TU/e

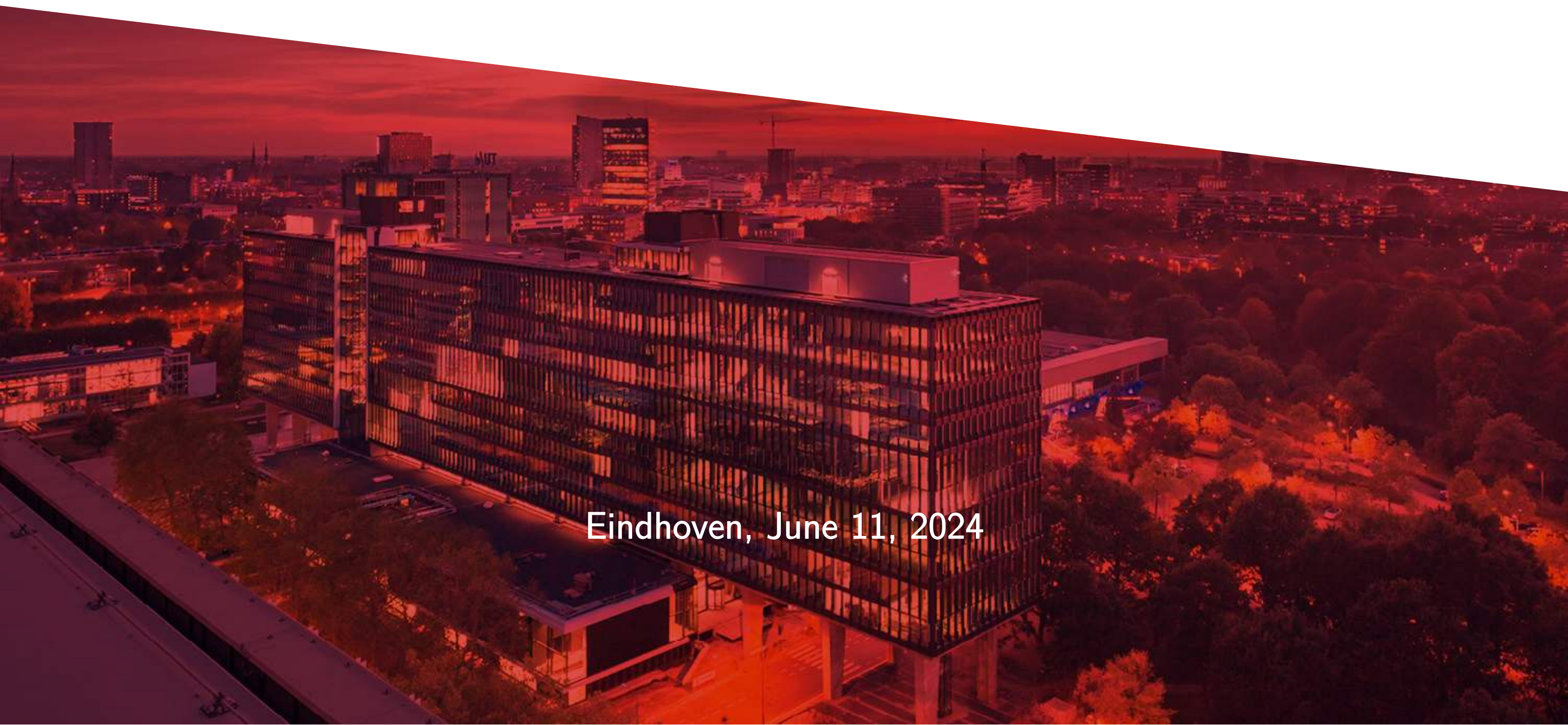
Effect of annealing on the crystal structure of $LiNiO_2$ PEALD thin films

Bachelor End Project 2023-Q4
Department of Applied Physics
Plasma and Materials Processing
10 ECTS

S.T.J. Beijers 0915183

Supervisors:
Prof. Dr. M. Creatore
M.J. Pieters, MSc

This work follows the TU/e Code of Scientific Integrity



Eindhoven, June 11, 2024

Abstract

The demand for high performance batteries powering such things as the internet of things and EVs, have pushed lithium-ion batteries (LIBs) to ever-higher capacities. To this end, Ni-rich cathode materials with high specific capacities have been exploited. However, to further improve them, challenges concerning the structural instabilities and interfacial reactions between electrolyte and cathode must be overcome. To investigate and gain insight into these problems, $LiNiO_2$ (LNO) thin films may be used as a model. In this report, the annealing of LNO thin films, deposited using plasma enhanced atomic layer deposition on stainless steel substrates (SS) is investigated. Based on literature, the effects of the annealing parameters consisting of the atmospheric composition, maximum temperature, holding time, heating rate and cooling rate on the crystallinity of LNO thin films were considered. LNO thin films were grown using Alanis and Lider as precursors, and O_2 plasma as a co-reactant in an ALD supercycle approach to obtain the desired stoichiometry. The thin films were characterized using X-Ray Diffraction (XRD), Spectroscopic Ellipsometry (SE) and X-Ray Photoelectron Spectroscopy (XPS) In-situ SE showed a growth per supercycle (GPSC) of 0.19 nm/cycle for a total thin film thickness of 73 nm. XRD confirmed that the pristine LNO thin films showed no crystalline LNO. As a reference point, also based on literature, a baseline anneal was done whereafter, the mentioned annealing parameters were systematically varied and compared to reference powder diffractograms using XRD. XRD revealed that the samples showed peaks likely belonging to rocksalt NiO (111) and spinel $NiFeO_4$-like (111) and (222) structures. Faint evidence was found for LNO presence from the (018) peak. This resulted from the SS substrate and LNO thin film mixing, which was confirmed by an XPS depth profile. Finally, a combined anneal was done for which the annealing parameters are based on the values for which the highest crystalline growth were observed by XRD. The combined anneal showed a lower presence of $NiFeO_4$-like phases than a previous sample, which indicating interplay between the annealing parameters. In conclusion, the annealing results in severe mixing of the thin film and the SS substrate. This is paired with the formation of NiO and the $NiFeO_4$ family of crystal phases, but not the desired layered LNO phase. The fabrication of layered LNO by PEALD and annealing remains promising, given the potential for using alternative substrates or coatings to prevent mixing, as well as the availability of a wide variety of annealing methods and parameters.