High Quality Al₂O₃ IPD With NH₃ Surface Nitridation

Yeong Yuh Chen, Chao Hsin Chien, and Jen Chung Lou

Abstract—In this letter, the effect of surface NH_3 nitridation on the electrical properties and reliability characteristics of aluminum oxide $(Al_2\,O_3)$ interpoly capacitors is studied. With NH_3 surface nitridation, the formation of an additional layer with lower dielectric constant during post-annealing process can be significantly suppressed, compared to that without nitridation treatment. Furthermore, the presence of a thin Si-N layer can make post-deposition annealing more effective in eliminating traps existing in the as-deposited films. As a result, a smoother interface and smaller electron trapping rate can contribute to the drastically reduced leakage current, enhanced breakdown field and charge to breakdown $(Q_{\rm b\,d})$ of $Al_2\,O_3$ interpoly capacitors with surface NH_3 nitridation.

Index Terms—Al $_2$ O $_3$, aluminum oxide, interpoly dielectric, IPD, surface NH $_3$ nitridation.

I. INTRODUCTION

CALING of nonvolatile flash memories requires continuous thickness reduction of both the tunnel dielectric and interpoly dielectric (IPD) layers in order to improve the program/erase performance, reduce the applied voltage as well as avoid the degradation of the coupling ratio [1]. However, thickness scaling of both dielectrics using current thermal and/or CVD oxynitride technologies is not sufficient to meet the stringent data retention requirement due to the unavoidable leakage current [2], [3]. Therefore, there is a strong demand to incorporate alternative high- κ dielectrics on nonvolatile memories for enhancing performance while suppressing charge loss. Among the potential candidates, Al₂O₃ is attractive for IPD applications in nonvolatile flash memories because of its higher conduction band offset with respect to the underneath poly-Si electrode and higher dielectric constant than Si₃N₄ [4]. Previously, W. -H. Lee et al. had shown the benefits of using an Al₂O₃ IPD for low voltage/high speed flash memories in simulations [5]. In this paper, the effect of surface NH₃ nitridation on the electrical properties and reliability characteristics of Al₂O₃ interpoly capacitors is studied. It is found that the incorporation of nitrogen on the floating gate surface can not only reduce leakage current by one order of magnitude but also enhance the breakdown field and the charge-to-breakdown (Q_{bd}) as well. This is ascribed to the resultant smoother in-

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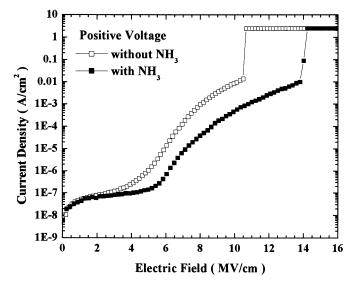


Fig. 1. J-E characteristics of Al_2O_3 interpoly capacitors with and without surface NH₃ nitridation under positive voltage applied to the top poly-Si.

terface between the dielectric and the floating gate by surface nitridation and less electron traps in the bulk.

II. EXPERIMENTAL

A 2000 Å buffer oxide was thermally grown on the 6-inch p-type (100)-oriented silicon substrate. The 2000 Å bottom poly-Si film was deposited on the buffer oxide in LPCVD and implanted with phosphorous at 5E15 cm⁻², 20 keV. Prior to Al₂O₃ deposition, several samples were subjected to NH₃ nitridation in LPCVD furnace at 800 °C for 1 h. 100 Å Al₂O₃ dielectric was then deposited by reactive sputtering in Ar/O₂ ambient, followed by rapid thermal annealing (RTA) at 800 °C in O₂ ambient for 30 s. Subsequently, a 2000 Å top poly-Si layer was deposited in LPCVD and implanted with phosphorous at 5E15 cm⁻², 20 keV. Dopants were activated at 950°C RTA for 30 s. The cross-sectional view of the interpoly capacitor was similar to [3]. The equivalent oxide thickness (EOT) was obtained from high frequency capacitance-voltage (C-V) measurement using a Hewlett-Packard (HP) 4284. The electrical properties and reliability characteristics of interpoly capacitors were measured by a HP 4156B semiconductor parameter analyzer.

III. RESULTS AND DISCUSSIONS

Fig. 1 shows the positive current density-electric field (J-E) characteristics, i.e., electron injection from the bottom electrode, of the Al_2O_3 interpoly capacitors with and without

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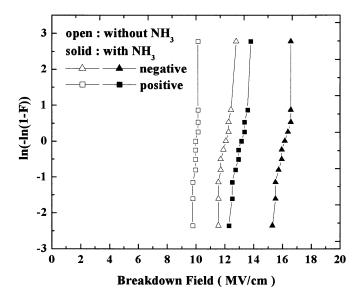


Fig. 2. Weibull plots of effective breakdown field (breakdown voltage/EOT) of Al_2O_3 interpoly capacitors with and without surface NH_3 nitridation in both polarities.

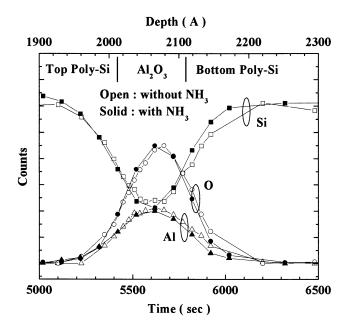


Fig. 3. AES depth profiles of Al₂O₃ interpoly capacitors with and without surface NH₃ nitridation.

surface NH₃ nitridation at 800 °C for 1 h. Surface NH₃ nitridation results in almost one order of magnitude reduction in leakage current density, compared to the sample without surface nitridation. Fig. 2 compares the Weibull distributions of effective breakdown field (breakdown voltage/EOT) of the Al₂O₃ interpoly capacitors with and without surface NH₃ nitridation for both polarities. More than 2 MV/cm breakdown field improvement has been clearly observed on the surface nitrided samples for both positive and negative polarities. The reasons might be two-fold. First, higher breakdown field in positive polarity may be attributed to the smoother surface of the bottom poly-Si films with NH₃ nitridation. This hypothesis is supported by the results of atomic force spectrum (not shown). The roughness of the bottom interface

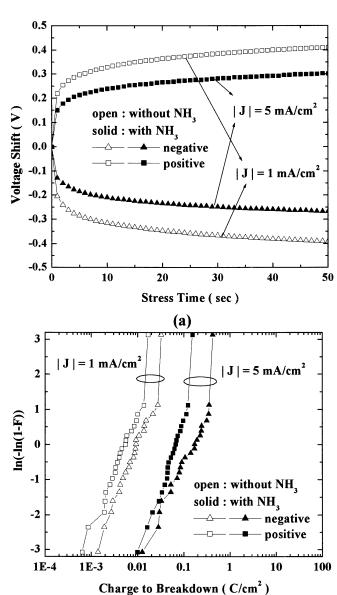


Fig. 4. (a) Curves of gate voltage shift (b) Weibull plots of charge-to-breakdown ($Q_{\rm bd}$) of Al_2O_3 interpoly capacitors with and without surface NH_3 nitridation under constant current stresses.

(b)

with and without surface nitridation are 2.76 nm and 3.32 nm, respectively, after selective IPD removal. Smoother interface is helpful in reducing the localized field and, hence, leads to lower leakage current and higher breakdown field [3], [6], [7]. The origin of the resultant smoother interface is hypothesized to be closely related to the capability of Si-N layer in blocking oxygen diffusion during post-deposition O2 annealing, as is evidenced by the high frequency C-V measurements and Auger electron spectra (AES). The EOTs of the Al₂O₃ IPD layers with and without NH₃ nitridation are 4.6 nm and 5.6 nm, respectively. In addition, Auger electron spectra of the Al₂O₃ interpoly capacitors, shown in Fig. 3, indicate that the presence of Si-N layer can effectively suppress the diffusion of oxygen species into the bottom poly-Si. Without surface passivation, Al and O atoms are easier to react with Si and may form additional silicon dioxide and/or aluminum silicate with relatively lower

 κ value [8]. Therefore, higher EOT value and rougher surface are obtained.

Second, the improvement of electrical properties in negative polarity might not be fully interpreted in term of surface roughness. Thus, we suspect that surface nitridation may effectively reduce the concentration of oxygen vacancies during post-deposition high temperature annealing due to its capability to block oxygen diffusion; In this case, oxygen molecules could have higher probability to compensate the unsaturated bonds in the as-deposited Al₂O₃. Fig. 4(a) depicts the charge trapping curves of the Al₂O₃ interpoly capacitors with and without nitridation under constant current stress of 5 mA/cm² and 1 mA/cm², respectively, in both polarities. The increase in the absolute gate voltage is obviously due to electron trapping. It is noted that the Al₂O₃ interpoly capacitors with surface nitridation, albeit subjecting to a larger stressing current, show a much smaller electron trapping rate than those without nitridation. Fig. 4(b) demonstrates the corresponding Weibull distributions of charge-to-breakdown (Q_{bd}) for two splits. Clearly, the Al₂O₃ interpoly capacitor with NH3 nitridation has nearly one order of magnitude improvement. This trend is fully consistent with the results in Fig. 4(a), i.e., higher trapping rate will lead to lower Q_{bd}.

IV. CONCLUSION

In this letter, the effect of surface NH_3 nitridation on the electrical properties and reliability characteristics of the Al_2O_3 interpoly capacitors is studied. With surface NH_3 nitridation, the EOT of Al_2O_3 IPD can be reduced to 4.6 nm due to the

suppression of interface silicate growth. Significant improvements on leakage current density, breakdown field and charge to breakdown ($Q_{\rm bd}$) are obtained in the Al_2O_3 interpoly capacitors with surface NH_3 nitridation. The Al_2O_3 dielectric with surface NH_3 nitridation thus appears to be very promising for future flash memory devices.

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