

Deposition of High-Quality SiO₂ Insulating Films at Low Temperatures by means of Remote PECVD

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Abstract—Silicon dioxide films were deposited by means of remote inductively coupled plasma enhanced chemical vapor deposition (ICPECVD) in Ar-N₂O-SiH₄ plasma at 150 °C and pressures between 1 and 6 Pa. The gas phase contained 0.08% of SiH₄ and 18% of N₂O. We observed that, at a total pressure of 1 Pa, the oxide films were formed with a density equal to that of thermally grown oxide. The films had a low oxide charge. Deposition at higher pressures resulted in the formation of oxides having a lower density than the film deposited at 1 Pa, and a higher oxide charge. We measured a strong dependence of the oxide charge on the film thickness. The films deposited at 1 Pa further exhibited leakage currents at an electric field strength of 6.5 MV/cm which were comparable to the leakage currents known for thermally grown (1000°C) oxides. The film deposited at 2 Pa also exhibited a low leakage current, but the current increase was observed at lower electric fields compared to the 1 Pa film. The films deposited at 6 Pa exhibited significantly higher leakage currents.

Index Terms— ICP, PECVD; silicon dioxide; electrical characterization; oxide charge

I. INTRODUCTION

The fabrication of electronic devices at relatively low deposition temperatures (100–150°C) becomes increasingly important. At low temperature, one can fabricate devices on glass or polymer substrates, or one can add extra functionalities to standard ICs by post-processing [1]. In order to realize good devices, high-electrical quality should be obtained, which is a challenge at such low temperatures.

In the present work, silicon dioxide films were deposited in Ar-N₂O-SiH₄ inductively coupled plasma (ICP) at 150 and 400°C, and pressures between 1 and 6 Pa. The gas phase contained 0.08% of SiH₄ and 18% of N₂O. In comparison with our previous work [2, 3] where the layers were deposited at a SiH₄ fraction of 0.8%, the new layers were grown at the same total pressures, but at a lower silane fraction of 0.08% in the

total gas flow. Although this lower fraction of silane resulted in a reduced deposition rate, the dielectric quality of the films was considerably improved.

Our aim is to deposit high-quality silicon dioxide films at low substrate temperatures in a remote inductively coupled plasma enhanced chemical vapor deposition system (ICPECVD). This paper is a part of an intensive study combining the film deposition, the plasma characterization by a Langmuir probe and optical emission spectroscopy [4, 5], and modeling the chemical reactions in Ar-N₂O-SiH₄ plasmas [6] to obtain optimal process conditions.

We focused in this paper on the effects of total pressure and temperature on deposition rate and film properties.

II. EXPERIMENTAL

Figure 1 schematically shows the system set-up. The inductively-coupled plasma source (supplied by Alcatel Micro Machining Systems; 13.56 MHz, max. electric power of 2 kW) is placed on top of the chamber (also supplied by Alcatel). Quoted electric powers are measured at the output of the rf generator (RF power products, model FR20S), and are not corrected for possible losses in the matching network. The wafer is placed in the load lock on a molybdenum susceptor and positioned on the chuck. The chuck is situated at the bottom of this chamber. The chuck can be heated up to 400 °C. Temperature is controlled by a PID (proportional-integral-derivative) controller via a thermo-couple inserted into the chuck. The wafer is mechanically clamped to the chuck. Argon backing pressure of 10 mbar between the susceptor and the chuck and between the wafer and the susceptor guarantees a fairly good heat transfer between the chuck and the wafer [7, 8]. The chuck can be rf-biased and can be moved upwards into the chamber, i.e., towards the plasma source. Furthermore, in Figure 1 two gas inlets are shown: one above the plasma source and one below, in the chamber. Mass flow controllers (Bronkhorst High-Tech B.V.) are used to control the gas flows. The system is evacuated with an oil-free turbo molecular pump (Adixen ATH 1300 M, argon pumping speed 800 l/min) backed by a dry pump (Adixen ACP 40 G); base pressure is 5·10⁻⁷ mbar. A set of Pfeiffer capacitance gauges is used for accurate measurement of process pressures (Pfeiffer

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CMR 261 and CMR 263), whereas a combined cold wall and Pirani gauge (Pfeiffer PKR 261) measures from base pressure to atmospheric pressure.

Argon was used as a carrier gas, the process pressure ranged from 1 to 6 Pa, while the argon flow was 190 sccm. The process pressure was controlled by a feedback loop to the gate valve. A flow of 44 sccm of nitrous oxide (N_2O) was added to the carrier gas in the plasma zone, while 10 sccm of Ar-SiH₄ mixture (2% silane (SiH₄) in argon) was added downstream of the plasma. This resulted in precursor fractions of 0.08% (SiH₄) and 18% (N_2O) in argon.

Si wafers (*n*-type, 100-mm (100)-orientation) having a resistivity of 1-10 Ω -cm were used for the experiments. The wafer cleaning consisted of a 10-min immersion into 100% fuming HNO₃ and a 10-min immersion into boiling 69% HNO₃, followed by a 30-s dip into 1% HF in order to remove the chemical oxide and passivate the surface by hydrogen atoms.

SiO₂ films with a thickness of approximately 50 nm were deposited at an ICP power of 300 W, a wafer position of 250 mm (see the vertical axis in Fig. 1) and a substrate temperature of 150 or 400 °C.

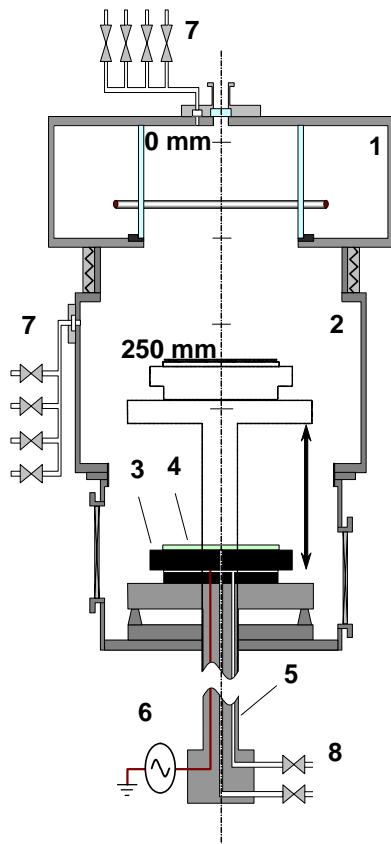


Figure 1. A schematic drawing of the remote-plasma CVD system: (1) ICP source, (2) chamber, (3) chuck and susceptor, (4) wafer, (5) motor-driven arm, (6) rf-source for chuck biasing, (7) gas-inlets, (8) gas-inlet to control pressure between wafer, susceptor and chuck; the gas distribution system, load lock and vacuum pumps are not shown.

The thickness, density and roughness of the deposited oxides were determined by a M2000 spectroscopic ellipsometer (SE), manufactured by J.A. Woollam, Inc., and covering the

spectral range of 245–1700 nm. The SE data were analyzed by a two-layer optical model; from bottom to top: silicon, silicon oxide.

The MOS capacitors were realized by sputtering a 1- μ m thick aluminum layer over the deposited oxide, followed by lithography and etching processes to define 0.1 and 0.2 mm² capacitors. An aluminum layer of the same thickness was also sputtered on the backside of the Si wafer. Wafers were divided into halves and one half was subjected to post-metallization annealing (PMA) for 5 min, at 400 °C in wet N₂ ambient (N₂ bubbled through de-ionized water at room temperature).

The high frequency (10 kHz) capacitance-voltage (*C-V*) and current density-voltage (*J-V*) measurements were carried out using a Hewlett-Packard 4275A multi-frequency meter and a Hewlett-Packard 4140B pA meter, respectively.

III. RESULTS AND DISCUSSION

SiO₂ layers in the thickness range from 30 to 50 nm were deposited at deposition rates of about 0.6 nm/min. The effects of total gas pressure and film annealing conditions on the electrical properties were investigated. Unless stated otherwise, all depositions were done at a substrate temperature of 150 °C.

The layers deposited at a pressure of 6 Pa exhibit a relatively high leakage current (Fig. 2a). The current density has already a maximum at a low electric field of 2 MV/cm, which indicates a high concentration of traps. Such traps can be caused, for example, by extra silicon [9]. However, our earlier work [2, 3] indicated a lower material density rather than the formation of such silicon-rich layers. So, traps are more likely to be caused by a lower material density as a result of building inappropriate chemical network (e.g., dangling bonds partially or fully satisfied with hydrogen instead of Si-O bonds). The ledges between 2 and 10 MV/cm, noticeable in Fig. 2a, are probably related to a conduction mechanism caused by bulk traps. The leakage current decreases within approximately two orders of magnitude when the pressure during the deposition is decreased to 2 Pa, and another 2 orders of magnitude when the pressure is decreased to 1 Pa.

As denser layers should be grown at higher temperatures due to enhanced surface migration and better hydrogen desorption, depositions at 400°C were carried out. By comparing the 2Pa/150°C-curve from fig. 2a with the 2Pa/400°C-curve from fig. 2b one can see that the film deposited at 400°C indeed shows low leakage currents up to an electric field of 6.5 MV/cm. However, the *J-V* characteristics of the film deposited at 150°C but 1 Pa exhibit similar low leakage current (indicating the important role of pressure) comparable to that of thermal oxide.

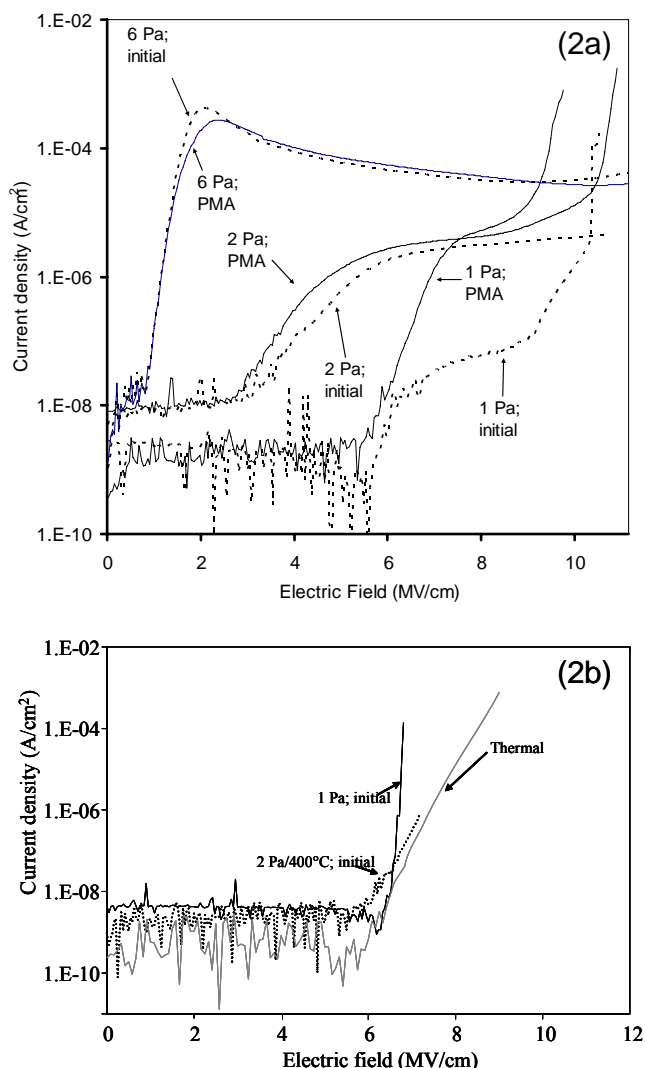


Figure 2. J - V characteristics of oxide layers (~ 50 nm thick) (a) deposited at pressures of 1 and 6 Pa, with and without PMA, and (b) deposited at 1 Pa/150 °C, 2 Pa/400 °C and for thermally grown oxide (1000 °C). The electric field (E) was calculated as $(V-V_{th})$ divided by the optical thickness.

Fig. 3 reveals a strong influence of total pressure on C - V curves. Table 1 compares the oxide thickness calculated using the dielectric constant of a stoichiometric SiO_2 and the optical film thickness of the ellipsometry measurements. The use of the dielectric constant of SiO_2 resulted in the electrical film

thickness lower than the measured optical thickness for the film deposited at 6 Pa. In contrast to this, both the electrical (C - V) and optical (SE) methods measure similar thicknesses of films deposited at 1 and 2 Pa. Furthermore, Fig. 3 shows that the PMA drastically decreases the oxide capacitance for the film deposited at 6 Pa. However, Table 1 shows that even after PMA this film is still electrically much thinner than it can be obtained from optical measurements.

In fig.4 the C - V characteristics of the thermally grown oxide film and those of the oxide film deposited at 1 Pa are compared. One can notice that, in the depletion region, the slope of the thermal oxide film is steeper than that of the 1-Pa film. This decreased slope indicates more interface traps. Oxide fixed charges are charge states in the oxide that do not change their occupancy during the C - V sweep. Accordingly, the oxide fixed charge induces a parallel shift of the entire C - V curve. In contrast to this, the interface charge is trapped by the states changing their occupancy with applied voltage. For example, a trap acting as an acceptor is neutral when empty and negatively charged when occupied by an electron. When free carriers are present in quantities that are not significantly greater than the interface trap density (i.e. weak accumulation or weak inversion), interface traps add a measurable parallel capacitance. Eventually, this leads to a decreased slope of the curves when more interface traps are present [10]. It is well-known that annealing of aluminum-gate devices in H_2O -containing ambient can provide hydrogen atoms for the trap passivation [11]. Indeed, Fig. 3 shows that the slope of the C - V curves increases when PMA is applied to the 6-Pa film, which indicates less interface traps after PMA. However, Fig. 4 indicates that the PMA does not passivate interface traps of the 1-Pa film entirely to the level of the thermally grown oxide. The PMA however significantly decreases the fixed oxide charge in the 1-Pa film (see Fig. 3 and Table 1) as expected from literature [12].

Table 1 summarizes the oxide charge calculated for ~ 50 -nm thick films. We found however that the oxide fixed charge was a function of the layer thickness. This very important observation is shown in Fig. 5 for two deposition conditions. The oxide charge appears to be more positive for thicker films. Extrapolating to zero thickness would give a negative interface charge for both films. With increasing the thickness,

TABLE 1. PROPERTIES OF SiO_2 LAYERS DEPOSITED AT SEVERAL PRESSURES. OXIDE CHARGE WAS CALCULATED ACCORDING TO [2]

total pressure during deposition (Pa)	deposition temperature (°C)	deposition rate (nm/min)	Optical film thickness (nm)	Etch rate in BHF (nm/min)	electrical film thickness		Oxide Charge	
					as-deposited (nm)	after PMA (nm)	as-deposited (10^{11} cm^{-2})	after PMA (10^{11} cm^{-2})
1	150	0.6	4	95	48	50	2.3	-0.42
2	150	0.6	50	100	53	55	-1.6	-0.58
2	400	0.5	49	100	50	50	6.5	0.88
6	150	0.6	51	120	28	32	3.1	5.5

this negative charge seems to be overcompensated by a positive oxide charge so that the total charge becomes positive. As the growing films receive a continuous flux of positive ions from the plasma (both films seem to collect a positive charge of $5 \cdot 10^9 \text{ cm}^{-2}$ per nanometer of their growth, as derived from the slopes in Fig. 5), more positive charge can be collected in a thicker film. The elevated chuck temperature of 400°C is not expected to have an influence on the plasma parameters; this is confirmed by the fact that there is no difference in slope for both films. However, these measurements suggest that the film deposited at 400°C has a less negative interface charge. This might be explained in terms of surface reactions, surface migration and hydrogen desorption, enhanced at 400°C , which resulted in a better interface quality.

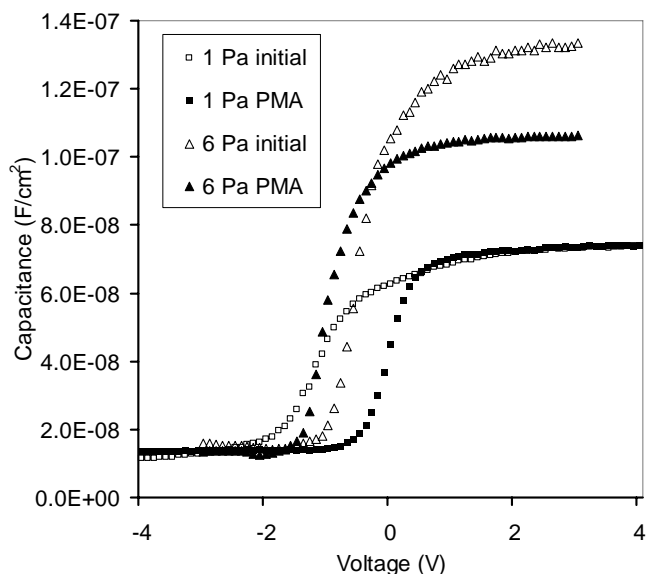


Figure 3. C-V curves of layers deposited at various total pressures, with and without PMA. C-V measurements were done at 10 kHz.

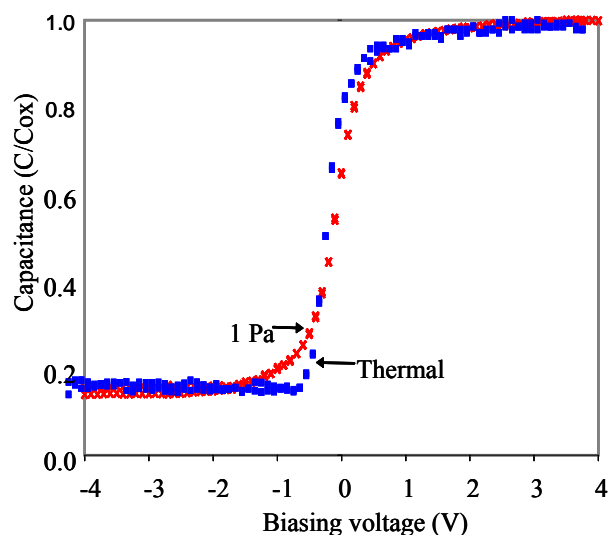


Figure 4. Comparison C-V characteristic of the thermal grown oxide film and the film deposited at 1 Pa and 150°C (both after PMA).

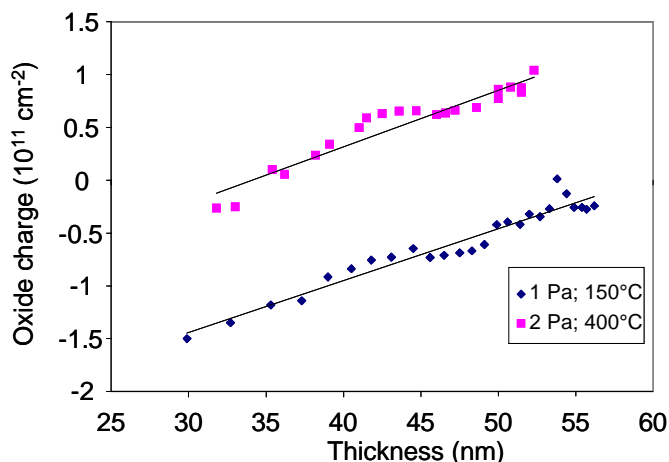


Figure 5. Oxide charge plotted vs. film thickness for layers deposited at 1 Pa/ 150°C and 2 Pa/ 400°C .

We concluded from Fig. 5 that, due to the observed linear behavior, the positive charge should be constantly added to the growing oxide layer during the deposition process. It is important to bear in mind that, for thermally grown SiO_2 , the oxide charge is always fixed-in-space near the SiO_2 -Si interface. The use of this method to calculate, for example, the same absolute charge but spread-in-space over the entire film thickness can lead to obtaining different values. In other words, the same absolute charge values for thermal and plasma oxides are not trivial to measure using the conventional C-V method.

Table 1 also shows the etch rate of our oxides in a 5:1 BHF solution (5 volume parts of 40% NH_4F mixed with 1 volume part of 49% HF). The etch rate of our 1Pa/ 150°C -film is 95 nm/min; this value is close to that of thermally grown oxide (80 nm/min) which confirms that this film is not only electrically but also chemically resembles thermally grown oxide.

IV. CONCLUSIONS

The silicon dioxide films were deposited by means of remote inductively coupled plasma chemical vapor deposition (ICPECVD), from SiH_4 and N_2O mixed with Ar carrier gas. The total gas pressure ranged between 1 and 6 Pa (7.5-45 mTorr), and the substrate temperature was either 150 or 400°C . The gas phase contained 0.08% of SiH_4 and 18% of N_2O , and the applied electrical RF (13.56 MHz) power was 300 W.

At a deposition temperature of 150°C and a total pressure of 1 Pa, the films exhibited very low leakage currents at an electric field strength of 6.5 MV/cm, comparable to the leakage currents known for thermally grown (1000°C) oxides. The best ICPECVD films contained a low concentration of oxide charge in the order of $2 \cdot 10^{11} \text{ cm}^{-2}$. The etch rate in BHF was comparable to that of thermally grown oxide. The deposition at higher pressures (2-6 Pa) resulted in the formation of oxide films with a higher density of electron traps and higher leakage currents. We found that the oxide fixed charge was a function of the layer thickness.

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REFERENCES

- [1] J. Schmitz, "Adding functionality to microchips by wafer post-processing," *Nuclear Instruments & Methods in Physics Research Section a-Accelerators Spectrometers Detectors and Associated Equipment*, vol. 576, pp. 142-149, 2007.
- [2] A. Boogaard, A. Y. Kovalgin, I. Brunets, A. A. I. Aarnink, J. Holleman, R. A. M. Wolters, and J. Schmitz, "Characterization of SiO₂ films deposited at low temperature by means of remote ICPECVD," in *Surface and Coatings Technology*, vol. 201, 2007, pp. 8976-8980.
- [3] A. Boogaard, A. Y. Kovalgin, I. Brunets, J. Holleman, and J. Schmitz, "Optical and Electrical Characterization of SiO₂ films deposited at low temperature by means of remote ICPECVD " *Proceedings of the 10th Annual Workshop on Semiconductor Advances for Future Electronics and Sensors*, pp. 404-407, 2007.
- [4] A. Boogaard, A. Y. Kovalgin, A. A. I. Aarnink, R. A. M. Wolters, J. Holleman, I. Brunets, and J. Schmitz, "Langmuir-probe Characterization of an Inductively-Coupled Remote Plasma System intended for CVD and ALD," *ECS Transactions*, vol. 2, pp. 181-191, 2007.
- [5] A. Boogaard, A. Y. Kovalgin, I. Brunets, A. A. I. Aarnink, J. Holleman, R. A. M. Wolters, and J. Schmitz, "On the Verification of EEDFs in Plasmas with Silane using Optical Emission Spectroscopy," *ECS Transactions*, vol. 6, pp. 259-270, 2007.
- [6] A. Y. Kovalgin, A. Boogaard, I. Brunets, J. Holleman, and J. Schmitz, "Chemical modeling of a high-density inductively-coupled plasma reactor containing silane," in *Surface and Coatings Technology*, vol. 201, 2007, pp. 8849-8853.
- [7] A. Hasper, J. E. J. Schmitz, J. Holleman, and J. F. Verwey, "Heat-Transport in Cold-Wall Single-Wafer Low-Pressure Chemical-Vapor-Deposition Reactors," *Journal of Vacuum Science & Technology a-Vacuum Surfaces and Films*, vol. 10, pp. 3193-3202, 1992.
- [8] A. M. van Graven and R. A. M. Wolters, "Wafer temperature measurement in PVD systems using the Co-Si reaction," *Microelectronic Engineering*, vol. 50, pp. 495-499, 2000.
- [9] V. S. Lysenko, I. P. Tyagulski, Y. V. Gomeniuk, and I. N. Osiyuk, "Effect of traps in the transition Si/SiO₂ layer on input characteristics of SOI transistors," Barcelona, Spain, 2000.
- [10] P. E. Nicollian, "Effect of interface traps and oxide fixed charge," in *Physics of Trap Generation and Electrical Breakdown in Ultra-thin SiO₂ and SiON Gate Dielectric Materials*. Enschede: University of Twente, 2007, pp. 23-24.
- [11] P. Balk, "40 years MOS technology -- from empiricism to science," *Microelectronic Engineering*, vol. 48, pp. 3-6, 1999.
- [12] A. R. Stivers and C. T. Sah, "A study of oxide traps and interface states of the silicon-silicon dioxide interface," *Journal of Applied Physics*, vol. 51, pp. 6292-304, 1980.