

PACS numbers: 81.15.Gh, 85.30.Tv

**PROPERTIES OF SILICON DIOXIDE FILMS PREPARED USING
SILANE AND OXYGEN FEEDS BY PE-CVD AT LOW POWER PLASMA**

**S.P. Gore¹, A.M. Funde¹, T.S. Salve², T.M. Bhawe³, S.R. Jadkar¹,
S.V. Ghaisas¹**

¹ University of Pune, 411007, Pune, India
E-mail: svg@electronics.unipune.ac.in

² Politecnico di Milano,
Piazza L. da Vinci, 32 – 20133, P.IVA 04376620151 - CF 80057930150,
Milano, Italy

³ Defence Institute of Advanced technology Girinagar,
411025, Pune, India

In this paper we report on synthesis of thin films of silicon dioxide (SiO₂) using conventional plasma enhanced chemical vapor deposition (PE-CVD) from pure silane (SiH₄) and oxygen (O₂), gas mixture at low RF power (30 Watt) and at moderate substrate temperature (250 °C). We have systematically investigated the material properties of these films as a function of oxygen partial pressure in view of their use in MOS devices. The formation of SiO₂ thin films is confirmed by Fourier transform infrared (FTIR) spectroscopy. The thickness and refractive indices of the films measured by ellipsometry. C-V measurement shows that the electrical properties are directly related to process parameters and Si/SiO₂ interface. The MOS structures were also fabricated from optimized SiO₂ layer to study C-V measurement and to estimate interface, oxide and effective border traps density.

Keywords: PLASMA ENHANCED CVD, C-V PLOTS, METAL OXIDE SEMI-CONDUCTOR, FTIR, UV-VISIBLE SPECTROSCOPY, ELLIPSOMETRY.

(Received 04 February 2011)

1. INTRODUCTION

Silicon dioxide (SiO₂) thin films are extensively studied for various applications in micro-electronics and multi-dielectric optical components because of their low refractive index. In thin film transistors (TFT) for active matrix liquid crystal displays (AMLCD), a low-temperature processing has to be developed to utilize low-cost glass substrates. This reduction in deposition temperature degraded material properties and electrical performance of the devices. It is therefore required to develop a low-temperature process which can give acceptable material and electrical properties. The low-temperature SiO₂ film deposition has been widely studied with different methods such as plasma-enhanced chemical vapor deposition (PE-CVD) [1], photo-CVD [2], ECR plasma CVD [3], Remote-PE-CVD [4] etc. Of these only PE-CVD has been proved to be the low temperature, fast and high growth rate deposition technique for the growth of SiO₂ films [5-7]. However, it has been observed that the low temperature oxide property is

inferior to thermal oxides resulting from the incorporation of the hydrogen related impurities, such as Si-H, Si-OH, and H₂O [8].

The most widely used precursors for the deposition of SiO₂ films using PE-CVD at low substrate temperature are silane (SiH₄) and tetraethoxysilane (TEOS, Si(OC₂H₅)₄) with oxygen (O₂) and nitrous oxide (N₂O). The SiO₂ film deposited using TEOS and O₂ gives excellent step coverage but due to low temperature can incorporate impurities like silanol (SiOH), carbon dioxide (CO₂) and water content. These impurities can degrade device reliability [9]. The films grown using SiH₄ and N₂O shows Si-N, N-H and Si-H bonding groups with high hydrogen content in the films [10]. However, the SiO₂ films deposited from mixture of SiH₄ and O₂ displays only Si-H and O-H bonds along with Si-O-Si bonds. The films produced from SiH₄, O₂ and hydrogen (H₂) mixture shows low hydrogen content with good structural and electrical properties [11,12]. With this motivation an attempt has been made to prepare SiO₂ films from the mixture of SiH₄ and O₂ using PE-CVD method. The electrical and optical properties of these films are studied as a function of oxygen partial pressure. The SiH₄ flow rate is intentionally kept low to ensure better control on film thickness which is essential for MOS structure to improve the dielectric quality [13]. Apart from this, stoichiometry, refractive index, and percentage of incorporated oxygen in the film have been also studied.

2. EXPERIMENTAL DETAILS

The SiO₂ films were deposited simultaneously on corning #7059 glass and p-type Si (100) wafers (3-5 Ωcm⁻¹) by PE-CVD technique using silane, oxygen and hydrogen mixture. Prior to the deposition, the Si wafers were treated with HF to remove any native oxide layer. Initially the deposition chamber evacuated to the base pressure of 3 × 10⁻⁵ Torr. Then the oxygen partial pressure in the deposition chamber was adjusted using micro-needle valve by controlling the oxygen flow rate while silane and hydrogen flow rates were kept constant. Other system parameters are listed in Table 1.

Table 1 – Deposition parameters employed for the synthesis of the SiO₂ films by PE-CVD

| | |
|---------------------------------------|-------------------------------------------------|
| Deposition pressure (P_{dep}) | 0.4 Torr |
| RF power | 30 W |
| Inter-electrode distance | 4 cm |
| Substrate temperature (Ts) | 250 °C |
| Silane flow rate | 1.5 sccm |
| Hydrogen flow rate | 20 sccm |
| Oxygen partial pressure (P_{O_2}) | 3 × 10 ⁻⁴ -3 × 10 ⁻³ Torr |

Fourier transform infrared (FTIR) spectra of the films were recorded by using FTIR spectrophotometer (JASCO, Japan). Bonded oxygen content (C_O) was calculated from stretching mode of IR absorption peak using the method proposed by *Iftiqar* [14]. The thickness of films is measured by using ellipsometry and further confirmed UV-Visible spectroscopy using the

method proposed by *Swanepoel* [15]. All samples were annealed at 450 °C in ambient environment for 15 min and allowed to cool them to room temperature. Gold dots are thermally evaporated through a metal shadow mask on top surface of SiO₂ films to form the gate electrode. Aluminum was also thermally evaporated on the back surface of Si wafer for ohmic contacts. The MIS structures were fabricated for C-V measurements and for interface characterization. The C-V measurements were achieved with LCR meter by varying voltage from - 3 V to 3 V at 1 MHz frequency.

3. RESULT AND DISCUSSION

3.1 FTIR spectroscopic analysis

The FTIR spectra of SiO₂ films deposited at various oxygen partial pressures (PO₂) by PE-CVD is shown in Fig. 1.

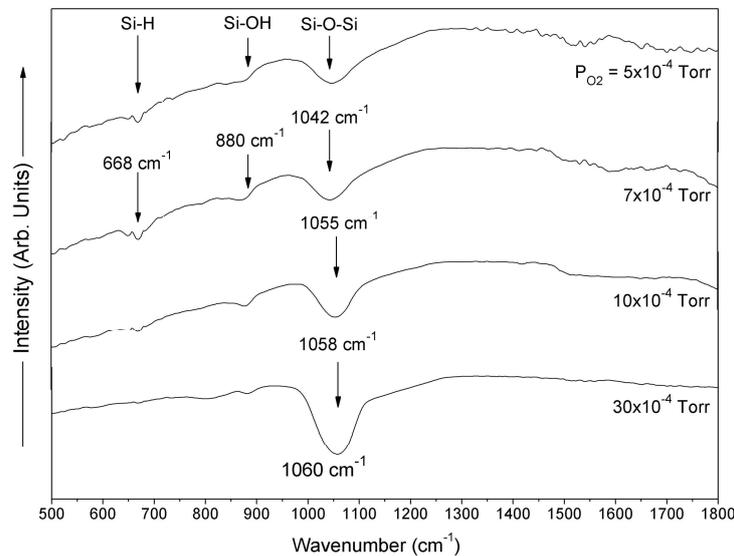


Fig. 1 – FTIR transmission spectrum of the series of samples deposited at different oxygen partial pressures. The spectra are arbitrarily shifted vertically for clarity

Following observations have been made from the FTIR spectra for the films deposited at various oxygen partial pressures;

- All films have major absorption bands at ~ 668 cm⁻¹ due to Si-O-Si bending vibrational mode [16], at ~ 880 cm⁻¹ due to bending vibrational mode of Si-OH bonded species [17] and at ~ 1042 cm⁻¹ due to anti-symmetric stretching vibrational mode of Si-O-Si [18].
- 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 SiH₄ and H₂ plasma whereas the shifting of absorption of band towards higher wave number indicates the formation of stoichiometric SiO₂ [10].

- The presence of only one broad peak in figure 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 $\sim 880\text{ cm}^{-1}$ in the FTIR spectra may be due to silanol which is formed due to unreacted silane, oxygen, and hydrogen in the plasma [18].

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

3.2 Ellipsometry analysis

Fig. 2 shows the variation of static refractive index (n_0) and deposition rate (r_d) as a function of oxygen partial pressure (P_{O_2}) for SiO_2 films deposited by PE-CVD as a function of oxygen partial pressure (P_{O_2}).

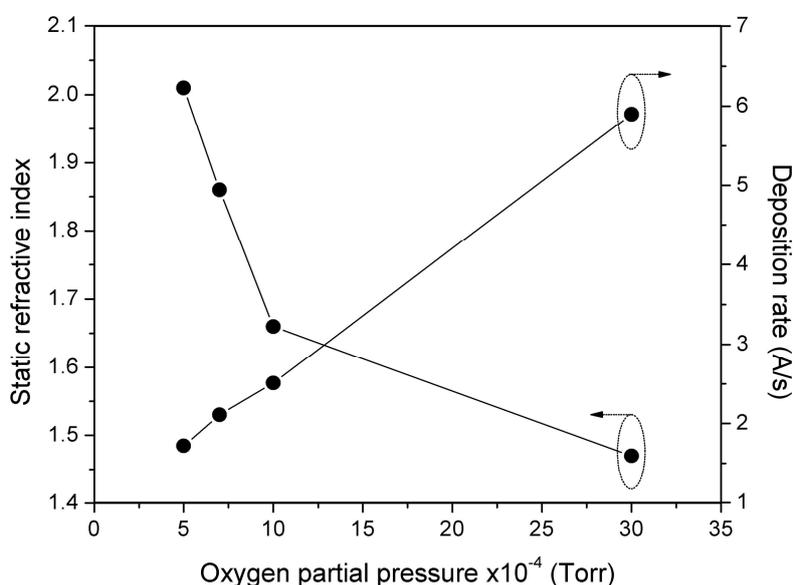


Fig. 2 – Variation of static refractive index and deposition rate as a function of oxygen partial pressure for SiO_2 thin films deposited by PE-CVD

As seen from the figure the deposition rate of SiO_2 films increases from $1.72\text{ \AA}/\text{s}$ to $5.90\text{ \AA}/\text{s}$ as oxygen partial pressure increases from 5×10^{-4} to 30×10^{-4} Torr. The increase in deposition rate with increase in oxygen partial pressure is as expected. With increasing P_{O_2} 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_{O_2} . 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 $P_{\text{O}_2} = 30 \times 10^{-4}$ Torr further support this inference.

Also as seen from the figure, the static refractive index for SiO_2 films decreases from 2.01 to 1.47 as the oxygen partial pressure 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 \AA (1.47) is same as that of bulk SiO_2 . This result indicate that the dense SiO_2 films exhibiting very similar optical characteristics that of bulk SiO_2 can be obtained from PE-CVD technique using silane and oxygen mixture.

3.3 Capacitance-Voltage (C-V) measurements

Fig. 3 shows the high frequency C-V measurement curves for the SiO_2 film (thickness - 924 \AA) before and after annealing.

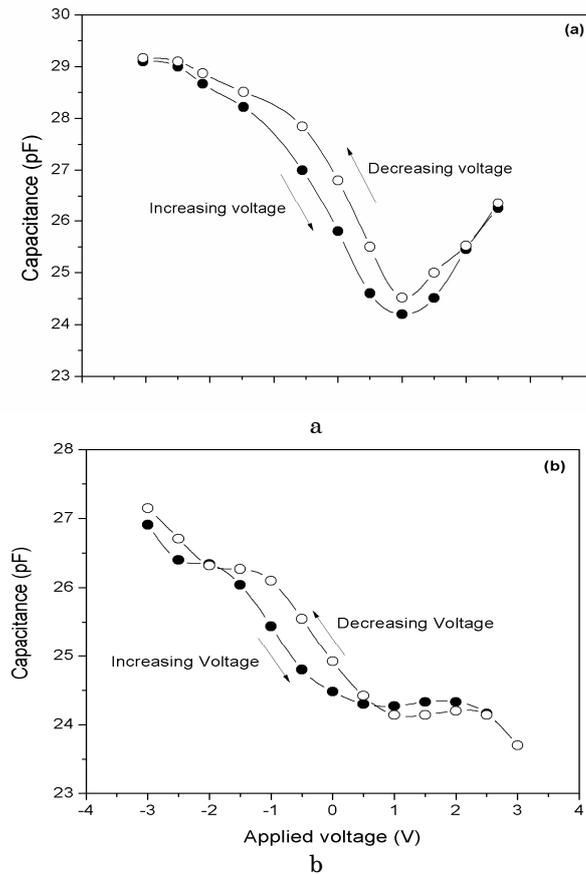


Fig. 3 – The C-V plot for SiO_2 film of thickness 924 \AA annealed (a) and unannealed (b)

As seen from the figure 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 2) is agrees with previously reported values [19]. 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 [20].

Table 2 – Interface trap, Border traps and oxide traps are calculated from C-V measurements. The corresponding thickness and refractive index measured from ellipsometry are also shown in the table

| Sample thickness(E) | $Q_{it} \times 10^{12}$ | $Q_{bt} \times 10^{11}$ | $Q_{ot} \times 10^9$ | 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 |

4. CONCLUSION

Silicon dioxide (SiO₂) films were successfully deposited by plasma enhanced chemical vapor deposition (PE-CVD) using silane and oxygen 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 oxygen partial pressure. The formation of SiO₂ films has been confirmed by FTIR spectroscopic analysis. We observed that static refractive index and interface states for ultra-thin SiO₂ film are same as that of bulk SiO₂. This result indicates that the ultra-thin SiO₂ film having device quality optical properties can be obtained from PE-CVD technique using silane and oxygen gas mixture.

The authors are thankful Indian Space Research Organization ISRO and University of Pune science and technology center (ISRO-UOP-STC) for the financial support.

REFERENCES

1. A.C. Adams, F.R. Alexander, C.D. Capio, T.E. Smith, *J. Electrochem. Soc.* **128**, 1545 (1981).
2. S. Szikora, W. Krauter D. Bauefle, *Mater. Lett.* **2**, 263 (1984).
3. S. Matsuo, M. Kiuchi, *Jpn. J. Appl. Phys.* **22**, L210 (1983).
4. G. Lucovsky, D.V. Tsu, *J. Vac. Sci. Technol. A* **5(4)**, 2231 (1987).
5. G.B. Raupp, T.S. Cale, H.P.W. Hey, *J. Vac. Sci. Technol. B* **10/1**, 37 (1992).
6. Y.-C. Chen, M.-Z. Yang, I-C. Tung, et al., *Jpn. J. Appl. Phys.* **38**, 4226 (1999).
7. A.M. Mahajan, L.S. Patil, J.P. Bange, D.K. Gautam, *J. Opt. (India)* **31**, 53 (2002).
8. S.S. Kim, D.J. Stepleen, G. Lueovsky, *J. Vac. Sci. Technol. A* **8(3)** 2039 (1990).
9. J. Lee, E. Chung, W. Moon, D.H. Suh, *Microelectron. Eng.* **83**, 2001 (2006).
10. P.G. Pai, S.S. Chao, Y. Takagi, G. Lucovsky *J. Vac. Sci. Technol. A* **4 (3)**, 689 (1986).
11. G. Lucovsky, D.V. Tsu, R.J. Markunas, *Mater. Res. Soc. Symp. Proc.* **68**, 323 (1986).
12. J. Batey, E. Tierney, *J. Appl. Phys.* **60**, 3136 (1986).
13. A. Boogaard, R. Roesthuis, I. Brunets et al., *Proceedings of the 11th annual workshop on semiconductor advances for future electronics and sensors (SAFE 2008)*, 452 (2008).
14. S.M. Iftiquar, *J. Phys. D: Appl. Phys.* **31**, 1630 (1998).
15. R. Swanepoel, *J. Phys. E: Sci. Instrum.* **16**, 1214 (1983).
16. G. Lucovsky, *Solar Energy Mater.* **8**, 165 (1982).
17. M. Hinoand, T. Sato, *Bul. Chem. Soc. Jap.* **44**, 33 (1971).
18. J. Osswald, K.T. Fehr, *J. Matter. Sci.* **41**, 1335 (2006).
19. D.M. Fleetwood, N.S. Saks, *J. Appl. Phys.* **79**, 1583 (1996).
20. E.A. Bobrova, N.M. Omeljanovskaya, *Semiconductors* **42**, 1351 (2008).