Growth processes of YF_3 epitaxial thin films using fluorine-anion conducting substrates

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[Introduction] Metal fluorides have attracted much attention due to a wide variety of electrochemical applications such as fluorine ion battery [1]. To understand the ionic conduction and ion transfer at the interface, a use of epitaxial thin films is a good way to control the size, roughness and orientation. Compared with oxide thin films, in general, fabrication of fluoride thin films is more challenging due to toxicity of fluorine gas, limiting the epitaxial growth of metal fluorides [2]. We have reported a simple route to fabricate EuF_2 thin films on F^--conducting CaF_2 substrates with no fluorine gas supply [3]. To extend this growth technique to other metal fluorides, here, we fabricate yttrium trifluoride (YF_3, orthorhombic, a = 6.353 Å, b = 6.850 Å, c = 4.393 Å) epitaxial thin films.

[Experiment] Yttrium-based thin films were deposited on CaF_2 (111) (cubic, a = 5.45 Å) and MgF_2 (100) (tetragonal, a = 4.597 Å, c = 3.038 Å) substrates using reactive magnetron sputtering. A Y metal plate (2 inch) was used as a target, and only Ar gas was introduced into a vacuum chamber for the sputtering. During the deposition, the pressure of Ar was fixed at 1.0 Pa with a constant flow rate of 10 SCCM in the growth chamber. The RF power supply at the Y target was maintained at 50 W. Substrate temperature and deposition time were set as 600°C and 5 min. After deposition, the samples were annealed at 700ºC for 1 hour in the growth chamber. The structural properties were characterized using X-ray diffraction (XRD).

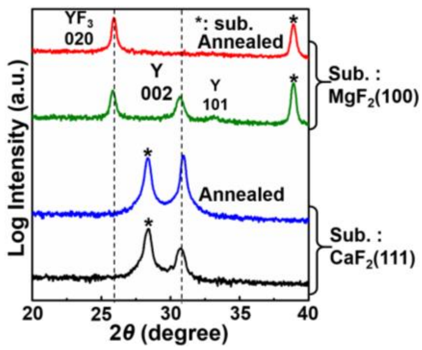

Fig.1. Out-of-plane XRD scan obtained from thin films on CaF_2(111) and MgF_2(100) substrates.

[Results & Discussion] Figure 1 shows XRD patterns of thin films grown on CaF_2(111) and MgF_2(100) substrates. Only metallic Y phase was observed on CaF_2(111) substrates, whereas a diffraction peak of fluoride phase (YF_3) also appeared on MgF_2(100) substrate. This difference can be explained by the relationship of standard Gibbs energy of formation at 600ºC between each fluoride: $\Delta G^0(CaF_2) = -1067.63$ kJ/mol < $\Delta G^0(YF_3) = -983.90$ kJ/mol < $\Delta G^0(MgF_2) = -937.84$ kJ/mol [4]. Namely, this growth technique requests higher chemical potential of substrate than that of thin films. To enhance the crystallization of YF_3, we further annealed the thin film sample grown on a MgF_2(100) substrate. As a result, we finally obtained single-phase YF_3(010) epitaxial thin films. In addition, pole figure measurements determined the in-plane epitaxial relationship as $[100]_{YF3}$ // $[001]_{MgF2}$. These results provide a thermodynamical guide to select a suitable substrate for metal fluoride epitaxial growth.

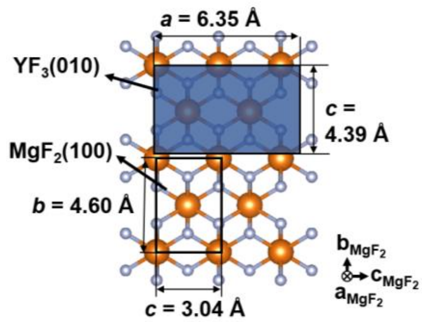

Fig.2. In-plane epitaxial relationship between YF_3 thin film and MgF_2 substrate.

References:

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[3] D. Xin, *et al*. JSAP. 10p-W323-13 (2019). [4] S.M. Howard. Ellingham Diagrams. (2006).