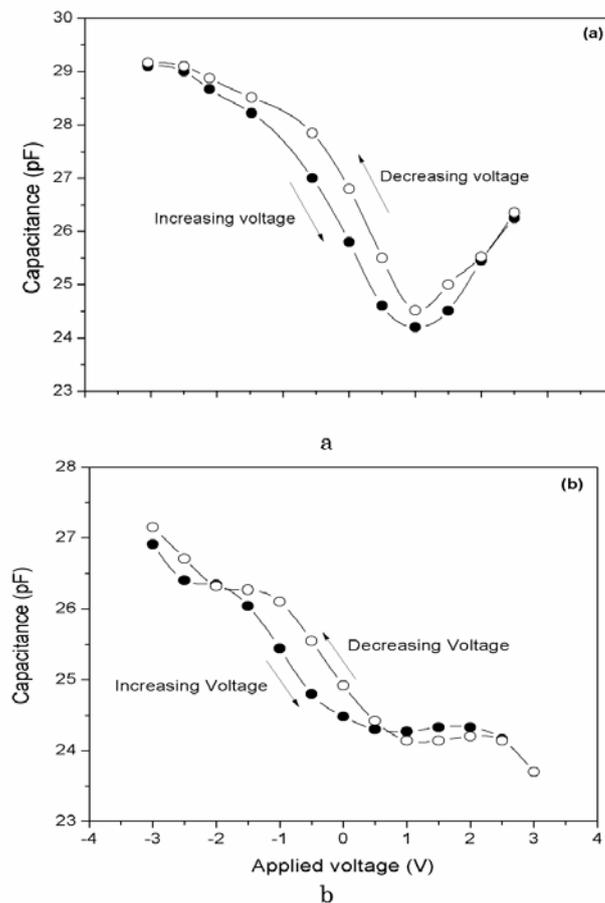Fig. 7 shows the high frequency C-V measurement curves for the SiO_2 film (thickness – 924 Å) before and after annealing.

Fig. 7. The C-V plot for SiO_2 film of thickness 924 Å annealed (a) and unannealed (b)

As seen from Fig. 7 a significant hysteresis is observed in C-V plot for both annealed as well as unannealed films. This result shows the presence of border traps in the films. The estimated density of border trap (see Table 1) is agrees with previously reported values [11]. Furthermore, a jump like change in C-V curve is observed for the unannealed film which is due to the effect of electric field during deposition of SiO_2 film. Similar results have been observed for ultra-thin SiO_2 films [12].

Table 1 Interface traps Qit, border traps Qbt and oxide traps Qot are calculated from C-V measurements. The corresponding thickness and refractive index measured from ellipsometry are also shown in this table

Sample thickness (Å)	$Qit \times 10^{12}$	$Qbt \times 10^{11}$	$Qot \times 10^{9}$	Refractive index
88	1.5	3.0	5.32	1.47
264	3.2	4.08	8.43	1.47
924	3.9	4.56	24	1.47
3940	2.5	0.88	1.35	1.48

Conclusion

Silicon dioxide (SiO_2) films were successfully deposited by plasma enhanced chemical vapor deposition (PECVD) using silane and nitrous oxide (N_2O) gas mixture. The effect of oxygen partial pressure on material properties has been investigated.

It is observed that the deposition rate increases with increase in RF power and gases partial pressure. The formation of SiO_2 films has been confirmed by FTIR spectroscopic analysis. We observed that static refractive index and interface states for ultra-thin SiO_2 film are the same as that of bulk SiO_2. This result indicates that the ultra-thin SiO_2 film having device quality optical properties can be obtained from PECVD technique using silane and oxygen gas mixture.

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