Annealing effects on the interface and insulator properties of plasma-deposited Al/SiO$_{x}$N$_{y}$H$_{z}$/Si devices

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Abstract

We have studied and compared the effects of conventional annealing in a forming gas atmosphere (430 $^\circ$C, 20 min) and rapid thermal annealing (RTA) in an inert Ar atmosphere (400–1000 $^\circ$C, 30 s) on Al/SiO$_{x}$N$_{y}$H$_{z}$/Si devices. The samples were deposited by the electron cyclotron resonance plasma method at low temperature ($T=200$ $^\circ$C). The devices were characterized by surface photovoltage measurements before applying contacts and by capacitance–voltage measurements.

All the as-deposited samples containing N had positive flat-band voltage, which corresponds to negative charge in the insulator and/or in the interface states ($Q_{\text{INS}}$). Additionally, trapping of positive charge is observed when measuring from inversion to accumulation after measuring from accumulation to inversion. This behaviour is tentatively attributed to the presence of defects related to N, such as the K centre ($N_2=Si^+$) or the N dangling bond ($Si=N^+$), which may be present in a negatively charged state. For samples of SiO$_2$ composition, with a negligible N content, $Q_{\text{INS}}$ is positive. High densities of interface states ($D_{\text{it}}$), above $10^{12}$ eV$^{-1}$ cm$^{-2}$, are observed in the as-deposited samples.

Both the annealing in a forming gas atmosphere and the RTA result in the change of the sign of $Q_{\text{INS}}$ from negative to positive and a decrease of its absolute value, as well as a decrease of $D_{\text{it}}$ of about one order of magnitude. The trapping of positive charge is also greatly reduced. These improvements of the electrical properties are attributed to the passivation of defects by H present in the forming gas atmosphere or in the SiO$_{x}$N$_{y}$H$_{z}$ film itself in a non-bonded state. For RTA temperatures above 700 $^\circ$C the properties of the devices degrade due to the release of H. The combination of RTA and annealing in a forming gas atmosphere results in the best properties.

1. Introduction

Silicon oxide (SiO$_2$) is widely used as a gate dielectric in metal–oxide–semiconductor (MOS) devices, due to its excellent electrical properties, especially the high quality of the SiO$_2$/Si interface [1, 2]. However, the increase of the integration scale requires ultra-thin SiO$_2$ films, about 3–6 nm thick [3, 4], or even thinner [5], resulting in too high tunnel leakage currents [3] and the diffusion of dopants from the p-type polysilicon gate, such as boron [3, 4]. The use of silicon oxyxnitride (SiO$_{x}$N$_{y}$H$_{z}$) instead of SiO$_2$ offers many advantages. First, SiO$_{x}$N$_{y}$H$_{z}$ has a higher dielectric permittivity than SiO$_2$, allowing physically thicker films with the same capacitance–voltage (C–V) characteristic, therefore reducing tunnel currents [3, 6]. Secondly, the incorporation of N improves the barrier properties against the diffusion of boron and alkali ions [3, 7]. Finally, the reliability of the devices is improved, with an increase of the charge to breakdown [8, 9].
a decrease of the generation of interface states due to charge injection [9, 10], and an improvement of the immunity to hot carrier effects [8, 11].

Another important issue of the ultra large scale integration (ULSI) technology is the requirement of low thermal budget processes to obtain the dielectric films. One of the most extended low-temperature techniques to grow SiO$_x$N$_y$H$_z$ films is plasma-enhanced chemical vapour deposition (PECVD) [12–14], with the remote PECVD variant, in which the substrates are placed outside the plasma region [3, 15, 16], and the electron cyclotron resonance (ECR-PECVD) variant [17–20]. The latter technique has several advantages. As in the case of the remote PECVD technique, substrates are placed outside the plasma region, thus reducing damage due to ion bombardment; the presence of a cathode is not required, which is especially important in processes using corrosive gases. Finally, a very high activation of the precursor gases is achieved, allowing the use of N$_2$ instead of NH$_3$ as a source of N atoms, thus reducing the incorporation of H to the films.

Although the PECVD techniques meet the low thermal budget requirement, the quality of the as-deposited dielectric films is not as good as that of thermally grown SiO$_2$ films [21, 22]. So, post-deposition annealing treatments are required to improve the electrical properties of the plasma-deposited films [5, 15, 18, 21–24].

The aim of this work is to perform a systematic and comparative study of the influence of different post-deposition annealing treatments on the electrical properties of SiO$_x$N$_y$H$_z$ films deposited by ECR-PECVD. Therefore, we have not focused on optimizing the deposition of the films for technological application, and relatively thick films were deposited, to ensure the absence of pinholes in the samples.

Two different annealing processes are studied: conventional annealing at 430 °C for 20 min in a forming gas atmosphere, and rapid thermal annealing (RTA) at temperatures ranging between 400–1000 °C for 30 s in an argon atmosphere. The effects of both treatments, as well as the combination of both processes, are studied for samples with different compositions, ranging from SiN$_2$ to SiO$_2$. The annealing effects will be related to the microstructural properties of the as-deposited films. In the case of RTA, we propose optimum annealing temperatures to minimize the density of interface defects and flat-band voltage.

2. Experiment

SiO$_x$N$_y$H$_z$ films were deposited using a commercial ECR reactor (Astex AX4500) attached to a stainless-steel deposition chamber [25]. SiH$_4$, O$_2$ and N$_2$ were used as precursor gases. Total gas flow, pressure and microwave power were kept constant at 10.52 sccm, 9 × 10$^{-4}$ mbar and 100 W, respectively. The deposition temperature was 200 °C. In all depositions, the SiH$_4$ gas flow $\phi$(SiH$_4$) was set at 1.76 sccm and the flows of O$_2$ and N$_2$, $\phi$(O$_2$) and $\phi$(N$_2$), were varied from 0 to 8.76 sccm in order to obtain films with compositions ranging from SiN$_2$ ($\phi$(O$_2$) = 0 sccm; $\phi$(N$_2$) = 8.76 sccm) to SiO$_2$ ($\phi$(O$_2$) = 8.76 sccm; $\phi$(N$_2$) = 0 sccm). The ratio $R = [\phi$(O$_2$) + $\phi$(N$_2$)]/$\phi$(SiH$_4$) was kept constant at $R = 5.0$. Throughout this paper, the SiO$_x$N$_y$H$_z$ samples will be denoted by the parameter $\alpha$:

$$\alpha = \frac{2x}{2x + 3y}.$$  (1)

This parameter characterizes the composition of the films, with $\alpha = 0$ representing SiN$_2$, and $\alpha = 1$ representing SiO$_2$. For the samples studied in this paper, $\alpha$ was calculated from H-ERDA measurements performed on samples deposited under the same conditions [26, 27].

The films were deposited on n-type Si (100) substrates with a resistivity of 5 Ω cm and a doping concentration of around 10$^{15}$ cm$^{-3}$. The substrates were cleaned using standard procedures [28]. The thickness of the deposited films was about 100 nm. The exact thickness of each sample was measured by ellipsometry using a Plasmos E2302 ellipsometer with incidence and detection angles both set at 70°.

For two selected compositions ($\alpha = 0.30$ and $\alpha = 0.91$), several $1 \times 1$ cm$^2$ samples were deposited in the same process in order to perform RTA treatments at different temperatures, as well as keeping an as-deposited sample for reference. The RTA annealing processes were performed in a Modular Process Technology furnace, model RTP-600, equipped with a graphite susceptor. Samples were annealed at temperatures ranging from 400 to 1000 °C for 30 s in argon atmosphere.

After deposition, before applying metallic contacts, the samples were characterized by surface photovoltage (SPV) measurements, in order to study the quality of the SiO$_x$N$_y$H$_z$/Si system without any influence of the contacts or the evaporation process. This technique measures the modifications in the band bending of the semiconductor when carriers are generated as a consequence of a light pulse. This allows us to determine the surface potential ($\phi_S$) as a function of the gate voltage [29]

$$-q\phi_S = E_{FS} - E_{Fi}$$  (2)

where $E_{FS}$ is the intrinsic Fermi level at the surface of the semiconductor and $E_{Fi}$ is the intrinsic Fermi level in the bulk, where no band bending takes place. For an n-type semiconductor, $\phi_S$ is positive in accumulation and negative in depletion and inversion.

The measurements were performed using an artificial metal–insulator–semiconductor (MIS) structure, with a transparent contact oxide (TCO) on a quartz slice as the gate electrode, and a foil of mica, 38 µm thick, working as the insulator [30]. This set-up allows the characterization of semiconductor interfaces. For our SiO$_x$N$_y$H$_z$/Si device, the capacity of the mica foil is in series with the SiO$_x$N$_y$H$_z$ film.

After the SPV measurements, aluminium contacts were evaporated. Several dots were defined in order to produce different Al/SiO$_x$N$_y$H$_z$/Si devices in each sample. The area of the gate electrodes was 0.87 mm$^2$. In this way we obtained MIS devices with different SiO$_x$N$_y$H$_z$ compositions without any annealing treatment. Additionally, for the compositions $\alpha = 0.30$ and $\alpha = 0.91$, MIS devices in which SiO$_x$N$_y$H$_z$ had been treated by RTA were also obtained. These MIS devices were characterized by $C$–$V$ measurements at high frequency (1 MHz). The density of interface states was evaluated from these measurements following the method of Terman [31].

The next step for all samples was a conventional annealing at 430 °C, for 20 min in a forming gas atmosphere. After this step, we obtained MIS devices with forming gas annealing and
Table 1. Summary of the different annealing treatments and measurements performed on the different samples.

<table>
<thead>
<tr>
<th>Sample composition</th>
<th>As-deposited</th>
<th>As-deposited</th>
<th>F. gas</th>
<th>Al/SiO$_2$N$_x$H$_y$/Si (forming gas)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha = 0.04$</td>
<td>SiO$_2$N$_x$H$_y$/Si</td>
<td>Al</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha = 0.30$</td>
<td>SiO$_2$N$_x$H$_y$/Si</td>
<td>Al/SiO$_2$N$_x$H$_y$/Si</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha = 0.50$</td>
<td>SiO$_2$N$_x$H$_y$/Si</td>
<td>Al</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha = 0.91$</td>
<td>SiO$_2$N$_x$H$_y$/Si</td>
<td>Al/SiO$_2$N$_x$H$_y$/Si</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha = 1.00$</td>
<td>SiO$_2$N$_x$H$_y$/Si</td>
<td>Al/SiO$_2$N$_x$H$_y$/Si</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Measure</td>
<td>SPV</td>
<td>C–V</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 1. Surface potential $\phi_s$ as a function of the total voltage applied to the structure formed by the mica foil and the non-annealed as-deposited SiO$_2$N$_x$H$_y$/Si device, for different compositions of the SiO$_2$N$_x$H$_y$ dielectric film.

MIS devices with RTA + forming gas annealing. The devices were once again characterized by C–V measurements. Table 1 summarizes the different fabrication steps and annealing treatments performed on the different samples, as well as the characterization technique used after each step.

3. Results

3.1. As-deposited samples

Figure 1 shows the surface potential $\phi_s$ (see equation (2)) measured by SPV as a function of the total gate voltage applied to the structure formed by the mica foil and the SiO$_2$N$_x$H$_y$/Si device. The actual voltage on the SiO$_2$N$_x$H$_y$/Si device is of the order of a few volts. The following qualitative results can be derived from figure 1. For the sample of composition closest to SiN$_x$H$_y$ ($\alpha = 0.04$), the flat-band condition $\phi_s = 0$ is achieved for positive applied voltage, which means a positive flat-band voltage. For higher values of $\alpha$, the surface potential ($\phi_s$) remains negative over the whole measured voltage range and the flat-band condition can be achieved for higher positive applied voltage. This means that the films are either in the inversion or the depletion regions, with a relatively high positive flat-band voltage. The result for the sample of SiO$_2$ composition ($\alpha = 1.00$), with a negligible N content, breaks the trend observed for the other samples. For this sample, the flat-band condition is achieved for negative applied voltage. Therefore the flat-band voltage of this sample is negative.

Figure 2 shows the high-frequency C–V characteristics of as-deposited Al/SiO$_2$N$_x$H$_y$/Si devices, for different compositions of the SiO$_2$N$_x$H$_y$ dielectric film. The complete measurement cycle is shown from accumulation to inversion followed by measurement from inversion to accumulation.

\[ V_{FB} = W_{MS} - \frac{Q_{INS}}{C_{INS}} \]  

where $C_{INS}$ is the SiO$_2$N$_x$H$_y$ capacitance and $W_{MS} = -0.34$ V is the work function difference for Al and n-Si with a 10$^{15}$ cm$^{-3}$ doping concentration [1]. Here, the insulator charge $Q_{INS}$ includes the contribution of the dielectric fixed charge ($Q_f$), the trapped charge ($Q_t$), the mobile charge ($Q_m$) and the charge associated with interface states ($Q_{INS}$) [1]. Equation (3) assumes that $Q_{INS}$ is located in the SiO$_2$N$_x$H$_y$/Si interface [1].

Table 2 summarizes the values of $V_{FB}$ and $Q_{INS}$ (estimated from equation (3)) obtained from the C–V measurements
Results obtained from the C–V measurements performed on the as-deposited Al/SiO$_2$/NH$_3$/Si devices: $\alpha = 2x/(2x + 3y)$; $V_{FB} =$ flatband voltage; $Q_{INS} =$ charge in the dielectric (see equation (3)). $\Delta Q_{INS} =$ charge trapping during the measurement cycle (from accumulation to inversion followed by from inversion to accumulation); $D_{IT,min} =$ minimum value of the density of interface states; $D_{IT(0.1)} =$ density of interface states for $E - E_F = -0.1$ eV; $D_{IT(0.3)} =$ density of interface states for $E - E_F = 0.3$ eV.

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>$V_{FB}$ (V)</th>
<th>$Q_{INS}/q_e$ $(\times 10^{11}$ cm$^{-2}$)</th>
<th>$\Delta Q_{INS}/q_e$ $(\times 10^{11}$ cm$^{-2}$)</th>
<th>$D_{IT,min}$ (eV$^{-1}$ cm$^{-2}$)</th>
<th>$D_{IT(0.1)}$ (eV$^{-1}$ cm$^{-2}$)</th>
<th>$D_{IT(0.3)}$ (eV$^{-1}$ cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04</td>
<td>2.6</td>
<td>9.8</td>
<td>2.3</td>
<td>1.1 $\times 10^{12}$</td>
<td>2.9 $\times 10^{12}$</td>
<td>3.5 $\times 10^{12}$</td>
</tr>
<tr>
<td>0.30</td>
<td>2.4</td>
<td>6.9</td>
<td>4.6</td>
<td>1.6 $\times 10^{12}$</td>
<td>4.7 $\times 10^{12}$</td>
<td>3.6 $\times 10^{12}$</td>
</tr>
<tr>
<td>0.50</td>
<td>6.5</td>
<td>15</td>
<td>3.8</td>
<td>1.7 $\times 10^{12}$</td>
<td>5.3 $\times 10^{12}$</td>
<td>5.0 $\times 10^{12}$</td>
</tr>
<tr>
<td>0.91</td>
<td>10.9</td>
<td>20</td>
<td>8.4</td>
<td>2.8 $\times 10^{12}$</td>
<td>11 $\times 10^{12}$</td>
<td>9.0 $\times 10^{12}$</td>
</tr>
<tr>
<td>1.00</td>
<td>-6.8</td>
<td>11</td>
<td>14</td>
<td>3.3 $\times 10^{12}$</td>
<td>5.1 $\times 10^{12}$</td>
<td>9.7 $\times 10^{12}$</td>
</tr>
</tbody>
</table>

Figure 3. Distribution of the density of interface states ($D_{IT}$) obtained from the C–V characteristics shown in figure 2, for as-deposited Al/SiO$_2$/NH$_3$/Si devices, with different compositions of the SiO$_2$/NH$_3$ dielectric film.

shown in figure 2. Negative $Q_{INS}$ is obtained for all samples, except for the sample with SiO$_2$ composition ($\alpha = 1.00$), which has positive $Q_{INS}$.

In all the samples, a shift of the C–V curve to the left ($V_{FB}$ decreases) is observed during the measurement cycle (the curve measured from inversion to accumulation is shifted with respect to the curve measured from accumulation to inversion). This clockwise hysteresis is opposite to that expected for the drift of mobile ions and corresponds to either the trapping of positive charge in the insulator when high negative fields are applied or the trapping of negative charge for high positive fields [32]. The change of $Q_{INS}$ associated with this shift is also shown in table 2 ($\Delta Q_{INS}$). There is a trend for $\Delta Q_{INS}$ to increase as $\alpha$ is increased, except for the SiO$_2$ sample, which shows the lowest charge trapping.

The energy distribution of the density of interface states obtained from the C–V measurements ($D_{IT}$) is shown in figure 3. The distribution has the characteristic ‘U’ shape, which is associated with stretched silicon–silicon bonds and Si dangling bonds (Si$_{3}\bar{\text{Si}}$) in the Si lattice [30]. The shape of the distribution is slightly distorted by the presence of peaks around $E - E_F = -0.1$ eV and $E - E_F = 0.3–0.4$ eV. In the SiO$_2$/Si system, Si dangling bonds back bonded to one or two O atoms (Si$_2$O or Si$_3$O$_2$) produce donor-like defects inside the silicon bandgap at specific energies [30]. It is suggested that the peaks observed in figure 3 may be related to Si dangling bonds with different chemical environments, involving O, N and Si atoms. The minimum of $D_{IT}$ for the different samples is shown in table 2 ($D_{IT(min)}$). The $D_n$ values corresponding to $E - E_F = -0.1$ eV ($D_{IT(0.1)}$) and $E - E_F = 0.35$ eV ($D_{IT(0.35)}$) are also shown, because most samples show clear peaks for these energies. (The peak around $E - E_F = 0.35$ becomes more clear after the annealing in a forming gas atmosphere, which will be discussed in the following sections.) The obtained densities of defects are above $10^{12}$ eV$^{-1}$ cm$^{-2}$, but it must be taken into account that these are as-deposited Al/SiO$_2$/NH$_3$/Si devices, which have not undergone any annealing treatment at all. $D_n$ values above $10^{12}$ eV$^{-1}$ cm$^{-2}$ have been also reported by Hernández et al [19] for ECR-deposited SiO$_2$/NH$_3$ films after a conventional post-metallization annealing in N$_2$ atmosphere at 460 °C.

3.2. Samples annealed in a forming gas atmosphere (430 °C, 20 min)

Figure 4 shows the high-frequency C–V characteristics of the Al/SiO$_2$/NH$_3$/Si devices after annealing in a forming gas atmosphere for 20 min at 430 °C. The calculated distribution of the density of defects appears in figure 5. After the annealing in a forming gas atmosphere, all samples show a clear peak for $E - E_F$ in the 0.3–0.4 eV range. Table 3 summarizes the characteristic parameters derived from the C–V measurements.

The most significant effect of the annealing in a forming gas atmosphere is the change of the sign of the flat-band voltage ($V_{FB}$) and the corresponding insulator charge ($Q_{INS}$).
for all the samples, except for that of SiO\(_2\) composition (\(\alpha = 1.00\)). After the annealing in a forming gas, all samples show negative values of \(V_{FB}\), which corresponds to positive \(Q_{DSS}\). Additionally, the magnitude of \(Q_{DSS}\) is lower than in non-annealed samples. The hysteresis observed over the measuring cycle is greatly reduced by the annealing in a forming gas atmosphere, as shown in figure 4. Finally, the density of interface states decreases by about one order of magnitude, as can be observed by comparing figures 3 and 5 and tables 2 and 3. All these results show an improvement of the electrical properties of the films.

### 3.3. Samples subjected to RTA

The influence of RTA treatments was studied for the samples of compositions \(\alpha = 0.30\) and \(\alpha = 0.91\). The surface potential \(\phi_s\) obtained from SPV measurements is shown for the sample with \(\alpha = 0.30\) in figure 6 as a function of the total voltage applied, for different annealing temperatures. Similar results were obtained for the sample with \(\alpha = 0.91\).

As previously shown in figure 1, the as-deposited sample has negative surface potential over the whole measured voltage range, indicating that the SiO\(_2\)/Si device remains in the inversion or in the depletion regions, with a high positive flat-band voltage value. The RTA process significantly affects the behaviour of the device, in a similar way as the annealing in a forming gas atmosphere described in the previous section. For all the RTA temperatures the flat-band condition \(\phi_s = 0\) is achieved for negative applied voltage, indicating a change of the sign of the flat-band voltage, and therefore a change of the sign of \(Q_{DSS}\). Additionally, figure 6 suggests that the flat-band voltage decreases in absolute value as RTA temperature increases from 400 °C to about 600–700 °C, but increases for higher annealing temperatures.

These qualitative results derived from the SPV measurements are perfectly consistent with the \(C–V\) measurements performed on Al/SiO\(_2\)/Si devices. The \(C–V\) curves for selected RTA temperatures are shown in figure 7 for \(\alpha = 0.30\) and in figure 8 for \(\alpha = 0.91\). The flat-band voltage and the minimum of the density of interface states are shown in figures 9 and 10, for the samples of composition \(\alpha = 0.30\) and \(\alpha = 0.91\), respectively, as a function of RTA temperature. The temperature of 200 °C corresponds to the
non-annealed as-deposited sample. The results after a forming gas annealing following the RTA are also shown. These results will be discussed in the next section.

The flat-band voltage is positive for the non-annealed samples and negative for all the annealed samples, regardless of the RTA temperature. So, the RTA has the same effect as the annealing in a forming gas atmosphere concerning the change of the sign of $Q_{\text{INS}}$. A decrease of the absolute value of $V_{\text{FB}}$ is observed for RTA temperatures up to 600–700 °C. For higher temperatures, $V_{\text{FB}}$ increases in absolute value, reaching higher values than in the as-deposited sample. The hysteresis during the measurement cycle is also greatly reduced by the RTA, as shown in figures 7 and 8. Concerning the density of interface states ($D_i$), the RTA results in a decrease of $D_i$, with the minimum value obtained for 400 °C. For the sample of composition $\alpha = 0.30$ the improvement in $D_i$ induced by RTA is more significant than for the sample of composition $\alpha = 0.91$, and comparable to the effect of the annealing in a forming gas atmosphere.

3.4. Effect of RTA followed by annealing in a forming gas atmosphere

Finally, we have studied the effect of RTA followed by annealing in a forming gas atmosphere. The flat-band voltage $V_{\text{FB}}$ and the minimum of the density of interface states $D_i$ as a function of RTA temperature, for the sample of composition $\alpha = 0.30$. The results after annealing in a forming gas atmosphere following the RTA are also shown. Lines are guides to the eye.

3.4. Effect of RTA followed by annealing in a forming gas atmosphere

Finally, we have studied the effect of RTA followed by annealing in a forming gas atmosphere. The flat-band voltage $V_{\text{FB}}$ and the minimum of the density of interface states $D_i$ as a function of RTA temperature, for the sample of composition $\alpha = 0.30$. The results after annealing in a forming gas atmosphere are shown in figures 9 and 10 for the compositions $\alpha = 0.30$ and $\alpha = 0.91$, respectively, as a function of RTA temperature. The annealing in a forming gas atmosphere further improves the interface, with a decrease of $D_i$, especially for the samples of composition $\alpha = 0.91$, in which the effect of RTA alone was less significant. For the sample of composition $\alpha = 0.30$, $D_i$ values below $10^{11}$ eV$^{-1}$ cm$^{-2}$ are obtained for RTA temperatures ($T = 400$ °C). These values are close to the results obtained by Ma et al [3] for SiO$_2$N$_x$H$_y$ films of similar composition, deposited by remote PECVD after a previous in situ plasma oxidation of the Si surface, and rapid thermally annealed at 900 °C.

No significant changes in $V_{\text{FB}}$, and therefore in $Q_{\text{INS}}$, are observed.

4. Discussion

4.1. Electrical properties of as-deposited samples

In order to explain the results obtained for the as-deposited samples, it is necessary to take into account the microstructural properties of the SiO$_2$N$_x$H$_y$ films, in particular the structure of defects. In a previous work, the paramagnetic defects of our SiO$_2$N$_x$H$_y$ films were studied in detail [27]. For SiO$_2$ films, the main defect is the E’ centre, which corresponds to a Si dangling bond back bonded to three O atoms (O3≡Si↑) [33]. This defect produces donor-like states in the Si conduction band, which are unoccupied in equilibrium and therefore positively charged [30]. It is suggested that the positive $Q_{\text{INS}}$ measured in the SiO$_2$ films ($\alpha = 1.00$) is related to positive fixed charge associated to the E’ centre.

It is suggested that the negative $Q_{\text{INS}}$ measured for the other compositions is related to the presence of N, which is not present in the SiO$_2$ films. The most important defects involving
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N are the K centre (Nᵢ=Si⁺) [34] and the N dangling bond (Si=N) [35, 36]. According to previous measurements, the K centre is present in our SiO₂,N,H films deposited at those conditions used in this work (R = 5.0) [27]. This defect is more stable in the diamagnetic negatively charged state than in the paramagnetic neutral one [34]. In fact, the K centre signal can be enhanced by ultraviolet (UV) illumination [34]. The negatively charged N dangling bond lies very close to the valence band in SiN₃H₅ films [37], which makes it very likely to be occupied, especially when K centres are also present and charge transfer between both defects may take place [37]. This makes the N dangling bond difficult to detect by EPR. For our SiO₂,N,H films deposited at R = 5.0 of intermediate compositions, a signal which may be related to the N dangling bond defect was observed [27]. He et al also reported a signal for PECVD SiO₂,N,H films with a structure very similar to that of the N dangling bond [14]. The intensity of this signal was enhanced as the composition approached SiO₂. Taking these results into account, we tentatively propose that the negative charge in our Al/SiO₂,N,H./Si devices may be related to the presence of negatively charged K centres and/or N dangling bonds. An increase of the N dangling bond concentration when composition changes from SiN₃H₅ (α = 0) to SiO₂ (α = 1) may explain the trend observed for Q_{INS}, which increases in absolute value when α increases (see table 2).

The hysteresis observed in the C–V curves (figure 2) may also be explained by the presence of K centres and N dangling bonds in the as-deposited films. When these defects are present in a negatively charged state, they are able to capture positive charge when high negative fields are applied [34], therefore resulting in the observed hysteresis cycle. This same mechanism of trapping positive charge under high negative fields was proposed by Perera et al [38] to explain hysteresis cycles in Si/SiO₂,N/Al devices before post-metallization annealing.

4.2. Effect of conventional annealing in a forming gas atmosphere

As described in the previous section, the annealing in a forming gas atmosphere results in significant changes concerning the insulator charge Q_{INS}. For the SiO₂ sample (α = 1.00), Q_{INS} decreases after annealing, without showing any change in its sign. This result is understood as a decrease of the fixed charge in the oxide as a consequence of the passivation or actual healing of defects during the annealing. For the other samples the annealing results in a change of the sign of Q_{INS}. In any case, the trend for Q_{INS} to increase as α is increased (excluding the SiO₂ sample) is maintained, so that the highest value of Q_{INS} before and after the annealing is obtained for α = 0.91. This result suggests a change in the charge state of the defects. However, the exact mechanisms taking place during the annealing are not fully understood.

The decrease of the hysteresis after annealing is consistent with the previous conclusion that the hysteresis is due to the trapping of positive charge by negatively charged centres. The disappearance of these centres (or a change in its charge state from negative to positive) results in a great decrease of the positive charge trapping, and therefore a decrease of the hysteresis.

Finally, the decrease of the density of interface states is attributed to the passivation of defects by H, coming from the forming gas atmosphere or from OH groups or water molecules covering the surface of the films before Al evaporation [30].

4.3. Effect of RTA

A network thermal relaxation process is known to be induced in SiO₂,N,H films by RTA treatments. This relaxation can contribute to reduce the defect concentration in the bulk and interface of SiO₂,N,H films. In previous works, our group observed this mechanism to take place for annealing temperatures up to 900 °C in SiN₃H₅ films, while for SiO₂,N,H films with α = 0.36 and higher values (including SiO₂), an improvement of the structural order was observed for annealing temperatures up to 1000 °C [25, 39, 40]. This mechanism may be to some extent responsible for the decrease of the interface charge density Dₙ and the decrease of the absolute value of V_{FB} (and therefore Q_{INS}) shown in figures 9 and 10. However, the relaxation process is more significant for temperatures above 600–700 °C than for lower temperatures [25, 39, 40], while the best values of Dₙ and V_{FB} are obtained for 400 and 600–700 °C, respectively, which suggests additional processes related to the electrical properties taking place during the RTA.

Although the RTA was performed in an Ar inert atmosphere, passivation of defects is possible by non-bonded H present in the films. We have previously reported the presence of non-bonded H in our SiO₂,N,H films deposited at R = 5.0 [41], as well as an increase of the N–H bond concentration for low RTA temperatures (T = 400–500 °C) [39], which supports the conclusion that defects are being passivated by H during the RTA. This effect is more significant for compositions closer to SiN₃H₅, which have a higher non-bonded H content [41]. In fact, no significant increase of the N–H bond concentration as a result of the RTA was observed for compositions of α = 0.7 and higher [39]. So, the decrease of DₙRTA is more significant for the sample of composition α = 0.30 (figure 9) than for the sample with α = 0.91 (figure 10).

For annealing temperatures above 400–500 °C, the bonded H content was observed to decrease [39]. We attribute the increase of the density of interface states for RTA temperatures higher than 400 °C to the release of H, which seems to be dominant with respect to the thermal relaxation at the interface. On the other hand, Q_{INS} is reduced for annealing temperatures up to 600–700 °C, as evidenced by the behaviour of V_{FB}, which suggests that the network relaxation process dominates over the H release mechanism in the bulk in this temperature range. For the highest RTA temperatures (T ≥ 800 °C), the H release is enhanced [39], resulting in an overall degradation of the electrical properties, as evidenced by the increase of both Q_{INS} and Dₙ.

4.4. Effect of RTA followed by conventional annealing in a forming gas atmosphere

As previously described, a conventional annealing in a forming gas atmosphere following RTA further improves the interface properties of the devices, reducing the density of interface states. This improvement is less significant in those samples.
of composition close to SiN$_x$H$_y$ (sample with $\alpha = 0.30$ in figure 9). These samples show a significant non-bonded H content, as explained above, which efficiently passivates the defects during RTA. On the other hand, samples of composition close to SiO$_2$ (sample with $\alpha = 0.91$ in figure 10) show much lower or negligible non-bonded H content, so that the passivation obtained after RTA in an argon atmosphere can be significantly improved by the annealing in a forming gas atmosphere.

5. Conclusions

The influence of different annealing treatments on the electrical properties of Al/SiO$_2$/Si devices has been investigated. The as-deposited samples, without any annealing treatment, exhibit high densities of interface states (over $10^{12}$ eV$^{-1}$ cm$^{-2}$). Positive flat-band voltage ($V_{FB}$), which corresponds to negative charge in the insulator ($Q_{INS}$), is observed in all samples containing N. On the other hand, for the sample of SiO$_2$ composition, $V_{FB}$ is negative and $Q_{INS}$ is positive. Trapping of positive charge is observed during the measurement cycle. This trapping is higher in those samples with higher negative values of $Q_{INS}$. It is suggested that the negative charge is associated with defects related to N, such as the K centre or the N dangling bond, which may be present in a negatively charged state. These defects may also be responsible for the charge trapping phenomenon.

Both the conventional annealing in a forming gas atmosphere and the RTA in an Ar atmosphere result in the change of the sign of $Q_{INS}$ from negative to positive in those samples containing N. Upon annealing in a forming gas atmosphere at 430 °C, the absolute value of $Q_{INS}$ decreases and the density of interface states ($D_q$) is reduced by about one order of magnitude. This improvement of the electrical properties is attributed to the passivation of defects by the H present in the annealing atmosphere.

The effect of RTA depends on the temperature. For low annealing temperatures $D_q$ decreases with respect to the as-deposited sample, with the minimum value obtained for $T = 400$ °C. The minimum value of $Q_{INS}$ is achieved for temperatures about 600–700 °C. These improvements are also attributed to the thermal relaxation of the network and the passivation of bonds by H. Although H was not present in the RTA atmosphere, there is H present in the films in a non-bonded state, which plays the role of passivation. The effect is more significant for the sample of composition $\alpha = 0.30$ (closer to SiN$_x$H$_y$) than for the sample of composition $\alpha = 0.91$, as the non-bonded H content in the former sample is higher.

For RTA temperatures of 800 °C and higher, the release of H during the process results in the degradation of the electrical properties, with an increase of $D_q$ and $Q_{INS}$. An annealing in a forming gas atmosphere following the RTA further improves the properties of the films, especially in those samples in which the RTA was less efficient.

The results presented in this work suggest that the combination of low-temperature ECR deposition and low-temperature annealing ($T = 400–500$ °C) is a promising process for the production of SiO$_2$/N$_x$/H$_y$ insulator films for application within the ULSI technology context.

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