Oxygen Potential Lowering in N-doped GeO₂ for Ge MIS Gate Stack Design in Extremely Thin EOT Region

The Univ. of Tokyo¹, JST-CREST² T. Tabata¹,² C. H. Lee¹,² T. Nishimura¹,² K. Nagashio¹,², and A. Toriumi¹,²

E-mail: tabata@adam.t.u-tokyo.ac.jp

1. Background
For Ge CMOS, a Ge MIS gate stacks with sub-nm EOT at 600°C is necessarily required. Then, an extremely thin GeO₃ interface layer (IL) is needed to passivate the interface states [1]. However, it is difficult in a sub-nm Ge MIS interface, because the oxidant in O₂ PDA to improve the high-κ gate oxide should diffuse very fast through the very thin gate dielectrics and lead an increase of GeO₃ IL thickness due to Ge oxidation. Therefore, we have to make oxygen potential lowering at the interface thermodynamically to suppress the oxidation. Although a simple thermodynamic consideration deals with only temperature and pressure as its parameters, the oxygen potential lowering is then expected to suppress the oxidant diffusion dramatically.

We have already reported that N doping can make the oxygen potential lowering in GeO₂ [2]. In this paper, we will demonstrate the effect of the oxygen potential lowering by the N doping into GeO₂ on Ge from the viewpoint of the suppression of GeO desorption from GeO₂/Ge and Ge MIS interface stabilization.

2. Experimental Procedure
HF-last Ge (100) wafers were used for the substrate. N-doped GeO₂ (GeON) films were deposited by N₂ sputtering of a GeO₂ target. N atom composition in GeON (N:O in at. %) and the film thickness were determined by XPS and GIXR, respectively. For MIS capacitors, Au and Al were evaporated as the gate electrode and the back contact, respectively.

3. Results and discussion
First, we investigated the effect of N doping on GeO desorption from GeO₂/Ge stacks. Fig. 1 shows that the GeO desorption is dramatically suppressed in GeON (20 at. % N)/Ge stacks. Considering that oxygen vacancy (Vo) formation plays a key role for the GeO desorption [3], the N doping is expected to increase the Vo formation energy due to the oxygen potential lowering in GeO₂. The suppression of the GeO desorption by N doping is quite advantageous for achieving both sub-nm EOT and interface stabilization at 600°C at the same time. However, bulk traps and/or interface states might be still there because their passivation can be achieved by a kinetic process. Therefore, we investigated the effect of N doping on GeO₂/Ge MIS characteristics. Fig. 2 shows the C-V characteristics of a 6.3-nm-thick GeON (15 at. % N)/Ge MIS gate stack annealed in pure N₂ at 600°C for 5 min. Almost zero hysteresis and well-suppressed frequency dispersions are found. Considering that the GeO desorption terribly degrades the MIS properties in such a thin pure GeO₂/Ge stacks [4], N doping dramatically affect to stabilize the GeO₂/Ge MIS gate stacks.

4. Conclusions
To control oxygen potential at the interface is the key to stabilize Ge MIS gate stacks with sub-nm EOT. N doping successfully works to stabilize Ge MIS gate stacks without inducing the GeO desorption, bulk traps, and interface states at 600°C.

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**Fig. 1** The GeO desorption temperature from pure GeO₂/Ge [3] and GeON (20 at. % N)/Ge stacks in TDS spectra.

**Fig. 2** The C-V characteristics of GeON (15 at. % N)/Ge MIS gate stacks with different frequencies.