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（博士課程）
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論 文 要 旨

THESIS SUMMARY

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

This thesis investigates the plasma-enhanced atomic layer deposition (PEALD) process for the conformal coating of manganese oxide (MnOx) thin films on carbon nanowalls (CNWs). CNWs are vertically aligned graphene-based nanostructures with high surface area, electrical conductivity, and mechanical stability, making them promising candidates for energy storage applications. MnOx, a low-cost and environmentally friendly metal oxide, is widely used in supercapacitors and other electrochemical energy storage devices. However, the uniform deposition of MnOx on CNWs is challenging due to their complex structure, which conventional deposition techniques fail to achieve. PEALD is explored as a potential method to address these challenges while preserving the CNWs' morphology and structural integrity.

This study begins with a review of carbon-based nanomaterials and their applications in energy storage and conversion devices. CNWs, synthesized through plasma-enhanced chemical vapor deposition (PECVD), offer unique structural advantages that facilitate ion transport and charge storage. However, their application is hindered by difficulties in achieving conformal coatings. Conventional deposition methods such as chemical vapor deposition (CVD) and electrochemical anodic deposition result in uneven coatings and agglomeration, failing to penetrate the intricate inter-wall regions of CNWs. The thesis introduces atomic layer deposition (ALD), particularly its plasma-enhanced variant, as a promising solution. ALD provides precise thickness control through self-limiting surface reactions, making it ideal for coating high-aspect-ratio structures like CNWs. PEALD offers additional benefits such as lower processing temperatures and enhanced surface reactivity.

This thesis details the synthesis of CNWs using a microwave plasma-enhanced chemical vapor deposition (MPECVD) process. CO and H2 gases were introduced into a quartz discharge tube at controlled flow rates and pressure conditions to initiate CNW growth. The resulting CNWs were analyzed using scanning electron microscopy (SEM), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). Raman spectra confirmed the characteristic D and G bands, indicative of a nanocrystalline graphene structure. XPS analysis revealed the presence of oxygen-containing functional groups, which play a crucial role in ALD nucleation. To optimize the PEALD process, the effect of oxygen plasma treatment on CNWs was examined at varying plasma distances. SEM analysis showed that closer plasma exposure led to significant structural degradation, while longer plasma distances (40 cm) minimized damage while still enhancing surface reactivity. Raman spectroscopy confirmed a decrease in the D/G intensity ratio with closer plasma distances, indicating defect reduction. XPS analysis showed an increase in oxygen functional groups at shorter plasma distances, further supporting the need for an optimized plasma exposure distance to balance functionalization and structural preservation.

The deposition of MnOx thin films was carried out in a custom-built remote plasma ALD system. A manganese precursor, tris(2,2,6,6-tetramethyl-3,5-heptanedionato) manganese (Mn(thd)3), was used alongside oxygen plasma as a reactant. The ALD process consisted of four sequential steps: precursor injection, evacuation, oxidation, and a final evacuation. The remote plasma setup was

designed to prevent CNW structural degradation while ensuring uniform deposition. Growth per cycle (GPC) measurements showed a deposition rate of approximately 5 pm/cycle, with negligible incubation delays. The optimization of precursor feed time and plasma exposure conditions led to uniform MnOx coatings on CNWs, including in the inter-wall regions, which had been a major challenge in previous studies.

Various characterization techniques were employed to confirm the conformal deposition and material properties of MnOx thin films. SEM and SEM-EDS confirmed the uniform coating of MnOx along the CNW structure without agglomeration or preferential deposition at the edges. X-ray Diffraction (XRD) showed the crystalline Mn3O4 phase after 5000 ALD cycles. Raman Spectroscopy verified that the graphene lattice was preserved post-deposition. X-ray Photoelectron Spectroscopy (XPS) analyzed the chemical composition, oxidation states, and surface bonding characteristics of MnOx films. Electrochemical Characterization through cyclic voltammetry (CV) measurements demonstrated superior capacitance behavior in MnOx/CNW composites compared to untreated CNWs, indicating improved energy storage performance.

This study successfully demonstrated that PEALD enables the conformal coating of MnOx on CNWs while preserving their structural integrity. The optimization of plasma distance (40 cm) was critical in achieving uniform deposition without damaging the CNWs. Electrochemical tests confirmed that MnOx/CNW composites are promising candidates for supercapacitors and other energy storage applications. Future work will explore the scalability of the PEALD process for large-area applications, the effect of varying MnOx film thickness on electrochemical performance, and the potential integration of other functional materials to enhance the capacitance and stability of MnOx/CNW electrodes. This research contributes to the development of high-performance electrode materials by addressing the longstanding challenge of conformal coating on complex nanostructures, paving the way for advancements in energy storage technologies.