論文 / 著書情報
Article / Book Information

題目(和文)	
Title(English)	Studies on structural and electronic properties of dimensionality- and composition-tuned molybdenum bronzes films
著者(和文)	ZHANG Shuxin
Author(English)	Shuxin Zhang
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12731号, 授与年月日:2024年3月26日, 学位の種別:課程博士, 審査員:大友 明,平山 雅章,川路 均,鈴木 耕太,吉松 公平
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Tokyo Institute of Technology, Report number:甲第12731号, Conferred date:2024/3/26, 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 系 応用化学 コース	申請学位（専攻分野）： Academic Degree Requested	博士 （工学） Doctor of
学生氏名： Student's Name	ZHANG Shuxin	審査員主査： Chief Examiner	大友 明

要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

This thesis entitled "Studies on Structural and Electronic Properties of Dimensionality- and Composition-tuned Molybdenum Bronzes Films" is composed of six chapters and written in English. This study has been conducted on well-defined epitaxial films of molybdenum bronzes with a variety of crystal structures and tunable valence states, obtained by using pulsed-laser deposition (PLD).

Chapter 1 "General Introduction" describes the background and general interest for this study. The complex interplay of charge, lattice, and spin degrees of freedom that are inherent in transition-metal oxides gives rise to a variety of correlated phases and emergent phenomena in condensed matter physics. However, the fundamental studies on elucidation of mechanisms in correlated phases and comprehensive theories that deal with uncovered physical properties still remain one of the greatest challenges. The exploration and synthesis of new materials allow us to exploit more possibilities. The combined approach of epitaxial film growth and solid-state chemistry is expected as a new driving force to open up an interdisciplinary field.

Chapter 2 "Epitaxial Growth of MoO_3 Polymorphs and Impacts of Li-ion Electrochemical Reactions on Their Structural and Electronic Properties" investigates the crystal phase control of α- and β-MoO_3 in epitaxial thin-film growth and precise control of electron doping to β-MoO_3 films via Li-ion electrochemical reactions. The detailed structural characterization and analysis conducted by using x-ray reciprocal space mapping method first reveal the unique growth dynamics in epitaxially stabilized β-MoO_3 films. From cyclic voltammetry measurements, β-MoO_3 films exhibit better reversibility than α-MoO_3 films and a ReO_3-type structure of the formers is able to be maintained against heavy intercalations of Li ions into the interstitial sites. Systematic evolution in β-Li_xMoO_3 film from band insulator to correlated metal with electrical conductivity change over several orders of magnitude shows the potential to be utilized in novel ion-intercalation-based functional oxide devices.

Chapter 3 "Orientation Control of MoO_2 Films and Orbital–selective Anisotropic Electronic Properties" is concerned with the correlated metal MoO_2 with a $4d^2$ configuration and a rutile-type structure. We realize the orientation control by choosing a number of substrate planes deliberately to investigate the impacts of orientation on the structural instability and electrical properties. The results show anisotropic conductivity and transport properties depending on film orientations. The characteristic splits of the $d_{\|}$ orbitals clearly observed in synchrotron-radiation photoemission and O 1*s* x-ray absorption spectra suggest the formation of Mo-Mo dimers along the $[001]_R$ (rutile's *c*-axis) direction. It is found that the $(001)_R$-oriented MoO_2 films exhibit unusually high electrical conductivity with metallic behaviors despite lower crystallinity, which arises from the combination between orbital occupation and intrinsic anisotropic properties.

Chapter 4 "Epitaxial Film Growth of $LiMoO_2$ and Structural Changes by Li-ion De-intercalation" studies the layered rock-salt type $LiMoO_2$ with an unconventional $4d^3$ configuration. The fabrication of high-quality (001)-oriented stoichiometric $LiMoO_2$ epitaxial films is demonstrated for the first time by using a Li-excess PLD target with [Li]/[Mo] = 1.5, strong reductive gas conditions, and elevated temperatures. The band structure is characterized from synchrotron-radiation photoelectron spectroscopy and x-ray absorption spectroscopy measurements. The Li-ion de-intercalations through electrochemical and soft chemical methods are carried out to reduce the valence states of Mo and to survey a hidden electronic phase transition. Mott-insulating behaviors are found to be robust even in Li_xMoO_2 with $x \approx 0$.

Chapter 5 "$AMoO_2$ (A = Li, Na, K): Two-dimensional Mott Insulators with Tunable MoO_2 Interlayer Distance" demonstrates the first systematic epitaxial growth of $AMoO_2$ (A = Li, Na, K) thin films. A new crystal phase of $K_{0.67}MoO_2$ is discovered with a well-defined layered structure and largely extended interlayer distance. The high degrees of cation orders in three types of layered oxides are elucidated by simulation of intensity ratios for a series of 00*l* reflections, which clearly indicates the feasibility of our concept proposed in this study: dimensionality- and composition-tuning on functional oxide materials.

Chapter 6 "General Conclusions" summarizes the above scientific findings.

This thesis contains original and valuable scientific results and contributes to new insights into the film synthesis of molybdenum bronzes with various crystal structures and modulation of physical properties through newly established chemical methods.

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).

注意：論文要旨は、東工大リサーチリポジトリ(T2R2)にてインターネット公表されますので、公表可能な範囲の内容で作成してください。
Attention: Thesis Summary will be published on Tokyo Tech Research Repository Website (T2R2).