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論文審査の要旨 (2000 字程度)

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 MoO₃ Polymorphs and Impacts of Li-ion Electrochemical Reactions on Their Structural and Electronic Properties” investigates the crystal phase control of α - and β -MoO₃ in epitaxial thin-film growth and precise control of electron doping to β -MoO₃ 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 -MoO₃ films. From cyclic voltammetry measurements, β -MoO₃ films exhibit better reversibility than α -MoO₃ films and a ReO₃-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_xMoO₃ 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 MoO₂ Films and Orbital-selective Anisotropic Electronic Properties” is concerned with the correlated metal MoO₂ 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 1s 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 MoO₂ 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 LiMoO₂ and Structural Changes by Li-ion De-intercalation” studies the layered rock-salt type LiMoO₂ with an unconventional $4d^3$ configuration. The fabrication of high-quality (001)-oriented stoichiometric LiMoO₂ 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_xMoO₂ with $x \approx 0$.

Chapter 5 “AMoO₂ (A = Li, Na, K): Two-dimensional Mott Insulators with Tunable MoO₂ Interlayer Distance” demonstrates the first systematic epitaxial growth of AMoO₂ (A = Li, Na, K) thin films. A new crystal phase of K_{0.67}MoO₂ 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. Therefore, this thesis is considered to be of sufficient value for the doctor’s degree of engineering.

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