**Mechanism of Epitaxial Growth of Rutile-type GeO2 by PLD**

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Ultra-wide band gap oxide semiconductors, with band gap energies (*E*g) exceeding those of GaN and SiC, have been extensively studied for next-generation power electronics and deep ultraviolet optoelectronics applications. Although *β*-Ga2O3 (*E*g = 4.8–4.9 eV) has been the primary focus, it has a critical limitation in the difficulty of achieving p-type doping. In contrast, rutile-type GeO2 (r-GeO2) with *E*g = 4.68 eV has been emerged as a promising material owing to its potential controllability of both p- and n-type conduction, which is predicted theoretically by first-principles calculations[1]. The extraordinarily short O–O distances in the r-GeO2 crystal structure enhance O 2*p* – O 2*p* antibonding interactions, raising the energy level of the valence band maximum and making hole doping feasible[2]. Although the number of reports on epitaxial growth of r-GeO2 films has been increasing[3,4], synthesis of high-quality epitaxial films remains challenging due to competing polymorphs, such as *α*-quartz and amorphous phases. These phases hinder effective doping with aliovalent ions.

In this study, we systematically investigate effects of deposition conditions, especially focusing on oxygen pressure (*P*O2) and growth temperature (*T*g), on growth of GeO2 films by pulsed laser deposition (PLD). We successfully controlled the growth phase of GeO2.

**Figure** shows the growth phase diagram of GeO2 films grown by PLD as a function of *T*g and *P*O2. Epitaxial films of r-GeO2 are obtained at *T*g = 500 – 600℃ under low *P*O2 ≤ 10-1 Pa, while the *α*-quartz phase does not appear under any growth conditions. However amorphous phase coexists under higher *P*O2 ≥ 10-2 Pa at *T*g = 500℃, and only amorphous phase is formed under lower *T*g ≤ 400℃ and higher *P*O2 ≥ 1 Pa. On the other hand, severe re-evaporation of the film occurs with increasing *T*g and decreasing *P*O2, and finally no film growth is observed at 700℃. These results indicate that low *P*O2 is inevitable to obtain pure r-GeO2 film; however, re-evaporation of the GeO2 film becomes serious at the same time. These competing phenomena not only complicate phase stabilization but also hinder precise control of chemical composition particularly when dopant ions are introduced. We will discuss it in more detail at the conference.

**Figure**. Growth Phase diagram of GeO2 film deposited by PLD at different *T*g and *P*O2.

[1] S. Chae, et al., *Appl Phys Lett*, **114**, 102104, (2019). [2] C. Niedermeier et al. *J.Phys.Chem*., **124**, 25721, (2020). [3] S. Chae, et al., *Appl Phys Lett*, **117**, 072105, (2020). [4] H. Takane, et al., *Appl Phys Lett*, **119**, 062104, (2021).