

# Low-Temperature SiO<sub>2</sub> Layers Deposited by Combination of ECR Plasma and Supersonic Silane/Helium Jet

## Alexey Y. Kovalgin,<sup>\*,z</sup> Gratiela Isai, Jisk Holleman, and Jurriaan Schmitz

MESA + Institute for Nanotechnology, University of Twente, 7500 AE Enschede, The Netherlands

As the semiconductor industry strives toward wafer postprocessing and three-dimensional integration, a demand has arisen for high-quality thin films deposited at temperatures below 400 °C. In this work, we present SiO<sub>2</sub> films deposited at near room temperature, using a multipolar electron cyclotron resonance (ECR) plasma source, introducing the SiH<sub>4</sub> gas by using a high-velocity jet of silane diluted in helium. The electrical properties were studied under varying deposition parameters, such as gas flow rate, deposition pressure, and postdeposition and postmetallization annealing processes. At a low pressure, low SiH<sub>4</sub> flow and high helium flow, device-quality SiO<sub>2</sub> layers were obtained after a deposition combined with a 5 min postmetallization annealing at 400 °C. These layers exhibited a refractive index of 1.46, an O/Si ratio of 2, an interface trap density in the order of  $10^{11}$  cm<sup>-2</sup> eV<sup>-1</sup>, an oxide charge density down to  $10^{10}$  cm<sup>-2</sup>, and a breakdown field up to 11 MV/cm. They are thus suitable as a gate dielectric in a thin-film transistor.

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Lowering the thermal budget of deposition of dielectrics, without deteriorating the film properties, has become a priority in the last several years. A broad range of applications, including wafer postprocessing,<sup>1</sup> thin-film transistors (TFTs) for large displays,<sup>2</sup> and three-dimensional integrated circuits (3D ICs), such as stacked memory devices,<sup>3</sup> require very good dielectrics with excellent interfaces.<sup>4</sup> However, these applications constrain the thermal budgets to the processing temperature below 400–450°C. Such a low temperature generally leads to inferior film properties.

Many works have reported that an electron cyclotron resonance (ECR) plasma source, either in its classical configuration or in the distributed configuration,<sup>5</sup> is a powerful tool to obtain device-quality  $SiO_2$  at low temperatures.<sup>5-8</sup> A multipolar ECR plasma source<sup>9</sup> is reported to provide very good film properties.<sup>10-12</sup> The multipolar source has several advantages over the other ECR plasma sources, such as a magnetic field parallel to the substrate minimizing the plasma damage, a tunable microwave cavity, and a quartz dome that reduces the metal contamination.

In our previous work,<sup>10,12</sup> a study of the conduction and trapping mechanisms in SiO<sub>2</sub> layers deposited by the multipolar ECR Plasma-enhanced chemical vapor deposition (PECVD) was carried out, without the use of a supersonic jet of silane in helium. It was shown that the total pressure and silane partial pressure mainly determined the film properties in terms of their leakage current, oxide charge, interface trap density, and charge-to-breakdown characteristics. It appeared that the best-quality films could only be grown at low pressures. However, as lowering the pressure below a certain level is undesirable due to an increased surface bombardment causing both the extra charge and interface damage, an extra tool needed to be found, to enable better films at a higher pressure. In this work, we added a high-velocity jet of diluted silane as such a tool, to ensure extra energy transfer to the growing film (it reduces the need to heat the wafer during deposition) for obtaining good dielectric properties. The multipolar ECR plasma source was used for dissociation of N<sub>2</sub>O gas, whereas a high-velocity (supersonic) jet of silane diluted with helium was introduced downstream of the plasma region, through a specially designed convergent-divergent nozzle. Although a jet vapor deposition (JVD) technique combined with a conventional microwave plasma (not ECR plasma) has proven to be successful in depositing very thin silicon nitride films,<sup>13</sup> we explore deposition of SiO<sub>2</sub> layers using a combination of ECR plasma and high-velocity jet of silane (i.e., ECR-JVD deposition method).

In this work, the optimal deposition parameters for obtaining  $SiO_2$  films with both high-quality interface and bulk electrical properties have been explored. The influence of deposition parameters,

such as gas pressure and precursor flow rate on film properties, was investigated. Correlations between the composition and electrical properties were made, in order to explain the influence of the deposition conditions on film properties. The impact of various annealing processes on electrical film properties was investigated.

### Experimental

The deposition system (Fig. 1) consisted of an adapted microwave plasma disk reactor (MPDR-300),<sup>9</sup> in which the manner of introducing the reactive gases was modified. Multipolar ECR plasma was created in the quartz dome, by superposing a microwave radiation of 2.45 GHz and a multipolar magnetic field. The magnetic field lines were directed parallel to the substrate and formed by eight permanent magnets. The magnets were placed in such a way that the polarity changed from one magnet to the next. An electronic grade N<sub>2</sub>O gas was introduced directly into the plasma generation zone (i.e., inside the quartz dome, see Fig. 1). A mixture of 2% SiH<sub>4</sub> diluted in He (i.e., SiH<sub>4</sub>–He mixture) was introduced downstream the plasma, not using a shower ring as for the original ECR plasma system,<sup>14</sup> but through a convergent-divergent nozzle with a throat diameter of 0.15 mm. The base pressure in the reaction chamber was  $10^{-7}$  Torr.

In this design, the nozzle is employed as a gas accelerator. By pushing a large flow of gas through a very small nozzle, a high pressure can be obtained in the inner  $SiH_4$ -He gas line. Because of



Figure 1. (Color online) Deposition chamber (see text for description).

<sup>\*</sup> Electrochemical Society Active Member.

<sup>&</sup>lt;sup>z</sup> E-mail: a.y.kovalgin@utwente.nl

the huge pressure difference between the  $SiH_4$ -He gas line and the reaction chamber, the gas is accelerated, reaching supersonic velocity in the divergent part of the nozzle.

A quartz shield is bonded to the quartz dome (Fig. 1) in order to avoid the backstream diffusion of silane into the plasma generation zone. To prevent deposition on the quartz dome, it is preferred that SiH<sub>4</sub> does not dissociate in this zone but downstream, in the afterglow region. Because of the high-velocity SiH<sub>4</sub>–He jet directed perpendicular to the substrate and the position of the nozzle just a few centimeters above the wafer surface, the deposition is strongly localized on the wafer. In order to achieve good film uniformity over the entire wafer surface, a movable holder having two independent movements is designed. The holder enables the rotation around its axis in addition to the independent translational movement along a segment of a circle within an angle of 60°.

In the experiments, the N<sub>2</sub>O flow ranged between 20 and 100 sccm, and the SiH<sub>4</sub>–He mixture flow varied from 5 to 20 sccm. To verify the nozzle effect, an extra helium flow of 20 sccm was added to the lowest SiH<sub>4</sub>–He flow in a number of experiments. The total pressure in the deposition chamber varied between 7 and 20 mTorr. The pressure in the SiH<sub>4</sub>–He line ranged between 60 and 190 Torr.

For our experiments, we used 3 in. (100)-oriented n-type Si wafers having a resistivity of 1–10  $\Omega$  cm. The wafer cleaning consisted of a 10 min immersion into 100% fuming HNO<sub>3</sub> and a 10 min immersion into boiling 69% HNO<sub>3</sub>, followed by a 30 s dip into 1% HF in order to remove the chemical oxide and passivate the surface by hydrogen atoms. SiO<sub>2</sub> films with a thickness between 10 and 60 nm were deposited at a microwave power of 400 W and floating substrate temperature, i.e., without active heating or cooling the substrate. Because of plasma heating, the temperature of the wafer holder, as measured by an embedded thermocouple, could reach 30–50°C. The temperature of the wafer surface was however expected to be higher due to the limited thermal conductivity between the holder and the wafer at the low deposition pressures used.

A PHI Quantum 2000 Scanning ESCA microprobe was used to determine the chemical composition with a relative error of <2%, by means of X-ray photoelectron spectroscopy (XPS). Analyzing the Si  $2p_{3/2}$  peak position in the spectra, one can distinguish (see Ref. 15, for details) between a fully oxidized Si atom (i.e., a Si atom having four chemical bonds to the surrounding O atoms; Si<sup>4+</sup>), a partially oxidized silicon atom (i.e., Si atom in the so-called suboxidation state with either one, two, or three chemical bonds to the surrounding O atoms; Si<sup>1+</sup>, Si<sup>2+</sup>, or Si<sup>3+</sup>, respectively), and nonoxidized silicon (i.e., Si atom with four chemical bonds to the surrounding Si atoms only; Si<sup>0+</sup>). Partially oxidized silicon atoms are expected to have an additional relevant number of Si-Si bonds, Si-H bonds, or just dangling bonds. We made no attempt to identify the suboxidation states (which requires deconvolution of the spectra and a model to calculate absolute concentrations). The oxidized-silicon peak was therefore always attributed to the Si<sup>4+</sup> states. In this light, only the Si<sup>4+</sup> and Si<sup>0+</sup> states were considered and measured by XPS. The system was calibrated using a stoichiometric thermally grown oxide, assuming an O/Si<sup>4+</sup> ratio of 2.

Spectroscopic ellipsometry (SE) measurements were carried out using a variable-angle spectroscopic phase-modulated ellipsometer (a UVISEL model from Jobin Yvon), in the spectral range from 1 to 4.5 eV. The angle of incidence was varied between 70° and 80° in order to obtain a maximum sensitivity of the SE measurements. Assuming (from the XPS measurements) a stoichiometric SiO<sub>2</sub> layer and based on the measured refractive index, the effective film density was calculated from Bruggeman's effective medium theory.<sup>16</sup> The film in this case was modeled as a mixture of uniformly distributed spherical inclusions, i.e., stoichiometric SiO<sub>2</sub> and volumes not containing matter (voids). The ratio between the obtained density and that of a stoichiometric nonporous thermally grown SiO<sub>2</sub> (i.e., relative film density) was used to illustrate a density decrease caused by, for example, dangling bonds, nano- and microporosity, etc.

Metal-oxide-semiconductor (MOS) capacitors with an area of



Figure 2. Shape and dimensions of the realized nozzle.

0.1 mm<sup>2</sup> were realized by sputtering a 1  $\mu$ m thick aluminum layer over the deposited oxide, followed by lithography and etching steps. An aluminum layer of the same thickness was also sputtered on the back side of the Si wafer, after removing the oxide by buffered oxide etchant (BOE). If not mentioned explicitly in the text, then the samples were subjected to postdeposition annealing (PDA) in a wet N<sub>2</sub> ambient (i.e., N<sub>2</sub> bubbled through deionized (DI) water at room temperature) for 60 min at 500°C, and postmetallization annealing (PMA) for 5 min at 400°C in the same ambient. In the annealing effect, the properties of annealed and nonannealed layers are compared. High-frequency (10 kHz) and quasistatic capacitance-voltage (C-V) measurements were carried out using a Hewlett-Packard 4275A multifrequency meter and a Hewlett-Packard 4140B pA meter, respectively. A Hewlett-Packard 4156 parameter analyzer was used to measure the current density-voltage (J-V) characteristics. A positive voltage was applied to the gate, injecting electrons from the substrate. The breakdown fields were extracted by averaging the J-V curves over 25 capacitors and correcting for the flatband voltage, leading to a statistical error of 3%.

#### **Theoretical Considerations**

In our experimental reactor, the SiH<sub>4</sub>–He mixture was introduced into the chamber through a quartz tube. At the tube outlet, a quartz nozzle was mounted to accelerate the gas flow by converting its static enthalpy into kinetic energy. The convergent-divergent shape and dimensions of the nozzle were optimized using fluid mechanics principles,<sup>17</sup> to create a supersonic jet. A convergent nozzle can only provide sonic speeds. Because of the gas pressure difference between the quartz tube and the chamber, the gas accelerates to supersonic velocity after exiting the throat, i.e., in the divergent part of the nozzle. For an isentropic expansion of helium, Eq. 1 gives the relation between the nozzle cross-sectional area *A*, gas pressure *P*, temperature *T*, and velocity  $v^{17}$ 

$$T = T_0 \left(\frac{P}{P_0}\right)^{\kappa/(\kappa-1)}, \quad v = \sqrt{2c_p(T_0 - T)}, \quad A = \frac{QRT}{vPM}$$
 [1]

where  $T_0$  and  $P_0$  are the temperature and pressure at the nozzle inlet, R is the gas constant,  $\kappa$  is the specific heat ratio for helium,  $c_p$  is the constant pressure specific heat for helium, M is the mole weight for helium, and Q is the mass flow rate of helium.

Based on Eq. 1, we calculated the nozzle dimensions (Fig. 2) enabling the gas pressure and velocity distributions drawn in Fig. 3. The gas reaches sonic speeds at the throat of the nozzle, and the velocity rises over the sonic limit in its divergent part. This acceleration is associated with a huge pressure drop. Based on the simulations, a nozzle of 2 mm in length with a throat diameter of



Figure 3. Pressure and gas velocity distributions through the nozzle.



**Figure 4.** *J-V* characteristics of layers (16, 20, 30, and 50 nm thick; curves upward, respectively) deposited at various  $N_2O$  and  $SiH_4$ –He flows. Total pressure: 20, 20, 19, and 19 mTorr; curves upward, respectively.

150  $\mu$ m was made from quartz and bonded to the outlet of the quartz pipe for introducing the SiH<sub>4</sub>-He mixture, as shown in Fig. 1.

### **Results and Discussion**

 $SiO_2$  layers in the thickness range from 10 to 60 nm were deposited at deposition rates varying between 0.5 and 1 nm/min. The effects of total gas pressure, gas flow rates, film thickness, and film annealing conditions on the refractive index, chemical composition, and the film's electrical properties were investigated in order to obtain layers with superior properties.

SiH<sub>4</sub>/N<sub>2</sub>O flow ratio effect.— At a fixed N<sub>2</sub>O flow of 20 sccm, the layers deposited at a SiH<sub>4</sub>–He flow of 5 sccm exhibit relatively high leakage current (Fig. 4). The current density reaches the saturation level at a low electric field of 2–4 MV/cm, which indicates a high concentration of traps. After the N<sub>2</sub>O flow is increased up to 100 sccm, the leakage current decreases by approximately two orders of magnitude. Increasing the SiH<sub>4</sub>–He flow up to 10 sccm and further to 20 sccm, at the fixed N<sub>2</sub>O flow, again results in a higher leakage current. The ledges between 2 and 4 MV/cm, very noticeable in Fig. 4, are likely related to a conduction mechanism caused by bulk traps in the oxide.<sup>10,18</sup> Such traps can be caused, for example, by excess silicon.<sup>19</sup> However, the refractive index of 1.45, measured by the spectroscopic ellipsometer (see Table I), indicates a near-stoichiometric O/Si ratio and normal material density. Therefore, the traps are more likely related to an inappropriately formed chemical network, containing dangling bonds partially or fully saturated with hydrogen instead of Si–O bonds.

To confirm the near-to-stoichiometric O/Si ratio in the films, we carried out the XPS measurements. Only the measurements showing no etching through the oxide layer were considered. One can expect a lowering O/Si ratio in the films when the SiH<sub>4</sub>/N<sub>2</sub>O ratio in the gas phase is increased. Such below-stoichiometric silicon atoms can likely be introduced in their lower oxidation states. If the SiH<sub>4</sub>/N<sub>2</sub>O ratio becomes sufficiently high, then one can even expect the appearance of a peak attributed to nonoxidized silicon. This peak is clearly separated from the peak of fully oxidized silicon, Si<sup>4+</sup>.<sup>15</sup> One should bear in mind that the spectra deconvolution was not performed for the suboxidation states of silicon and the entire peak area of the oxidized silicon was attributed to the Si<sup>4+</sup> states only.

For the SiH<sub>4</sub>/N<sub>2</sub>O ratios shown in Fig. 4, our XPS measurements indicated neither the appearance of the nonoxidized silicon nor a noticeable deviation of the  $O/Si^{4+}$  ratio from 2. The refractive index measured by SE (the most reliable measurement technique for such thin layers) was also hardly influenced, at least for the films deposited under 100 sccm of N<sub>2</sub>O flow (see Table I). However, the oxide

Table I. Properties of SiO<sub>2</sub> layers deposited at various process conditions.

Conditions			SE measurements <sup>a</sup>				Single wavelength <sup>b</sup>			Electrical	Optical/electrical thickness ratio	
SiH <sub>4</sub> –He flow (sccm)	N <sub>2</sub> O flow (sccm)	Total pressure (mTorr)	Ref. index	Film thicknesses (nm)	Dep. rate (nm/min)	Rel. density	Ref. index	Film thickness (nm)	Dep. rate (nm/min)	thickness from C-V curves	SE <sup>c</sup>	He–Ne <sup>d</sup>
5	20	7	1.44	18	0.30	0.96	1.36	21	0.35	19	0.95	1.11
5	20	20	1.41	20	0.57	0.89	1.37	22	0.63	21	0.95	1.05
5	100	20	1.45	16	0.46	0.98	1.35	19	0.54	17	0.94	1.12
5 <sup>e</sup>	$100^{\rm e}$	$20^{\rm e}$	1.45	27	0.66	0.99	1.37	30	0.73	25	1.08	1.20
10	100	22	1.45	34	1.13	0.97	1.36	40	1.33	16	2.13	2.50
10	100	19					1.35	32	1.03	25		1.28
20	100	19					1.38	55	1.83	39		1.41

<sup>a</sup> Measured by SE, by fitting experimental  $\Psi$  and  $\Delta$  functions in the energy range from 0.7 to 3.7 eV. The refractive index is extracted at 1.96 eV (632.8 nm), which corresponds to a He–Ne laser.

<sup>b</sup> Measured by a single-wavelength ellipsometer at a He-Ne laser wavelength of 632.8 nm.

<sup>c</sup> Determined as a ratio between the thickness measured by the SE ellipsometer and the thickness extracted from the C-V measurements.

<sup>d</sup> Determined as a ratio between the thickness measured by the single-wavelength ellipsometer and the thickness extracted from the *C-V* measurements. <sup>e</sup> Retarded plasma ignition time of 25 min (see text for details).



Figure 5. C-V curves of layers deposited at 5 sccm of  $SiH_4$ -He flow, 20 sccm of  $N_2O$  flow, and various total pressures.

capacitance obtained from the *C*-*V* measurements was noticeably higher for the layers deposited under the higher  $SiH_4$ –He flows, compared to the theoretical capacitance calculated using the dielectric constant of stoichiometric  $SiO_2$  and the physical film thickness of the SE measurements. The use of the  $SiO_2$  dielectric constant resulted in an extracted electrical film thickness lower than the measured physical thickness. To equalize the physical and electrical thicknesses, one has to assume an increased dielectric constant of the layers.

The latter is in contradiction with the stoichiometric O/Si ratio of 2 and the refractive index of 1.45 measured by XPS and SE, respectively. The observed dielectric constant increase can be explained in terms of water absorption in the films due to the inappropriate chemical network with dangling bonds (see above). Roughly estimating,  $\varepsilon_{\text{film}} = x\varepsilon_{\text{H}_2\text{O}} + (1 - x)\varepsilon_{\text{SiO}_2}$ , where  $\varepsilon_{\text{film}}$  is the measured dielectric constant of the films, *x* is the volume fraction of the adsorbed water,  $\varepsilon_{\text{SiO}_2} = 3.9$  and  $\varepsilon_{\text{H}_2\text{O}} = 80$  are the dielectric constants of a thermal oxide and water, respectively. We can calculate that a 50% decrease of the electrical thickness can be caused by only 5% of water. Such a small amount will hardly affect both the refractive index ( $n_{\text{H}_2\text{O}} = 1.33$ ) and film density within the measurement error.

Although the O/Si<sup>+4</sup> ratio remained 2 for the lowest  $N_2O$  flow of 20 sccm, the relative film density decreased from 0.98 to 0.89 (see Table I). This resulted in lowering the refractive index from 1.45 to 1.41. We interpreted this as a consequence of the insufficient energy transfer from the plasma to the surface at low  $N_2O$  flows, expressed in terms of the insufficient surface bombardment. This could suppress both hydrogen desorption from the growing layers and surface migration of adsorbed species and finally result in a higher concentration of incorporated hydrogen and a lower material density.

Total pressure effect.— The C-V curves shown in Fig. 5 reveal a strong influence of total pressure on the fixed oxide charge. The measured flatband voltage ( $V_{\rm FB}$ ) is about -1.9 V for the film obtained at a deposition pressure of 7 mTorr. Using a value of -0.3 V for the metal-semiconductor work-function difference ( $\phi_{\rm ms}$ ) between the Al contact and n-type Si substrate with a doping level of  $3 \times 10^{15}$  cm<sup>-3</sup>,<sup>20</sup> one can calculate a net positive oxide charge of  $1.8 \times 10^{12}$  cm<sup>-2</sup> from the expression  $V_{\rm FB} = \phi_{\rm ms} - Q_{\rm ox}/C_{\rm ox}$ , where  $Q_{\rm ox}$  is the oxide charge and  $C_{\rm ox}$  is the capacitance. The  $V_{\rm FB}$  shifts to approximately -0.7 V with increasing the total pressure from 7 to 12 mTorr, which corresponds to a charge of  $4 \times 10^{11}$  cm<sup>-2</sup>. The further increase of pressure up to 20 mTorr results in a net negative oxide charge of  $-2 \times 10^{11}$  cm<sup>-2</sup>.

As the floating wafer potential is normally negative with respect to the plasma potential, positive ions are attracted to the wafer. At lower pressures, one can expect a higher energy of positive ions in the plasma because the ions experience fewer collisions during their



Figure 6. J-V characteristics of layers shown in Fig. 5.

transport to the film surface. Furthermore, the increased electron energy causes a higher ionization degree. Although a decreased pressure results in a lower total ion density, the increased ion energy can significantly affect the growing film because of the surface bombardment. This will cause an extra damage (not only the film but also the surface Si layer can be affected) and create a positive charge. The latter is clearly noticeable in Fig. 5. This can also occur due to the implantation of H<sup>+</sup> atoms as they can penetrate deeply and have less chance to be neutralized. The high-energy film-surface bombardment will enhance the surface migration and hydrogen desorption and thus densify the layers. The latter is confirmed by the refractive index, increased from 1.41 at a pressure of 20 mTorr to 1.44 at a pressure of 7 mTorr; compare the first two lines in Table I.

The interface trap density is slightly affected by the pressure, as can be seen from the slope of the corresponding *C*-*V* curve in Fig. 5. A possible explanation is that the extra bombardment causes an additional damage of the interface. The interface trap density, as calculated for the film deposited at 20 mTorr, is in the order of  $10^{11}$  cm<sup>-2</sup> eV<sup>-1</sup>.

Comparing the *J-V* characteristics in Fig. 6, one can see that a higher-pressure oxide has a higher leakage current. Thus, although the current flowing through the low-pressure oxide [highest resistivity of  $6 \times 10^{15} \Omega$  cm measured at the onset of Fowler-Nordheim (F-N) tunneling at 6 MV/cm] is mainly due to F-N tunneling, the currents through the high-pressure oxides are ruled by trap-related mechanisms.<sup>10,21</sup>

The XPS measurements indicate that the O/Si<sup>4+</sup> ratio is 2 and hardly changes within the experimental error. Nevertheless, the refractive index (extracted at 1.96 eV) decreases considerably with increasing the pressure (Fig. 7). This behavior is best explained in terms of a lower film density. As mentioned, this can likely be caused by unsatisfied (dangling) bonds, nano- or microvoids, and/or incorporation of hydrogen. Assuming a stoichiometric SiO<sub>2</sub> layer, the dependence of a relative film density on total pressure is calculated (Fig. 7). The relative density decreases from 0.96 to 0.89 with raising the pressure from 7 to 20 mTorr.

Summarizing, the pressure influence has two counteracting effects. First, the positive oxide charge increases together with deteriorating the interface at a lower pressure. In this light, deposition at a higher pressure is desired. Second, the bombardment will likely enhance the surface migration and hydrogen desorption at near room temperatures<sup>22</sup> and results in a denser layer having a lower leakage current. In this regard, deposition at a lower pressure is needed to improve film integrity.

*Nozzle effect.*— To verify whether silane molecules, escaping the nozzle, have sufficient energy for their dissociation (as a result of their collisions with the substrate), the plasma ignition was retarded



Figure 7. Refractive index and relative density (both measured by SE) of the layers shown in Fig. 5 and 6.

for 25 min. During this retardation time, all the precursors were continuously flowing through the reactor. As measured by the SE ellipsometer, the retardation time resulted in an 8 nm thick film grown prior to the plasma ignition. A deposition rate of  $\sim 0.3$  nm/min can therefore be estimated at room temperature in the absence of plasma, provided by the nozzle only.

To theoretically confirm that oxygen-containing layers can be deposited by the high-speed jet, the following considerations are done. It is assumed that SiH4 molecules and He atoms have similar velocities in the jet (Fig. 3). For a SiH<sub>4</sub> molecule, a velocity of 1000 m/s corresponds to a kinetic energy of  $\sim 0.17$  eV, which is much less than the lowest activation energy  $(E_a)$  required for the dissociation of silane (SiH<sub>4</sub> + M  $\rightarrow$  SiH<sub>2</sub> + H<sub>2</sub> + M;  $E_a = 2.2 \text{ eV}$ and M is a third body, which is the wafer surface in this case). However, such a low energy can still result in a measurable dissociation rate, if the collision frequency of the molecules with the surface is sufficiently high. For deposition conditions listed in the caption to Fig. 8, the calculated SiH<sub>4</sub> flux  $(F_{SiH_4})$ to the wafer surface is in the order of  $10^{18}$  molecules cm<sup>-2</sup> s<sup>-1</sup> (assuming a spot diameter of 1 cm on the surface). The dissociation rate of silane  $(R_{SiH_4})$ , obtained from the Arrhenius expression  $R_{\text{SiH}_4} = F_{\text{SiH}_4} \exp(-2.2/0.17 \text{ eV})$ , is then in the order of  $10^{12}$  molecules cm<sup>-2</sup> s<sup>-1</sup>. For a sticking probability of 1 for SiH<sub>2</sub>



Figure 8. *J-V* characteristics of layers obtained at a plasma-ignition retardation time of 0 or 25 min; total pressure of 20 mTorr,  $N_2O$  flow of 100 sccm, and SiH<sub>4</sub>–He flow of 5 sccm.



**Figure 9.** *J-V* characteristics of layers deposited at 12 mTorr, 5 sccm of  $SiH_4$ -He flow, 20 sccm of  $N_2O$  flow, and an extra He flow of 0 sccm (16 nm film) and 20 sccm (13 nm film).

radicals, this will result in a deposition rate in the order of  $10^{14}$  Si atoms per min (approximately one monolayer) and is in agreement with the measured deposition rate.

Following a similar procedure, the dissociation rate of N2O molecules  $(R_{\rm N_2O})$  can be estimated. It is known that  $\rm N_2O$ can dissociate by the reaction  $N_2O + M \rightarrow N_2 + O(^3P) + M$ , where  $E_a \approx 55-60$  kcal/mol or 2.4–2.6 eV.<sup>23</sup> Assuming the kinetic energy transfer from He atoms to  $N_2O$  molecules (i.e., M = He) gives an insignificant  $R_{N_2O}$  due to the low energy of He atoms  $(\sim 0.02 \text{ eV})$  because of their light mass. Considering M = SiH<sub>4</sub> and taking the pre-exponential factor A in the order of  $10^{-10}$  cm<sup>3</sup> s<sup>-1</sup> <sup>23</sup> reveal a dissociation constant  $k_{dis}$  $10^{-10}$  cm<sup>3</sup> s<sup>-1</sup>  $k_{dis}^{23}$  reveal a dissociation constant  $k_{dis}^{23}$   $k_{dis}^{23} = 10^{-17}$  cm<sup>3</sup> s<sup>-1</sup>  $[k_{dis} = A \exp(-2.5/0.17 \text{ eV})]$ . Then the O(<sup>3</sup>P) dissociation rate, calculated from the expression  $R_{\rm O} = k_{\rm dis} n_{\rm N_2O} n_{\rm SiH_4}$  $(n_{N_2O} \text{ and } n_{SiH_4} \text{ are the concentrations of } N_2O \text{ and } SiH_4 \text{ molecules}^4$ in the jet, respectively; the total pressure in the jet is chosen to be 100 Torr, which corresponds to a velocity of 1000 m/s shown in Fig. 3), appears to be in the order of  $10^{14}$  cm<sup>-3</sup> s<sup>-1</sup>. Assuming all the generated oxygen atoms reaching the surface, the generation rate of oxygen atoms is similar to that of SiH<sub>2</sub> radicals. From this, the deposition of  $SiO_rH_v$  films can already be expected in the absence of plasma, provided only by the jet.

From the *C-V* measurements, the net oxide charge was hardly influenced by the retardation time, but the interface trap density was clearly increased. Measuring the *J-V* curves, we observed that the leakage current increased by four orders of magnitude when the retardation time was 25 min (Fig. 8). The XPS data showed a marginal decrease of the O/Si<sup>4+</sup> ratio from 2.0 to 1.98, whereas the refractive index and relative film density hardly changed (see Table I). The calculated  $\varepsilon_{\rm film}/\varepsilon_{\rm SiO_2}$  ratio was 1.08. These results confirmed that the interfacial layer grown without plasma at room temperature contained both silicon and oxygen. The high leakage current and the ledge in Fig. 8 suggest a high concentration of traps. Thus, a minimum possible retardation time is required to achieve better film properties.

To further verify whether the role of the nozzle was beneficial for deposition of  $SiO_2$  layers, an extra helium flow of 20 sccm was added to the  $SiH_4$ -He flow. After this, the pressure in the  $SiH_4$ -He line increased from 60 to 190 Torr. The chamber pressure remained unchanged at 12 mTorr. A beneficial impact on the film properties was that the leakage current considerably decreased (see Fig. 9). Because of the extra He flow, the silane partial pressure (as it could roughly be estimated from the conditions, at the wafer surface and not inside the tube/nozzle) was reduced by approximately two times. The deposition rate decreased then from 0.53 to 0.25 nm/min. Such a double decrease of the deposition rate, caused by lowering the



**Figure 10.** Oxide charge plotted vs film thickness for layers deposited under 5 sccm (7 mTorr) or 2.5 sccm (10 mTorr) of SiH<sub>4</sub>–He flow, and 20 sccm of N<sub>2</sub>O flow;  $\phi_{\rm ms}$  is assumed to be -0.3 V. The fit curve for extrapolating to zero thickness can be approximated by  $y = 7 \times 10^9 \times x^2 + 10^{10} \times x - 9 \times 10^{11}$ , where y is the charge and x is the thickness.

silane partial pressure by two times, could be expected. The film thicknesses in Fig. 9 were comparable (16 and 13 nm, see the legend); thus, the film thickness influence on the interface should not play a role. The improved film properties in Fig. 9 could not be explained by a lower silane partial pressure only because this effect was not observed for the films grown at similar conditions (i.e., N2O flow increased from 20 to 50 sccm at a pressure of 12 mTorr, and SiH<sub>4</sub>-He mixture flow kept at 5 sccm) but without the extra helium flow. In addition, the deposition rate decreased much less in the latter case, namely, from 0.53 to 0.43 nm/min. This likely pointed to an increased energy flux to the surface from the plasma, caused an enhanced dissociation of SiH<sub>4</sub>, which was not the case when only the extra He flow was added. Our results suggested that high-quality layers, comparable to those deposited at a lower pressure of 7 mTorr (Fig. 6), could also be deposited at a higher pressure, when the jet kinetic energy was increased. In this light, the jet suppressed the trap formation probably by enhancing the surface mobility and hydrogen desorption.

As mentioned in the previous subsection, a lower pressure is normally needed to obtain low leakage currents. However, a higher pressure is desired for minimizing the net oxide charge and improving the interface quality. A high-velocity jet enables lower-leakage currents at higher deposition pressures, thus, minimizing both the leakage current and oxide charge. The jet can therefore be considered as an extra tool to improve the film quality.

Film thickness influence.— When analyzing high-frequency C-V curves, it appears that thinner layers contain less net oxide charge compared to thicker films (Fig. 10). Extrapolating to zero thickness suggests a negative interface charge in the order of  $-10^{12}$  charge/cm<sup>2</sup>. With increasing thickness, this negative charge seems to be overcompensated by a positive oxide charge so that the total charge becomes positive. This can be explained in terms of the film exposure time to plasma. The growing films receive a continuous flux of positive ions from the plasma. As a thicker film has a longer exposure time, more positive charge can be collected.

The refractive index, as measured by the SE at 1.96 eV, decreases from 1.45 for a 18 nm thick film down to 1.38 for a 10 nm thick film (see the conditions in the legend to Fig. 10, both the films are deposited at 7 mTorr). This is most probably due to a material density gradient, with the lowest density closest to the interface. A clear downward trend of both the relative film density and the refractive index is observed together with increasing  $O/Si^{+4}$  ratio (measured by XPS) when approaching the interface (Fig. 11), i.e., for the thinner layers. For the XPS measurements, the films were



**Figure 11.** Refractive index at 1.96 eV and relative film density plotted vs  $O/Si^{4+}$  ratio, obtained for differently thick layers (16, 34, 27, 18, 20, 21, 18, and 10 nm) deposited at various pressures (20, 22, 20, 7, 20, 12, 12, and 7 mTorr), SiH<sub>4</sub>–He flows (5, 10, 5, 5, 5, 5, 5, and 5 sccm), and N<sub>2</sub>O flows (100, 100, 20, 20, 50, 20, and 20 sccm), respectively. The symbols with a higher  $O/Si^{4+}$  ratio (i.e., >2) correspond to thinner films; the thinnest film of 10 nm exhibited a ratio of about 2.18.

sputtered and consequently measured, step by step. The measured  $O/Si^{4+}$  ratio was then averaged over the number of sputter/ measurement steps. This made the interface influence smaller for the thicker layers. The effect was mostly pronounced when approaching the interface, but this would certainly need further investigation. When calculating the ratio, only the XPS spectra not showing any appearance of the nonoxidized Si peak were considered, i.e., without etching through the oxide. The XPS measurements confirmed a somewhat higher  $O/Si^{+4}$  ratio for the thinnest (10 nm) layer with respect to the thicker films.

One can use the following considerations to explain the layer formation with a slightly above-stoichiometric  $O/Si^{4+}$  ratio (Fig. 11). A stoichiometric  $SiO_2$  has two neighboring  $SiO_2$  tetrahedrons with one bridging O atom bonded to two Si atoms. For  $SiO_x$  with *x* slightly higher than 2, there can be two nonbridging O atoms instead of one bridging O atom. Each of these O atoms is bonded to a Si<sup>4+</sup> atom of the corresponding tetrahedron and has the second chemical bond either dangling or passivated by a hydrogen atom.

Annealing effect.- All the films described above received both the PDA and PMA steps. In this section, we report on the influence of each of these annealing steps upon bulk and interface electrical properties. It is well known that annealing in H2O- or H2-containing ambient can significantly reduce the amount of oxide charge and interface states by passivating the traps. At least two types of traps are identified for thermally grown oxide,<sup>24</sup> which are located close to the Si-SiO<sub>2</sub> interface. The first type is attributed to trivalent silicon ( $\equiv$ Si, also called a silicon atom with a dangling bond) and appears to be neutral before releasing an electron (or capturing a hole). These traps, positively charged after the electron release (or hole capture), become efficient electron traps. The second type is attributed to nonbridging oxygen,  $\equiv$  Si–O·. Such a nonbridging oxygen atom requires an extra electron to complete the outer electron orbital, or an extra chemical bond to become a bridging atom. It is likely that these traps can capture electrons and become negatively charged.

Annealing the initial (i.e., before capturing a charge) traps in H<sub>2</sub>O- or H<sub>2</sub>-containing ambient can provide the required H or OH groups for passivation, forming the relatively stable  $\equiv$ Si–H and  $\equiv$ Si–OH groups and disabling the electron capturing centers. It is reported that Si–OH bonds can be broken again by ionizing radiation or secondary impact ionization with the formation of negatively charged OH<sup>-</sup> ions drifting away.<sup>25</sup> To balance the charge, this for-



Figure 12. Influence of PDA at 500°C for 30 min and PMA at 400°C for 5 min upon *J-V* characteristics of layers (12–14 nm) deposited at 7 mTorr, 5 sccm of SiH<sub>4</sub>–He flow, and 20 sccm of  $N_2O$  flow.

mation requires the appearance of positively charged trapping centers such as  $\equiv$ Si<sup>+</sup>, causing again a positive charge in the film. The removal of hydroxyl groups during a vacuum anneal above 600°C is also reported.<sup>26</sup>

It is known that annealing in  $H_2$  under polysilicon gates or no gates (i.e., our PDA step) is slower and less effective than that with metal gates due to the formation of molecular hydrogen.<sup>27</sup> In contrast to this, atomic hydrogen is responsible for annealing the traps when an aluminum gate (i.e., our PMA step) is present.<sup>28</sup> Annealing of aluminum-gate devices is both faster and more effective.

*PDA effect.*— The as-deposited film shown in Fig. 12 exhibits no part in the *J*-*V* curve, which can be described by F-N tunneling mechanism. The leakage current is low and slightly increases with increasing voltage. It is likely that traps, randomly distributed in the film bulk, causes such a conduction behavior. After the PDA process, the bulk quality is improved and the leakage current exhibits a large part attributed to FN tunneling. It is important to note that after applying the PDA step, our *C*-*V* measurements indicate that the positive oxide charge, probed through the  $V_{\text{FB}}$  shift toward negative voltages, increases however by two to three times, compared to the nonannealed films.

*PMA effect.*— Based on the high-frequency *C-V* curves, the PMAonly step greatly reduces the net oxide charge, by more than 10 times. In Fig. 13, none of the samples received the PDA step. After



**Figure 13.** Influence of PMA at 400°C for 5 min upon high-frequency C-V curves of a 15 nm thick layer received no PDA step, and deposited at 12 mTorr, 5 sccm of SiH<sub>4</sub>–He flow, and 20 sccm of N<sub>2</sub>O flow.



**Figure 14.** Relative *C-V* curves of high-quality  $SiO_2$  layers (12 and 14 nm thick films correspond to the dotted and solid curves, respectively) received PMA-only step at 400°C for 5 min, and deposited at 5 sccm of SiH<sub>4</sub>–He flow, 20 sccm of N<sub>2</sub>O flow, and various total pressures.

aluminum gates were formed, the first structures were annealed at  $250^{\circ}$ C in a wet ambient for 5 min, whereas the second structures received PMA at a higher temperature of  $400^{\circ}$ C. For the asdeposited film, one can extract a positive charge in the order of  $10^{12}$  cm<sup>-2</sup>. After PMA at  $400^{\circ}$ C, the net charge is as low as  $10^{10}$  cm<sup>-2</sup>. Furthermore, the slope of the *C-V* curves increases with annealing temperature indicating less interface traps. A low interface trap density in the order of  $10^{11}$  eV<sup>-1</sup> cm<sup>-2</sup> can be obtained from both the quasistatic and high-frequency measurements presented in Fig. 14. When both PDA and PMA are applied, the final oxide charge is higher compared to that obtained after PMA only. This is a consequence of the positive charge increase after the PDA step.

The PMA-only influence on the J-V curves is also more beneficial compared to the PDA-only influence. It appears that the samples received the PMA-only step at 250°C already exhibit a lower leakage current compared to the samples received the PDA-only step at 500°C. The same holds for the oxide charge and interface states. Applying PMA at 400°C (no PDA) results in much lower leakage current with respect to that obtained after the PDA-only step (Fig. 12). When both PDA and PMA are applied, the leakage current is higher compared to that obtained after PMA only.

Because the PMA step involved annealing of aluminum-gate devices, it should occur faster and more effective due to the fast diffusion of atomic hydrogen. This was generally accepted for thermally grown oxides. In this work, we demonstrated that PMA had similar advantages over PDA for ECR-JVD plasma oxides. Applying the PMA-only step at a lower temperature and for a shorter time with respect to the PDA-only step allows for achieving better results in terms of leakage current, oxide charge, and interface state density.

Comparison between ECR-JVD, radio frequency PECVD (rf-PECVD), and low pressure chemical vapor deposition (LPCVD) oxides.— In Fig. 15, we compare J-E curves of the best films deposited in our system with those of the layers obtained by rf-PECVD at 300°C and LPCVD at 600°C. All the realized MOS capacitors had the same surface area and only received the PMA step (i.e., no PDA). We observed that our ECR-JVD oxides exhibit a lower leakage current and a higher breakdown field. Furthermore, the electrical current through the ECR-JVD oxides can accurately be described by Fowler–Nordheim tunneling. One can therefore conclude that our SiO<sub>2</sub> layers, deposited by a combination of multipolar ECR plasma and a high-velocity jet of silane, have superior electrical properties compared to those of LPCVD and rf-PECVD oxides.

A detailed reliability study of the jet-deposited films certainly remains an objective for future work. Based on our earlier study of



Figure 15. A comparison of J-V curves of layers deposited by different methods and at various deposition temperatures.

the conduction and trapping mechanisms in  $SiO_2$  layers deposited by the multipolar ECR PECVD without a supersonic jet,<sup>10</sup> we however expect a better reliability of the films grown with the jet. The latter is because the jet-grown films initially exhibit a better quality compared to the layers obtained without the jet.

### Conclusion

We demonstrated a deposition method as a promising tool to obtain high-quality dielectrics at a low thermal budget not exceeding 400°C. High-electrical quality SiO<sub>2</sub> films with a refractive index of 1.46, stoichiometric O/Si ratio of 2, and a relative film density of 0.99 with respect to thermal SiO<sub>2</sub> were deposited. The best-quality layers exhibited a breakdown field up to 11 MV/cm, a resistivity in the order of  $10^{16} \Omega$  cm, an oxide charge density down to  $10^{10}$  cm<sup>-2</sup>, and an interface trap density in the order of  $10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$ .

The films were deposited using a multipolar ECR plasma source combined with a high-velocity jet of silane diluted with helium. In order to study and optimize the deposition process, the effects of total gas pressure and gas flows on film properties were explored. It appeared that a low pressure ( $\sim 10$  mTorr) is desired to obtain lowleakage currents. However, a higher pressure (~20 mTorr) is needed for minimizing net oxide charge and improving interface quality. A high-velocity jet of silane diluted with helium is an extra tool to improve the film quality at higher pressures. Using the jet allows for achieving lower-leakage currents at higher deposition pressures, thus, minimizing both the leakage current and oxide charge.

Postdeposition annealing in N2-H2O ambient at 500°C for 30 min, applied to as-deposited films, decreased the leakage current, whereas the positive oxide charge became two to three times higher. Postmetallization annealing in the same ambient at 400°C for 5 min, optimally applied without PDA, tremendously improved electrical properties in terms of decreasing the leakage current and oxide charge. The ECR-JVD oxides possessed better electrical properties than the oxides deposited by rf-PECVD and LPCVD methods.

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