



Title	Improved performance of yttrium-doped Al₂O₃ as inter-poly dielectric for flash-memory applications
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Citation	IEEE Transactions on Device and Materials Reliability, 2011, v. 11 n. 3, p. 490-494
Issued Date	2011
URL	http://hdl.handle.net/10722/155655
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Improved Performance of Yttrium-Doped Al_2O_3 as Inter-Poly Dielectric for Flash-Memory Applications

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Abstract—Yttrium-doped Al_2O_3 ($\text{Y}_x\text{Al}_y\text{O}$) 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_2O_3 and Y_2O_3 films, the optimized $\text{Y}_x\text{Al}_y\text{O}$ 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 $\text{Y}_x\text{Al}_y\text{O}$ film is a promising candidate as the IPD for flash memory.

Index Terms—Flash memory, high-dielectric constant (high- k), inter-poly dielectric (IPD), $\text{Y}_x\text{Al}_y\text{O}$, 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_2O_3 seems to be a promising candidate due to its large band-gap (~ 8.8 eV, which is only next to that of SiO_2) and higher k value (~ 9) than SiO_2 (~ 3.9) [1]. However, the formation of a poor low- k SiO_2 interfacial layer between Al_2O_3 and floating gate (poly-Si) is unavoidable during the Al_2O_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_2O_3 scavenging layer inserted between the Al_2O_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_2O_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_2O_3 may lead to an unstable and low- k lanthanum hydroxide, further limiting its applications [4]. Gadolinium-doped Al_2O_3 dielectric film was also proposed to improve the dielectric constant of Al_2O_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_2O_3), and no magnetic characteristics (compared with Gd_2O_3), thus attracting increasing interest [6], [7]. The main shortcomings of Y_2O_3 lie in its poor thermal property and relatively small band-gap (~ 6 eV) compared with Al_2O_3 [1]. In this paper, a novel method to engineer Y-doped Al_2O_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_2O_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 $0.17 \sim 0.23 \Omega \cdot \text{cm}$. The wafers were cleaned by the RCA method, and then $\text{Y}_x\text{Al}_y\text{O}$ with different Y contents was deposited on the wafers by co-sputtering of Al and Y targets in a mixed ambient ($\text{Ar}/\text{O}_2 = 24:10$). 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_2O_3 or Y_2O_3 as the dielectric film were also fabricated using the same process, and denoted as Al_2O_3 and Y_2O_3 samples, respectively. Note that all the samples had similar EOT ($\sim 31 \text{ \AA}$).

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.

Manuscript received March 2, 2011; revised April 20, 2011; accepted May 5, 2011. Date of publication May 19, 2011; date of current version September 2, 2011. This work is supported by the RGC of HKSAR, China (Project HKU 713308E), the Small Project Funding of the University of Hong Kong (Project 200707176147), the University Development Fund (Nanotechnology Research Institute, 00600009) of the University of Hong Kong, and the National Nature Science Foundation of China (Grant 60976091).

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Digital Object Identifier 10.1109/TDMR.2011.2156796

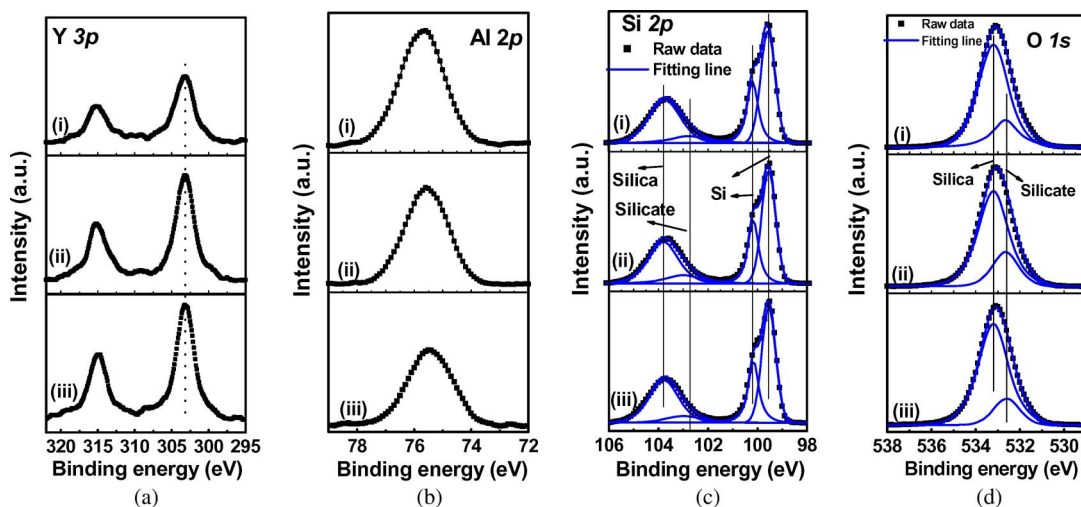


Fig. 1. XPS spectrum of the samples, where (i), (ii), and (iii) represent $\text{Y}_{0.22}\text{Al}_{0.78}\text{O}$, $\text{Y}_{0.33}\text{Al}_{0.67}\text{O}$, and $\text{Y}_{0.43}\text{Al}_{0.57}\text{O}$, respectively. (a) Y 3p, (b) Al 2p, (c) Si 2p, (d) O 1s.

III. RESULTS AND DISCUSSION

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 $\text{Y}_x\text{Al}_y\text{O}/\text{Si}$ interface, a thin $\text{Y}_x\text{Al}_y\text{O}$ 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 $\text{Y}_{0.22}\text{Al}_{0.78}\text{O}$, $\text{Y}_{0.33}\text{Al}_{0.67}\text{O}$, and $\text{Y}_{0.43}\text{Al}_{0.57}\text{O}$, 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 $\text{Y } 3p_{1/2}$ and $\text{Y } 3p_{3/2}$, respectively. These two peaks are at higher binding energy than the values (300 eV for $\text{Y } 3p_{1/2}$, and 290 eV for $\text{Y } 3p_{3/2}$) for Y_2O_3 [8], indicating different bonding structures from Y_2O_3 . 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 Al_2O_3 (74.9 eV) [9]. The above observations demonstrate that the dielectric films present a homogenous material without phase-separated Al_2O_3 and Y_2O_3 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 $\text{Si } 2p_{3/2}$), silica (103.8 eV for $\text{Si } 2p$), and silicate (103.0 eV for $\text{Si } 2p$) [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 SiO_2 (~ 533.1 eV) and Y_2O_3 (~ 529.5 eV [10]) [or Al_2O_3 (~ 532.2 eV [9])], and assigned to the silicate. It is noted that a SiO_2 -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 SiO_2 -like interlayer due to O-radical enhanced oxidation with the Si substrate [11]. The atomic ratio of silicon (and

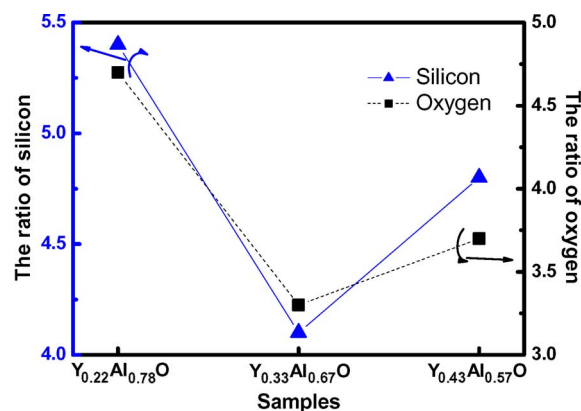


Fig. 2. Atomic ratio of silicon or oxygen component corresponding to silica and silicate for the $\text{Y}_{0.22}\text{Al}_{0.78}\text{O}$, $\text{Y}_{0.33}\text{Al}_{0.67}\text{O}$, and $\text{Y}_{0.43}\text{Al}_{0.57}\text{O}$ samples.

oxygen) component corresponding to the silica and silicate is also summarized in Fig. 2. The ratio of silicon (and oxygen) for the $\text{Y}_{0.22}\text{Al}_{0.78}\text{O}$ sample is largest among the three samples, corresponding to lowest Y content in the film and indicating its thickest silica interlayer. However, the $\text{Y}_{0.43}\text{Al}_{0.57}\text{O}$ sample also has a larger ratio than the $\text{Y}_{0.33}\text{Al}_{0.67}\text{O}$ 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 SiO_2 -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 Al_2O_3 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

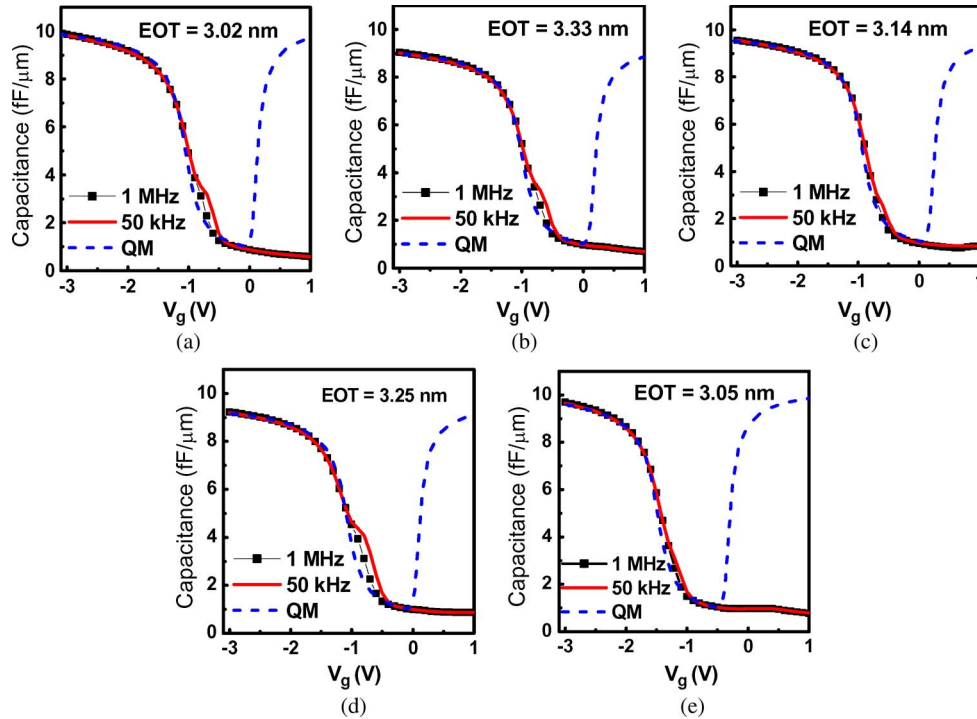


Fig. 3. C - V characteristics of the samples measured at 50 kHz and 1 MHz. The quasi-static (QM) simulated C - V curves are also shown. (a) The Al₂O₃ sample; (b) the YAIO-1 sample; (c) the YAIO-2 sample; (d) the YAIO-3 sample; (e) the Y₂O₃ sample.

TABLE I
PHYSICAL AND ELECTRICAL PARAMETERS OF THE SAMPLES

	Al ₂ O ₃	YAIO-1	YAIO-2	YAIO-3	Y ₂ O ₃
V_{fb} (V)	-1.0	-0.92	-0.85	-0.99	-1.4
D_{it} (cm ⁻² eV ⁻¹)	2.7e+12	2.1e+12	5.3e+11	2.0e+12	2.4e+12
Q_{ox} (cm ⁻²)	1.4e+12	1.5e+12	6.9e+11	1.4e+12	4.0e+12
T_{ox} (Å)	45.7	54.8	68.2	70.2	55.6
EOT (Å)	30.2	33.3	31.4	32.5	30.5
k	5.9	6.4	8.5	8.4	7.1

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})

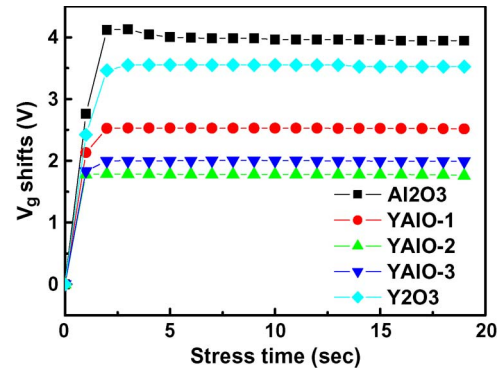


Fig. 4. Gate-voltage shifts versus time under a 10- μ A/cm² constant-current stress.

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 $k = \epsilon_{SiO_2} T_{ox} / EOT$, where ϵ_{SiO_2} is the dielectric constant of SiO₂. Among the samples, the YAIO-2 sample shows the smallest D_{it} (5.3×10^{11} cm⁻²eV⁻¹), smallest Q_{ox} (6.9×10^{11} 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

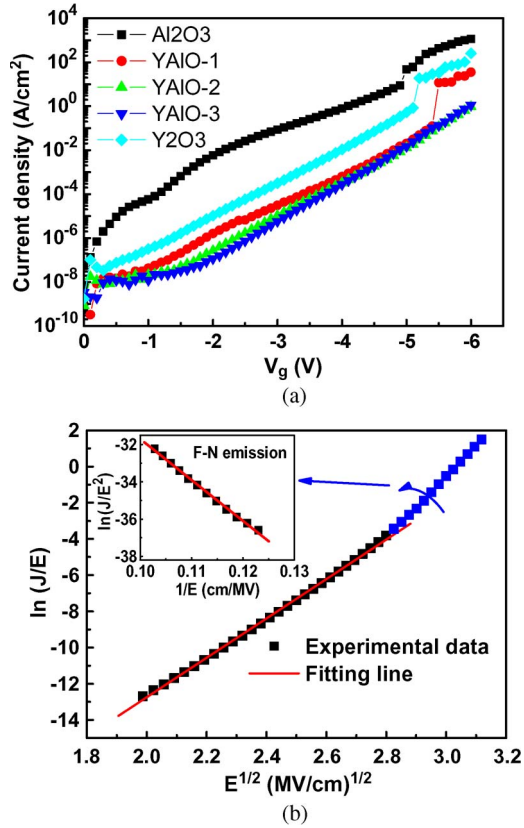


Fig. 5. (a) I - V characteristics of the samples under negative gate voltage corresponding to gate injection. (b) P-F emission plot in the low- and medium-field regions. The inset shows the F-N emission plot in the high-field region.

Y-doped Al_2O_3 is demonstrated by the YAIO-2 sample with the lowest D_{it} , smallest Q_{ox} and highest k value.

Fig. 4 displays the gate-voltage shift (ΔV_g) of the MOS devices under a $10\text{-}\mu\text{A}/\text{cm}^2$ constant-current stress. ΔV_g is induced by charge trapping in the dielectric film, and therefore, larger ΔV_g indicates larger amount of charge trapped in the dielectric film [15]. It is shown that both of the Al₂O₃ ($\Delta V_g = 3.98$ V) and Y₂O₃ ($\Delta V_g = 3.55$ V) samples show much larger ΔV_g than the $\text{Y}_x\text{Al}_y\text{O}$ samples, indicating their large quantity of traps in the films due to their poor interface and thermal properties, respectively. Among the samples, the YAIO-2 sample exhibits the smallest ΔV_g (1.78 V), demonstrating its good dielectric properties with fewer charge traps even after undergoing the 950°C annealing.

Fig. 5(a) shows the I - V characteristics of the samples under negative gate voltage corresponding to gate injection. The Al₂O₃ sample shows the largest leakage, mainly due to its poor interface. The Y₂O₃ sample also has considerable leakage compared with the $\text{Y}_x\text{Al}_y\text{O}$ samples due to thermally induced defects after the 950°C annealing. Furthermore, the YAIO-2 sample shows the smallest leakage and highest breakdown voltage, indicating few defects in the dielectric bulk and at the interface, further supporting its excellent qualities. To gain deep insight on the conduction mechanism of the YAIO-2 sample, the current density (J) as a function of electric field (E) is also investigated. It is found that the leakage current of this sample is well consistent with the Frenkel-Poole (F-P) emission under low and medium electric fields as shown in Fig. 5(b), where

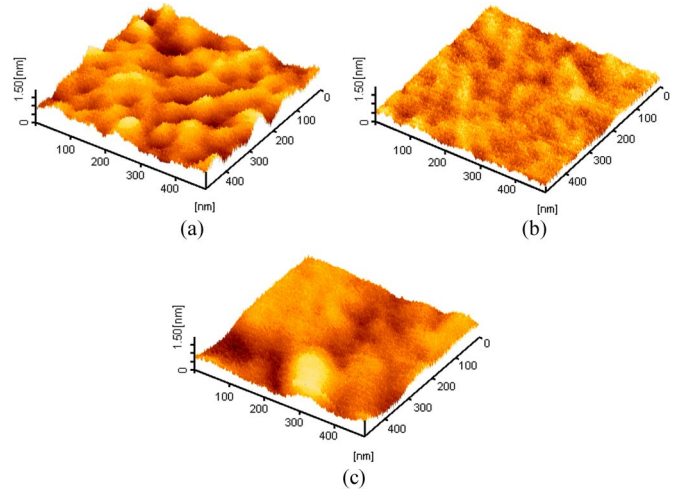


Fig. 6. AFM image of the samples. (a) The Al₂O₃ sample, RMS = 2.33 Å; (b) the YAIO-2 sample, RMS = 1.04 Å; (c) the Y₂O₃ sample, RMS = 2.18 Å.

$\ln(J/E)$ varies linearly with $E^{1/2}$. For the (F-P) emission, the current density can be expressed as

$$J_{\text{FP}} = CE \exp\left(\frac{q\sqrt{qE/\pi\epsilon_0\epsilon_r} - \phi_{\text{FP}}}{k_B T}\right) \quad (1)$$

where C is a trap-related constant; q is the electron charge; ϵ_0 is the permittivity of vacuum; ϵ_r is the dynamic dielectric constant; k_B is the Boltzmann's constant; T is the Kelvin temperature; and ϕ_{FP} is the trap energy level from the conduction band of the insulator. The extracted ϕ_{FP} is 0.8 eV from the conduction band of the $\text{Y}_{0.33}\text{Al}_{0.67}\text{O}$ film. From the slope of the line, the ϵ_r value is evaluated to be 7.9. It is worth pointing out that the extracted ϵ_r value is in agreement with the k value from high-frequency C - V measurement ($k \sim 8.5$), 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

$$J_{\text{FN}} = \frac{q^2}{8\pi h} \frac{E^2}{\phi_{\text{FN}}} \exp\left(-\frac{8\pi\sqrt{2m^*}(q\phi_{\text{FN}})^{3/2}}{3qhE}\right) \quad (2)$$

where ϕ_{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 ϕ_{FN} is 2.8 eV, which lies between the Al/Y₂O₃ barrier height (~ 2.5 eV) and Al/Al₂O₃ barrier height (~ 3.1 eV) [1], [16]. This large barrier height is beneficial to suppress the leakage, demonstrating the potential of AIYO as the inter-poly dielectric for memory applications.

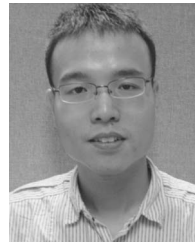
Fig. 6 shows the AFM image of the Al₂O₃, YAIO-2 and Y₂O₃ samples with a scanning area of $0.5 \times 0.5 \mu\text{m}^2$. Both of the Al₂O₃ (RMS = 2.33 Å) and Y₂O₃ (RMS = 2.18 Å) samples show much rougher morphology than the YAIO-2 sample (RMS = 1.04 Å), corresponding to their thicker interlayer and poorer thermal property, respectively, which are consistent with the conclusions mentioned above.

IV. CONCLUSION

In summary, based on MOS capacitors, the characteristics of $Y_xAl_{1-y}O$ film with different Y contents were investigated as the inter-poly dielectric of flash memory. Compared with the Al_2O_3 and Y_2O_3 films, the optimized Y-doped Al_2O_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 $Y_xAl_{1-y}O$ is a promising candidate as inter-poly dielectric for flash-memory applications.

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