Fabrication of fluorine-ion conducting LaF_3 epitaxial thin films assisted by CF_4 reactive gas

°(D)Xin DAI[1], Ryota Shimizu[1 2], Taro Hitosugi[1]
Tokyo Tech[1], JST-PRESTO[2]
E-mail:dai.x.ab@m.titech.ac.jp

[Introduction] Metal fluorides (e.g., MgF_2, LaF_3) exhibit unique properties ranging from high broadband optical transmittance [1] to high F-ion conduction.[2] These properties open up novel optoelectronic and electrochemical applications. For the understanding of the intrinsic properties of metal fluorides, it is essential to fabricate high-quality epitaxial thin films. For the fabrication of metal fluoride thin films using magnetron sputtering, reactive gases such as CF_4 and SF_6 are commonly used to compensate many fluorine deficiencies [3]. In these cases, the impurities from the reactive gases are inevitable [3], deteriorating the intrinsic physical properties. Here, we show the fabrication of F-ion conducting LaF_3 epitaxial thin films using CF_4 gas as a model case. We found that the addition of H_2 to CF_4 during the sputtering successfully suppress the incorporation of carbon impurities into LaF_3 thin films.

[Experiment] LaF_3 thin films with a thickness of 90 nm were deposited on CaF_2(111) substrates using reactive magnetron sputtering. A LaF_3 sintered disk (diameter: 2 inches) was used as a target, and a mixture of Ar, CF_4, and Ar(96%)-H_2(4%) premixed gases was introduced to the chamber at a total pressure of 1.0 Pa. The radio-frequency power supply was maintained at 100 W. Substrate temperature and deposition time were set as 600˚C and 30 min, respectively. The structural and optical properties were characterized using X-ray diffraction (XRD) and spectrophotometry, respectively.

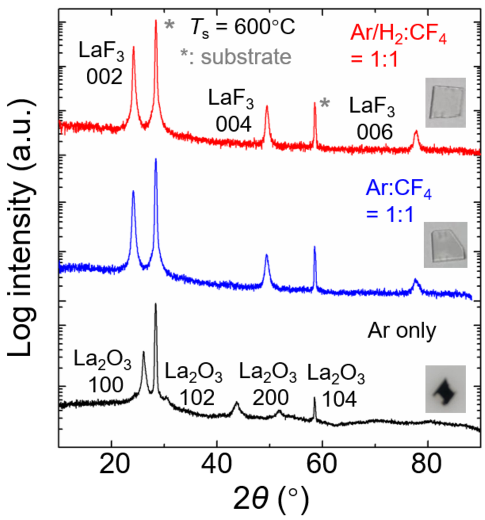

Figure. Out-of-plane XRD patterns obtained from LaF_3 thin films on CaF_2(111) with Ar only (black), Ar:CF_4 = 1:1 (blue), Ar(96%)-H_2(4%):CF_4 = 1:1 (red). Insets show the photographs of each sample.

[Results & Discussion] Figure shows XRD patterns of thin films grown on CaF_2(111) substrates at 600˚C with different ratios of Ar: H_2:CF_4. With only Ar gas, only the signals from La_2O_3 were obtained (black), possibly due to extreme fluorine deficiencies at the LaF_3 target surface during sputtering. Next, a mixture of Ar and CF_4 (1:1) gases was used for the fluorination. As a result, we obtained LaF_3 thin films (blue). However, the color of the film is gray (transmittance of 84.3% at 500 nm), suggesting the incorporation of carbon impurities from CF_4. To suppress the carbon impurities, we additionally introduce H_2 gas, aiming for the promotion of evaporation of carbon species (C (s) + H_2 (g) → C_xH_y (g)). Finally, we succeeded in the fabrication of LaF_3 thin film with high transmittance (88.9% at 500 nm) with Ar(96%)-H_2(4%) and CF_4 (1:1) gases.

References:

[1] M. Bischoff, *et al.*, Appl. Opt., **47,** C157 (2008).
[2] M. Vijayakumar, *et al.*, J. Fluor. Chem., **125,** 1119 (2004).
[3] S. Mertin, *et al.*, Adv. Eng. Mater., **17,** 1652 (2015).