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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 "Thin Film Synthesis of Coordination-Compounds by Dry Process" comprises five chapters. This work reports on a novel route to fabricate coordination compound thin film by dry process.

In Chapter 1, the author reviews the coordination compounds focusing on the metal complex hydrides and metal-organic frameworks (MOFs). For thin film growth of the coordination compounds, the author explains the problem in conventional thermal evaporation for the materials with low decomposition temperature and claims the necessity of a new dry process. In this study, the author demonstrates the thin film synthesis of a calcium imide, CaNH using reactive magnetron sputtering, and MOF, Cu<sub>3</sub>(HHTP)<sub>2</sub> (HHTP = 2,3,6,7,10,11-hexahydroxytriphenylene) using multilayer deposition followed by vapor-assisted annealing.

In Chapter 2, the author describes the experimental procedures employed in fabricating and characterizing thin films of CaNH and Cu<sub>3</sub>(HHTP)<sub>2</sub>. The details of each method, including the operating principles and measurement techniques, are thoroughly described.

In Chapter 3, the author fabricates epitaxial thin films of CaNH using reactive magnetron sputtering. Two phases in Ca-N-H system, namely Ca<sub>2</sub>NH (ionic crystal) and CaNH (metal complex hydride), are selectively grown by controlling H<sub>2</sub> partial pressure ( $P_{H_2}$ ): CaNH at  $P_{H_2} > 0.04$  Pa and Ca<sub>2</sub>NH at  $P_{H_2} < 0.04$  Pa. *In-situ* plasma emission spectroscopy suggests that the modification of Ca-metal target surface to CaH<sub>x</sub> under high  $P_{H_2}$  leads to the formation of CaNH phase. Notably, this study is the first report on the metal complex imide thin film, providing a novel strategy to form complex imide thin films.

In Chapter 4, the author demonstrates the fabrication of (001)-oriented Cu<sub>3</sub>(HHTP)<sub>2</sub> thin films. The developed process is comprised of two steps: 1) multilayer deposition of Cu(OAc)<sub>2</sub> and HHTP precursors on Al<sub>2</sub>O<sub>3</sub> (0001) by infrared pulsed laser deposition and 2) subsequent post-deposition annealing under pyridine and H<sub>2</sub>O vapor in the air. The author finds the multilayer precursor film is successfully crystallized and (001)-oriented after the post-deposition annealing. In addition, the conductivity of the (001)-oriented thin film is 0.5 S cm<sup>-1</sup>, comparable to the film reported by the wet process. This is the first report on fabricating Cu<sub>3</sub>(HHTP)<sub>2</sub> thin films using the dry process.

In Chapter 5, the author summarizes and concludes this work and describes the guidelines for future research on thin films of coordination compounds based on the developed dry processes.

To sum up, this thesis demonstrates the fabrication of coordination-compounds thin films which have not been achieved by conventional dry processes based on thermal evaporation. The author deserves a Doctor of Engineering from the Tokyo Institute of Technology.

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