

論文 / 著書情報  
Article / Book Information

題目(和文)	
Title(English)	Fluorination processes for growing metal fluoride epitaxial thin films
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出典(和文)	学位:博士(工学), 学位授与機関:東京工業大学, 報告番号:甲第12102号, 授与年月日:2021年9月24日, 学位の種別:課程博士, 審査員:一杉 太郎,平山 雅章,荒井 創,大友 明,鈴木 耕太,清水 亮太
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Tokyo Institute of Technology, Report number:甲第12102号, Conferred date:2021/9/24, Degree Type:Course doctor, Examiner:,,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

(博士課程)  
Doctoral Program

## 論文要旨

THESIS SUMMARY

系・コース: Department of, Graduate major in	応用化学 応用化学	系 コース	申請学位 (専攻分野): Academic Degree Requested	博士 Doctor of (工学)
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要旨 (英文 800 語程度)

Thesis Summary (approx.800 English Words)

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  $\text{YF}_3$  (010) and  $\text{EuF}_2$  (111) epitaxial films on  $\text{MgF}_2$  (100) (Chapter 3) and  $\text{CaF}_2$  (111) (Chapter 4), respectively. The other method is fluorination assisted by the non-toxic  $\text{CF}_4\text{-H}_2$  mixed gas. This method was demonstrated in the fabrication of  $\text{LaF}_3$  (001) epitaxial films on  $\text{CaF}_2$  (111) and Nb-doped  $\text{SrTiO}_3$  (100) substrates (Chapter 5).

In Chapter 3, through the fabrication of  $\text{YF}_3$  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 ( $\text{CaF}_2 > \text{YF}_3 > \text{MgF}_2$ ), the F ions spontaneously diffuse from  $\text{MgF}_2$  substrate to Y thin films at  $700^\circ\text{C}$ , forming  $\text{YF}_3$  (010) epitaxial thin films. In contrast, spontaneous F-ion diffusion does not occur on the  $\text{CaF}_2$  substrates; thus, Y metal films grow on the  $\text{CaF}_2$  substrate. Transmission electron microscopy and secondary ion mass spectroscopy measurements show the uniform distribution of F ions in the  $\text{YF}_3$  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  $\text{YF}_3$  film is  $\sim 40$  nm, smaller than the theoretical calculation of diffusion distance ( $4.2 \mu\text{m}$ ). 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  $\text{EuF}_2$  (111) epitaxial thin films, which have not been reported yet. Because  $\text{EuF}_2$  has the highest thermodynamical stability among the metal fluorides, the author expects that the Eu metal is fluorinated to  $\text{EuF}_2$  on  $\text{CaF}_2$  substrates. Indeed, the  $\text{EuF}_2$  (111) epitaxial thin films are successfully fabricated on  $\text{CaF}_2$  (111) substrates at  $700^\circ\text{C}$  with a maximum thickness of  $\sim 80$  nm. The  $\text{EuF}_2$  epitaxial thin films exhibit higher transmittance in the visible-light region than that of polycrystalline  $\text{EuF}_2$ . The clear two absorption bands at 3.75 and 5.45 eV are clearly observed, suggesting the ideal  $\text{Eu}^{2+}$  states in the  $\text{EuF}_2$ . This method is applied to oxides;  $\text{EuO}$  (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  $\text{CF}_4$  gas. The author confirmed that the fabrication of thick  $\text{LaF}_3$  thin films is difficult because of the limitation in the fluorination using F-conducting substrates. Here, non-toxic  $\text{CF}_4$  gas is introduced during the sputtering processes as the fluorination source. As a result, the  $\text{LaF}_3$  (001) epitaxial thin films are successfully fabricated with the assistance of  $\text{CF}_4$  gas. With the increase of the  $\text{CF}_4$  ratio to 50%, the crystallinity of  $\text{LaF}_3$  films improves obviously. Furthermore, a mixture of  $\text{CF}_4$  and  $\text{H}_2$  decreases the level of carbon impurities originating from  $\text{CF}_4$ . In addition, the author evaluates the ionic conductivity of the 400-nm-thick  $\text{LaF}_3$ (001) thin on Nb-doped  $\text{SrTiO}_3$  (100) substrates. At room temperature, the ionic conductivity of  $\text{LaF}_3$  (001) thin films is  $4.3 \times 10^{-6} \text{ S cm}^{-1}$ , which is comparable to the previously reported value of bulk  $\text{LaF}_3$ . These results indicate that high-quality metal-fluoride epitaxial thin films are fabricated using  $\text{CF}_4$ - $\text{H}_2$  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.

備考 : 論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

Note : Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1copy of 800 Words (English).

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