Rapid Thermal and Anodic Oxidations of LPCVD Silicon Nitride Films

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Introduction

For CMOS devices shrink further into the deep submicron range, alternative high k materials should be considered for reducing the gate leakage current. Siliconbased Si₃N₄ is attractive because of the material compatibility and high permittivity (k=7.2). However, nonstoichiometric Si-rich Si₃N₄ films can severely degrade the dielectric quality. In this work, we focus on the postoxidation effects on the quality of CVD silicon nitride. Experiment

Ultra-thin Si₃N₄ (T_{ox}=20Å-30Å) is grown by LPCVD with SiH_2Cl_2 and NH_3 . These CVD Si_3N_4 films were then oxidized by rapid thermal oxidation at 850 $^\circ\!C$ in O_2 ambient and constant field anodic oxidation in DI water followed by N2 annealing. SIMS, XPS were utilized to analyze the depth profile and atomic concentration. Also, electrical property is analyzed by J-V measurement.

Results and Discussions

Oxidant species react with the silicon nitride by substituting the unstable nitrogen bonding or Si dangling bond, and move toward the underneath silicon. Therefore, "SiO₂"-like layers on the surface and around the interface, and "Si₃N₄"- like layer between them are observed as shown in Fig.1. More oxygen was found to be incorporated in the anodic Si₃N₄ film and reduce the nitrogen bonding rather than the thermal oxidation one. Atomic concentration of as grown $\mathrm{Si}_3\mathrm{N}_4$ and oxidized $\mathrm{Si}_3\mathrm{N}_4$ are observed in Fig. 2. The native oxide is easy to form in the ultra-thin CVD Si₃N₄ as shown in Fig. 2(a). After oxidation, SiO₂-like layers are grown on the surface of both samples as shown in Fig. 2(b) and 2(c). A nearly stoichiometric SiO_2 is observed on the anodic Si_3N_4 surface that may attribute to the field enhanced replacement of unstable nitrogen. We believe the imperfect Si₂=N and Si dangling bonds can be oxidized into Si₂=N-O or SiO₂, and the stoichiometric Si₃=N bonding is not affected during oxidation. Gate leakage current comparison is shown in Fig.3. Post-oxidation presents a dramatic improvement in the nitride property. Moreover, the Si₃N₄like layer between two SiO2-like layers can maintain the high-k characteristic, thus an almost two orders of magnitude lower leakage current than SiO2 under EOT=20Å is observed. For the rapid thermal and anodic oxidations treated samples under EOT=30Å, the more oxygen incorporation in the anodic Si₃N₄ may account for the lower leakage current since the higher bandgap (~9eV) of SiO₂-like layer can block the carrier from migrating through the dielectric and reduce the trap-assisted tunneling.

Conclusion

Post-oxidation plays an important role to enhance CVD nitride quality. It is found that the O atom is easier to incorporate into the Si₃N₄ film by anodic oxidation than thermal oxidation that is helpful to reduce the gate leakage current. Therefore, if one can well control the oxidation condition, Si₃N₄ could be a promising high-k dielectric for the advanced process utilization.



Fig. 1 SIMS depth profile analysis of rapid thermal oxidation and anodic oxidation treated CVD Si₃N₄.



Fig. 2 XPS atomic concentration analysis of (a) as-grown CVD Si₃N₄, (b) followed by rapid thermal oxidation and (c) by anodic oxidation.



Fig. 3 J-V comparison of conventional SiO₂, as grown CVD Si₃N₄ and rapid thermal oxidation and anodic oxidation treated Si₃N₄.