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# Suppressed Boron Penetration in p<sup>+</sup> poly-Si/Al<sub>2</sub>O<sub>3</sub>/Si Metal-Oxide-Semiconductor System by Remote Plasma Nitridation of Al<sub>2</sub>O<sub>3</sub> Surface

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# ABSTRACT

We examine boron penetration in p<sup>+</sup> poly-Si/Al<sub>2</sub>O<sub>3</sub>/n-Si pMOS capacitors with various treatments. Suppressed B penetration was attained in p<sup>+</sup> poly-Si/Al<sub>2</sub>O<sub>3</sub>/n-Si pMOS capacitors by the surface nitridation of Al<sub>2</sub>O<sub>3</sub> gate dielectric using remote plasma nitridation (RPN). The flatband shift of pMOS capacitor was negligible up to 850 °C, effectively blocking the B penetration using RPN- Al<sub>2</sub>O<sub>3</sub> compared to the Al<sub>2</sub>O<sub>3</sub> only or Al<sub>2</sub>O<sub>3</sub>/SiN<sub>x</sub> structure. However, the gate leakage current of RPN-Al<sub>2</sub>O<sub>3</sub>/Si MOS capacitors was higher than that of nominal Al<sub>2</sub>O<sub>3</sub> due to the reduced energy bandgap (E<sub>g</sub>) of RPN-Al<sub>2</sub>O<sub>3</sub>.

# INTRODUCTION

Al<sub>2</sub>O<sub>3</sub> has attracted a lot of attention as an alternative gate dielectric because of good thermal stability when in direct contact with Si, excellent interface characteristics, and low leakage current [1,2]. Especially, good compatibility of Al<sub>2</sub>O<sub>3</sub> with poly-Si gate allows us to maintain conventional CMOS technologies. However, the p<sup>+</sup> poly-Si/Al<sub>2</sub>O<sub>3</sub>/Si structure showed an extraordinary positive flatband shift  $(\triangle V_{FB})$  due to the B penetration into the Si substrate through Al<sub>2</sub>O<sub>3</sub> at elevated temperatures [3], resulting in the critical issues for CMOS applications. In this study, we employed an unique RPN approach on the Al<sub>2</sub>O<sub>3</sub> surface to block the B penetration and attained negligible  $\triangle V_{FB}$  up to 850 °C.

#### EXPERIMENTAL

Poly-Si/RPN-Al<sub>2</sub>O<sub>3</sub>/Si MOS capacitors were fabricated on the n-type and p-type (100) Si substrates (8-inch dia.). HF last cleaning was carried out, followed by the atomic layer deposition (ALD) of Al<sub>2</sub>O<sub>3</sub> (55 Å) gate dielectric using Al(CH<sub>3</sub>)<sub>3</sub> and H<sub>2</sub>O vapor at 350 °C. Some samples were subjected to the gate dielectric improvement anneal in O<sub>2</sub> at 800 °C for 30min. RPN process was employed on the Al<sub>2</sub>O<sub>3</sub> surfaces at 650-850 °C using a remotely controlled He/N<sub>2</sub> plasma reactor. Undoped and n<sup>+</sup> poly-Si were deposited for pMOS and nMOS, respectively. Then, <sup>11</sup>B<sup>+</sup> was implanted on the undoped poly-Si at 4 keV and 3 × 10<sup>15</sup> B ions/cm<sup>2</sup>. To activate the implanted B ions, furnace anneals were carried out from 800 °C to 900 °C in N<sub>2</sub> for 30 min. For comparison, p<sup>+</sup> poly-Si/Al<sub>2</sub>O<sub>3</sub>/SiN<sub>x</sub>/n-Si MOS capacitors were also prepared using NH<sub>3</sub> anneals on the Si surfaces for SiN<sub>x</sub> formation. Physical and electrical properties of MOS capacitors were examined.

# **RESULTS AND DISCUSSION**

Shown in Figs. 1-2 are high-frequency C-V curves of p<sup>+</sup> poly-Si/Al<sub>2</sub>O<sub>3</sub>/n-Si and p<sup>+</sup> poly-Si/Al<sub>2</sub>O<sub>3</sub>/SiN<sub>x</sub>/n-Si MOS capacitors with anneal temperatures. Our previous results showed that the  $\triangle V_{FB}$  of Al<sub>2</sub>O<sub>3</sub> only was +1.54V after activation anneal from 800°C to 850°C [3]. On the contrary, the  $\triangle V_{FB}$  of Al<sub>2</sub>O<sub>3</sub>/SiN<sub>x</sub>/n-Si was reduced to +0.15 V at the same condition, indicating somewhat retarded B penetration. However, the negative V<sub>FB</sub> shift and non-ideal C-V hump of Al<sub>2</sub>O<sub>3</sub>/SiN<sub>x</sub>/n-Si system was pronounced due to the SiN<sub>x</sub>-Si interfaces. Fig. 3 exhibits C-V curves of RPN-Al<sub>2</sub>O<sub>3</sub>/n-Si pMOS capacitor, demonstrating negligible  $\triangle V_{FB}$  (< 10 mV) up to 850°C. A normalized inversion capacitance (C<sub>inv</sub>/C<sub>ox</sub>) measured from this structure was about 83% at 850°C (not shown). Fig. 4 shows B profiles in the p<sup>+</sup> poly-Si/RPN-Al<sub>2</sub>O<sub>3</sub>/n-Si structures, depicting an effective B blocking in

the Al<sub>2</sub>O<sub>3</sub> up to 850°C. This may be feasible because of the thermally stable RPN-Al<sub>2</sub>O<sub>3</sub> surfaces at 850°C (Fig.5). In addition, the  $\triangle V_{FB}$  even after 900°C was +0.52V, that is remarkably reduced value compared to the one of Al<sub>2</sub>O<sub>3</sub> after 850°C (Fig.1). Fig. 6 exhibits the conductance loss (G/ $\omega$ )-V plots of RPN-Al<sub>2</sub>O<sub>3</sub>/Si MOS capacitors for D<sub>it</sub> extraction. The D<sub>it</sub> level was decreased from ~8x10<sup>11</sup> cm<sup>-2</sup>-eV<sup>-1</sup> to ~2x10<sup>11</sup> cm<sup>-2</sup>-eV<sup>-1</sup> with activation temperatures.

Figure 7 shows J-V characteristics of n<sup>+</sup> poly/Al<sub>2</sub>O<sub>3</sub>/p-Si nMOS capacitors as a function of RPN. An increase of leakage current ( $I_{LC}$ ) at high electric field is noted with RPN, where the capacitance equivalent thickness (CET) with RPN is ~3Å thicker than that without RPN. For a better understanding of  $I_{LC}$  increase with RPN, the energy bandgap ( $E_g$ ) of Al<sub>2</sub>O<sub>3</sub> was measured using electron energy loss spectra of O 1s on Al<sub>2</sub>O<sub>3</sub>/Si-substrate [4]. The  $E_g$  of asdeposited Al<sub>2</sub>O<sub>3</sub> is about 6.8 eV, while that of RPN-Al<sub>2</sub>O<sub>3</sub> is 6.1eV. The  $E_g$  of those after N<sub>2</sub> anneal at 800°C was increased to 6.94 eV for Al<sub>2</sub>O<sub>3</sub> and 6.5 eV for RPN-Al<sub>2</sub>O<sub>3</sub> (Table 1).

Shown in Fig. 9 are XPS core level spectra of Al 2p and N 1s as a function of RPN on Al<sub>2</sub>O<sub>3</sub>. The Al 2p spectra of Al2O3 only and RPN-Al2O3 showed no distinct difference between those because the binding energy (B.E.) of Al 2p for Al<sub>2</sub>O<sub>3</sub> and AlN is similar (74 - 74.7 eV). On the other hand, the N 1s spectra exhibited two clear peaks at 396 eV and 403 eV after RPN. The B.E. at 396 eV corresponds to the atomic nitrogen and that at 403 eV to the adsorbed NO or N<sub>2</sub>O on Al<sub>2</sub>O<sub>3</sub> [5]. From the presence of N 1s peak at 403 eV after anneal at 800°C, the bonding at 403 eV appears to be stronger than the one at 397 eV. Based on our observation, the N incorporation into the interstitial or substitutional site is related with the formation of AlN. A partial modification of Al<sub>2</sub>O<sub>3</sub> surfaces into AlN, of which has the E<sub>g</sub> of ~5.9 eV [6], may result in the  $E_g$  decrease into 6.1 eV. It is thought that reduced E<sub>g</sub> by RPN, in turn, decreases the barrier height of RPN-Al<sub>2</sub>O<sub>3</sub>/Si junction, led to the increase of the I<sub>LC</sub> in Fig. 7. This can be inferred from the increase of  $E_g$  (6.5 eV) of RPN-Al2O3 after N2 anneal at 800°C, which may be resulted from the N outdiffusion (Fig. 10). Our experiments suggest that an optimization process for a pertinent N content is required for the least B penetration and bandgap reduction.

#### CONCLUSION

The B penetration in the  $p^+$  poly-Si/Al<sub>2</sub>O<sub>3</sub>/n-Si pMOS capacitors was effectively suppressed up to 850 °C by the surface nitridation of Al<sub>2</sub>O<sub>3</sub> using RPN. We found I<sub>LC</sub> increase due to the E<sub>g</sub> reduction of RPN-Al<sub>2</sub>O<sub>3</sub>, that requires optimization for B suppression and bandgap engineering.

## REFERENCES

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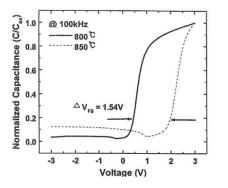


Fig. 1. C-V plots of p+ poly-Si/Al<sub>2</sub>O<sub>3</sub>/n-Si MOS capacitors with anneal temperatures. After Ref. [3].

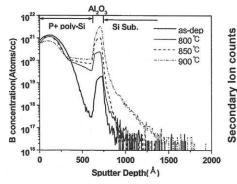


Fig. 4. B profiles in the p+ poly-Si/RPN-Al<sub>2</sub>O<sub>3</sub>/n-Si structure with temperatures using SIMS.

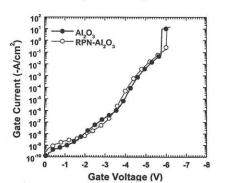
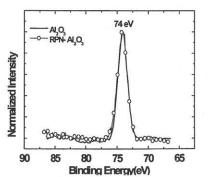


Fig.7. J-V curves of n+ poly-Si/Al<sub>2</sub>O<sub>3</sub>/p-Si nMOS capacitors as a function of RPN.



(a) core level spectra of Al 2p.

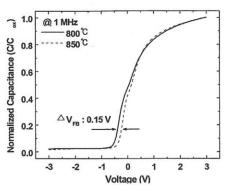


Fig. 2. C-V plots of p+ poly-Si/  $Al_2O_3$  /SiN<sub>x</sub>/n-Si MOS capacitors with anneal temperatures.

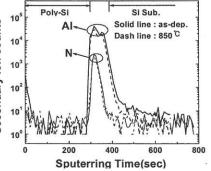


Fig. 5. SIMS profiles in the p+ poly-Si/RPN- $Al_2O_3/n$ -Si with activation anneal.

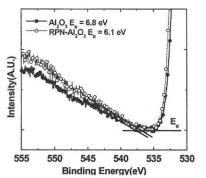
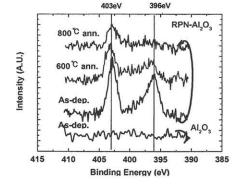


Fig. 8. XPS electron energy loss spectra of O 1s with  $Al_2O_3/Si$  sub. as a function of RPN.



(b) core level spectra of N1s.

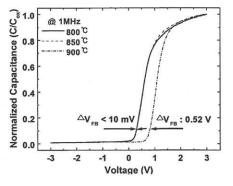


Fig. 3. C-V plots of p+ poly-Si/ RPN-Al<sub>2</sub>O<sub>3</sub> /n-Si MOS capacitors with anneal temperatures.

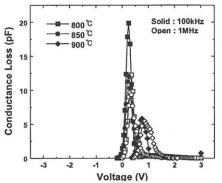


Fig. 6. Conductance loss  $(G/\omega)$  -V plot of the p+ poly-Si/RPN-Al<sub>2</sub>O<sub>3</sub>/n-Si with activation anneal.

	As-dep.	After ann. 800℃
Al <sub>2</sub> O <sub>3</sub>	6.8 eV	6.94 eV
RPN-Al <sub>2</sub> O <sub>3</sub>	6.1 eV	6.5 eV

Table 1. Energy bandgap (Eg) of  $Al_2O_3$  as a function of RPN by electron energy loss spectra.

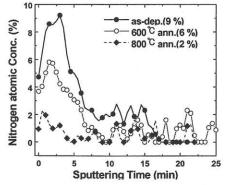


Fig. 10. AES depth profiles of RPN-Al<sub>2</sub>O<sub>3</sub>/Si sub. with anneal temperatures.

Fig. 9. XPS core level spectra of Al 2p and N 1s with Al\_2O\_3/Si sub. as a function of RPN.