

Study of kinetics in GeO desorption, GeO<sub>2</sub> crystallization and Ge oxidation in GeO<sub>2</sub>/Ge system  
(GeO<sub>2</sub>/Ge系におけるGeO脱離反応、GeO<sub>2</sub>結晶化過程およびGe酸化反応に関する速度論的研究)

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Ge is a promising candidate to replace Si for future complementary metal oxide semiconductor (CMOS) devices because of its high mobility. And GeO<sub>2</sub>/Ge stack is considered as the most fundamental for Ge CMOS. In order to meet the requirement for the control of GeO<sub>2</sub>/Ge stack of high performance Ge CMOS, understanding the kinetics in GeO<sub>2</sub>/Ge becomes quite important. In this thesis, the kinetics in GeO desorption, GeO<sub>2</sub> crystallization and Ge oxidation in GeO<sub>2</sub>/Ge system are systematically investigated.

First, the desorption kinetics of GeO from GeO<sub>2</sub>/Ge system have been investigated. On the basis of the direct observation of Ge substrate consumption during GeO desorption, GeO has been confirmed to mainly desorb due to the redox reaction between GeO<sub>2</sub> and Ge. Moreover, the diffusion species has been clarified to be the oxygen vacancy (Vo) by the <sup>73</sup>Ge and <sup>18</sup>O labeling technique in thermal desorption spectroscopy (TDS) analysis. It is concluded that the GeO desorption initiates from the GeO<sub>2</sub> surface in the uniform-desorption region. A Vo diffusion model has been proposed to explain the desorption mechanism of GeO from a GeO<sub>2</sub>/Ge stack. The activation energy of about 2eV was obtained from the kinetic calculation. Moreover, two kinds of GeO desorption (uniform and nonuniform) have been demonstrated, and the uniform one is likely to occur at relatively lower temperature. Furthermore, the relationships between GeO desorption and the degradation of electrical properties of GeO<sub>2</sub>/Ge stacks is studied. It is confirmed by interface trap density measurement that GeO desorption deteriorates the GeO<sub>2</sub>/Ge

interface by creating more interface traps within the bandgap.

Moreover,  $\alpha$ -quartz like  $\text{GeO}_2$  crystallization on Ge substrate at around 660 °C has been observed in this study. A  $\text{Vo}$  diffusion induced crystallization model has been proposed, where  $\text{GeO}_2$  crystallization is attributed to the network rearrangement through  $\text{Vo}$  incorporation. The disproportionation reaction at the  $\text{GeO}_2/\text{Ge}$  interface is discussed from the viewpoint of thermodynamic calculation, where  $\text{GeO}$  is considered to become Ge and  $\text{GeO}_2$  due to the higher free energy of  $\text{GeO}$ . In addition, the nonuniform desorption with voids formation is studied. The voids formation in the nonuniform desorption region is attributed to the faster diffusion of  $\text{Vo}$  at  $\text{GeO}_2$  crystalline boundary. And a unified model integrates uniform/nonuniform  $\text{GeO}$  desorption,  $\text{GeO}_2$  crystallization and  $\text{GeO}_2/\text{Ge}$  interface redox reaction is finally proposed.

The oxidation of Ge is proved to not follow the Deal-Grove model. The active oxidation of Ge has been observed and studied. A transition region where both active oxidation and passive oxidation path occurs comparably has been found under some certain conditions. A  $p\text{O}_2$ -T diagram that summarizes the active oxidation, passive oxidation, the transition region,  $\text{GeO}$  desorption,  $\text{GeO}_2$  crystallization is proposed. Towards the processing technique of Ge-MOS, guidelines for preparing a high-quality  $\text{GeO}_2/\text{Ge}$  stack are proposed. Finally, concerning the difference between  $\text{GeO}_2/\text{Ge}$  and  $\text{SiO}_2/\text{Si}$ , a fundamental consideration in the direction of atomistic structure is discussed. The inertness of Ge 4s electrons is attributable to the strong coulomb repulsion within the 3d shell.