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論文審査の要旨及び審査員

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論文審査の要旨（2000 字程度）

This doctoral thesis entitled “Fluorination processes for growing metal-fluoride epitaxial thin films” is composed of six chapters in total. This work reports novel routes to fabricate metal-fluoride epitaxial thin films using the magnetron sputtering method.

In Chapter 1, the author reviews the importance of fluorination processes to fabricate metal-fluoride epitaxial thin films for wide applications, including optics and F-ion batteries. The author proposes new approaches to fluorinate thin films based on the drawbacks of the conventional fluoride film-growth technology, such as incorporating F deficiencies and using toxic fluorination sources.

In Chapter 2, the author provides experimental information, including crystal structures of related materials, thin-film fabrication techniques, and characterization methods. The experimental fluorination processes, the main topics of this thesis, are classified as two methods. One method is fluorination using F-conducting substrates as the F--ion sources. This method was demonstrated in the fabrication of YF_3 (010) and EuF_2 (111) epitaxial films on MgF_2 (100) (Chapter 3) and CaF_2 (111) (Chapter 4), respectively. The other method is fluorination assisted by the non-toxic CF_4-H_2 mixed gas. This method was demonstrated in the fabrication of LaF3(001) epitaxial films on CaF_2 (111) and Nb-doped $SrTiO_3$ (100) substrates (Chapter 5).

In Chapter 3, through the fabrication of YF_3 epitaxial thin films, the author shows the basic concept of fluorinating metals using F-ion-conducting substrates. This method uses Y metal as the target material, ensuring that fluoride ions are supplied only from the substrate. Following the thermodynamic stability ($CaF_2 > YF_3 > MgF_2$), the F ions spontaneously diffuse from MgF_2 substrate to Y thin films at 700 °C, forming YF_3 (010) epitaxial thin films. In contrast, spontaneous F-ion diffusion does not occur on the CaF_2 substrates; thus, Y metal films grow on the CaF_2 substrate. Transmission electron microscopy and secondary ion mass spectroscopy measurements show the uniform distribution of F ions in the YF_3 epitaxial thin films. Although fluorination was insufficient at low substrate temperature, single-phase fluoride thin films are obtained after post-deposition-annealing. The maximum thickness of YF_3 film is ~40 nm, smaller than the theoretical calculation of diffusion distance (4.2 μm). This result suggests the importance of the kinetics of the F diffusion process in fluorination. Taken together, the fluorination method using F-ion conducting substrate is effective for the fabrication of metal-fluoride epitaxial thin films.

In Chapter 4, the author further demonstrates the feasibility of the method proposed in Chapter 3. The author focuses on the growth of EuF_2 (111) epitaxial thin films, which have not been reported yet. Because EuF_2 has the highest thermodynamical stability among the metal fluorides, the author expects that the Eu metal is fluorinated to EuF_2 on CaF_2 substrates. Indeed, the EuF_2 epitaxial thin films are successfully fabricated on CaF_2 (111) substrates at 700 °C with a maximum thickness of ~ 80 nm. The EuF_2 epitaxial thin films exhibit higher transmittance in the visible-light region than that of polycrystalline EuF_2. The clear two absorption bands at 3.75 and 5.45 eV are clearly observed, suggesting the ideal Eu^{2+} states in the EuF_2. This method is applied to oxides; EuO (100) epitaxial thin films are fabricated using yttria-stabilized zirconia (100) as an O-conducting substrate. Hence, this method using anion-conducting substrates has great potential to fabricate epitaxial thin films of a wide variety of ionic compounds.

In Chapter 5, the author investigates the fluorination processes using the non-toxic CF4 gas. The author confirmed that the fabrication of thick LaF_3 thin films is difficult because of the limitation in the fluorination using F-conducting substrates. Here, non-toxic CF_4 gas is introduced during the sputtering processes as the fluorination source. As a result, the LaF_3 (001) epitaxial thin films are successfully fabricated with the assistance of CF_4 gas. With the increase of the CF_4 ratio to 50%, the crystallinity of LaF_3 films improves obviously. Furthermore, a mixture of CF_4 and H_2 decreases the level of carbon impurities originating from CF_4. In addition, the author evaluates the ionic conductivity of the 400-nm-thick LaF_3 (001) thin on Nb-doped $SrTiO_3$ (100) substrates. At room temperature, the ionic conductivity of LaF_3 (001) thin films is 4.3 × 10-6 S cm^{-1}, which is comparable to the previously reported value of bulk LaF_3. These results indicate that high-quality metal-fluoride epitaxial thin films are fabricated using CF_4-H_2 mixed gases during the magnetron sputtering processes.

In Chapter 6, the author summarizes and concludes this work, and describes the prospect of future research.

To sum up, this thesis proposes novel routes to fabricate metal-fluoride epitaxial thin films. The author deserves to receive a Doctor of Engineering from the Tokyo Institute of Technology.