Extended Abstracts of the 2005 International Conference on Solid State Devices and Materials, Kobe, 2005, pp.514-515

P1-14

Germanium Out-Diffusion in HfO_2 and its Impact on Electrical Properties

Qingchun Zhang, Nan Wu, Chunxiang Zhu, L.K.Bera*

Silicon Nano Device Lab, Department of Electrical and Computer Engineering
Phone: +65-68748930 E-mail: elezhucx@nus.edu.sg
National University of Singapore, 10 Kent Ridge Crescent, Singapore
*Institute of Microelectronics, Singapore

1. Introduction

Ge MOSFET with high-κ gate dielectric shows strong potential for future high performance application due to its high mobility. Recent works revealed that a large amount of germanium was incorporated inside HfO_2 deposited by either MOCVD or PVD with post deposition annealing (PDA) [1, 2]. However, there is no detailed investigation on the relationship of Ge incorporation with PDA conditions. Besides, it is not clear about the change in HfO_2 film properties after germanium-incorporation (i.e. HfGeO). Kamata et al [3] studied the dielectric constant variation by Si MOS capacitor with a very thick HfGeO gate dielectric (100nm). However, this thickness is not applicable to real Ge MOS device. Additionally, other important electrical properties, such as leakage current, trap states, and fixed charge etc., are still unknown. In this paper, we report the PDA-dependant Ge incorporation in HfO_2 and its impact on the electrical properties of HfO_2.

2. Experiment

A. Germanium incorporation

HfO_2 was directly deposited on diluted-HF cleaned Ge substrate by reactive sputtering method with pure Hf target in O_2 ambient. PDA was performed in RTP at different temperatures under N_2 or O_2 ambient.

B. Electrical characterization of HfGeO

The MOS capacitors were fabricated on p-type Si wafers. Pure HfO_2 and HfGeO gate dielectrics with three different Ge compositions were deposited using PVD followed by 700°C PDA. TaN metal gate was then deposited and patterned by lithography and dry etching. For some MOS capacitors, post-metal-anneal (PMA) was performed at 800 °C and 950 °C for 30s in nitrogen ambient. Backside Al contact deposition and alloy (400 °C 10% H_2) were performed as final steps.

3. Results and Discussion

Fig. 1 shows Ge profiles in HfO_2 after PDA as well as that in the as-dep film. No germanium is found in the as-dep film. Obvious Ge incorporation is observed in the film with PDA at 500 °C and above. Fig. 2 shows that PDA in O_2 enhances the germanium incorporation.

The impact of Ge-incorporation on HfO_2 dielectric constant was first studied. Fig. 3 exhibits the EOTs of devices with different Ge contents. By fitting thickness and refractive index together using spectroscopic ellipsometer, the HfO_2 and $Hf_{1-x}Ge_xO$ (x=5%, 10% and 15%) film are 8.1nm, 8.2nm, 6.9nm and 7.2nm respectively including IL. Although a more precise dielectric constant should be calculated from dielectric thickness series, the impact of Ge incorporation on HfO_2 dielectric constant can be discussed qualitatively by considering effective dielectric (ε_{eff}=Dielectric Thickness/EOT). The HfGeO samples show comparable ε_{eff} with HfO_2. This implies that the Ge incorporation into HfO_2 will not degrade dielectric constant obviously. In addition, the Ge incorporation into HfO_2 does not increase the leakage current (shown in Fig. 4). Fig. 5 shows the TEM pictures of HfO_2 and HfGeO. The HfGeO sample shows a rougher and thicker interfacial layer than the one with HfO_2. Adding Ge to HfO_2 does not increase crystallization temperature significantly as incorporating Si into HfO_2 does. Both of the films are crystallized after 700 °C PDA.

Fig. 6 shows the CV characteristics of HfO_2 and HfGeO measured at different frequency. Obvious kink and frequency dispersion are observed when germanium is present. The kinks reduce with increasing measurement frequency implies that there exist some “slow” surface states. Increasing PMA temperature relieves the frequency dispersion (Fig. 7). The kink effect and frequency dependence are often observed in Ge MOS devices [4-6]. It is also noted that the flat-band voltage shifts to positive side by >0.3V with germanium addition. This indicates Ge incorporation introduces a large amount of negative fixed charge into dielectrics. And those negative fixed charge can not be annealed out by PMA.

All devices have anti-clockwise hysteresis due to interface stats (Fig. 8). However, devices with HfGeO exhibit a 2 times higher hysteresis (170-200 mV) than pure HfO_2 (95 mV). PMA can effectively reduce the hysteresis of HfGeO while it is still larger than that of HfO_2. High-low dual frequency method is used to measure the interface state densities (Fig. 9).It is clearly observed that the quasi-static CV curve of HfGeO is significantly distorted due to the huge density interface states. A very large D_{it} is observed with HfGeO (6.6×10^{12} $eV^{-1}cm^{-2}$) near mid-gap.

4. Summary

The dependences of germanium incorporation in HfO_2 on PDA conditions have been evaluated. It is found that apparent Ge out-diffusion, from Ge substrate, is observed after annealing temperature higher than 500°C. The incorporation of germanium into HfO_2 does not degrade the dielectric constant and leakage current apparently but introduces a large amount of negative fixed charge and interface states. Therefore, for Ge MOSFET fabrication, a novel Ge surface passivation method or a new high-k material must be developed to prevent Ge out-diffusion.

Reference

[1] S. Van Elshocht *et al*, Appl. Phys. Lett., **85** (2004) 3824.
[2] K. Kita *et al*, *SSDM Tech. Dig.* (2003) 292.
[3] Y. Kamata *et al*, *SSDM Tech. Dig.* (2004) 36.
[4] C. O. Chui *et al*, Electron Device Lett., **23** (2002) 473.
[5] H. Kim *et al*, Appl. Phys. Lett., **85** (2004) 2902.
[6] A. Dimoulas *et al*, Appl. Phys. Lett., **86** (2005) 2908.

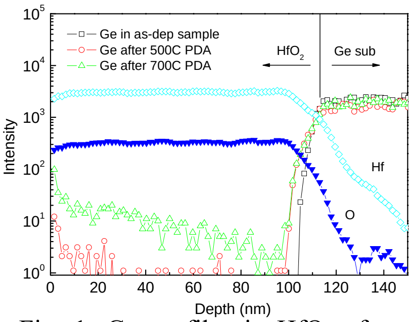


Fig. 1. Ge profiles in HfO_2 after different temperature annealing. Since Hf and O profiles are identical for all samples, only one group is plot here.

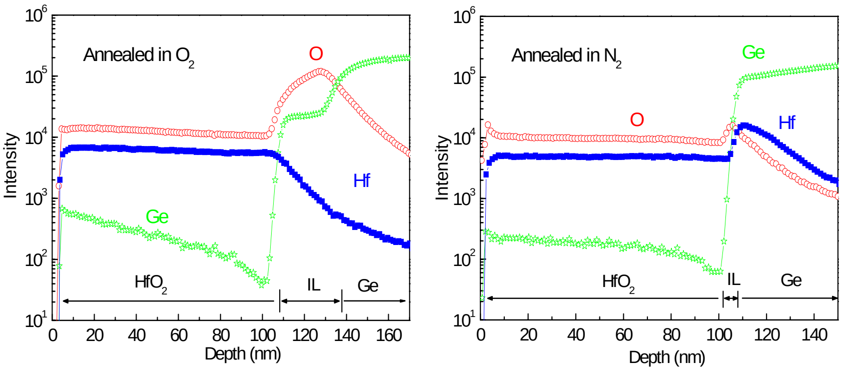


Fig. 2. SIMS profiles of HfO_2 after 700°C 2min annealing under O_2 (left) and N_2 (right) ambient.

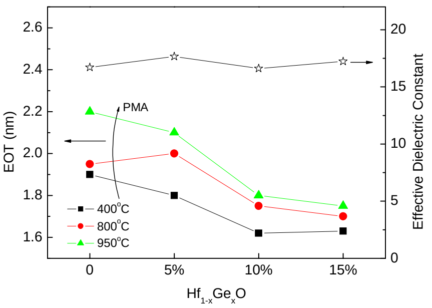


Fig. 3. EOTs of MOS capacitors with HfO_2 and HfGeO dielectrics. Different post-metal-annealings (PMA) were applied including 400°C forming gas annealing (FGA), 800°C PMA+FGA, and 950°C PMA+FGA.

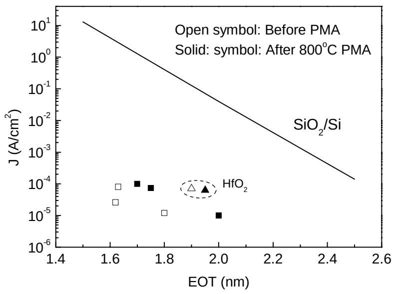


Fig. 4. Leakage currents (J) of HfO_2 compared to HfGeO for various composition. Leakage currents were measure at $|V_g-V_{fb}|=1V$.

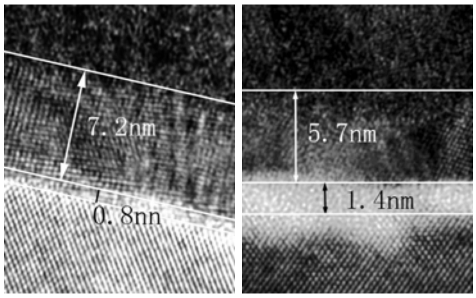


Fig. 5. TEM pictures of samples with HfO_2 and $Hf_{1-x}Ge_xO$ (x=15%). The thickness measured by TEM is consistent with that measured by ellipsometer.

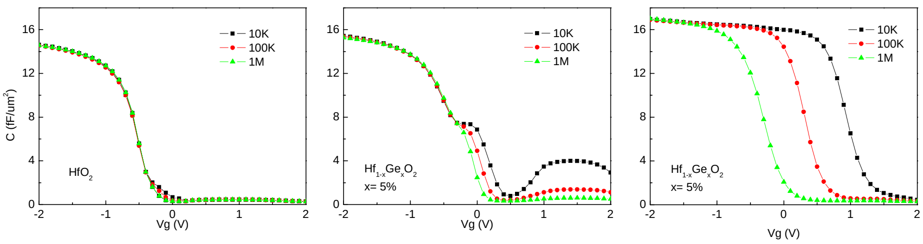
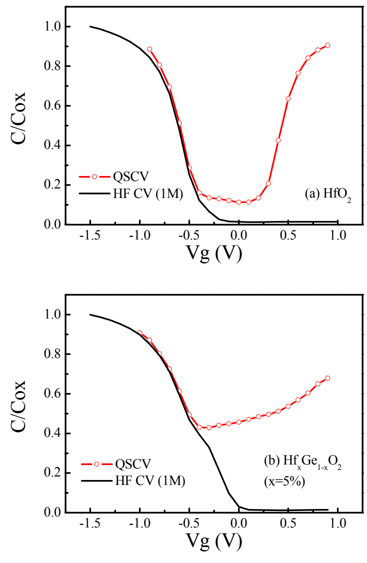


Fig. 6. CV characteristics of MOS capacitors with HfO_2 and HfGeO dielectrics. Severe kink and frequency dependence are observed on sample with HfGeO.



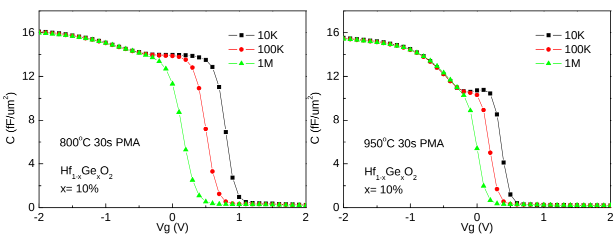


Fig. 7. PMA at high temperature can gradually anneal out part of interface states.

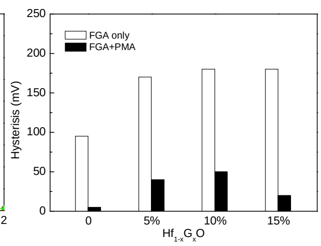


Fig. 8. Hysteresis of MOS capacitors with HfO_2 and HfGeO dielectrics defined as the difference between V_{fb} of CV curves swept from 2V to -2V and vice versa.

Fig. 9. High-low frequency CV of samples with HfO_2 and $Hf_{1-x}Ge_xO$ (x=5%).