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Physical and Electrical Characteristics of Poly-Si/ZrO2/SiO2/Si MOS Structures

Kwan-Yong Lim, Dae-Gyu Park, Heung-Jae Cho, Joong-Jung Kim, Jun-Mo Yang, Il-Sang Choi, Jung-Kyu Ko,

Jae-Young Kim, In-Seok Yeo, Jin Won Park, and Hee-Koo Yoon

Advanced Process Team, Memory R&D Division, Hyundai Electronics Industries Co. Ltd., Ichon P.O. Box 1010, Ichon-si,

Kyoungki-do, 467-701 Korea (Phone:+82-31-630-4468, Fax:+82-31-630-4545, e-mail: kylim@sr.hynix.com)

ABSTRACT

We examine the physical and electrical characteristics of poly-Si/ZrO₂/SiO₂/p-Si metal-oxide-semiconductor (MOS) structures for the poly-Si gate compatibility with ZrO₂ gate dielectric. The MOS capacitors gated with n⁺ poly-Si exhibited ideal high-frequency C-V curves up to the furnace anneal of 750°C for 30 min with an interface trap density (D_{it}) as low as ~5x10¹⁰ eV⁻¹cm⁻². We found several orders of magnitude lower gate leakage current from the small size (< 50x50/m2) gate electrode pattern. Electrical and physical analyses revealed that the formation of interfacial ZrSi. nodule was responsible for the high gate leakage and was strongly dependent on the gate area and line width. Further, Boron penetration was observed from the p⁺ poly-Si gated pMOS capacitors after activation anneal above 800°C.

INTRODUCTION AND EXPERIMENTAL

Most recently, ZrO₂ has been assessed for MOS device applications as an alternative gate dielectric due to the high dielectric constant (k~25) and good thermal stability with Si [1,2]. Because of critical issues such as severe thickness variation and reliability of gate oxide at the isolation edges [3], we employed ZrO₂ gate dielectric prepared by atomic layer chemical vapor deposition (ALCVD) for giga-scale CMOS devices ensuing excellent step coverage.

MOS capacitors having n⁺ and p⁺ poly-Si gates were fabricated on the ZrO2/SiO2/Si structure. The ZrO2 films were deposited by ALCVD at ASM Microchemistry using ZrCl₄ and H₂O vapor at 300 °C. Prior to the ZrO₂ deposition, an ultrathin (~ 7 Å) SiO₂ was grown for the smooth ZrO₂ nucleation [2]. The ZrO₂/SiO₂/Si stack was annealed in O₂ for dielectric improvement, followed by the preparation of poly-Si gate electrodes at 550°C, i.e., in-situ PH3 doped n⁺ poly-Si and 11B⁺ implanted p⁺ poly-Si. The process compatibility of poly-Si electrode with ZrO₂ gate dielectric was examined via dopant activation at 650-900 °C for 30 min in N₂.

RESULTS AND DISCUSSION

Figures 1-2 show high-frequency C-V hystereses and conductance loss (G/w)-V curves of n⁺ poly-Si/ZrO₂/SiO₂/p-Si nMOS capacitors as a function of activation anneal, exhibiting ideal MOS characteristics up to 750°C. The hysteresis (V_H) and interface state density (D_{it}) as determined by the $riangle V_H$ and G/ω were reduced with anneal temperature. The $riangle V_H$ and the D_{it} after anneal at 750 °C is ~ 10 mV and ~5x10¹⁰ eV⁻¹cm⁻². There was slight positive shift in the flat-band voltage (VFB) with anneal. This may be related with the phosphorus (31P) diffusion into the ZrO₂/SiO₂ layer with temperature (Fig.3), which was also observed from the n⁺ poly-Si/Al₂O₃/Si system [4]. However, the C-V measurements were not able to carried out for the samples annealed over 800°C (Fig. 1). Shown in Fig 4 is J-V plots of MOS capacitors measured from the 200x200 µm² square electrodes. It is observed that the gate leakage current

 (I_{LC}) was abruptly increasing with the activation anneal above 750 °C, displaying \sim 3 orders of magnitude higher I_{LC} (-1.5V) at 800°C compared with the ILC at 700°C. Fig. 5 depicts cross-sectional TEM images of n⁺ poly-Si/ZrO₂/SiO₂/ p-Si structure, showing interfacial precipitates for asdeposited and annealed samples. The size and density of those nodules are increasing with anneal temperature. The high-resolution TEM images(Fig.5) and Fourier transformed digital diffractogram (Fig.6) identified the precipitate as ZrSi_x, in consistent with recent report [5]. Shown in Fig. 7 are SEM images of ZrO2 surfaces after poly-Si removal, where the ZrSi_x nodules were etched out during the poly-Si removal. The size and distribution of pinholes are well matched with ZrSi, nodules, and increased with anneal temperature as well. Notably, we found a pattern-size dependent I_{LC} variation that ~ 3 orders of magnitude lower I_{LC} at -1.5V were attained even after activation anneal of 800 °C-30min. This indicates that the presence and/or density of interfacial ZrSix nodule may be rare on the smaller pattern size (< $50 \times 50 \mu m^2$) due to the limited silicidation reaction at the narrow gate area and line width (Fig. 8).

The cumulative I_{LC} distribution of p⁺ poly-Si gated pMOS capacitors (200x200 /m2) and pattern-size dependent ILC characteristics were plotted with anneal in Figs 9-10. The smaller size (< $50 \times 50 \mu m^2$) capacitors exhibited ~4 orders of magnitude lower ILC than the large size capacitors. However, the capacitors annealed at 900°C showed very leaky ILC characteristics regardless of pattern size, resulting in the incompatible poly-Si gate with ZrO₂ at 900°C. Figs.11-12 displayed C-V and SIMS profiles of p⁺ poly-Si gated pMOS capacitors. The V_{FB} shifts of +0.18V with the anneal from 800 to 850°C and +0.2V from 850°C to 900°C were observed due to the boron penetration, although the C-V data from 900 °C was too leaky to compare each other (Fig. 11). The boron profiles in p⁺ poly-Si/ZrO₂/SiO₂/n-Si structure (Fig.12) confirmed the conspicuous boron penetration responsible for the noted $riangle V_{FB}$ in Fig.11. The diffusion path of B can be the grain boundaries of polycrystalline ZrO₂ or ZrSi, at the elevated temperatures.

In summary, we attained ideal C-V characteristics from the n^+ poly-Si gated nMOS capacitors up to 750 °C with the D_{ir} of $-5x10^{10}$ eV⁻¹cm⁻², whereas boron penetration was observed from the p⁺ poly-Si gated pMOS capacitors after activation anneal over 800°C. While several orders of lower ILC was obtained from small-size capacitors, the formation of interfacial ZrSix nodules at 900°C was hardly capable of prohibiting even at 0.8^{µm}-wide gate line.

REFERENCES

- [1] W.-J. Qi et al., IEDM Tech. Dig., p.145 (1999).
 [2] M Copel et al., Appl. Phys. Lett. 76, p.436 (2000).
 [3] C.T. Liu et al., VLSI Tech. Dig., p.75 (1999).
 [4] J.H. Lee et al., IEDM Tech. Dig., p.645 (2000).
 [5]C. Hobbs et al. Int. Symp. on VLSI-TSA, p.204 (2001).



Fig.1. C-V hysteresis curves of the n⁺ poly-Si/ZrO₂(50 Å)/SiO₂(7 Å)/p-Si nMOS capacitors.



Fig.4. I-V characteristics of the n⁺ poly-Si/ZrO₂(50 Å)/SiO₂(7 Å)/p-Si nMOS capacitors as a function of activation temperature.



Fig. 7. SEM images of ZrO_2 surfaces as a function of activation temperature: (a) asdeposited ZrO_2 , (b) no activation, (c) 800°C, and (d) 900°C in N₂-ambient for 30min. The surface morphologies of $ZrO_2/SiO_2/Si$ were examined after poly-Si removal.



Fig. 10. Pattern-size dependency of leakage currents of the p⁺ poly-Si/ZrO₂(100 Å)/SiO₂(7 Å)/n-Si : plotted as a function of activation anneal.



Fig.2. Conductance loss (G/ω) -V curves of the n⁺ poly-Si/ZrO₂(50 Å)/SiO₂(7 Å)/p-Si nMOS capacitors.



Fig. 5. Cross-sectional TEM images of n⁺ poly-Si/ZrO₂/SiO₂(7 Å)/p-Si nMOS capacitors: (a) no activation for ZrO₂ 50 Å and (b) N₂-800C-30m for ZrO₂ 140 Å.



Fig. 8. Pattern-size dependency of leakage currents of the n⁺ poly-Si/ $ZrO_2(50 \text{ Å})$ /SiO₂(7 Å)/p-Si: plotted as a function of activation anneal.



Fig. 11. C-V curves of the p⁺ poly-Si/ ZrO₂(100 Å)/SiO₂(7 Å)/n-Si pMOS capacitors.



Fig.3. Phosphorus profiles in the n⁺ poly-Si/ZrO₂(50 Å)/SiO₂(7 Å)/p-Si as a function of activation anneal.



Fig. 6. XTEM images of n⁺ poly-Si/ZrO₂/SiO₂(7 Å) /p-Si with 800C anneal in N₂ (left) and its Fourier transformed digital diffractogram image (right): the structure of ZrSi_x nodule is expected to be Zr_3Si_4 (tetragonal: PDF #72-2097) or ZrSi₂ (orthorhomic: PDF #74-1053).



Fig. 9. Cumulative probability of leakage currents of p⁺ poly-Si/ZrO₂(100 Å)/SiO₂(7 Å)/n-Si pMOS capacitors: measured at V_g =1.5V.



Fig. 12. Boron profiles in the p^+ poly-Si/ZrO₂/SiO₂/n-Si as a function of activation anneal.