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Thesis Title

"Studies on structural and electronic properties of dimensionality- and composition-tuned molybdenum bronzes films"

Thesis Outline

The study in this thesis has been conducted on molybdenum bronzes with a variety of crystal structures and flexible valence states, aiming to discover emergent crystal phases and modulate unique electronic properties originating from electron correlation, carrier concentration, low-dimensionality, and chemical composition modulation.

Chapter 1 "General Introduction"

In Chapter 1, background and general interest for this work are described. 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 in elucidation of mechanism in correlated phases and comprehensive theory to deal with uncovered physical properties still remain one of the greatest challenges. Besides theoretical understanding and predictions, synthesis of new materials can allow us to exploit more possibilities. The discovery of high-temperature superconductivity in cuprates started a new era. Moreover, the combined approaches of epitaxial film growth and solid-state chemistry can be expected as a new driving force to open up an interdisciplinary field. One the one hand, control of film growth with different chemical composition and dimensionality brings about various crystal phases with atomic-scale well-defined structures, with possibility towards integration into devices exhibiting novel functionalities that cannot be realized in conventional semiconductors. One the other hand, the solid-state chemistry can be efficient way to manipulate the competition of localization and itinerancy in correlated oxides through powerful chemical treatments.

Chapter 2 "Epitaxial Growth of MoO_3 Polymorphs and Impacts of Li-ion Electrochemical Reactions on Their Structural and Electronic Properties"

In Chapter 2, phase control of two major polymorphs of MoO_3 (α and β phase) in epitaxial thin-film growth using PLD is discussed. Especially, growth dynamics of thermodynamically unstable β-MoO_3 films was first revealed through detailed structural analysis using X-ray reciprocal space mapping (RSM) method. Electrochemical reversibility of α- and β-MoO_3 thin films and control of electronic phases are discussed. In particular, insulator-metal transition (IMT) was first observed in β-MoO_3 films. The electronic condition of β-MoO_3 and origins of the transition were revealed by detailed analysis and comparing relating materials.

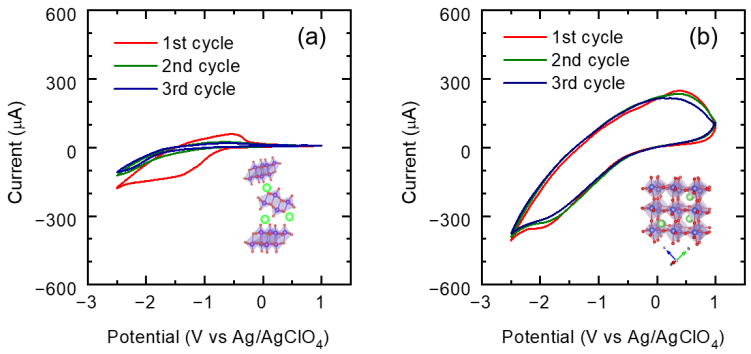

Fig. 1 Cyclic voltammogram for α- and β-MoO_3|$LiClO_4$:PC|$LiCoO_2$/Al electrochemical cells taken during repeated Li-ion electrochemical reactions.

Chapter 3 "Orientation Control of MoO_2 Films and Orbital–selective Anisotropic Electronic Properties"

In Chapter 3, the impacts of orientation control on transport properties of MoO_2 epitaxial films are investigated for the first time. The anisotropy in conductivity and magnetoresistance in different-oriented MoO_2 films were clearly observed. In addition, thickness-dependent metal-insulator transition was shown in the epitaxial grown MoO_2 films regardless of crystal orientation. As a rutile-related compound, the possible orbital occupancy effect on this anisotropy in transport properties are discussed combined with theoretical calculations on the orbital-selective band structure.

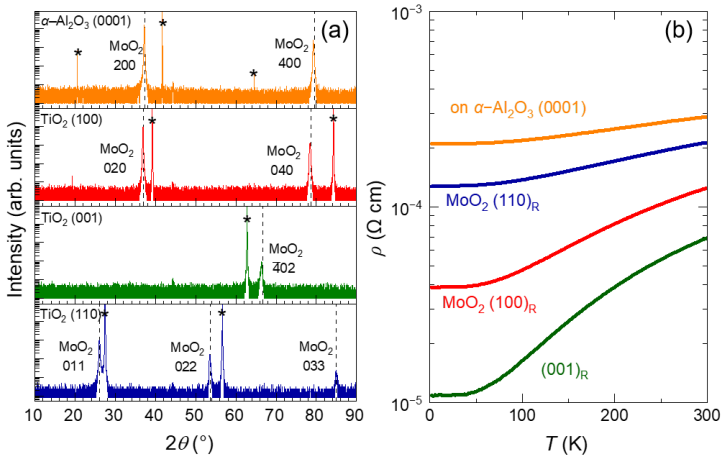

Fig. 2 (a) XRD profiles of MoO_2 films grown on various substrates. (b) Temperature dependence of resistivity for MoO_2 films grown on various substrates.

Chapter 4 "Epitaxial Film Growth of $LiMoO_2$ and Structural Changes by Li-ion De-intercalation"

In Chapter 4, highly crystalline $LiMoO_2$ epitaxial films were successfully fabricated for the first time. Through careful control of Li composition during PLD growth, nearly stoichiometric composition and epitaxial growth was achieved for the first time. The Li-ion de-intercalation

through electrochemistry and soft chemistry methods was carried out to reduce the valence states of Mo for possible electronic phase transition. And the structural changes during the de-intercalation process were observed. Nearly x~0 in Li_xMoO_2 was achieved through Li-ion deintercalation.

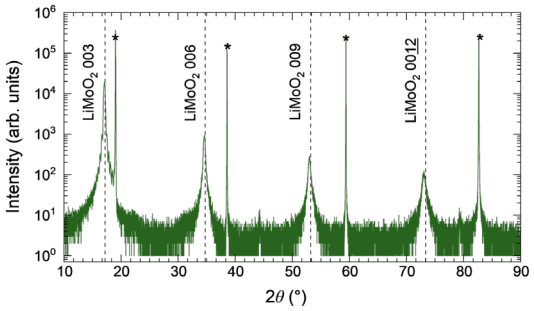

Fig. 3 XRD profile of $LiMoO_2$ film grown on $MgAl_2O_4$ (111) substrate.

Chapter 5 "AMoO$_2$ (A = Li, Na, K): Two-dimensional Mott Insulators with Tunable MoO$_2$ Interlayer Distance"

In Chapter 5, Na_xMoO_2 and K_xMoO_2 thin films were fabricated for the first time. The interlayer distance was largely enlarged through alkali-metal substitution in the layered oxides AMoO$_2$. Among them, K_xMoO_2 is the new crystal phase that has not been reported before. Degree of order analysis suggested well-defined layered structure in epitaxially grown AMoO$_2$ films. The optical properties as well as band structure of $Na_{0.6}MoO_2$ and $K_{0.67}MoO_2$ sample were also measured for the first time.

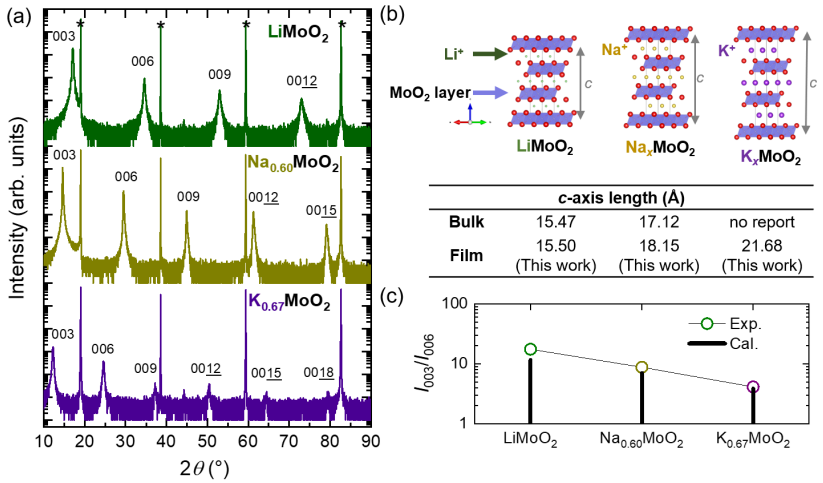

Fig. 4 (a) XRD profiles of A_xMoO_2 films grown on $MgAl_2O_4$ (111) substrates. The substrate reflections are marked with asterisks. (b) The crystal structures of A_xMoO_2. (c) I_{003}/I_{006} ratios obtained from XRD profiles.

Chapter 6 "General Conclusions"

In Chapter 6, the results are summarized to discuss the impact of this thesis generally. Finally, an outlook of the future development for the study is presented.