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<tr>
<td>Citation</td>
<td>IEEE Transactions on Device and Materials Reliability, 2011, v. 11 n. 3, p. 490-494</td>
</tr>
<tr>
<td>Issued Date</td>
<td>2011</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/10722/155655">http://hdl.handle.net/10722/155655</a></td>
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Improved Performance of Yttrium-Doped Al$_2$O$_3$ as Inter-Poly Dielectric for Flash-Memory Applications

X. D. Huang, L. Liu, J. P. Xu, and P. T. Lai, Senior Member, IEEE

Abstract—Yttrium-doped Al$_2$O$_3$ (Y$_x$Al$_y$O) with different yttrium contents prepared by co-sputtering method is investigated as the inter-poly dielectric (IPD) for flash memory applications. A poor SiO$_2$-like interlayer formed at the IPD/Si interface is confirmed by X-ray photoelectron spectroscopy, and can be suppressed by Y doping through the transformation of silica into silicate. Compared with Al$_2$O$_3$ and Y$_2$O$_3$ films, the optimized Y$_x$Al$_y$O film shows lower interface-state density, lower bulk charge-trapping density, higher dielectric constant, and smaller gate leakage, due to the suppressed interlayer and good thermal property ascribed to appropriate Y and Al contents in the film. Therefore, the optimized Y$_x$Al$_y$O film is a promising candidate as the IPD for flash memory.

Index Terms—Flash memory, high-dielectric constant (high-$k$), inter-poly dielectric (IPD), Y$_x$Al$_y$O, yttrium doping.

I. INTRODUCTION

HIGH-DIELECTRIC constant (high-$k$) dielectrics have been widely proposed to replace SiO$_2$ as inter-poly dielectric (IPD) in flash memory for good data retention properties and continual scaling down of the dimensions of flash memory. Among various high-$k$ dielectrics, Al$_2$O$_3$ seems to be a promising candidate due to its large band-gap ($\sim$8.8 eV), which is only next to that of SiO$_2$ and higher $k$ value ($\sim$9) than SiO$_2$ ($\sim$3.9) [1]. However, the formation of a poor low-$k$ SiO$_2$ interfacial layer between Al$_2$O$_3$ and floating gate (poly-Si) is unavoidable during the Al$_2$O$_3$ deposition which can reduce the effective dielectric constant and increase the leakage of the flash memory [2], [3]. To remove the interfacial layer, Jayanti et al. [3] suggested a La$_2$O$_3$ scavenging layer inserted between the Al$_2$O$_3$ and poly-Si because the rare-earth metal oxides are known to consume SiO$_2$. The main problem of this method is that the extra La$_2$O$_3$ layer may increase the equivalent oxide thickness (EOT) of the IPD and complicate the processing due to the double dielectric layers. Moreover, the hydroscopic characteristics of La$_2$O$_3$ may lead to an unstable and low-$k$ lanthanum hydroxide, further limiting its applications [4]. Gadolinium-doped Al$_2$O$_3$ dielectric film was also proposed to improve the dielectric constant of Al$_2$O$_3$, while maintaining a moderate conduction-band barrier to suppress the gate leakage [5]. Among rare-earth metal oxides, yttrium oxide shows the strongest affinity for oxygen, no humidity absorption (compared with La$_2$O$_3$), and no magnetic characteristics (compared with Gd$_2$O$_3$), thus attracting increasing interest [6], [7]. The main shortcomings of Y$_2$O$_3$ lie in its poor thermal property and relatively small band-gap ($\sim$6 eV) compared with Al$_2$O$_3$ [1]. In this paper, a novel method to engineer Y-doped Al$_2$O$_3$ film as IPD is proposed by co-sputtering Y and Al targets in an Ar/O$_2$ mixed ambient for further improvement of the dielectric performance. Experimental results have demonstrated that the optimized Y-doped Al$_2$O$_3$ is a promising candidate as IPD for flash-memory applications.

II. EXPERIMENTS

Silicon MOS capacitors were fabricated on p-type (100) substrate with a resistivity of $0.17 \sim 0.23$ $\Omega \cdot$ cm. The wafers were cleaned by the RCA method, and then Y$_x$Al$_y$O with different Y contents was deposited on the wafers by co-sputtering of Al and Y targets in a mixed ambient (Ar/O$_2 = 24:10$). To explore the ability of Y doping to consume the interlayer, a high ratio of oxygen was used for the reactive sputtering because it could lead to a thicker interlayer. Al sputtering power was fixed at 25 W, while Y sputtering power was set as 20, 25, and 30 W to obtain samples with different amounts of Y incorporation, denoted as YAIO-1, YAIO-2, and YAIO-3 samples, respectively. Following that, the samples received post-deposition annealing (PDA) at 950 °C for 30 s in N$_2$ ambient. Subsequently, aluminum was evaporated and patterned as electrodes. Finally, forming-gas annealing was performed at 300 °C for 20 min. For comparison, samples with Al$_2$O$_3$ or Y$_2$O$_3$ as the dielectric film were also fabricated using the same process, and denoted as AL2O3 and Y2O3 samples, respectively. Note that all the samples had similar EOT ($\sim$31 Å).

The chemical composition and bonding states of the films were analyzed by X-ray photoelectron spectroscopy (XPS). The thickness of the dielectrics was determined by ellipsometry. Their surface morphology was detected by atomic force microscope (AFM). Capacitance–voltage characteristics were measured by HP4284A LCR meter. Gate leakage was measured by HP4156A semiconductor parameter analyzer. All the electrical tests were performed under a light-tight and electrically shielded condition at room temperature.
Thus the dielectrics are denoted as Y when the Y sputtering power is set as 20, 25, and 30 W, and Al is determined to be 0.22/0.78, 0.33/0.67 and 0.43/0.57 on HF-treated silicon with the same PDA treatment is used as higher binding energy than the values (300 eV for Y 3p1/2 and Y 3p3/2). Fig. 1 shows the Y 3p, Al 2p, Si 2p, and O 1s XPS spectra of the samples. To study the interfacial bonding states at the Y2AlO5/Si interface, a thin Y2AlO5 film (~2 nm) deposited on HF-treated silicon with the same PDA treatment is used as the XPS sample. According to the XPS analysis, the ratio of Y and Al is determined to be 0.22/0.78, 0.33/0.67 and 0.43/0.57 when the Y sputtering power is set as 20, 25, and 30 W, and thus the dielectrics are denoted as Y0.22Al0.78O, Y0.33Al0.67O, and Y0.43Al0.57O, respectively, where the Y content increases with increasing Y sputtering power. Fig. 1(a) shows the Y 3p spectrum of the samples. It is noted that all the samples show peaks located at 315.2 and 303.1 eV corresponding to Y 3p1/2 and Y 3p3/2, respectively. These two peaks are at higher binding energy than the values (300 eV for Y 3p1/2, and 290 eV for Y 3p3/2) for Y2O3 [8], indicating different bonding structures from Y2O3. Similar phenomenon is also observed in the Al 2p spectrum shown in Fig. 1(b). The Al 2p peak at 75.5 eV also shifts to higher binding energy compared with that of Al2O3 (74.9 eV) [9]. The above observations demonstrate that the dielectric films present a homogenous material without phase-separated Al2O3 and Y2O3 after the PDA. To confirm the bonding structures of the dielectric films, Si 2p spectrum as well as the curve-fitting lines is also shown in Fig. 1(c). Each fitting peak is assumed to follow the general shape of the Lorentzian–Gaussian function. The spectrum can be decomposed into three components corresponding to the Si substrate (99.5 eV for Si 2p3/2), silica (103.8 eV for Si 2p), and silicate (103.0 eV for Si 2p) [10]. The formation of silicate can further be confirmed by the O 1s spectrum shown in Fig. 1(d), where the peak at 533.1 eV is consistent with silica [10], while the peak at 532.6 eV is intermediate between SiO2 (~533.1 eV) and Y2O3 (~529.5 eV [10]) [or Al2O3 (~532.2 eV [9])], and assigned to the silicate. It is noted that a SiO2-like interlayer can be observed in all the samples. Since the O radical has small radius and is highly reactive, it seems unavoidable to form such a poor SiO2-like interlayer due to O-radical enhanced oxidation with the Si substrate [11]. The atomic ratio of silicon (and oxygen) component corresponding to the silica and silicate for the Y0.22Al0.78O, Y0.33Al0.67O, and Y0.43Al0.57O samples is also summarized in Fig. 2. The ratio of silicon (and oxygen) for the Y0.22Al0.78O sample is largest among the three samples, corresponding to lowest Y content in the film and indicating its thickest silica interlayer. However, the Y0.43Al0.57O sample also has a larger ratio than the Y0.33Al0.67O one, even though it shows higher Y content than the latter. The reason should be that reoxidation occurs during the PDA due to the poor thermal stability of the sample with high Y content [12]. Consequently, the SiO2-like interlayer can be effectively suppressed by optimizing the Y content through the transformation of silica into silicate.

Fig. 3 shows the C–V curves of the MOS samples, swept from the inversion to accumulation region at 50 kHz and 1 MHz, and the related simulated quasi-static (QM) C–V curves obtained by a software developed by UC Berkeley are also shown in Fig. 3. The curves of the Al2O3 and YAlO-1 samples exhibit obvious frequency dispersion, and their C–V curves measured at 50 kHz show a bump in the transition region related to high interface-state density at their interface, indicating their poor dielectric qualities. Moreover, obvious deviation of the measured curves from the simulated ones

![Image](319x339 to 532x488)
Fig. 3. C–V characteristics of the samples measured at 50 kHz and 1 MHz. The quasi-static (QM) simulated C–V curves are also shown. (a) The Al2O3 sample; (b) the YAIO-1 sample; (c) the YAIO-2 sample; (d) the YAIO-3 sample; (e) the Y2O3 sample.

Table I
Physical and Electrical Parameters of the Samples

<table>
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<tr>
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<th>Al2O3</th>
<th>YAIO-1</th>
<th>YAIO-2</th>
<th>YAIO-3</th>
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<tr>
<td>(V_{fb}(V))</td>
<td>-1.0</td>
<td>-0.92</td>
<td>-0.85</td>
<td>-0.99</td>
<td>-1.4</td>
</tr>
<tr>
<td>(D_{it}(\text{cm}^2\text{eV}^{-1}))</td>
<td>2.7e+12</td>
<td>2.1e+12</td>
<td>5.3e+11</td>
<td>2.0e+12</td>
<td>2.4e+12</td>
</tr>
<tr>
<td>(Q_{ox}(\text{cm}^2))</td>
<td>1.4e+12</td>
<td>1.5e+12</td>
<td>6.9e+11</td>
<td>1.4e+12</td>
<td>4.0e+12</td>
</tr>
<tr>
<td>(T_{ox}(\text{Å}))</td>
<td>45.7</td>
<td>54.8</td>
<td>68.2</td>
<td>70.2</td>
<td>55.6</td>
</tr>
<tr>
<td>(EOT(Å))</td>
<td>30.2</td>
<td>33.3</td>
<td>31.4</td>
<td>32.5</td>
<td>30.5</td>
</tr>
<tr>
<td>(k)</td>
<td>5.9</td>
<td>6.4</td>
<td>8.5</td>
<td>8.4</td>
<td>7.1</td>
</tr>
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Further confirms a large quantity of defects in the films. For the Al2O3 sample, this should be due to a large number of interfacial defects existing in the poor interlayer between the Al2O3 and Si substrate. It also indicates that the Y content in the YAIO-1 sample may be not enough to scavenge the poor interfacial layer, thus resulting in a large quantity of interface states. In addition, the C–V curves of the YAIO-3 and Y2O3 samples also show obvious frequency dispersion and deviation between the measured data and the simulated one in the transition region. This should be associated with the defects due to their poor thermal stability because the Y2O3 film has a low crystallization temperature [12]. On the contrary, the YAIO-2 sample shows negligible frequency dispersion and the measured C–V data is also in good agreement with the simulated one, implying its excellent film quality with little defects. Moreover, the Al2O3 and Y2O3 samples show deep depletion phenomenon that their capacitance decreases with increasing positive gate voltage in the inversion region, indicating their poor leakage characteristics [13], which can be further confirmed by the \(I–V\) characteristics shown in Fig. 5 below. For further comparison, the flatband voltage (\(V_{fb}\)), oxide-charge density (\(Q_{ox}\)), and interface-state density near mid-gap (\(D_{it}\)) of the samples extracted by the Terman’s method are summarized in Table I, [14]. Table I also lists some other physical parameters including the physical thickness (\(T_{ox}\)) obtained by ellipsometry, \(EOT\) extracted by fitting the measured 1-MHz C–V data to the simulated one in the accumulation region, and the dielectric constant (\(k\)) calculated by \(k = \varepsilon_{SiO_2}T_{ox}/EOT\), where \(\varepsilon_{SiO_2}\) is the dielectric constant of SiO2. Among the samples, the YAIO-2 sample shows the smallest \(D_{it}(5.3 \times 10^{11} \text{cm}^{-2}\text{eV}^{-1})\), smallest \(Q_{ox}(6.9 \times 10^{11} \text{cm}^{-2})\) and highest \(k\) value (≈8.5), further supporting its good dielectric quality. It is worth pointing out that its \(k\) value is still below the value of Al2O3 (≈9), even though Y incorporation into Al2O3 tends to improve the dielectric constant. This indicates that the low-\(k\) SiO2-like interlayer has not been fully consumed, which should be due to the high ratio of oxygen used during the reactive sputtering, leading to a thick interlayer at the interface. Anyway, the improvement of the IPD quality by optimizing

Fig. 4. Gate-voltage shifts versus time under a 10-μA/cm^2 constant-current stress.
compared with the Y2O3 sample also has considerable leakage. The Al2O3 sample shows the largest leakage, mainly due to its negative gate voltage corresponding to gate injection. The current density

\[ J \propto \exp \left( \frac{qE}{k_BT} - \frac{\phi_{FP}}{k_B T} \right) \]

(F–N) emission as shown in the inset of Fig. 5(b). The \( \phi_{FP} \) is the Al/dielectric barrier height and can be extracted from the slope of the fitted line shown in the inset of Fig. 5(b). The F–N current density can be described

\[ J_{FN} = \frac{q^2 E^2}{8\pi \hbar \phi_{FN}} \exp \left( -\frac{8\pi \sqrt{2m^* (q\phi_{FN})^{3/2}}}{3\hbar E} \right) \]

where \( C \) is a trap-related constant; \( q \) is the electron charge; \( \varepsilon_0 \) is the permittivity of vacuum; \( \varepsilon_r \) is the dynamic dielectric constant; \( k_B \) is the Boltzmann’s constant; \( T \) is the Kelvin temperature; and \( \phi_{FP} \) is the trap energy level from the conduction band of the insulator. The extracted \( \phi_{FP} \) is 0.8 eV from the conduction band of the Y0.33Al0.67O film. From the slope of the line, the \( \varepsilon_r \) value is evaluated to be 7.9. It is worth pointing out that the extracted \( \varepsilon_r \) value is in agreement with the \( k \) value from high-frequency \( C−V \) measurement (\( k \approx 8.5 \)), further supporting the (F–P emission mechanism in the low and medium field regions. However, it is also shown that the current density deviates from the fitted curve in the high field region (\( E > 8.0 \) MV/cm), where it obeys the Fowler–Nordheim (F–N) emission as shown in the inset of Fig. 5(b). The F–N current density can be described

\[ J_{FN} = \frac{q^2 E^2}{8\pi \hbar \phi_{FN}} \exp \left( -\frac{8\pi \sqrt{2m^* (q\phi_{FN})^{3/2}}}{3\hbar E} \right) \]

where \( \phi_{FN} \) is the Al/dielectric barrier height and can be extracted from the slope of the fitted line shown in the inset of Fig. 5(b). The extracted \( \phi_{FN} \) is 2.8 eV, which lies between the Al/Y2O3 barrier height (\( \sim 2.5 \) eV) and Al/Al2O3 barrier height (\( \sim 3.1 \) eV) [11, 16]. This large barrier height is beneficial to suppress the leakage, demonstrating the potential of AlYO as the inter-poly dielectric for memory applications.

Fig. 6 shows the AFM image of the Al2O3, YAlO-2 and Y2O3 samples with a scanning area of 0.5 × 0.5 μm². Both of the Al2O3 (RMS = 2.33 Å) and Y2O3 (RMS = 2.18 Å) samples show much rougher morphology than the YAlO-2 sample (RMS = 1.04 Å), corresponding to their thicker interlayer and poorer thermal property, respectively, which are consistent with the conclusions mentioned above.
IV. Conclusion

In summary, based on MOS capacitors, the characteristics of Y$_2$Al$_2$O$_5$ film with different Y contents were investigated as the inter-poly dielectric of flash memory. Compared with the Al$_2$O$_3$ and Y$_2$O$_3$ films, the optimized Y-doped Al$_2$O$_3$ film with a Y/Al ratio of 0.33/0.67 showed the lowest interface-state density, lowest bulk-trap density, highest dielectric constant, smallest leakage and smallest surface roughness. The reason should be that the poor SiO$_2$-like interlayer can be effectively suppressed by optimizing the Y content through the transformation of silica into silicate, while the film still maintains good thermal stability even at 950 °C due to its appropriate Al content. Therefore, the optimized Y$_2$Al$_2$O$_5$ is a promising candidate as inter-poly dielectric for flash-memory applications.

REFERENCES


