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# The effect of annealing on the crystal structure of $\text{LiNiO}_x$ thin films deposited by atomic layer deposition

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# 1 Abstract

Nickel-rich layered oxides show high potential for use as cathodes in lithium-ion batteries (LIB), as they can offer high energy densities. The downside of Ni-rich layered oxides lies in its structural instability and the interfacial reactions between cathode and electrolyte. To get an insight in the problems surrounding the Ni-rich layered oxides and to find solutions to the structural instability, a pure Ni layered oxide, LiNiO<sub>2</sub> (LNO) thin film was developed in this project, for further use as a cathode model system. LNO thin films were deposited using plasma enhanced atomic layer deposition (PEALD) and were annealed after deposition in order to change the amorphous structure to a layered structure. LNO was grown by deposition of supercycles and the ALD process used LiHMDS and NiMeAMD as precursors and a  $O_2$  plasma as coreactant. The thin films were deposited on a silicon substrate with and without a TiN barrier layer. The thin films were studied using in-situ spectroscopic ellipsometry (SE), x-ray diffraction (XRD) and x-ray photoelectron spectrometry (XPS). The in-situ SE measurements showed a growth per supercycle of LNO of 0.4 nm. Annealing the LNO thin films on the silicon substrates resulted in Si-migration from the substrate into the thin film, as seen in the elemental depth profiles measured by XPS. These depth profiles showed a larger presence of Si up to 20 atomic % in the thin film after annealing, while a lower Si-content of 10 atomic % was present before annealing. The Si-content before annealing is most likely present due to the LiHMDS precursor used in the ALD recipes. To prevent the Si-migration, a TiN barrier layer was used. From the XRD spectra of the annealed LNO thin films on TiN, the TiN barrier material was found to oxidise due to annealing at a temperature of 550 °C and higher. From the depth profiles of the annealed LNO on the TiN barrier, it was found that the Ti from the TiN barrier material migrates through the LNO sample due to annealing at temperatures between 500 - 700 °C. It was concluded that the TiN on its own is not likely to not function well as a barrier material in the case of annealing the LNO thin films above 500 °C. Either a different barrier material should be used, or a second barrier layer should be deposited over the TiN to prevent oxidation and migration of the TiN.

Some evidence of layered LNO was found after annealing the LNO thin films on the TiN layer above temperatures of 600 °C, although more research is necessary to determine the quality of these findings. Annealing the LNO thin films deposited using ALD is a promising method for creating layered LNO thin films, if the barrier layer can be optimised and the Si-contamination can be removed.

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# 2 Introduction

Currently, potential buyers of electric vehicles (EVs) are steered away from buying EVs due to concerns about the range the cars can travel on a single charge. However, EVs are preferred to gas-powered cars, as the carbon emissions of EVs is lower compared to that of gas-powered cars [1]. Ideally, the range of EVs should be increased in order to convince the potential buyers of EVs to drive these cars, such that current climate goals can be met.

EVs store their energy in batteries, which require a high energy density, such that they do not take up a large volume in the EV and do not excessively weigh down the car. Thus, increasing the energy density of the batteries is the best way to increase the range of the EVs compared to increasing the battery size. Currently, the batteries which offer the highest energy capacity on the market are lithium-ion batteries (LIBs). For LIBs, the energy density mostly depends on the choice of anode and cathode. Currently, the anode material is still the same graphite anode as it has been for decades and the most common cathode material is a layered  $\text{LiCoO}_2$  (LCO) cathode [2]. The best way to improve the battery energy density is by choosing a cathode material with better characteristics than the LCO cathode. Currently, promising cathode materials are Ni-rich layered oxides, as they offer higher energy densities than the LCO cathode.

The LIB with a LCO cathode has a theoretical capacity of 274 mAh  $g^{-1}$  [3]. However, the LCO cathode batteries suffer from a severe capacity decay after cycling the battery at maximum capacity. To reduce the capacity decay, the battery is used to half its maximum capacity. Thus, the practical capacity of LCO lies at 135 mAh  $g^{-1}$  with a voltage of 3.0 to 4.2 V vs. Li/Li<sup>+</sup>[3, 4]. The energy density of the LCO battery can be improved by substituting cobalt by a different transition metal, such as manganese or nickel. In general, the energy density increases with increasing Ni-content. When the Ni-content in these materials with a layered crystal structure is above 80 %, we speak of Ni-rich layered oxides [2]. The downside of increasing the Ni-content in the cathode material is the increase in structural instability. As such, Ni-rich layered oxide cathodes will show large structure changes due to cycling, making them not viable for LIBs. In order to increase the structure stability, different elements such as aluminium and manganese can be added to the cathode [2]. This is the case for Ni-rich layered  $\text{LiNi}_x \text{Mn}_u \text{Co}_z O_2$  (NMC) cathodes, which currently are the most interesting cathodes for the industry [3, 5]. The Ni-rich layered oxides are interesting, because of their high capacity, which is expected to increase when the structure stability of the layered oxides is increased. In addition, the current trend is to increase the Ni-content in the layered oxides to increase the capacity, which would ideally lead to a 100 % Ni-content. We can then speak of LiNiO<sub>2</sub> (LNO), which would have the highest theoretical capacity of all the Ni-rich layered oxides. The LNO has about the same theoretical capacity as LCO, with it being at 275 mAh  $g^{-1}$ , but as LNO is not limited to a practical capacity of half its maximum capacity, the cathode offers a higher rechargeable capacity of 150 mAh  $g^{-1}$  for a voltage range of 2.5 - 4.2 V vs. Li/Li<sup>+</sup>[3, 6]. However, it is expected that the capacity of the LNO cathode can be increased above 150 mAh  $g^{-1}$  when the stability of the LNO material is improved. This high capacity would be useful for electric vehicle batteries.

The LNO material was already identified in the 1990s [7]. LNO has not yet been commercialized due to difficulty in producing the material and due to the structural instabilities of the material [2, 8]. However, LNO is a useful material in research for new batteries, as its material properties can be investigated in order to gain an insight in other Ni-rich layered oxides. For the LNO cathodes, the problems at the cathode-electrolyte interface are the main bottlenecks, as unknown processes at this interface prevent the commercialisation of Ni-rich layered oxides. In order to solve these problems, thin film model systems need to be made of the LNO cathodes, that can be used to study the interfacial processes.

This project focuses on developing crystalline LNO thin films using plasma Enhanced Atomic Layer Deposition (PEALD) and post-deposition annealing. ALD is a strong method for depositing uniform and conformal thin film layers onto substrates. There has as of yet not been much research done on creating structured LNO using this method. One paper has been published on the deposition of lithium-nickel-silicon-oxide thin films using ALD by Maximov et al. [9]. In this paper, the thin film as

deposited by ALD has been annealed at 800 °C in order to form structured LNO. Although they did not succeed in showing layered LNO using X-ray diffraction due to Si-contamination from the LiHDMS precursor, the presence of LiNiO<sub>2</sub> after annealing was showed using selected-area electron diffraction. ALD together with post-deposition annealing may provide an effective way to create layered LNO thin films, which can be used for thin film models of the LNO cathode material.

In this project, it has been observed that LNO as deposited using ALD has an amorphous structure. It is expected that the amorphous structure of the LNO material prevents the lithium-ions from being extracted out of, or inserted into, the LNO material, which is a necessary process for the discharging and charging of LIBs. In order to allow the Li-ions to diffuse through the LNO layer as grown by ALD, its structure must be changed from amorphous to crystalline. One way to do this is by annealing the sample after the ALD deposition. For different materials, it has been observed that annealing changes the crystal orientation or the lattice ordering of the material. This was the case for LCO [10], for Ni-rich layered LiNi<sub>x</sub>Mn<sub>y</sub>Co<sub>z</sub>O<sub>2</sub> cathodes [5] and for high voltage spinel LiNi<sub>0</sub>.5Mn<sub>1</sub>.5O<sub>4</sub> cathodes [11]. In addition, Maximov et al. has already attempted annealing LNO thin films as grown by ALD [9]. The goal of this BEP project is to determine the effect of annealing on the crystal structure of the LNO thin film as deposited by ALD.

In this project, the crystal structure of LNO thin films deposited by ALD are analysed before and after annealing. LNO thin films are deposited on silicon wafer substrates with and without a TiN barrier layer on the substrate. The characterisation is done using in-situ spectroscopic ellipsometry (SE), X-ray diffraction (XRD) and X-ray photoelectron spectrometry (XPS). From the characterisation, it was found that the TiN coating layer on its own is likely to not function well as a barrier layer, as the TiN oxidises above an annealing temperature of 550. It was concluded that other (combinations of) barrier layers should be tested. In addition, evidence of layered LNO was found by annealing at temperatures above 600 °C.

The report begins by introducing the theory behind the deposition methods and analysis methods in chapter 3. Afterwards, the experimental details concerning the set-up of the experiments and the procedures behind the measurements are shown in chapter 4. Next, the results of the experiments are shown and discussed in chapter 5; The growth, structure and material composition of the LNO films by ALD is shown. The change in the crystal structure and layer composition of the LNO films after annealing is shown for the LNO thin films on the Si-substrate with and without the TiN layer. Lastly, a conclusion on the effect of annealing on the crystal structure of LNO and the efficacy of the TiN barrier layer is drawn in chapter 6.

# 3 Theory

In this chapter, the theory behind the methods and tools for developing and analysing the LNO thin films will be shown. section 3.1 explains how ALD works what choices can be made in designing an ALD recipe. In section 3.2, the types of crystal structures which can be present in LIB thin film cathodes and why the layered crystal structure is preferred are explained. In addition, the method of annealing the thin films in order to change their structure type is described. Section 3.3 explains the theory behind Spectroscopic Ellipsometry and its uses in determining the thin film thickness, section 3.4 is about the theory behind X-ray diffraction and how it can be used to measure the thin film structure and finally, 3.5 shows the theory behind x-ray photoelectron spectrometry and how it can determine the thin film elemental composition.

## 3.1 Atomic Layer Deposition (ALD)

Atomic Layer Deposition (ALD) is a useful method for depositing uniform thin films with high control, over for example, the layer thickness and the elemental composition [12]. Similarly to Chemical Vapor Deposition (CVD), a substrate in a vacuum chamber is exposed to a reactive substance in gaseous phase. This reactive gas is termed as a precursor. For CVD, multiple precursors are present at the same time in the chamber; These precursors react in the gas phase and deposit on the substrate surface. This is not the case for ALD, where only one precursor is present at a time. This precursor will instead engage in a self-limiting reaction with the surface. The precursor forms bonds with the available surface sites, until the precursor has fully reacted with the surface. This self-limiting behaviour and uniformity of the thin films is what makes ALD a useful deposition method. The thin film will be a uniform thickness in every location, even when some areas experience a lower gas flow. ALD is also able to grow conformal thin films in more challenging 3D structures.

After the precursor step has saturated the surface, the precursor is pumped out of the vacuum chamber in a purge step. The purging duration should be long enough to get rid of a sufficient amount of precursor molecules. After the purging of the precursor has been completed, a different reactive substance, called the coreactant, is introduced into the chamber. This coreactant will also react with the surface by exchanging binding groups with the ligands of the adsorbed precursor of the precursor step. Again, this step is self-limiting. The coreactant will change the surface ligands such that the precursor can again react with the surface. Following the coreactant step is again a purging step. These four steps after each other form one whole cycle. These cycles can be repeated as often as is necessary to get the desired thin film thickness.

There are two kinds of coreactants, thermal coreactants and plasma coreactants, which both have their positives and negatives. When using thermal ALD to grow a thin film, a higher reactor temperature is required in order to let the reactions proceed [13]. Often, temperatures between 20 °C and 350 °C are used. H<sub>2</sub>O is used as coreactant for thermal processes. As water is very difficult to pump out of chambers, high purge times are required in thermal ALD processes. Thermal ALD leads to good thin film conformality for even difficult substrate surface structures. The downside of thermal ALD is the limited amount of precursors that can be used with this method.

Plasma enhanced ALD (PEALD) uses a plasma as coreactant for the ALD process. Due to the high reactivity of plasmas, lower reactor temperatures can be used. For PEALD, water does not need to be used as coreactant, thus reducing the purge times. PEALD has more variety in which plasmas can be used, although the most common plasmas are the  $H_2$  plasma and  $O_2$  plasma. PEALD also offers a higher choice of precursor materials, thus PEALD is a much more versatile method compared to thermal ALD. PEALD has a higher growth rate, offers better thin film material properties and has a good control over the film composition. The downsides of PEALD are the reduced conformality of the thin films and the increased reactor complexity due to the usage of plasma sources. In general, PEALD is seen as a better method compared to thermal ALD [14, 15]. Due to the benefits of growing thin films using plasma enhanced ALD, this method will be used for growing the LNO thin film layers.

It is possible to grow ternary materials, which are materials consisting of three elements, by ALD by using two different precursors [16]. This will lead to more complicated ALD recipes, which may use a supercycle approach. With the supercycle approach, one supercycle exists of a number of cycles of

precursor 1 followed by a number of cycles of precursor 2. The supercycles can be repeated as often as needed for the required thin film thickness. This approach is used for growing the LNO thin films in this project.

As has been mentioned before, the reactions in ALD steps require saturation to happen in order for the thin film to grow uniformly. This saturation must be investigated when creating new ALD recipes in order to get reproducible results. For this reason, the growth per cycle (GPC) is analysed as a function of the precursor and coreactant dose times. The GPC is found by measuring the thin film thickness as a function of the number of cycles deposited. For analysing the saturation, first the coreactant dose time and both purge times are chosen large enough such that saturation certainly takes place the corresponding steps. Then, the GPC of the ALD deposition is determined for several different precursor dose times and from these measurements, a saturation curve is plotted. The saturation curve, as seen in example figure 1(a), shows the GPC as a function of the dose time. It is possible to determine when we reach saturation for the precursor step by determining from which dose time and onward the GPC does not change. This same process is repeated for the coreactant step, where this time the precursor dose time is taken large enough for saturation to take place.

Also the saturation curves of the purge times must be determined. When the purge time is too small, both precursor and coreactant are present in the same chamber, causing reactions between the two, which leads to unwanted CVD growth, as seen in example figure 1(b).



**Figure 1:** Figure showing examples of ideal saturation curves for (a) the coreactant dosing time and for (b) the purge time. Saturation is reached at the plateau where the GPC does not change for increasing times. Figure taken from AtomicLimits [12].

#### 3.2 Effect of annealing on material structure

The crystal structure of the cathode material is of importance for its electrochemical characteristics. Most cathode materials have a layered crystal structure and as such, are layered oxides. Layered oxides with a rocksalt structure have a  $\alpha$ -NaFeO<sub>2</sub> structure type and belong to the R $\bar{3}$ m space group [3]. In the case of layered LNO, layers of lithium are followed by nickel layers in the form of alternating layers. The Li and Ni are surrounded by oxygen. For the case of layered  $\alpha$ -LiCoO<sub>2</sub>, the structure can be seen in figure 2a. The green spheres are the Li-ions and the blue octahedra are CoO<sub>6</sub> octahedra. From the structure, it can be seen that Li-diffusion is allowed in parallel planes.

Another possibility is the spinel structure type for LIB cathodes [17]. This structure also provides good qualities for LIB cathodes. Due to its structure, as seen in figure 2b, 3D lithium ion diffusion channels are present which allow for fast (dis)charging. In this project, layered oxides are preferred instead of spinel cathodes, because layered oxides have 1 Li-ion per transition metal, while spinel has 0.5 per transition metal. Thus, layered oxide materials have higher energy densities than spinel materials.

Before the start of this project. it has been seen that the growth of LNO with ALD does not result in the desired layered LNO structure. Instead, the structure appears to be amorphous. This has also been observed by Maximov et al. [9], who also deposited LNO thin films by using ALD. The amorphous structure is unwanted, both because it is desired to study the layered LNO structure and because it is expected that the amorphous structure prevents the Li-ions from diffusing out of the material, which would prevent its use for LIB cathodes.

One possibility to change the thin film structure from amorphous to crystalline is to anneal the amorphous thin films at high temperatures. It is often the case that cathode thin films are annealed after they have been deposited, in order to enhance its electrochemical properties. The positive effects of annealing have been shown for materials such as LCO thin films [18] and for Ni-rich layered  $\text{LiNi}_{0.6}\text{Co}_2\text{Mn}_{0.2}\text{O}_2$  thin film cathodes [19, 20]. Maximov et al. used the same approach of annealing LNO thin films grown by ALD and were able to show the presence of  $\text{LiNi}_{0.2}$  after annealing at 800 °C.





(a) Layered  $\alpha$ -LiCoO<sub>2</sub> (b) Spinel LiMn<sub>2</sub>O<sub>4</sub> **Figure 2:** Crystal structures of (a) Layered  $\alpha$ -LiCoO<sub>2</sub> and (b) Spinel LiMn<sub>2</sub>O<sub>4</sub>. Li ions are shown as the light green spheres. Figures taken from Chakraborty et al. [3].

#### 3.3 Spectroscopic Ellipsometry (SE)

The growth of the thin film layer can be investigated using in-situ Spectroscopic Ellipsometry (SE) [21]. This is a non-invasive, quick measurement method which uses the change in polarisation of light being reflected from the thin film surface to determine several thin film properties, such as its optical constants or the layer thickness. An ellipsometer measures the values of  $\Psi$  and  $\Delta$ , where  $\tan \Psi$  is the amplitude ratio upon reflection and  $\Delta$  is the phase difference upon reflection.  $\tan \Psi = X/Y$  gives the relative amplitude between the maximum of the x- and y-component when the oscillation of light takes place in the x,y-plane.  $\Delta$  gives the time interval between the maximal value of the y-component and that of the x-component.

Figure 3 shows an illustration of an in-situ SE mounted onto an ALD machine. When a SE measurement is started, the light source emits a light beam onto the thin film in the ALD chamber. This light gets reflected and experiences a polarisation shift due to the thin film layer and the substrate underneath. The reflected light hits the detector, which measures the polarisation of the light.

In-situ spectroscopic ellipsometry can be used in-between deposition steps of the ALD process, thus making it easy to measure the thickness of the thin film after every step or cycle. To determine the layer thickness from the measured polarisation, the data must be fitted to an optical model of the thin film layers. The optical model depends on the properties of the material, a Cauchy model can be used for transparent materials and a general oscillator model can be used for non-transparent materials.



**Figure 3:** Illustration showing the setup of an in-situ SE for ALD depositions. The light source at the left emits a light beam consisting of a spectrum of light waves onto the sample in the center. The sample reflects and shifts the polarisation of the incoming light. The detector on the right side receives the reflected light and measures the polarisation of the light. Figure taken from AtomicLimits [22].

#### 3.4 X-ray Diffraction (XRD)

Using X-ray Diffraction (XRD) measurements on the ALD thin films, it is possible to determine the crystal structures which are present in the thin film. In this section, an overview of the theory behind XRD and the practical applications of XRD will be given.

The wavelength of X-ray light is in the order of angströms. This small size allows X-ray beams to scatter due to the lattice planes, while the high energy of the X-rays lets the rays penetrate into the material. When an X-ray wave hits an electron of an atom in the material, its energy causes the electron to vibrate. This electron will then send out light of around the same energy as the incident beam. The electron thus scatters the incident X-ray wave in a circular wavefront. When a second electron scatters an X-ray, this causes a second circular wavefront, which can interfere with the first wavefront. This causes interference effects to take place. In the case that X-ray light is incident on a periodic lattice of atoms, this light will be diffracted into a linear wavefront due to the interference effects of the scattered light from the electrons (see fig 4)[23].



**Figure 4:** Figure showing the development of a linear wavefront from circular wavefronts in a periodic lattice. Figure taken from opengeology [23].

Following the theory of the above paragraph, Bragg has created a simple mathematical relation to determine the diffraction of light on parallel planes of atoms [24],[25]. When an X-ray beam is incident on a crystal, the periodic lattice planes in the crystal structure will partially reflect the X-ray beam, as shown in figure 5. Light which is incident on a lattice plane at an angle of incidence  $\theta$  will be

reflected under the same angle  $\theta$ .

When another parallel X-ray beam is reflected by a second parallel lattice plane which is spaced a distance d apart from the first, the beam will travel an extra distance compared to the beam reflected from the first plane. This extra distance, equal to  $2d\sin\theta$ , causes a phase delay. Due to this phase delay, the two beams interfere. Constructive interference of two beams from two nearest lattice planes will take place according to Bragg's law,

$$2d\sin\theta = n\lambda,\tag{1}$$

where n is an integral number and  $\lambda$  is the wavelength of the incident light. Bragg's law tells us that in order to have constructive interference of light, the difference in path length between the two reflected beams should be equal to an integer times their wavelength. Due to the high number of lattice planes in a crystal, only beams for which constructive interference takes place will survive. All other beams will destructively interfere. Thus, the angles  $\theta$  at which the constructive interference is present will let us know the lattice spacing d between the parallel lattice planes. When the relative intensities of the diffraction peaks are also known, it is possible to determine the structure cell of the crystalline material. The relation between the relative peak intensity and the structure cell composition is more intricate, but its derivation can be found in Introduction to Solid State Physics by Kittel [25].



Figure 5: Figure showing an X-ray beam incident under an angle  $\theta$  on parallel crystal lattice planes with lattice spacing d. The beams are reflected under the same angle and beams reflected from different planes experience a phase difference. Figure taken from Kittel [25].

X-ray diffractometers are used to measure the XRD spectra of thin films. As can be seen in figure 6, the diffractometer consists of an X-ray source which beams light onto a sample in the sample stage. The reflected light is detected by a detector. For the setup with the emitter and the detector, light will come in at an angle of incidence  $\theta$  and is reflected at the same angle  $\theta$ , thus the reflected X-ray beam makes an angle of  $2\theta$  with the emitter. This  $2\theta$  angle is measured by the detector. For this reason, it is usual that XRD spectra show the intensity peaks as a function of  $2\theta$  instead of  $\theta$ .

Both X-ray source and detector are usually rotated around the sample to scan for all reflection angles. However, it is also possible to keep the emitter at a fixed angle, while the detector moves around to measure the reflected light. This is the case for Grazing Incidence-XRD (GI-XRD), which will be used for this project. With GI-XRD, the emitter is kept at a fixed place making an angle of incidence of less than 2° to the thin film surface plane. This way, the X-ray beam can travel longer through the thin film material before it would enter the substrate. As thin film samples down to 20 nm thickness will be analysed, the usual XRD setup would have X-ray beams penetrating into the substrate, such that also X-ray beams reflected in the substrate will be detected and intensity peaks from the substrate are visible in the spectrum. With GI-XRD, the X-ray beam has a smaller penetration depth and therefore an increased surface sensitivity, allowing us to only measure peaks from the thin film sample.

In practice, XRD spectra of a large amount of materials in powdered form have already been determined and analysed to find their crystal structure. The data on XRD spectra of materials has been gathered into a database. One of these databases is the ICDS database from FIZ Karlsruhe. By simply comparing the measured XRD spectra to the XRD spectra of materials in the database, conclusions about the material structures present in the thin film can be drawn. As the materials in the database have been turned into powders, its crystal plane orientations have been randomly distributed, such that it is expected to see diffraction peaks of all possible crystal planes with the correct relative intensity [23][26]. When performing XRD measurements on thin films grown using ALD, it is not likely to see all crystal plane orientations in the thin film. There will be a preference to grow some orientations over others, leading to a difference in relative intensities compared to the powder spectra. Thus, it is not possible to determine the relative amount of material structures present in the thin film.



Figure 6: Figure showing an X-ray diffraction machine. At the left side, the X-ray source can be seen. This source emits X-rays onto the sample in the sample holder. The reflected X-ray beams are detected by a detector at the right side. Both source and detector are able to rotate around the sample, although it is usual for GI-XRD to keep the source fixed and move the detector twice the distance. Figure taken from opengeology [23].

#### 3.5 X-ray Photoelectron Spectrometry (XPS)

X-ray Photoelectron Spectrometry (XPS) is a measurement method which allows us to determine the elemental compositions in a material and the bindings of atoms with other elements [27, 28]. XPS makes use of the photoelectric effect, where core electrons hit by photons of sufficient energy can be launched away from the atom, as seen in figure 7. XPS is a surface sensitive measurement method, as the photoelectrons measured mostly come from the sample surface.



Figure 7: Illustration of the photoelectric effect. X-ray light is incident on a surface and hits an electron in the material, causing the electron to be emitted from the surface in the form of a photoelectron. Figure taken Diamond Light Source [29].

When X-ray light of sufficient energy hits an electron in an atomic orbital, the electron will be emitted with a certain kinetic energy. This kinetic energy can be measured using a hemispherical electron energy analyser [30]. The photon energy of the incoming X-ray light,  $E_{X-ray}$ , is known. In order for an electron to be emitted after being hit by a photon, the X-ray photon must overcome the electron binding energy barrier. Using the law of conservation of energy, we can find the binding energy of the emitted electron in a simplified case using

$$E_{\text{binding}} = E_{\text{X-ray}} - (E_{\text{kinetic}} + \phi), \qquad (2)$$

where  $E_{\text{binding}}$  is the electron binding energy,  $E_{\text{kinetic}}$  is the kinetic energy of the emitted photon and  $\phi$  is the work function of the electron energy analyser.

The X-ray energy is high enough for electrons from the inner atomic orbital to be kicked out of their shell. These electrons are bound the strongest to the core and have binding energy values that are unique to each element. This allows us to determine the elements present in a measurement sample. An XPS measurement of a thin film can be shown in a plot where the number of detected electrons is plotted against the binding energy of the detected electrons. From the plot, is can be seen for which binding energies a peak is present. By comparing the peak energies to the standard binding energies of the electron orbitals per element, it is possible to find out which elements are present in the thin film. It is possible to determine the elemental composition of the thin film from its XPS spectrum as the atomic percentages of the elements in the thin film can be determined from the peak areas of the XPS spectrum.

The electron binding energy of an element can also be shifted due to a change in the electronegativity of the surrounding atoms [31]. An element can have different bindings to other atoms. These atoms may vary in their electronegativity. More electronegative atoms will partially draw away the electrons of the element they are bonded to. As an example, carbon may be bonded as a C-H or a C-O bond. As oxygen is more electronegative than hydrogen, the electrons around the C in the C-O bond are drawn away stronger. The remaining electrons in the C of the C-O bond will then see a stronger positive charge of the carbon nucleus and as such are bound stronger to the nucleus. Elements which have more bonds with electronegative atoms will thus have a chemical shift to higher electron binding energies. From this chemical shift, the chemical state of an atom can be determined.

With usual XPS measurements, the signal of the surface is the greatest. It is not possible to measure the electron binding energies deeper in the thin film, as the emitted photoelectrons must find their way out the material and into the energy analyser without being stopped in their path. As emitted electrons can experience inelastic collisions, recombination or material excitation when travelling through the thin film, it quickly becomes less likely to detect electrons which come deeper from in the material. However, it is possible to study the composition deeper in the material by employing the use of ionbeam etching; By hitting the sample with an ion-beam, the surface layer can be sputtered away, leaving the inner part of the thin film exposed. By increasing the sputtering time, a thicker layer is sputtered away from the thin film. The material composition can then be determined as a function of the sputtering time.

Some elements are more prone to being sputtered away by the ions. In general, materials with lower atomic mass will be sputtered more than those with a higher atomic mass. We can thus see that preferential sputtering will take place during depth measurements [32]. Due to this preferential sputtering, it is not possible to accurately determine the amount of each element present at a certain thin film depth. The atomic ratios may be influenced due to this effect of preferential sputtering. Thus, only an estimate of the atomic ratios at a certain depth can be made. In addition to this preferential sputtering, the ion-beams also cause a change in charge composition on the material [33]. A positive charge is built up on the thin film surface, as the electrons are emitted from the thin film due to the ion-beam. The binding energy peaks are shifted and sometimes distorted due to the charge buildup. In order to compensate for this positive charge buildup, a flood gun shoots electrons onto the sample. However, it is possible that the flood gun emits too many electrons and causes a negative charge buildup onto the sample. In that case, there will still be a shift in the binding energy peaks and as the measured peaks positions are not accurate, it is not possible to determine the chemical state of the elements in the material when using ion-beam etching.

## 4 Experimental details

In this section, the steps that are taken when depositing and analysing the LNO thin films are explained. Section 4.1 shows the recipe of the ALD process. The details of the annealing oven, including the temperatures at which the samples are annealed, are explained in section 4.2, section 4.3 explains how the thin film thickness is measured using the in-situ SE. The measurement settings of the XRD setup are explained in section 4.4. The methods of determining the depth profile compositions of the thin films using XPS are explained in section 4.5 and lastly, the storage method of the thin films is shown in section 4.6.

#### 4.1 Growth of thin film LNO by ALD

The deposition of the LNO thin films is done using the Flexal1 ALD system from Oxford Instruments. The sample table is kept at a temperature of 200 °C. Li<sub>2</sub>O (LiO), NiO and LNO were deposited by ALD, where a bis(N,N'-di-tert-butylacetamidinato)nickel(II) (NiMeAMD) precursor was used to grow the NiO layers and a Lithium bis(trimethylsilyl)amide (LiHMDS) precursor was used to grow the LiO layers. The precursor structures can be seen in figure 8. The NiMeAMD precursor is heated to a temperature of 90 °C and is supplied to the chamber using a vapour drawn process, while the LiHMDS is heated to a temperature of 85 °C and is supplied using a bubbled process using an Ar carrier gas with a 100 sccm flow rate. For both the NiO and the LiO layer depositions, an O<sub>2</sub> plasma was used as a coreactant.



Figure 8: Molecular structures of (a) NiMeAMD and (b) LiHMDS.

At the start of the project, saturation curves for the PEALD growth of NiO thin films and LiO thin films on the same ALD machine were made. The saturation curves have not been finished, but can be found in appendix A. Based on these saturation curves, the dose times and purge times for the deposition recipes in this project were taken large enough to ensure saturation. The recipes of the NiO and the LiO cycles can be seen in figure 9.



Figure 9: Recipes of the (a) NiO and (b) LiO cycles A cycle consists of a precursor dose, followed by a purge step, then a 200 W, 50 mTorr, 50 sscm,  $O_2$  plasma coreactant step and lastly another purge step. A LNO supercycle consists of 3 cycles of NiO followed by 1 cycle of LiO.

The LNO thin film is grown by depositing supercycles consisting of 3 cycles of NiO followed by 1 cycle of LiO. The NiO:LiO cycle ratio of 3:1 is chosen, as previous results have shown that this cycle ratio results in near-stoichiometric LiNiO<sub>2</sub>. For the LiO and the NiO depositions an SE measurement is performed every 10 cycles. For LNO depositions, an SE measurement is performed after every supercycle instead.

Monocrystalline silicon wafers with orientation (100) were used as substrate. In addition, silicon substrates with a TiN coating were used for LNO depositions. In the paper of R. Janski et al. [34], TiN has been investigated for its use as a barrier material between the active components of a Liion battery and the surrounding crystalline silicon semiconductor material. The barrier material is tested for its capability for blocking Li-ion migration into a silicon substrate. The results from the electrochemical tests indicate that TiN significantly blocks the Li-ion migration.

During the experiments which were done on the LNO thin films, it has been noticed that the Si content in the thin films of the LiO and LNO depositions was unusually high. This high Si content was not present during the first depositions done in this project. This Si-contamination could effect the formation of crystalline LNO and as such, a change has been made to the ALD recipes. A 2 s  $H_2$  plasma step was added before the  $O_2$  plasma step for the LiO (sub)cycles, while the NiO (sub)cycle was kept the same. The addition of the  $H_2$  step was successful in removing silicon in depositions with only LiO cycles, but not in removing silicon in the LNO depositions. However, no large differences have been spotted in the elemental compositions and GPCs of the LNO deposition with the  $H_2$  plasma and without it and as such, both deposition types have been used in the comparison between the effect of different annealing temperatures on the thin film crystal structure. More information about the Si-contamination can be found in appendix D.

## 4.2 Annealing the LNO thin films

As explained in section 3.2, the LNO thin films are annealed to crystallise them. The thin films are annealed in an annealing oven for times between 45 minutes to 6.5 hours and temperatures between  $500 \degree \text{C}$  and  $700 \degree \text{C}$ . The annealing time is measured from the moment that the oven is turned on to the moment the thin films are taken out of the oven. A box oven was used for annealing, but this oven has some sulphur contamination on its surface. This sulphur contamination has been seen on XPS measurements of the LNO thin films after annealing them. For the last two annealing measurements, a tube furnace has become available. This oven has been cleaned and should not expose the thin films to contamination. This tube furnace, however, is expected to take a longer time to heat up compared to the box oven, which reached a set temperature of 700 °C in about 20 minutes. The thin films were exposed to air during the annealing process. In the box oven there was a nitrogen flow, but in the tube furnace there was no flow.

#### 4.3 Measuring the thin film thickness using in-situ SE

In-situ SE measurements are done in-between the ALD cycles as explained in section 4.1. The wavelength range of the emitted light used for the SE measurements is from 1.2eV to 5.0eV.

The SE data is fitted against a model of the thin film layers. Only thin films on Si substrates are modeled using SE. When the data is fitted sufficiently well, the thin film thickness as a function of the number of cycles can be determined from the fit parameters. From this, the GPC can be found.

NiO thin films are modeled using a NiO layer model that consists of a general oscillator and a double Tauc Lorentz oscillator. LiO thin films are modeled using a LiO layer model that consists of a cauchy model. In the case of LNO grown on the silicon substrate, its optical properties appear to be similar to that of NiO on the Si substrate. As such, LNO on the Si substrate is also modeled using the general oscillator plus a double Tauc Lorentz oscillator.

In order to determine the thin film thickness of LNO depositions on silicon substrates with a TiN barrier layer, a regular silicon substrate is placed in the ALD chamber such that the SE light beam reflects of the silicon surface. Thus, a model of LNO grown on a silicon substrate can be used. The SE measurement data could be better fitted when the LNO was deposited on standard silicon substrates compared to the TiN barrier substrate. Thus, the thin film thickness can be determined

more accurately in this way. It is assumed that the LNO growth on the silicon substrate with TiN layer is the same as the LNO growth on the regular silicon substrate.

## 4.4 Determining the thim film structures using XRD

The XRD measurements were performed using a D8 discover bruker GI-XRD machine. The thin film XRD spectra were measured for angles  $2\theta$  between 15 and 70° with a step size of 0.05° and a measurement time of 3 s per step. The angle between the thin film surface plane and the X-ray emitter is kept at 1°.

The measured XRD spectra have been compared to the spectra of relevant materials in the database of ICDS from FIZ Karlsruhe. The ICDS database codes for the powder spectra of the relevant materials can be found in appendix B. From the comparison between the thin film spectra and the powder spectra, conclusions can be drawn about the presence of relevant crystal structures in the thin film.

## 4.5 Depth profiles and compositions of LNO thin films

XPS measurements were done using a ThermoFisher Scientific K-Alpha XPS system. Survey scans of the thin films are made to determine the elements present and the possible contamination of foreign elements in the thin film. Surface scans are made to find the elemental compositions in the thin film. These scans determine the electron counts in intervals of binding energies that correspond to an electron orbital of each of the chosen elements. It is difficult to measure the presence of lithium using XPS as it contains only 3 electrons. In order to improve the signal to noise ratio for lithium measurements, extra measurements must be done in the surface scans of lithium.

The background energies of the elemental peaks are fitted, such that the atomic ratios can be determined of the elements in the thin film. As explained in the theory behind XPS in section 3.5, the binding energies of elements can be shifted when they are bound to different elements.

The depth profiles are determined by sputtering the thin film using an argon ion-beam and performing a quick scan after a certain amount of sputtering time has passed. The elemental composition for every quick scan is determined, such that a plot can be made of the elemental composition as a function of the sputtering time.

#### 4.6 thin film storage

As LiO and LNO react quickly with air and air exposure leads to the formation of lithium carbonate, the LiO and LNO thin films are kept in a nitrogen-atmosphere glovebox when stored for longer times. The exposure of the thin film samples is kept to a minimum by placing the thin films into a canister with a light vacuum of about 3 mbar when they are taken out of the ALD reactor. In addition, the thin films are transported in a nitrogen atmosphere to the XPS machine. Nonetheless, exposure to air for a duration of roughly one minute cannot be prevented.

## 5 Results and discussion

In this section, the results of the project is shown and discussed. Firstly, the growth of standard depositions of LiO, NiO and LNO as measured using in-situ SE is shown in section 5.1. Next, in section 5.2, the analysis of the XRD spectra and depth profiles of the atomic compositions of LNO deposited on a Si substrate is shown before and after annealing. Lastly, the same analysis is done for LNO on a Si substrate with a TiN barrier layer in section 5.3.

### 5.1 Growth of LiO, NiO and LNO thin films

Standard depositions were done for the LiO, NiO and LNO thin films. 150 cycles were deposited for the LiO film, 350 cycles for the NiO and 50 supercycles of LNO on silicon substrates. The film growth for these depositions was measured using in-situ SE. A plot of the thin film thickness versus the number of deposition cycles can be seen in figure 10. The figure shows the number of regular cycles on the horizontal axis, such that four cycles for LNO are equal to one supercycle. It can be seen that the curves of the thickness against the number of cycles are not perfectly straight, while it is expected for ALD processes where saturation takes place during depositions. The GPC is measured starting from the 50<sup>th</sup> cycle onward. For about the first 50 cycles, the GPC is not constant. Here, the substrate is not completely covered by the deposited layer. As the precursors can adsorb with a different strength to the substrate compared to the LNO thin film, we see that the layer growth is different for the first cycles.

In-situ SE measurements are performed during the ALD process. The data is fitted with the corresponding thin film model, resulting in a fit of the thickness against the number of cycles, from which the GPC can be found. The GPC for the standard LiO is 0.11 nm. For the standard NiO it is 0.04 nm. The growth per supercycle for the standard LNO deposition is 0.4 nm. It has been observed that the GPC shows some variance for different depositions using the same settings. As the data is also fitted using a model, extra error is introduced in the values for the GPC. The magnitude of the uncertainty is unknown. It is possible to measure the film thickness with a different technique, in order to verify the results from the in-situ SE. The thin film thickness can be measured using transmission electron microscopy (TEM).



Figure 10: The thin film thickness vs. the number of cycles for standard depositions of LiO, NiO and LNO. 1 supercycle of LNO exists of 4 cycles in total.

#### 5.2 Annealing LNO on Si substrate

In order to study the crystal structure composition of the LNO thin film as deposited on a silicon substrate, an XRD measurement has been done on a LNO thin film. The XRD measurement resulted in an XRD spectrum, which did not show any peaks. As no diffraction peaks have been observed, it is

likely that the LNO thin film does not have a structured layer. The LNO thin film has an amorphous structure in that case. We expect that crystalline LNO is not formed by a simple ALD deposition. As explained in section 4.2, the LNO sample will need to be annealed to see a structure change in the XRD sample spectra.

A LNO thin film on the silicon substrate is annealed at 500 °C for longer than 2 hours. The XRD spectrum of the annealed LNO sample is shown in figure 11. Peaks that were not present before annealing can be seen from the spectrum, which means that the annealing of the sample had an effect on the crystal structures in the thin film. The diffraction peaks belonging to a NiO powder can be seen in the XRD plot. Thus, the annealing resulted in the formation of crystalline NiO. However, no presence of crystalline LNO is found, as no LiNiO<sub>2</sub> peaks are present. A peak at 27.2° can be seen, this peak could belong to a crystalline  $\text{Li}_x \text{Si}_y \text{O}_z$  material, such as  $\text{Li}_2 \text{Si}_3 \text{O}_7$ . However, not enough evidence for the presence of crystalline  $\text{Li}_x \text{Si}_y \text{O}_z$  is found. In order to verify the presence of Si in the LNO thin film, an XPS profile of the elemental composition of the thin film is made.

For this XRD measurement, a low measurement time per increment of 2 s was used. In order to improve the signal-to-noise ratio, the measurement time per increment is increased to 3 s for further XRD measurements.



Figure 11: The XRD spectrum of a standard LNO deposition on a silicon substrate, which was annealed at 500 °C for longer than 2 hours. Powder spectra of NiO,  $LiNiO_2$  and  $Li_2Si_3O_7$  have been plotted as well.

The depth profiles of the unannealed and annealed LNO thin films on the Si substrate can be seen in figure 12. The depth profiles show the elemental compositions of the thin films as a function of the sputtering time. Scans were made for each measurement to find the sample composition of O, Si, C, Li and Ni. After sputtering for longer than 1300 seconds, the silicon substrate has been reached, a plateau of a high percentage of silicon can be seen.

The depth profile of the annealed LNO thin film in figure 12b shows that a small amount of carbon has deposited on the sample surface. In the short time that the sample has been exposed to air,  $CO_2$ from the air has reacted with the sample surface. This is expected, as both LiO and LNO materials react quickly when exposed to air. Most likely, the water in the air reacts with the surface Li<sub>2</sub>O, resulting in LiOH. The LiOH in turn reacts with  $CO_2$  in the air, resulting in Li<sub>2</sub>CO<sub>3</sub> [35]. Also, it can be seen that both the nickel and the lithium content does not stay constant in the LNO sample. Near the surface, the nickel content is high and rapidly declines, while the lithium content is higher deeper in the LNO thin film compared to the surface. Due to the annealing, the Li and Ni are not evenly spread across the LNO thin film. Ideally, the lithium and nickel is spread out evenly, as this would lead to a better crystallinity of the LNO material. Compared to the depth profile of the unannealed LNO thin film, a larger amount of silicon can be seen in the annealed LNO layer. Up to 20 atomic % can be seen. The silicon from the substrate could have migrated into the LNO sample due to the annealing of the sample. This is in line with the structure peak possibly belonging to  $\text{Li}_x \text{Si}_y \text{O}_z$  at 27.2 ° seen in the XRD plot in figure 11. As also 10 atomic % Si can be seen in the unannealed LNO thin film, it is expected that the silicon from the LiHMDS precursor has also been incorporated into the LNO structure of the sample. This Si-contamination is unwanted and should be removed. Still, the Si-content is higher in the annealed thin film, indicating Si-migration due to annealing.



(a) LNO on Si before annealing

(b) LNO on Si after annealing

**Figure 12:** Depth profiles of the LNO thin film (a) before annealing and (b) after annealing at 500 °C for longer than 2 hours. For each measurement, scans were done to find the sample composition of O, S, Si, C, Li and Ni.

#### 5.3 Annealing LNO on TiN substrate

A TiN barrier material may be able to prevent the Si migration into the LNO layer when annealing the thin film. In order to test the effectiveness of this barrier material, 120 supercycles of LNO are deposited on silicon substrates with a 150 nm TiN layer on top, resulting in a LNO layer thickness of about 40 nm. The structure and elemental compositions are determined for several LNO thin films. One thin film is measured as it was deposited. The others have been annealed at different temperatures for a different duration. The LNO thin films on the TiN-coated substrate have been annealed at 700 °C for 6.5 hours and 45 minutes and at 500 °C for 45 minutes. In addition to these measurements, a second LNO deposition is performed, where a H<sub>2</sub> plasma step is included before the O<sub>2</sub> plasma step in the LiO cycles, as described in section 4.1. For these samples, again 120 supercycles have been used. These samples have been annealed for 2 hours at 550 °C and 2 hours at 600 °C.

The XRD spectrum for the as-deposited LNO thin film on the TiN-coated substrate can be seen in appendix C figure 18b. The plot only shows peaks belonging to the crystalline TiN material. From the XRD spectrum, it can be seen that a shift has taken place in the diffraction peak positions of the thin film material compared to the TiN powder. This peak shift is likely to be caused by the usage of GI-XRD instead of standard XRD. This can cause peak shifts at higher values of  $2\theta$ .

After annealing the LNO thin film on the TiN-coated substrate for 6.5 hours at 700  $^{\circ}$ C, a clear change is observed. As shown in appendix C figure 19, the annealed sample on the top left has changed colour to grey/blue compared to the un-annealed sample on the right. On the surface of the annealed sample, spots of different colours can be observed. Based on these observations by eye, it is expected that the sample structure has largely been changed and possibly destroyed. The change in appearance after annealing makes us expect that the annealing temperature and/or time was too high.

The XRD spectrum of the LNO sample on the TiN-coated substrate after annealing for 6.5 hours at 700 °C can be seen in figure 13. As most peaks belong to rutile TiO<sub>2</sub>, it is concluded that the TiN has been oxidised to TiO<sub>2</sub> due to annealing. This result agrees with the paper of Hong-Ying Chen et al. [36]. In their paper, it was found using XRD that TiN deposited on Silicon substrates and annealed in air show rutile-TiO<sub>2</sub> peaks at annealing temperatures above 600 °C. In our XRD spectrum, the other peaks at 18.7°, 36.5° and 64.4° show overlap with the peaks of the powder spectrum of LNO, although the peaks are too small to clearly indicate the presence of crystalline LNO in the sample. In addition, if the peak at 18.7° belongs to LNO, then this peak would belong to the (003) LNO crystal orientation. However, the presence of the (003) peak would lead us to expect that the (006) LNO peak at 38.0° is also present in the spectrum, but this peak is not visible in the spectrum. This makes the presence of crystalline LNO in the thin film less likely.

The LNO thin film has also been annealed at 700 °C for a shorter time of 45 minutes instead of 6.5 hours. Appendix C figure 17 shows the two spectra. There is little difference between the spectra of the two annealing times. For both, the structure change has already taken place. It can be concluded that the annealing time does not strongly influence the change in structure.



Figure 13: XRD spectrum of LNO on TiN annealed for 6.5 hours at 700  $^{\circ}$ C compared to rutile TiO<sub>2</sub>, LiNiO<sub>2</sub> and TiN powder spectra.

Next, the effect of different annealing temperatures on the crystal structures of the LNO depositions is determined. Figure 14 shows the XRD spectra for LNO deposited on the TiN barrier material after being annealed at temperatures of 500 °C, 550 °C, 600 °C and 700 °C. The XRD spectra in figure 14 do not all belong to the same LNO deposition and have also been annealed in two different ovens. The LNO films annealed at 700 °C and at 500 °C are from a regular LNO deposition on a TiN-coated substrate and are annealed in the same box oven. The samples at 550 °C and 600 °C, however, are from a LNO deposition where a H<sub>2</sub> plasma has been implemented before the O<sub>2</sub> plasma step, as explained in section 4.1.

The samples at 550 °C and 600 °C have also been annealed in a different oven, a tube oven. This tube oven does not contaminate the sample due to a contaminated oven surface. However, it does take a longer time to heat up the sample, as the oven first has to heat up a hollow glass cylinder before the sample in the cylinder is annealed. For this reason, a longer annealing time of 2 hours instead of 45 minutes is taken for the tube oven.

From the XRD spectra in figure 14, it can be seen that the samples annealed at 500 °C and 550 °C are similar to each other. They both have two sharp peaks at 43 ° and at 63 °. These two peaks coincide with the peaks of the crystalline NiO powder. The sample at 550 °C does show more smaller peaks

compared to the one of 500 °, possibly belonging to some orientations of the  $\text{TiO}_2$  crystal powder. The sample at 550 °C also shows two peaks at 25.7 ° and 55.4, which have not been observed before. These peaks are likely to belong to anatase  $\text{TiO}_2$  as can be seen in appendix C figure 21. This would also explain the peak broadening to the right side of the peak at 62.5 °, as an extra anatase  $\text{TiO}_2$  peak is present at this position.

The peaks for 600 ° and 700 ° are very similar. Both show all the peaks belonging to the rutile  $TiO_2$  powder. Both XRD spectra also show a smaller peak at 19 ° plus peaks at 36 ° and 65 °. These last three peaks are at the same position as layered LNO diffraction peaks.

From these XRD spectra, it can be seen that the TiN oxidises to  $TiO_2$  from temperatures of 600 °C and above, with the oxidation already taking place at a temperature of 550 °C, where we find anatase  $TiO_2$  XRD peaks. These findings correspond quite well to the findings of Hong-Ting Chen et al. [36].

From figure 14, we find some evidence of crystalline LNO in the thin layer after annealing at a temperature above or equal to 600  $^{\circ}$ C. However, the TiN barrier material also oxidises in this same temperature regime. This oxidation has effect on the thin film structure and might affect the formation of structured LNO.



**Figure 14:** XRD spectra of LNO on TiN annealed at 500 °C, 550 °C, 600 °C and 700 °C. The diffraction peaks likely belonging to TiO<sub>2</sub> peaks are indicated by  $\diamond$ , LiNiO<sub>2</sub> peaks by \*, TiN peaks by • and NiO peaks by  $\bigtriangledown$ .

In order to investigate the structure of the thin films more closely after they have been annealed, XPS depth profiles are shown for three thin films; LNO as deposited on the TiN barrier substrate; LNO on TiN annealed for 6.5 hours at 700 °C and LNO on TiN annealed for 45 minutes at 500 °C. These depth profiles are shown in figure 15. Depth profiles of the samples deposited with the H<sub>2</sub> plasma step are similar to the ones shown here and can be found in appendix C figure 22.

Figure 15a shows the depth profile of LNO as deposited on TiN. An atomic ratio of 10 % silicon can be seen in the LNO layer. This contamination is not coming from the silicon substrate, as the sample has not been annealed and the TiN barrier does not contain any silicon. It is expected that the silicon from the LiHMDS precursor has been incorporated into the thin film structure during the ALD deposition. More on this Si-contamination can be found in appendix D.

The sample shows a clear boundary between the TiN layer and the LNO sample. Near the LNO-air thin film interface, a peak in the Ni-content and a drop in the Li-content can be seen. In the other parts of the LNO film, the Ni- and Li-content is stable. Also 5 atomic-% carbon can be seen in the thin film. This may also have been incorporated into the sample due to the LiHMDS precursor.

The depth profile of the LNO sample on TiN which was annealed for 6.5 hours at 700 °C can be seen

in figure 15b. This profile indicates that the sample structure has been destroyed due to the annealing. A large amount of titanium is present through the whole sample. Also the percentages of the other elements are close to constant throughout the sample. It can be noted that no nitrogen and lithium is present after annealing the thin film at this temperature.

If we anneal at a lower temperature of 500  $^{\circ}$ C, the sample structure is still broken as can be seen in figure 15c, although it is possible to see differences in the atomic percentages as a function of the sputtering depth. From this figure, it can be seen that the titanium of the TiN layer has partially migrated towards the center of the LNO sample. This migration is still an unwanted effect. Annealing for shorter times may help to prevent the titanium from migrating far from the barrier layer. In addition, the nickel has mostly migrated towards the surface layers and some lithium has found its way into the TiN barrier material. Even at this lower temperature, where the TiN has not been oxidised, it seems that the structure of the TiN barrier is broken. It is not able to completely prevent the lithium-ions from migrating into the substrate.

From the XRD spectra of the LNO thin films on the TiN-coated substrate, it is observed that the TiN oxidises at 550 °C into anatase TiO<sub>2</sub> and oxidises to rutile TiO<sub>2</sub> above 600 °C. Evidence of layered LNO can also be seen at annealing temperatures above 600 °C. From the XPS spectra of the thin films, it was seen that the thin film structure is completely broken for 700 °C and partially broken at 500 °C. The TiN migrates even at 500 °C, which is below its oxidation temperature. It can be concluded that the coating layer loses its structure after annealing and oxidises at annealing temperatures which we expect are required to create layered LNO. As such, TiN on its own does not seem a viable coating against Si-diffusion, nor against Li-diffusion, in the case of annealing the LNO thin film to create layered LNO.



(c) LNO on TiN annealed for 45 minutes at 500 °C

**Figure 15:** Depth profiles of (a) LNO as deposited on a TiN barrier substrate, (b) LNO on TiN annealed for 6.5 hours at 700 °C and (c) LNO on TiN annealed for 45 minutes at 500 °C.

# 6 Conclusion and outlook

LNO thin films have been deposited using Plasma Assisted ALD. The GPC for the thin films is determined using in-situ SE and for LiO it is found to be 0.11 nm. For the NiO it is 0.04 nm. The growth per supercycle for the LNO deposition is 0.4 nm.

From the XRD measurements on the LNO thin films on Si before and after annealing, it was found that no crystallographic order was present before annealing. After annealing, crystalline NiO could be seen together with an XRD diffraction peak possibly belonging to a  $\text{Li}_x \text{Si}_y O_z$  material. From the depth profile of the annealed LNO compared to the unannealed LNO, it was seen that Si has migrated from the substrate into the thin film layer due to the annealing.

In order to prevent the Si migration due to annealing, TiN has been tested for its use as a barrier material on the Si substrates. Here, it was tested whether it is able to reduce the Si-migration into the LNO layer and the Li-migration into the substrate.

From the XRD measurements and from the depth plots of the annealed LNO samples on the TiN barrier material, is can be concluded that TiN on its own does not function well as a barrier material. The TiN oxidises at the temperatures which are likely to be required to create structured LNO. Anatase TiO<sub>2</sub> was found after annealing at 550 °C and rutile TiO<sub>2</sub> was found starting from 600 °C. Evidence of layered LNO was found after annealing at temperatures above 600 °C. The Ti also migrates through the thin film layer when annealing even at lower temperatures of 500 °C, which is likely too low of a temperature to create structured LNO. These results indicate that combinations of other materials might need to be tested for its use as a barrier material to prevent Li and Si migration in the thin film due to annealing.

A possible solution is to add a second barrier material over the TiN material, which should prevent the Ti from migrating into the LNO layer. However, this layer should also be able to prevent the oxidation of TiN at higher temperatures, as it is not expected that  $TiO_2$  is able to prevent Li-diffusion, while TiN can.

We have not been able to obtain layered LNO thin films by depositing using ALD and annealing at high temperatures after deposition. From the XRD spectra of the annealed LNO samples, the presence of layered LNO cannot be concluded. However, some small peaks that may belong to structured LNO are present after annealing at temperatures above 600 °C. This indicates that it might be worth further researching the annealing of LNO samples deposited using ALD. Further research should first remove the high silicon contamination in the LNO thin films and should focus on finding a good barrier material capable of preventing Li- and Si-migration in addition to Ti-migration due to annealing if using the TiN layer. After these steps have been completed, it is possible to vary the annealing temperatures to more accurately find at which temperature LNO may be formed. The annealing time can also be changed in order to characterise the time it takes for the thin film structure to change due to annealing. For this, an in-situ annealing stage in the XRD machine could be used. This allows us to measure XRD spectra during the annealing process.

Overall, some signs of crystalline LNO were found after annealing at temperatures above 600 °C. If the barrier layer can be optimised, it is expected that crystalline LNO thin films can be obtained using annealing. The crystalline LNO thin films can afterwards be used for further research on the electrochemical properties of these thin film model systems of high-voltage cathodes.

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# Appendix

#### A. Saturation curves

The saturation curves of the ALD recipes in this project could not fully be determined due to issues with the ALD machine. The saturation curve of the NiMeAMD precursor at a fixed purge time of 5 s can be seen in figure 16. A fit using the Langmuir equation

$$y = \frac{abx^{1-c}}{1+bx^{1-c}} \tag{3}$$

was made through the measurement points. From the curve, it can be seen that the NiMeAMD precursor step experiences soft-saturation. The GPC is slowly increasing even for high dose times. An explanation of this is that a continuous argon flow is required through the ALD chamber, as the process uses a plasma as reactant. This flow must be pumped away, even during the precursor step, which means that the NiMeAMD precursor does not fill the room completely. As such, the process is not completely saturated. It is not worth it to increase the dose times further in order to satisfy saturation, this would be a waste of precursor material.



Figure 16: A fit of the saturation curve of the NiMeAMD precursor. The black dots are the measurement points and the red line is the fit. The purge time was kept at 5 s.

#### B. Powder spectra database

The powder spectra used in this project are from the ICDS database from FIZ Karlsruhe.

#### ICDS powder codes

- NiO: 92127-ICSD, space group: R -3 m H
- LiNiO<sub>2</sub>: 78687-ICSD, space group: R -3 m H, structure type:  $\alpha$ -NaFeO<sub>2</sub>
- $Li_2Si_3O_7$ : 100402-ICSD, space group: C m c 21
- Rutile TiO<sub>2</sub>: 9161-ICSD, space group: P 42/m n m, structure type: rutile
- Anatase TiO<sub>2</sub>: 9852-ICSD, space group: I 41/a m d S, structure type: anatase
- TiN: 26947-ICSD, space group: F m -3 m

#### C. Extra figures



Figure 17: XRD spectra of LNO deposited on a TiN barrier substrate annealed for 45 minutes and for 6.5 hours at 700 °C. TiO<sub>2</sub> peaks indicated by  $\diamond$ , LiNiO<sub>2</sub> peaks by \* and TiN peaks by •.

Figure 18 shows the XRD spectra of both the silicon substrate with the TiN barrier layer and the standard LNO deposition on the TiN barrier substrate. Two large peaks and one smaller peak are visible. Apart from the peak shift in the sample XRD spectra, the peaks match the powder spectrum of TiN. The peak shift may be present because of a difference in the lattice parameters of the TiN in the sample and that of the TiN powder. Again, no peaks belonging to LNO are visible in figure 18b, thus we will anneal the sample.



(a) TiN substrate

(b) LNO on TiN substrate

Figure 18: XRD spectra of (a) silicon substrate with the TiN barrier material and (b) LNO on TiN barrier substrate. The XRD spectra are compared with the powder spectrum of TiN.



**Figure 19:** Picture of two LNO samples deposited on the silicon substrate with TiN barrier. The left sample has been annealed for 6.5 hours at 700 °C. The right sample is the LNO as deposited on the TiN barrier material.

Figure 20 compares the XRD spectrum for (a) annealing for 6.5 hours at 700 °C and for (b) annealing for 45 minutes at 500 °C. It is clear that annealing at 500 °C prevents the oxidisation of TiN to TiO<sub>2</sub>. This result also agrees with Hong-Ying Chin et al. [36], which say that rutile-TiO<sub>2</sub> is detected using XRD after annealing TiN on silicon at 600 °C. However, as was also the case for annealing the LNO sample on a regular silicon substrate at 500 °C, spectrum (b) does not show LNO peaks. NiO peaks are again visible when annealing at 500 °C.



(a) LNO on TiN annealed for 6.5 hours at 700 °C (b) LNO on TiN annealed for 45 minutes at 500 °C compared to TiO<sub>2</sub>, LiNiO<sub>2</sub> and TiN powder spectra.

**Figure 20:** XRD spectra of (a) LNO on TiN annealed for 6.5 hours at 700 °C and (b) LNO on TiN annealed for 45 minutes at 500 °C.



Figure 21: XRD spectra of the LNO sample with the  $H_2$  plasma step deposited on TiN substrate and annealed for 2 hours at 550 °C. The reference spectrum of anatase TiO<sub>2</sub> is added for comparison.



(a) LNO with H<sub>2</sub> plasma step on TiN

(b) LNO with  $H_2$  on TiN annealed for 2 hours, 600 °C



(c) LNO with  $\rm H_2$  plasma step on TiN annealed for 2 hours at 500  $^{\circ}\rm C$ 

**Figure 22:** Depth profiles of (a) LNO with H2 plasma step as deposited on a TiN barrier substrate, (b) LNO with H2 plasma step on TiN annealed for 2 hours at 600 °C and (c) LNO with H2 plasma step on TiN annealed for 2 hours at 550 °C.

## D. High silicon contamination

During the depositions of the LIO and the LNO samples, it has been noticed that the Si-content of the samples has steadily increased since the start when the deposition method has first been used. One of the sample compositions of the latest LiO deposition can be seen in table 1. The most likely explanation for this contamination is the silicon groups in the LIHMDS precursor. These Si-groups can have been incorporated into the thin film structure, thus leading to the contamination. This is likely the reason, as there is no problem of the Si-contamination in the NiO thin films.

It has been tried to remove the Si-contamination by adding a 2 s  $H_2$  plasma step before the  $O_2$  plasma step for the LiO and LNO recipes. This step might be able to remove the silicon groups from the sample surface. For the LiO depositions, this was effective, as can be seen from the atomic composition of one such sample in table 1. For the LNO thin film, however, the silicon contamination was still present.

For the LNO depositions with the  $H_2$  plasma, the atomic compositions and GPCs are similar. The atomic composition of a LNO deposition with the  $H_2$  plasma step included for the LiO cycles, which was deposited on a Si substrate with TiN barrier layer, can be seen in table 2.

Table 1: Table of the atomic composition of the surface of a LiO deposition without and with a 2 s  $H_2$  plasma step before the  $O_2$  plasma step on a silicon substrate. The atomic compositions are found using a XPS surface scan.

	LiO without H2	LiO with H2
Name	Atomic $\%$	Atomic $\%$
0	47.07	46.64
Li	28.3	33.18
Si	14.46	0.08
С	6.65	19.25
F	3.21	0.71
Ν	0.31	0.14

**Table 2:** Table of the atomic composition of the surface of a LNO deposition with a 2 s  $H_2$  plasma step before the  $O_2$  plasma step in the LiO. The LNO is deposited on a Si substrate with TiN barrier layer. The atomic compositions are found using a XPS surface scan.

	LNO without H2	LNO with H2
Name	Atomic $\%$	Atomic %
0	43.4	44.7
Li	29.31	29.5
Si	8.7	6.1
С	13.1	13.2
F	-	3.6
Ν	0.9	0.4
Ni	4.7	2.5