The Effect of Growth Temperature on Aluminum Nanocrystal Embedded AlO_xN_y for Non-Volatile Memory

Nian-Huei Chen[1], Shu-Jen Huang[2], Jenn-Chang Hwang[3], and Fon-Shan Huang[1]

[1]Institute of Electronics Engineering, National Tsing Hua University, Hsinchu, Taiwan
[2] Department of Cosmetic Science and Application, Lan Yang Institute of Technology, Yilan, Taiwan
[3] Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu, Taiwan
E-mail:d9663801@oz.nthu.edu.tw Phone:886-3-5742586 Fax:886-3-5752120

ABSTRACT

An aluminum-based nonvolatile memory (NVM) of Al_2O_3/Al-rich AlO_xN_y/ $Al_{0.44}O_{0.38}N_{0.18}$ layered structure on SiO_2/n-Si was in situ fabricated by a simple rapid thermal processing (RTP) metal organic chemical vapor deposition (MOCVD) system. The composition of each layer is produced by modulating the flow rate of TMA and NH_3. The mole fraction of tunnel layer is $(AlN)_{0.87}(Al_2O_3)_{0.13}$. The control layer is polycrystalline Al_2O_3 with preferred orientation (510), (403), and (511). The Al-rich AlO_xN_y films containing excess Al nanocrystals (NCs) were utilized for charge storage layer. In order to find optimal condition, the Al-rich AlO_xN_y films were deposited at various temperatures. All films were investigated by TEM and XPS for structure and composition analysis. From TEM data, the charge storage films deposited at 560 ^oC has 2-4 nm Al NCs embedded in amorphous Al_2O_3 and AlN. Whereas, for deposition temperature at 700 ^oC, the films contain 15-20 nm Al NCs embedded in polycrystalline films of Al_2O_3 and AlN. In XPS analysis, the metallic Al increases as deposition temperature decreasing, whereas, the mole fraction of AlN increases as deposition temperature increasing.

Keywords: Al nanocrystal, Aluminum oxynitride, MOCVD, Flash memory

1 INTRODUCTION

The continuous trend of flash memory devices toward large storage density, fast transfer speed, and low power consumption drives the technology node scaling down. Al-based materials such as aluminum oxide (Al_2O_3), aluminum nitride (AlN), and aluminum oxynitride (AlON) have been considered as the attractive candidates for tunnel and control dielectric because of their high dielectric constant, high thermal stability, and compatible with the standard CMOS process. Furthermore, due to the good interface between Al and Al-based dielectrics, the low cost Al NCs embedded in AlN and Al_2O_3 is promising for NVM. S. Nakata *et al.* [1], in 2005, employed electron cyclotron resonance sputter to deposit Al_2O_3 (15 nm)/Al-rich Al_2O_3 (4.5 nm)/Al_2O_3 (15 nm) on p-Si. In 2008, Y. Liu *et al.* [2] demonstrated a single Al-rich Al_2O_3 films (60 nm) on p-Si by radio frequency (RF) magnetron sputtering with Al target in oxygen (O_2)/argon (Ar) plasma. Al NCs with size of 3-5 nm were embedded in Al_2O_3. Y. Liu *et al.* [3], in 2010, deposited Al-rich AlN (5 nm Al NCs) on p-Si by using RF magnetron sputtering with Al target in a gas mixture of nitrogen (N_2) and Ar.

Therefore, the aim of this paper is to present a Al-based memory structure of Al_2O_3/Al-rich AlO_xN_y/AlN/SiO_2/n-Si fabricated by a low cost RTP MOCVD system without breaking vacuum. The composition of each layer was produced by modulating the flow rate of TMA and NH_3 and deposition temperature. In order to find optimal condition, we focus on varies growth temperature of the Al-rich AlO_xN_y films for good electrical performance.

2 EXPERIMENT

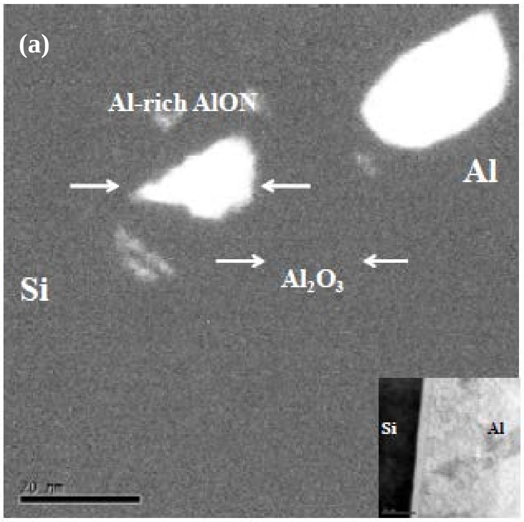
A high-quality SiO_2 with thickness about 2 nm was thermally grown on the n-type Si(100) wafer at temperature of 850 ^oC. The deposition of Al_2O_3/Al-rich AlO_xN_y/AlN layered structure was continuously carried out by homemade RTP-MOCVD system on SiO_2/n-Si without breaking vacuum. NH_3 and TMA precursor which was carried by Ar gas were flowed into the chamber through mass flow controllers to modulate the gases. The tunnel AlN films were deposited with TMA/NH_3 flow-rate ratio of 1:30 at temperature of 880 ^oC for 15 s under pressure of 4 mtorr. Due to the small O_2 leakage in the MOCVD system, the small amounts of Al_2O_3 were also formed [5]. The charge storage layer of Al-rich AlO_xN_y was fabricated by reaction of TMA, O_2, and NH_3. The Al NCs can be randomly 3-D precipitated in AlON matrix. TMA/ NH_3 with ratio of 1:4 were operated at pressure of 0.4 mtorr for 10 s. In order to find the optimal memory performance, various deposition temperature of 560, 600, and 700 ^oC (sample named S560, S600, and S700) were used to adjust the size, density of the Al NCs and quality of AlO_xN_y matrix. The control layer of Al_2O_3 films were grown by mixture gases of TMA/ NH_3 with a constant flow-rate ratio of 1:20 at temperature of 850 ^oC for 45 s under pressure of 4 mtorr with small O_2 leakage in the system. Then, Al layer was deposited onto the Al_2O_3 films through a evaporation and lift-off process to form the top electrodes with 60 μm^2 square. The backside of the wafer was finally coated with a 200 nm Al layer as the bottom electrode. The post metal annealing was then performed at temperature of 400 °C for 30 min in forming gases.

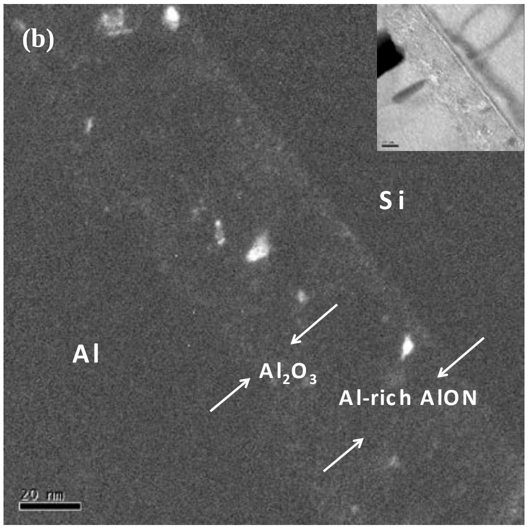
Physical thickness of memory stack layers and the size of Al NCs were analyzed using cross-section TEM (JEOL JEM-2010). The selected area of electron diffraction pattern (SAEDP) of S700, S600, and S560 are used to acquire the crystallinity of Al NCs and AlO_xN_y dielectrics. The X-ray photoelectron spectroscopy (XPS) measurements were carried out in a PHI 5600 CI system with a monochromatized Al Kα X-ray source (1486.6 eV). Sputtering depth profiling was achieved using a Thermo-VG-Scientific EXO5 Ar ion beam. The high-resolution spectra of O1s, Al2p, and N1s were examined. The high frequency (1 MHz) capacitance-voltage (C–V) tests were utilized to determine the P/E speed, retention and endurance characteristics of memory capacitors by using Agilent 4285 LCR meter and Agilent 81110 pulsed generator.

3 RESULTS AND DISCUSSIONS

3.1 TEM

Figures 1(a), (b) and (c) reveal the dark field images of memory stack layer of S700, S600, and S560. Al {200} reflections show the NCs with grain size of 3-7 and 2-4 nm in S600 and S560, respectively. The Al NCs are large with size of 20 nm in S700. Figures 1 also show the visible images of the interface among tunnel layer, charge storage layer, and control dielectric. The thickness of charge storage and control layer are about 28 and 22 nm, respectively. All three samples (S700, S600, and S560) have almost the same thickness.





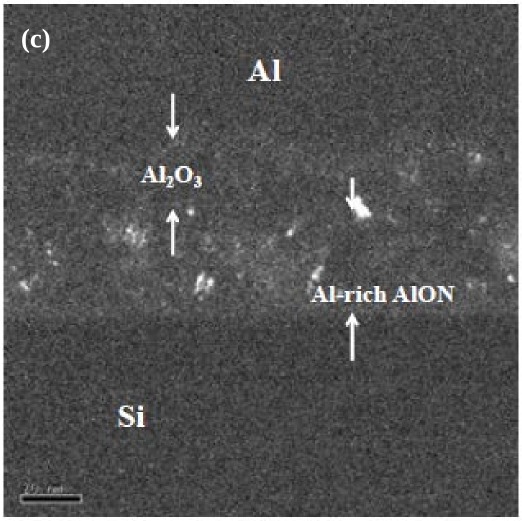


Figure 1. Dark field image of memory device (a) S700 (b) S600 (c) S560. The inset shows corresponding bight-field image

The associated selected area of electron diffraction pattern (SAEDP) of S700, S600, and S560 are shown in figures 2 (a), (b), and (c). A series of concentric spatty rings indexed as Al(111), Al(200), Al(220), Al(311), Al(222), Al_2O_3(510), and AlN (211) are shown in figure 2(a). The grain size of Al NCs is about 20 nm from the brightest spot of Al (200). The others show the size about 15-20 nm. The 3-4 nm AlN NCs is also found. Al(220) and AlN (211) are disappeared in figure 2(b). Al NCs are uniform and small. The grain size is about 3-7 nm. The ring indexed Al_2O_3(510) becomes dim. Figure 2(c) exhibits two diffuse halo rings corresponding to Al(111) and Al(200) with weaky broading outer ring. The grain size of Al NCs is around 2-4 nm.

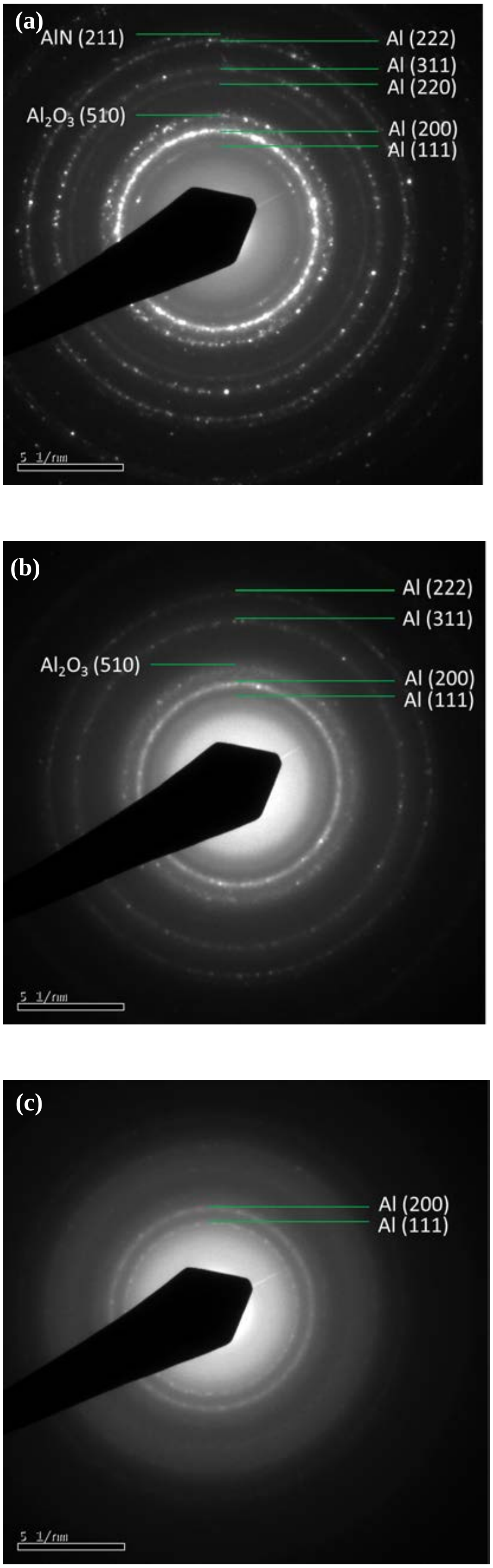


Figure 2. Selected area of electron diffraction pattern (SAEDP) (a) S700 (b) S600 (c) S560

3.2 XPS

XPS depth profiling analysis is carried out to observe the chemical bonding and determine atomic concentration of charge storage, tunnel, and control layers. Figures 4(a) and (b) show the Al2p and N1s XPS spectra of charge storage layer deposited at various temperatures. In figure 4(a), the Al2p spectra can be deconvoluted into three components of Al-N (73.5 and 73.9 eV), Al-O (74.9 and 75.3 eV), and Al-Al (72.1 and 72.5 eV) bonds [6]. The Al-Al binding shows the largest peak area in all three samples. Figure 4(b) exhibits N1s spectra with two peaks at 397 and 398 eV which represent N-Al and N-Al-O bonds. From XPS data, it demonstrates that the metallic Al is embedded in the dielectrics films of Al_2O_3 and AlN. The peak intensities are fitted from the total integrated area of the Al2p, O1s, and N1s spectra. The atomic concentration of Al:O:N can be estimated from peaks areas with 0.549:0.395:0.056, 0.563:0.405:0.032, and 0.715:0.254:0.031 which can be depicted as the mole fraction of $(Al_2O_3)_{0.316}(AlN)_{0.135}Al_{0.549}$, $(Al_2O_3)_{0.315}(AlN)_{0.075}Al_{0.61}$, and $(Al_2O_3)_{0.134}(AlN)_{0.049}Al_{0.817}$ for samples S700, S600, and S560, respectively. The size of Al NCs, atomic concentration, and mole fraction of the charge storage layer are summarized in Table 1.

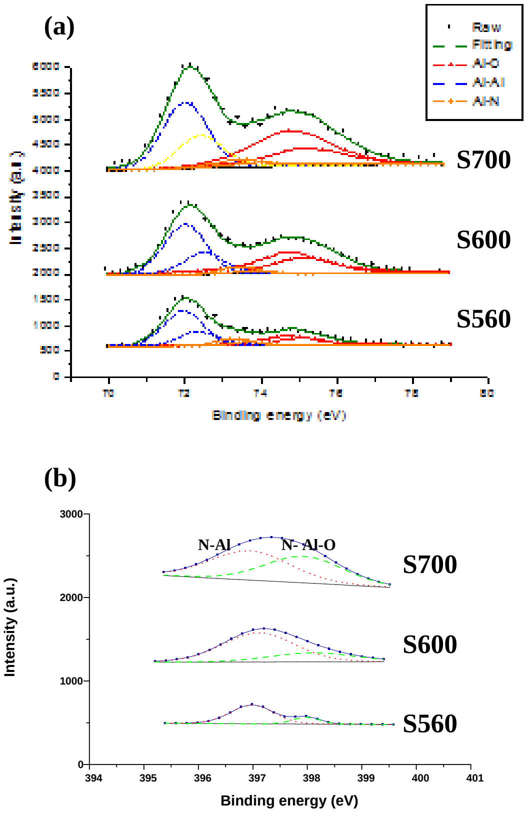


Figure 3. XPS analysis of (a) Al2p spectrum (b) N1s spectrum of charge storage layer deposited at different temperature

Table 1. The size, atomic concentration, and mole fraction of samples S700, S600, and S560

Sample	Size of Al NCs (nm)	Atomic concentration	Mole fraction
S700	15-20	$Al_{0.549}O_{0.395}N_{0.056}$	$(Al_2O_3)_{0.316}(AlN)_{0.135}Al_{0.549}$
S600	3-7	$Al_{0.563}O_{0.405}N_{0.032}$	$(Al_2O_3)_{0.315}(AlN)_{0.075}Al_{0.61}$
S560	2-4	$Al_{0.715}O_{0.405}N_{0.031}$	$(Al_2O_3)_{0.134}(AlN)_{0.049}Al_{0.817}$

From all above experiment results of HRTEM and XPS, S560 has mole fraction of $(Al_2O_3)_{0.134}(AlN)_{0.049}Al_{0.817}$ with 2-4 nm Al NCs embedded in amorphous Al_2O_3 and AlN. The mole fraction of S600 is $(Al_2O_3)_{0.315}(AlN)_{0.075}Al_{0.61}$. Al NCs with size 3-7 nm are embedded in crystallized Al_2O_3(510) and amorphous AlN. For S700, mole fraction is $(Al_2O_3)_{0.316}(AlN)_{0.135}Al_{0.549}$ with large Al NCs embedded in polycrystalline films of Al_2O_3 and AlN.

The variation in structure and chemical mole fraction will affect the reliability measurements of memory device. As we known, the barrier heights of AlN and Al_2O_3 are 2.2 eV and 4.9 eV, respectively. As S700 has more AlN mole fraction. AlN (211) is also found in the films. These will imply that the trapped holes are not easily remained in Al NCs. It can predict that the retention characteristic of S700 is not so good. Whereas, S560 has the least sum of mole fraction of AlN and Al_2O_3 among three samples. This means that It has poor insulation property. Therefore, the endurance characteristic of S560 can't meet ITRS requirement[7]. The optimum deposition condition for charge storage layer is S600. It demonstrates a memory window of 4 V with a programming/erasing (P/E) voltage of -12 V/12 V for 100 ms/10 ms. For reliability characteristics, it exhibits long data retention up to 10^5 s with only 4% charge loss and good endurance characteristic with 7.5% memory window closure after 10^4 cycling stress.

4 CONCLUSIONS

The memory structure of Al/Al_2O_3 (22 nm)/Al-rich AlO_xN_y (28 nm)/ $Al_{0.44}O_{0.38}N_{0.18}$ (3 nm)/SiO_2 (2 nm)/ n-Si was fabricated by RTA-MOCVD system. The optimal condition for charge storage layer is S600. From TEM data, the films contain 3-7 nm Al NCs with preferred orientation of Al(111), Al(200), Al(311), and Al(222) embedded in crystallized Al_2O_3(510) and amorphous AlN. In XPS analysis, the mole fraction of S600 is $(Al_2O_3)_{0.315}(AlN)_{0.075}Al_{0.61}$. For eletrical measurement, the sample S600 demonstrated a memory window of ~ 4 V with a P/E voltage of -12 V/12 V operated at 100 ms/10 ms. For reliability characteristics, it exhibited long data retention up to 10^5 s with only 5% charge loss and endurance after 10^4 cycles with small memory window closure of 0.2 V

REFERENCES

[1] S. Nakata, K. Saito, and M. Shimada, “Nonvolatile memory using Al_2O_3 film with an embedded Al-rich layer”, *Appl. Phys. Lett.*, Vol. 87, p. 223110 (2005)

[2] Y. Liu, T. P. Chen, W. Zhu, M. Yang, Z. H. Cen, J. I. Wong, Y. B. Li,S. Zhang, X. B. Chen, and S. Fung, "Charging effect of Al_2O_3 thin films containing Al nanocrystals" , *Appl. Phys. Lett.*, Vol. 93, p. 146102 (2008)

[3] Y. Liu, T. P. Chen, L. Ding, J. I. Wong, M. Yang, Z. Liu, Y. B. Li, and S. Zhang, "Charging Effect of Aluminum Nitride Thin Films Containing Al Nanocrystals", *Journal of Nanoscience and Nanotechnology*, Vol. 10, p. 599 (2010)

[4] N.H. Chen, H.C. Yu, G.Y. Huang, S.J. Huang, and F.S. Huang, "MOCVD $Al_{0.39}O_{0.6}$ $N_{0.01}$/Al-rich $Al_{0.4}O_{0.45}N_{0.15}$/$Al_{0.4}O_{0.4}N_{0.2}$ with High Density Aluminum Nanocrystal for Nonvolatile Memory", *Materials Research Society Symp. Proc.*, Q1.6 (2011)

[5] R.S. Ehle, B.J. Baliga, and W. Katz, "Low temperature aluminum oxide deposition using trimethylaluminum", *Journal of Electronic Materials*, Vol. 12, p. 587 (1983)

[6] L. Rosenberger, R. Baird, E. McCullen, G. Aunerc, and G. Shrevea, "XPS analysis of aluminum nitride films deposited by plasma source molecular beam epitaxy", *Surf. Interface Anal.*, Vol. 40, 1254 (2008)

[7] http://www.itrs.net, last accessed 2010