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Plasma-assisted atomic layer deposition of TiN/Al2O3 stacks for metal-oxide-semiconductor capacitor applications

D. Hoogeland,1 K. B. Jinesh,2,a) F. Roozeboom,1,2 W. F. A. Besling,2 M. C. M. van de Sanden,1 and W. M. M. Kessels1,b)
1Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
2NXP Semiconductor Research, High-Tech Campus 4, 5656 AE Eindhoven, The Netherlands

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By employing plasma-assisted atomic layer deposition, thin films of Al2O3 and TiN are subsequently deposited in a single reactor at a single substrate temperature with the objective of fabricating high-quality TiN/Al2O3/p-Si metal-oxide-semiconductor capacitors. Transmission electron microscopy and Rutherford backscattering spectroscopy analyses show well-defined interfaces and good Al2O3 stoichiometry, respectively. Electrical investigation of as-deposited test structures demonstrates leakage current densities as low as ~1 nA/cm². Current-voltage (I-V) measurements demonstrate clear Fowler–Nordheim tunneling with an average TiN/Al2O3 barrier height of 3.3 eV. Steep Weibull distributions of the breakdown electric field around 7.5 MV/cm indicate good reliability of these devices. Time-dependent dielectric breakdown measurements demonstrate that the devices can sustain high operating electric fields of 3–4 MV/cm for the 10 year lifetime criterion. From capacitance-voltage (C-V) measurements, a dielectric constant (k) of 8.7 ± 0.1 was extracted for the Al2O3. No direct dependence on the deposition temperature was found in the range 350–400 °C, although the stack deposited at 400 °C demonstrates significantly lower C-V hysteresis of ~50 mV. A negative fixed oxide charge density of (9.6 ± 0.2) × 10¹² cm⁻² was found to be present at the Al2O3/p-Si interface. © 2009 American Institute of Physics. [doi:10.1063/1.3267299]

I. INTRODUCTION

Thermal SiO2 and poly-Si still serve as the mainstay of dielectric and electrode layers in the current metal-oxide-semiconductor (MOS) technologies. Replacing SiO2 by high-k materials is the prime technological challenge. This is because, although high-k materials offer higher capacitance, high-k materials are often associated with lower dielectric breakdown voltages and decreased lifetimes. Also, leakage current and power consumption become unacceptably large for the technological demands. Leakage current depends not only on the band gap of the dielectric but also on the band offsets with the electrodes as well. Novel dielectric/conductor combinations should be tuned for the right metal work function as well as the optimum thermochemical stability of the layer stack. Therefore, much effort has been made to explore new combinations of dielectric and conductive layers such that miniaturization of MOS-based devices (both active and passive) can be continued following Moore’s law. The combination TiN/Al2O3 has been identified as a promising and especially reliable candidate because of its chemical compatibility and thermal stability, good adhesion properties on various substrates, and low interface trap densities in TiN/Al2O3/p-Si devices.1 Furthermore, both materials can relatively easily be synthesized by atomic layer deposition (ALD) under compatible processing conditions. Al2O3 is known for its modest dielectric permittivity of ~9 and the high breakdown electric field due to its large band gap (9 eV).2,3 It has a large band offset with Si, which is crucial in maintaining low leakage currents through devices.4 Al2O3 withstands the thermal budget of the various processing steps by remaining amorphous at temperatures up to 800 °C.5 It has been reported that Al2O3 can be deposited by ALD on Si even without an interfacial oxide layer6 and Al2O3 can be readily used as an oxidation barrier for ALD-based synthesis of other high-k layers as well.7 TiN is a well-established midgap metal with low electrical resistance.8 Therefore, it is commonly used as an electrode material that, in addition, also suppresses the outdiffusion of Si more efficiently than Al. This latter electrode material can cause significantly large leakage currents.9

To meet future requirements for miniaturization and package integration in Si device technology, high-quality thin films are required for both the electrode and the dielectric materials. This not only holds for CMOS technology but also for many other applications of MOS capacitors. More particularly, it also holds in passive integration platforms, which include both active and passive devices for which Al2O3 is considered a very relevant dielectric material. ALD is one of the preferred methods available to deposit such thin films with extremely good layer thickness control, uniformity, and step coverage,10 especially on challenging substrate topologies (e.g., substrates with high aspect ratio features).

a)Present address: Holst Centre (IMEC-NL), P.O. Box 8550, 5605 KN Eindhoven, The Netherlands.
b)Author to whom correspondence should be addressed. Electronic mail: w.m.m.kessels@tue.nl.
For example, using ALD, high-density trench capacitors have been processed and integrated in Si for use as rf decoupling capacitors.\textsuperscript{11–13}

This paper focuses on the characterization of the material properties and electrical performance of TiN/Al\textsubscript{2}O\textsubscript{3}/p-Si MOS capacitors. Particularly Al\textsubscript{2}O\textsubscript{3} films with a nominal thickness of 10 nm are investigated as this thickness is considered relevant for the applications of the decoupling MOS capacitors envisioned. Furthermore, this work distinguishes itself from other efforts by the fact that the TiN and Al\textsubscript{2}O\textsubscript{3} were deposited sequentially in a single deposition chamber using plasma-assisted ALD. In this method, plasma is used during the oxidation or nitridation step of the ALD cycle, and the plasma-assisted ALD processes of Al\textsubscript{2}O\textsubscript{3} and TiN have been reported previously by Heil et al.\textsuperscript{8} and Van Hemmen et al.,\textsuperscript{14} respectively. To date, the investigation of all plasma-assisted ALD stacks has not been extensively reported on, whereas the single-reactor processing of Al\textsubscript{2}O\textsubscript{3} and TiN is of interest for exploratory studies in ALD within research and development programs when cluster tools or multiple chambers are not available. No clear evidence of precursor cross contamination of the Al\textsubscript{2}O\textsubscript{3} and TiN deposition processes has been observed, even if the processes were separated by purging times as short as 5 min. This leads to minimal interface states and trap levels from the reaction residues at the TiN/Al\textsubscript{2}O\textsubscript{3} interface, as follows from the results presented in this paper.

\section*{II. EXPERIMENTAL SETUP}

\subsection*{A. ALD reactor}

The ALD reactor used in this work is a FlexAl\textsuperscript{TM} remote plasma and thermal ALD reactor, manufactured by Oxford Instruments.\textsuperscript{8} The reactor is equipped with an inductively coupled plasma source that can generate plasma powers of up to 600 W. A base pressure of 10\textsuperscript{−6} Torr in the reactor is maintained with a turbomolecular pump backed by a rotary pump. A loadlock for wafer loading is connected to the reactor chamber at a pressure of 10\textsuperscript{−5} Torr. From the loadlock, the substrate can automatically be placed on the wafer stage of the reaction chamber, which can be resistively heated up to a set temperature $T_{\text{set}}=400$ °C. The plasma precursor gases can be fed into the reactor chamber at programmable flow rates, whereas the pressure in the reactor can be independently controlled by adjusting the pumping speed. Precursor vapors can be dosed into the reactor by fast open-close valves, either vapor drawn or, if necessary, by bubbling with Ar as a carrier gas. The precursors can be independently heated to temperatures up to 150 °C.

\subsection*{B. Process Flow}

The thin films were deposited on 150 mm p-type Si (100) wafers with a resistivity of 10–30 $\Omega$ cm. Prior to each deposition, the wafers were cleaned using a diluted HF solution (1% HF) for 1 min, to remove the native oxide and, subsequently, rinsed with de-ionized water. Next, the wafers were immediately transferred into the ALD reactor chamber and a waiting time of at least 15 min was applied for the wafer to reach thermal equilibrium with the heated wafer stage. After the deposition of Al\textsubscript{2}O\textsubscript{3}, there was an intermission of at least 5 min before starting the TiN deposition in order to avoid possible cross contamination of the precursors. After the depositions, the wafer was placed in the loadlock for at least 30 min to allow the wafer to cool down to room temperature before transferring it into atmosphere. With four-point-probe (FPF) measurements, the average resistivity of the top TiN film was determined. For the electrical characterization of Al\textsubscript{2}O\textsubscript{3}, MOS devices were fabricated by patterning with standard lithography and subsequent selective etching (with a Br-based plasma) of the TiN on the TiN/Al\textsubscript{2}O\textsubscript{3}/p-Si wafer. This resulted in capacitors with a well-defined square footprint with areas ranging from 0.01 to 36 mm\textsuperscript{2}.

\section*{C. ALD conditions and processed stacks}

The plasma-assisted ALD process of Al\textsubscript{2}O\textsubscript{3}, more extensively described in Ref. 14, started with a saturated dose of Al(CH\textsubscript{3})\textsubscript{3} (trimethylaluminum or TMA from Akzo-Nobel, semiconductor grade), obtained by a 20 ms vapor injection. For the plasma process, an O\textsubscript{2} plasma of 400 W was ignited at a pressure of 15 mTorr and sustained for a duration of 2 s. O\textsubscript{2} also served as a purging gas because O\textsubscript{2} does not react with Al(CH\textsubscript{3})\textsubscript{3}.\textsuperscript{15} The O\textsubscript{2} flow was kept constant at 60 SCCM (SCCM denotes cubic centimeter per minute at STP) during the entire cycle. A cycle time of 4 s was obtained by employing an Al(CH\textsubscript{3})\textsubscript{3} purge of 1.5 s and a postplasma purge of 0.5 s.

For the plasma-assisted ALD process of TiN, first TiCl\textsubscript{4} (titanium tetrachloride, from Sigma-Aldrich with 99.995 +% purity) was dosed into the reactor by two subsequent 40 ms vapor injections. The plasma was ignited in a H\textsubscript{2}–N\textsubscript{2} gas mixture in a ratio of 8:1 (68 SCCM in total) and was sustained for a duration of 10 s. Argon was used as a purge gas at 150 SCCM flow rate. The pressure during the entire cycle was kept at 80 mTorr and the total cycle time was 27 s.\textsuperscript{8}

As mentioned, the Al\textsubscript{2}O\textsubscript{3} and TiN depositions took place at a single wafer stage temperature. This was done to exclude any possibility of undesired annealing effects due to a change in temperature after Al\textsubscript{2}O\textsubscript{3} deposition and before TiN deposition. A temperature change would also complicate our investigation of the deposition temperature dependence of the TiN/Al\textsubscript{2}O\textsubscript{3}/p-Si stacks. Furthermore, it is important to note that no postdeposition annealing was applied to the processed stacks.

For all of the stacks investigated in this work, the wafer stage temperature and the nominal Al\textsubscript{2}O\textsubscript{3} layer thicknesses are given in Table I. Two temperatures, i.e., 350 and 400 °C, were chosen as deposition temperatures. An Al\textsubscript{2}O\textsubscript{3} thickness series (10, 20, and 40 nm) was carried out at a wafer stage temperature of 350 °C to allow for an investigation of the Al\textsubscript{2}O\textsubscript{3} bulk properties. For instance, the amount of fixed charge or oxide-trapped charge in a TiN/Al\textsubscript{2}O\textsubscript{3}/p-Si stack of plasma-assisted ALD Al\textsubscript{2}O\textsubscript{3} can be investigated with the thickness series. The TiN film thickness was 30 nm for each TiN/Al\textsubscript{2}O\textsubscript{3} stack to allow for sufficient conductivity during electrical testing.
D. Analysis techniques

In situ spectroscopic ellipsometry (SE) was used to monitor film growth employing a visible to near-infrared (245–1700 nm) spectroscopic ellipsometer from J.A. Woollam, Inc. M2000U. For studying the composition of the Al$_2$O$_3$ films, Rutherford backscattering spectroscopy (RBS) was carried out in a singletron accelerator with a nominally 2 MeV He$^+$ probe beam. The scattering chamber contained two detectors for backscattered He$^+$ detection, one at a fixed angle of 10° relative to the incoming beam and one at a variable angle that was set at 70°. The TiN resistivity measurements were performed at room temperature using a Signatone FFP in combination with a Keithley 2400 sourcemeter. High-resolution transmission electron microscopy (HR-TEM) imaging was performed on TiN/Al$_2$O$_3$ stacks using a Tecnai F30ST TEM microscope operated at 300 kV. The $I$-$V$ measurements of MOS capacitors were performed using an Agilent 4155C semiconductor parameter analyzer. For $C$-$V$ measurements, an HP4275A multifrequency LCR meter was used. All $C$-$V$ measurements were performed at 10 kHz, with an oscillation level of 50 mV. A LABVIEW interface program was used to perform the $C$-$V$ measurements and to facilitate both forward and reverse $C$-$V$ measurements.

III. Al$_2$O$_3$ AND TIN MATERIAL PROPERTIES

The structural and electrical properties of individual plasma-assisted ALD Al$_2$O$_3$ films have been investigated previously by Van Hemmen et al.$^{14}$ For wafer stage temperatures in the range 200–300 °C, high uniformity, good stoichiometry, and low impurity levels of H (<3 at. %) and C (<1 at. %) were reported. The RBS results on a plasma-assisted ALD Al$_2$O$_3$ film deposited at 400 °C obtained in this work give results consistent with these earlier measurements: for Al$_2$O$_3$ deposited at temperatures between 200 and 400 °C, the [O]/[Al] ratio is 1.5 ± 0.1 and the mass density of the Al$_2$O$_3$ remains constant at approximately 3.0 ± 0.1 g/cm$^3$. The H content, which drops toward virtually zero with increasing temperature in the range 25–300 °C,$^{14}$ is 0.1 at. % at 400 °C. This trend is also consistent with the results obtained for thermal ALD Al$_2$O$_3$ by Groner et al.$^{16}$ For Al$_2$O$_3$ films deposited above room temperature, the carbon content in the film was below the detection limit of the RBS instrument (C content <1 at. %) for the previous experiments$^{14}$ as well as for the new experiment. For the latter, the detection limit was, however, significantly higher (~5 at. %), but based on the previous experiments and the electrical performance of the films (see Sec. IV), the C-content is also expected to be <1 at. % for 400 °C.

Figure 1 shows the growth per cycle as a function of the wafer stage temperature $T_{set}$. The figure contains data previously obtained within the temperature range 25–300 °C (Ref. 14) as well as new data in the temperature range 300–400 °C. Most data were obtained from in situ SE, whereas the two data points deduced from the HR-TEM images in Fig. 2 confirm these results. All data were obtained on the FlexAl™ ALD reactor covering a time span over more than 1 year. Figure 1 demonstrates therefore the good reproducibility of the plasma-assisted ALD process of Al$_2$O$_3$. A gradual decrease in the growth per cycle as a function of the deposition temperature is evident from Fig. 1. This trend has been attributed to a decrease in –OH surface groups with increasing temperature due to dehydroxylation reactions.$^{16–18}$

Plasma-assisted ALD TiN films deposited in the FlexAl™ ALD reactor was previously investigated by Heil et al.$^8$ They reported a decrease in resistivity of the TiN down to 147 $\mu\Omega$ cm for deposition temperatures increasing up to 350 °C in agreement with the results obtained in a similar plasma-assisted ALD reactor.$^{19}$ The resistivity of the nominally 30 nm thick TiN layers deposited in the current experiments varied between 230 and 275 $\mu\Omega$ cm, without any distinct dependence on the deposition temperature in the range

<table>
<thead>
<tr>
<th>$T_{set}$ (°C)</th>
<th>Al$_2$O$_3$ thickness (nm)</th>
<th>$k_{eff}$</th>
<th>$V_{FB}$ forward (V)</th>
<th>$\Delta V_{FB}$ (V)</th>
<th>$J_L$ (nA/cm$^2$)</th>
<th>$\Phi_B$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>10</td>
<td>7.1 ± 0.1</td>
<td>0.72 ± 0.04</td>
<td>0.06 ± 0.02</td>
<td>3.2 ± 0.5</td>
<td>3.27 ± 0.03</td>
</tr>
<tr>
<td>350</td>
<td>10</td>
<td>7.0 ± 0.1</td>
<td>1.0 ± 0.2</td>
<td>0.5 ± 0.2</td>
<td>2.3 ± 0.4</td>
<td>3.3 ± 0.2</td>
</tr>
<tr>
<td>350</td>
<td>20</td>
<td>8.2 ± 0.1</td>
<td>3.2 ± 1.0</td>
<td>2.6 ± 0.9</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>350</td>
<td>40</td>
<td>8.7 ± 0.1</td>
<td>7.1 ± 1.2</td>
<td>6.0 ± 1.2</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

![FIG. 1.](Image-url) (Color online) The growth per cycle as a function of the wafer stage temperature $T_{set}$. A consistent trend is visible from different experiments carried out over a period longer than 1 year but all in the same ALD reactor. The values have been measured by SE and TEM imaging. The data by Van Hemmen et al. have been taken from Ref. 14.
300–400 °C. This resistivity, combined with the uniform layer thickness, is sufficiently low to guarantee a good electrode performance.

The TEM images of the TiN/Al2O3/p-Si stacks in Fig. 2 reveal no structural differences for the bulk Al2O3 or TiN for the two deposition temperatures. The Al2O3 is clearly amorphous and the TiN is polycrystalline, both in accordance with literature reports for as-deposited (thermal or plasma-assisted) ALD Al2O3 (Refs. 5 and 20) and TiN,21 respectively. Both the Al2O3/p-Si and TiN/Al2O3 interfaces are smooth and well defined.

For the Al2O3/p-Si interfaces, a number of additional observations can be made in Fig. 2. First of all, the interface of the stack deposited at 350 °C depicts a bright line that is most likely the result of electrons scattered at the interface rather than an indication for interfacial SiOx because the Si crystal lattice with its (100) orientation is imaged throughout the white line. The interfacial SiOx is not recognizable possibly because of the low contrast between the oxides in the thinnest areas of the TEM sample. The Al2O3/p-Si interface of the stack deposited at 400 °C also shows a white or light area. However, this area reveals a more grainy structure at the interface, which is distinctly different from that of the bulk Al2O3. Therefore, this layer can be identified as interfacial SiOx and it is estimated to be 1.4 ± 0.4 nm thick. Since the effective k values of the 10 nm thick Al2O3 films deposited at 350 and 400 °C are comparable (see Table I), it is expected that the stack deposited at 350 °C has a similar SiOx thickness.

IV. ELECTRICAL PERFORMANCE

A. Current density versus electric field (J–E)

The current density-electric field (J–E) characteristics of the TiN/10 nm Al2O3/p-Si stacks are shown in Fig. 3(a). The J–E plots given for both deposition temperatures are representative for all deposited stacks. For both 350 and 400 °C, the onset of Fowler–Nordheim (FN) tunneling is around 6 MV/cm for the films deposited.

The TiN/Al2O3 barrier heights ΦB, i.e., the difference of conduction band edges of TiN and Al2O3, can be calculated with the FN equation22,23

\[ J_{FN} = \frac{e^3 m^*}{16\pi^2\hbar^2\Phi_B} E^2 \exp\left(-\frac{4\sqrt{2m^*\Phi_B}}{3eE}\right) \]

in which e is the electron charge and h is Planck’s constant divided by 2π. The parameter \( m^* \) is the electron effective mass in the Al2O3, which is taken as 0.23m, where m is the free electron mass.10 The data, replotted in Fig. 3(b), demonstrate excellent FN tunneling as indicated by the linear regime. Theoretically, the conduction band offset of Al2O3 to TiN is 3.8 eV.24 The TiN/Al2O3 barrier height ΦB estimated from the slope of the plot in Fig. 3(b) for the as-deposited samples is approximately 3.3 eV, in good agreement with the values of 3.2 eV for annealed TiN/Al2O3/Si samples reported in the literature.25 We note, however, that also other values for the effective electron mass than \( m^*_o = 0.23m \) have been reported, such as \( m^*_o = 0.5m \) or 0.45m.26,27 Due to this uncertainty, the reported experimental values of the barrier heights differ correspondingly. The fact that the theoretical ΦB value of 3.8 eV is higher than the experimental value of 3.3 eV can most likely be attributed to the assumption of...
crystallinity for the TiN and Al₂O₃ in the theoretical evaluation. For the current experimental case, the TiN is polycrystalline and the Al₂O₃ is amorphous.

Figure 3(a) shows that both TiN/Al₂O₃/p-Si stacks demonstrate similar leakage and tunneling current behavior, indicating little deposition temperature dependence. The leakage current densities \( J_L \) have been averaged over three devices per stack, each measuring 1000 current values at a fixed electric field of 4 MV/cm. The \( J_L \) values of the TiN/Al₂O₃/p-Si stacks are \( \sim 1 \) nA/cm² (see Table I). This is a significantly low leakage current for as-deposited samples at 4 MV/cm and it is among the lowest reported in the literature for Al₂O₃ layers with similar thicknesses (~5–10 nm). Similar leakage currents reported in the literature are only obtained for annealed samples at electric fields of 2 MV/cm or lower.²,¹⁶,²⁰,²³,²⁸ The aforementioned \( E_{FN} \) value of 6 MV/cm is a high value for the 10 nm Al₂O₃ compared to the \( \sim 3.8 \) MV/cm reported for a 12 nm thermal ALD Al₂O₃ sample.¹⁶ The high \( E_{FN} \) suggests an Al₂O₃ layer of excellent quality with low defect densities. The latter needs to be verified by future quasistatic C-V measurements.

**B. Lifetime and reliability measurements**

The lifetime and reliability of the stacks deposited at the two different deposition temperatures have been examined by means of time-dependent dielectric breakdown (TDBB) and dielectric breakdown field \( (E_{BD}) \) measurements, respectively. The latter are in the range 7–9 MV/cm, in agreement with the literature on other (plasma-assisted) ALD Al₂O₃ MOS capacitors.¹⁴,¹⁶,²⁵ Weibull distributions of the breakdown measurements are shown in Fig. 4. Each data point is an average over 30 breakdown measurements. Both plots show steep distribution curves, indicating that the breakdown is intrinsic in nature, not related to the deposition or processing artifacts. The Weibull plots show comparable average \( E_{BD} \) values of 7.4 ± 0.2 and 7.8 ± 0.2 MV/cm for the stacks deposited at 350 and 400 °C, respectively.

A common extrapolation method used to predict the 10 year lifetime criterion is based on the power law voltage dependence of TDDB:

\[
t_{BD} \approx V_{FA}^n,
\]

where \( V_{FA} \) is the fixed applied voltage on the MOS capacitor, \( n \) is a constant, and \( t_{BD} \) is the time to breakdown that is measured for a certain \( V_{FA} \). This power law is generally applicable to MOS capacitors.²⁹ The value of \( t_{BD} \) increases with decreasing \( V_{FA} \), as is clearly illustrated in Fig. 5(a). The exponent \( n \) can be estimated from the slope of a log(\( t_{BD} \)) versus log(\( V_{FA} \)) plot, shown in Fig. 5(b). All measurements have been performed at 125 °C to accelerate the breakdown events. The TDBB behavior of all capacitors tested satisfied the 10 year lifetime criterion within the operation voltage range, irrespective of the deposition temperature. The measurements where \( t_{BD} \) is below 1 s are not included in the linear fit, since for these values the resolution limit of the measurement system is approached.

**C. Capacitance versus voltage (C-V)**

Figure 6 shows the representative C-V curves for the TiN/10 nm Al₂O₃/p-Si stacks deposited at 350 and 400 °C. The applied voltage is the voltage with respect to the top TiN electrode. Both C-V curves are smooth for forward as well as reverse biasing. The positive flatband voltages \( V_{FB} \) indicate the presence of negative fixed charge in the TiN/Al₂O₃/p-Si stacks for both deposition temperatures. The C-V hysteresis \( \Delta V_{FB} \) is indicative for the amount of mobile charge drifting dissipatively under the applied electric field.³⁰
The most noticeable differences between the C-V curves for the two deposition temperature cases are (i) the considerably lower C-V hysteresis $\Delta V_{\text{FB}}$ of the stack deposited at 400 °C and (ii) the bump in the forward C-V curve of the stack deposited at 350 °C visible at approximately 1 V, indicating the presence of interfacial states. From these observations, a higher deposition temperature appears to have a similar effect as a postdeposition annealing; i.e., it improves the Al$_2$O$_3$/p-Si interface quality.

Based on a set of four C-V measurements of each TiN/Al$_2$O$_3$/p-Si device, a more quantitative overview of the C-V characteristics is given in Table I. In this table, the average forward and hysteresis values $\Delta V_{\text{FB}}$ are given for each deposition temperature and Al$_2$O$_3$ thickness. The $V_{\text{FB}}$ values are determined from Mott–Schottky plots of the associated C-V curves. No obvious influence of the deposition temperature is observed from the values of Table I. However, the data demonstrate an Al$_2$O$_3$ thickness dependence for the forward $V_{\text{FB}}$ and $\Delta V_{\text{FB}}$, which can be explained by the presence of the negative fixed charge $Q_f$. Fixed charge is a limiting factor for the capacitor’s lifetime since the associated shift in $V_{\text{FB}}$ requires a higher operating voltage and correspondingly in a higher power consumption. It also induces positive (mirror) charge trapping, resulting in a decreased lifetime and reliability of the MOS capacitors. However, we already demonstrated in Sec. IV B that the 10 year lifetime criterion of the deposited stacks is well above the operating voltage.

The fixed charge density $Q_f$ can be calculated from the equation:

$$V_{\text{FB}} = \Phi_{\text{MS}} - Q_f e_o e_k t_o,$$  \hspace{1cm} (3)

where $\Phi_{\text{MS}}$ is the work-function difference between the metal and the p-Si substrate, $e_o$ and $e_k$ are the vacuum and relative permittivities, respectively, and $t_o$ is the oxide thickness. This equation is valid only if the bulk oxide charge is negligible compared to the fixed charge located at the oxide/silicon interface, which can be confirmed by the minimal error in the linear fit given in Fig. 7. The slope of this plot gives an estimation of $Q_f$ and the intersect of the linear fit on the vertical axis gives $\Phi_{\text{MS}}$, the work-function difference between TiN and p-Si substrate. Since the samples are as deposited, some of the interface trapped charge $Q_{\text{tr}}$, which could in principle be annealed out, is possibly interpreted as $Q_f$. Note that in this work the forward $V_{\text{FB}}$ is used when calculating the fixed charge density $Q_f$ in order to minimize the contribution of oxide or interface trapped charge.

The slope of the linear fit of the forward $V_{\text{FB}}$ plot is $(20 \pm 4) \times 10^6$ V/cm. Using the $k$ value of 40 nm thick Al$_2$O$_3$, as given in Table I ($k=8.7 \pm 0.1$; for this thickness the influence of the dielectric interfacial SiO$_2$ is minimal), yields a fixed oxide charge density $Q_f$ of $(9.6 \pm 0.2) \times 10^{12}$ cm$^{-2}$. The error in $Q_f$ is based on the error in $k$ and the standard deviation of the linear fit. Similar values have been reported in the literature. Buckley et al. did the same calculation for MOS capacitors with thinner thermal ALD Al$_2$O$_3$ layers and found a $Q_f$ value of $1.15 \times 10^{13}$ cm$^{-2}$. It should be noted, however, that in the case of Buckley et al. the fixed charge is reported for samples that received a postdeposition annealing at 700 °C in O$_2$. With different measurement techniques, $Q_f$ has also been extracted by Hoex et al. for plasma-assisted ALD Al$_2$O$_3$ films deposited in the same reactor as used for the current work (at 200 °C and postdeposition annealed at 425 °C in N$_2$ for 30 min). From corona charging experiments, a $Q_f$ value of $1.3 \times 10^{13}$ cm$^{-2}$ was estimated, which is in good agreement with the $Q_f$ value found in this work. The offset of the linear fit in Fig. 7, which indicates the value of $\Phi_{\text{MS}}$, is $-1.1 \pm 0.5$ V and is also consistent with reports in the literature.

V. CONCLUSIONS

TiN/Al$_2$O$_3$ stacks were deposited on p-Si in a subsequent mode by plasma-assisted ALD performed in a single ALD reactor and at a single deposition temperature (either 350 or 400 °C). When separating the subsequent TiN and Al$_2$O$_3$ depositions by 5 min, no sign of cross contamination of precursors and/or reaction products was observed. This allowed for the synthesis of high-quality as-deposited TiN/Al$_2$O$_3$/p-Si MOS capacitors. Inspection by SE, RBS, and TEM imaging as well as extensive electrical characterization confirmed that the as-deposited TiN/Al$_2$O$_3$/p-Si devices have good structural and electrical properties compared to annealed devices with electrodes deposited ex situ. Capacitance-voltage measurements indicate a $k$ value of $8.7 \pm 0.1$, although for thinner Al$_2$O$_3$ films an interfacial
SiO\textsubscript{2} layer thickness of 1.4 ± 0.4 nm decreases the effective k value to some extent. Excellent electrical performance of the stack is demonstrated by I-V and C-V measurements, revealing low leakage (~1 nA/cm\textsuperscript{2}), good FN tunneling behavior (with a TiN/Al\textsubscript{2}O\textsubscript{3} barrier height of ~3.3 eV), and smooth C-V curves with low C-V hysteresis, indicating negligible interface charge trapping. C-V measurements reveal the presence of a large negative fixed charge density (9.6 ± 0.2) × 10\textsuperscript{12} cm\textsuperscript{-2} at the Al\textsubscript{2}O\textsubscript{3}/p-Si interface, which is comparable to Q\textsubscript{f} reported for annealed devices in the literature. The reliability of these MOS capacitors was demonstrated by steep Weibull distributions of breakdown electric fields combined with a good lifetime at high operating voltages (~4 MV/cm) at 125 °C for the 10 year lifetime criterion. The combination of good performance, lifetime, and reliability illustrates the merits of plasma-assisted ALD processes carried out in a single ALD chamber.

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