## Characterization of LiCoO2 Thin Film Grown by Pulsed Laser Deposition

by

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## Abstract

This thesis is a presentation of experiments of  $LiCoO_2$  thin film growth by pulsed laser deposition (PLD) for study using beta defected NMR of implanted <sup>8</sup>Li. The films were characterized by ellipsometry to figure out their optical properties. Other characterization techniques were also applied such as x-ray diffraction (XRD) and atomic force microscope (AFM). It shows that PLD is a convenient technique to deposit  $LiCoO_2$  thin film and the growth conditions have strong effect on the properties of the resulting films.

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## Chapter 1

## Introduction and Objectives

This thesis is a presentation of experiments of  $LiCoO_2$  thin film growth by pulsed laser deposition (PLD) for study using beta deflected NMR of implanted <sup>8</sup>Li. LiCoO<sub>2</sub> is an interesting cathode material and its magnetic properties are attracting the attentions of many researchers.

Lithium Cobalt  $Oxide(LiCoO_2)$  has been used as a positive electrode material in commercial Li-ion batteries since Goodenough and his colleagues demonstrated its ability to reversibly intercalate lithium in 1980[1]. Now there is an increasing interest in thin film batteries with smaller dimensions. An all solid state thin film battery has potential applications in microelectronics such as backup power for smart cards, implantable medical devices and on-chip static memory modules[2][3].

In batteries, electrode materials are required to have ionic and electronic conduction simultaneously. They need relatively open structures with partial occupancies of the mobile ion sites to obtain ionic conduction, and a mixed valence of one of the atoms to keep electronic conduction. In such material, electrons could migrate or hop simply in parallel with ions' migration. A typical Li battery scheme is shown in figure 1.1. The anode is made of lithium embedded in graphitic carbon making an intercalation compound, typically  $\text{LiC}_6$ . Li<sup>+</sup> can be easily released and then travels through a conducting polymer electrolyte to the cathode. Cathode material  $\text{LiCoO}_2$  is also intercalation host structure. It has empty channels or layers capable of accepting Li<sup>+</sup> ions and a mixed valence species in the host framework that is able to accept, and release electrons. The formula  $\text{LiCoO}_2$  refers to the fully intercalated, discharged state. On charging, Li<sup>+</sup> ions are removed and  $\text{Co}^{3+}$  is oxidized to  $\text{Co}^{4+}$ . The  $\text{Co}^{3+}/\text{Co}^{4+}$  couple gives a cell voltage of 4.0V against anode[8].

 $LiCoO_2$  has been extensively studied due to its reversible insertion and extraction of Li<sup>+</sup> from  $LiCoO_2$ , and interesting magnetic properties. Its electronic structures are studied by magnetic susceptibility measurements[10], x-ray photoelectron spectroscopic (XPS) analysis[11], x-ray absorption spectroscopy (XAS)[16] and band-structure calculations[12]. They indicate that

1



Figure 1.1: Diagram of a general battery. Requirement for electrode is high ionic conduction and high electronic conduction.

 $Co^{3+}$  ions are in a low spin state with S=0 at ambient temperature. It is thus believed that LiCoO<sub>2</sub> is non-magnetic. This conclusion was confirmed by  $\chi$ and NMR measurements down to 4.2K[13]. Although LiCoO<sub>2</sub> is known to be an insulator, Li deficient  $Li_x CoO_2$  with x=0.7-0.55 exhibits metallic behavior above 50K. As x decreases from 1, an insulator-to-metal transition occurred at around x=0.95 as shown by resistivity measurements[6]. The existence of long-range magnetic order in  $Na_x CoO_2$  was found at low temperatures by positive muon spin rotation and relaxation ( $\mu^+$ SR) experiments[14] and reconfirmed by neutron diffraction experiments[15]. This leads to the interests in magnetism of  $Li_xCoO_2$ , particularly for Li-deficient phases. Although all past bulk experiments suggested the absence of magnetic transitions at low T, Sugiyama and coworkers reported in Ref[9] that there was a magnetic transition around  $175K (=T_m)$  for  $Li_{0.7}CoO_x$ , and that weak transverse field (wTF-)  $\mu$ SR measurements showed the appearance of magnetism below  $65K(=T_C^{on})$ even for the sample with x=1.0. The volume fraction of the magnetic phase at 1.8K is estimated as 20% for LiCoO<sub>2</sub>. This means that the observed magnetism is not induced by impurities but is an intrinsic behavior. The magnetism at low T is probably induced by either a charge disproportionation  $(2\text{Co}^{3+}\rightarrow\text{Co}^{2+}+\text{Co}^{4+})$ , a spin state transition $(t_{2g}^6\rightarrow t_{2g}^5e_{2g}^1)$  of  $\text{Co}^{3+}$ , or an appearance of magnetic  $Co^{3+}$  at surface.

Magnetism of LiCoO<sub>2</sub> is not fully investigated, and no systematic studies of microscopic magnetism for Li-deficient phases at low temperatures were reported. We intend to study these interesting properties with <sup>8</sup>Li  $\beta$ NMR at

 $\mathbf{2}$ 

TRIUMF. The first task, prior to  $\beta$ NMR experiments, is to synthesize crystalline thin films of LiCoO<sub>2</sub>. We also intend to synthesize an electrochemical thin film heterostructure involving Li<sub>x</sub>CoO<sub>2</sub> such that the Li content x can be varied electrically in situ via solid state intercalation /deintercalation in order to study magnetic properties as a function of Li doping and Li mobility processes. My part is just starting the work, LiCoO<sub>2</sub> thin film deposition and characterization.

## Chapter 2

## **Basic properties of LiCoO\_2**

There are two principle phases of LiCoO<sub>2</sub> referred to by temperature required for their synthesis: the standard or high-temperature phase, HT-LiCoO<sub>2</sub>, and the low-temperature phase [4]. Both structures have the same oxygen framework (a cubic-closest-packed oxygen network). This structure can be thought of as an ordered rocksalt type with an ABCABC stacking of the oxygen planes and Li and Co atoms occupy the octahedral sites surrounded by 6 oxygen atoms, forming LiO<sub>6</sub> and CoO<sub>6</sub> clusters(figure 2.2). The layered HT-LiCoO<sub>2</sub> crystalizes in the rhombohedral system (figure 2.1) and belongs to the space group  $R\bar{3}m$ . Co and Li atoms show ordered arrangement in alternate octahedral sites of (111) plane. On the other hand, LT-LiCoO<sub>2</sub> crystalizes in space group Fd3m. 25% of Li and Co atoms are randomly arranged, forming alternating Co<sub>0.75</sub>Li<sub>0.25</sub> (Co-rich) and Li<sub>0.75</sub>Co<sub>0.25</sub> (Li-rich) layers (shown in figure 2.2. Both phases have potential applications as promising cathode materials in all-solid-state batteries. Delmas and coworker showed systematic changes in the lithium deintercalation from LiCoO<sub>2</sub>[6].

As mentioned in the first chapter, Li can be deintercalated from LiCoO<sub>2</sub>. The properties of Li<sub>x</sub>CoO<sub>2</sub> vary with the intercalation. Dahn *et al.* varied Li concentration x by electrochemical means and investigated the properties as functions of delithiation. In situ x-ray diffraction measurements of Li<sub>x</sub>CoO<sub>2</sub> showed that lithium ion ordering occurred at x=1/2 and was coupled to lattice distortion from hexagonal to monoclinic symmetry. A strong first ordering transition showed up in the region  $0.75 \le x \le 0.93$  [7]. Studies on Li<sub>x</sub>CoO<sub>2</sub> crystallized thin films showed that the electronic conductivity increases considerably with lithium deintercalation  $(0.9 \le x \le 1.0)$ [33]. Honders *et al.* indicated that the electrical transport takes place through moving electron holes in a Co<sup>III</sup> valance band[34]. Molenda *et, al.* performed the electronic conductivity upon deintercalation and observed a semiconductor behavior for the lithium-rich phases and a metallic one for the more deintercalated ones[35].



Figure 2.1: Structure of layer  $HT-LiCoO_2$ . A triangular oxygen network of edge sharing octahedra. Co and Li atoms occupy the center of O octahedra of (111) planes alternatively



Figure 2.2: (a) layered-hexagonal structure, (b)LT-cubic structure of  $LiCoO_2$ (c) Typical arrangement of Li and Co atoms in Co-rich and Li-rich layers. Solid circles represent Co, and open circles Li. Solid and open squares represent the substituted Co in Li-rich layers and the substituted Li in Co-rich ones, respectively. Oxygen layers are not shown here. The shadowed parts in (b) correspond to those in (c). These figures were cited from [5]

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## Chapter 3

## Approach

## 3.1 Available Techniques

LiCoO<sub>2</sub> thin films can be prepared by various techniques such as radio frequency(rf) sputtering, sol-gel coating, chemical vapor deposition, cobalt metal reaction, and pulsed laser deposition(PLD). Among them, rf sputtering and PLD are most commonly used for LiCoO<sub>2</sub> thin film growth. For rf sputtering, normally post-annealing is required to obtain better crystallization and preferred texture. As for PLD, it has many advantages for producing good quality thin films, such as high deposition rate, retaining the original stoichiometry of the target to the deposited films, and the capability of making a multilayer film by exchanging the targets inside the chamber. Therefore we used PLD to deposit LiCoO<sub>2</sub> thin film.

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### 3.2 PLD Historical Review

[17] Ever since the first high-power ruby laser became available, interest was increasing on the theoretical and experimental studies on the interactions of intense laser beams with solid surfaces, liquids and gaseous materials. The finding that material could be easily vaporized by a laser beam suggested that intense laser radiation could be used to deposit thin films. The first deposition was demonstrated by Smith and Turner in 1965, using a ruby laser to deposit thin films on semiconductors, dielectrics, chalcogenides, and organometallic materials[18]. They pointed out some features essential to later developments, including the stoichiometric preservation of a multiple component target. It succeeded in mimicking flash evaporation for stoichiometry control by laser irradiation. The use of a laser showed its obvious advantages in lowering the contamination level and the ease of process control. There are some limitations including the failure to evaporate and deposit films from a "transparent" target, which absorbed very little laser radiation. In general, film qualities were inferior to those deposited by the conventional techniques at that time. PLD remained in the stage of research and development for a long time.

During the 1970s, two major developments boosted a new research flood in PLD. First, reliable electronic Q-switch was generated to generate very short optical pulses to attain a peak power exceeding  $10^8$ W/cm<sup>2</sup>. Any material that absorbs laser radiation of this power level, will be transformed to form a plasma. Thus PLD can be used to deposit thin films of any material if the absorbed laser power density is high enough. And the use of short laser pulses for ablation is more likely to achieve congruent ablation<sup>1</sup> that allows PLD to preserve stoichiometry during mass transfer from the target to the thin film. The second significant technical advance was the development of high-efficiency second harmonic generator to deliver shorter wavelength radiation. Therefore, the absorption depth is shallower and the splashing is reduced. A smaller heated volume also favors congruent evaporation. These two developments greatly widened the material selection and improved the film quality.

In 1980s, with improved affordability and quality of commercial lasers, more and more researchers joined this field and made many breakthroughs. For example, epitaxial semiconductor films, heterostructures, and superlattices grown by PLD showed, for the first time, qualities comparable to those grown by MBE[19]. Quantum Hall Effect for two-dimensional carriers in a II-VI compound semiconductor was observed for the first time in a HgTe/CdTe superlattice grown by PLD[20]. Silicon epitaxy by PLD was also briefly investigated with promising results except the rough surface morphology due to the condensation of a large number of micron-sized molten globules[21]. In addition, there was a large collection of work on the growth of oxide and fluoride films by PLD, which were used as optical coatings. An improvement in crystallinity over electron-beam-deposited films was observed and attributed to the high surface mobility due to hyperthermal impact energy[22]. However, the presence of surface particulates due to "splashing" still poses a major problem.

The success of in situ growth of high-temperature superconducting films by PLD[23] in 1987 brought an overwhelming interest to this field. The total number of publications in PLD since 1987 is over 10 times more than the combined publications in the previous 25 years. The simplicity and versatil-

<sup>&</sup>lt;sup>1</sup>Exactly the same composition in the resulting plume as that in the target.

ity of the experimental setup makes it an affordable technique to explore new frontiers in material science. The new trends in PLD development include the heteroepitaxy of oxides on semiconductors. It provides potential for new devices based on the integration of semiconductors and oxides in material research. The growth of ferroelectric perovskite oxide films is another promising area. It is a natural extension of the work on high  $T_c$  oxide superconductors because of the structural similarity of these materials. These layers can be grown by PLD in situ without high-temperature post annealing. Therefore, epitaxial multilayer structures can be grown by incorporating matching electrodes to improve the performance endurance of the devices subjected to repetitive cycling. Nitrides are another material that researchers have attempted to grow by PLD, although results were far from satisfactory, maybe due to the inactivity of nitrogen. Further, production-related issues concerning reproducibility, large-area scale-up, and multiple-level devices have also begun to be addressed with PLD development.

## Chapter 4

## Pulsed Laser Deposition (PLD)

## 4.1 Principles

The principle of PLD is pretty simple both conceptually and experimentally, probably the simplest among all thin film growth techniques. The beam from an excimer laser<sup>1</sup> is reflected and focused by a set of optical components then on to the target inside the chamber. When the target absorbs the laser radiation, electromagnetic energy is converted first into electronic excitation and then into thermal, chemical, and even mechanical energy to cause evaporation, ablation excitation, plasma formation, and exfoliation. Evaporants form a "plume" consisting of a mixture of energetic species including atoms, molecules, electrons, ions, clusters, micron-sized solid particulates, and molten globules. The collisional mean free path inside the dense plume is pretty short. Therefore immediately after the laser irradiation, the plume rapidly expands into the vacuum from the target surface with hydrodynamic flow characteristics. This process leads to many advantages as well as disadvantages. The advantages are flexibility, fast response, energetic evaporants and congruent evaporation. The disadvantages include the presence of micron-sized particulates and the narrow forward angular distribution that makes large-area scale-up and growth rate monitoring a very difficult task. The resulting plume goes directly forward to the substrate just sitting across the target and the particles inside the plume are deposited together with thin films on the substrate.

The decoupling of the vacuum hardware and the evaporation power source makes this technique so flexible that it is easily adaptable to different operational modes without the constraints imposed by the the use of internally powered evaporation sources. Film growth can be carried out in a reactive environment containing any kinds of gases with or without plasma excita-

<sup>&</sup>lt;sup>1</sup>Excimer laser usually is a form of ultraviolet chemical laser. It typically uses an inert gas and a reactive gas under the appropriate conditions of electrical stimulation to ignite laser light in the ultraviolet range.

tion. It can also be operated in conjunction with other types of evaporation sources in a hybrid approach. The substrate temperature, ambient pressure and substrate lattice constants will affect the quality of the resulting film. Although the main principle seems simple, the theoretical descriptions of the laser-target interaction are complicated. In order to optimize the PLD process, several issues have to be taken into consideration. PLD is so versatile that with the choice of an appropriate laser, it can be used to grow thin films of any kind of material. The versatility is reflected in the rapidly growing list of materials deposited.

### 4.2 The PLD process

In general, PLD is a four-stage process, including: 1) laser ablation of the target material and creation of a plasma; 2) dynamics of the plasma; 3) deposition of the ablated material on the substrate; and 4) nucleation and growth of the film on the substrate surface. Each of these four steps is crucial for the crystallinity, uniformity and stoichiometry of the resulting film.

### 4.2.1 Laser Ablation and Plasma Creation

The laser irradiation upon the target material and the creation of plasma are very complex processes. The incident laser pulse penetrates into the surface of the material within the penetration depth which is dependent on the laser wavelength and the refraction index of the target material at the applied laser wavelength. The electrical field generated by the laser light is sufficiently strong to remove the electrons from the bulk material in the penetrated volume. This process occurs within 10ps of a nanosecond laser pulse and is caused by non-linear processes such as multiphoton ionization which are enhanced by microscopic cracks at the surface, voids, and nodules which increase the electric field. The free electrons oscillate within the electromagnetic field of the laser light and can collide with the atoms of the bulk material within the surface region. The surface of the target is then heated up and the material is vaporized. The temperature of the generated plasma plume is typically  $10^4$ K.

### 4.2.2 Dynamics of the Plasma

The material expands in a plasma parallel to the normal vector of the target surface towards the substrate surface. Figure 4.1 shows a plume ejected from a LiCoO<sub>2</sub> target during pulsed laser deposition. The spatial distribution of the plume is dependent on the background pressure inside the PLD chamber. The density of the plume can be described by a  $\cos^n(x)$  law. The dependency of the plume shape on the pressure can be described in three stages: 1) the vacuum stage, where the plume is very narrow and forward directed; almost no scattering occurs with the background gases. 2) The intermediate region where a splitting of the high energetic ions from the less energetic species can be observed. 3) High pressure region where we find a more diffusion-like expansion of the ablated material. Naturally this scattering is also dependent on the molecular mass of the background gas and can influence the stoichiometry of the deposited film. The most important consequence of increasing the background pressure is the slowing down of the highly energetic species in the expanding plasma plume. It has been shown that particles with kinetic energies around 50eV can resputter the film already deposited on the substrate. This results in a lower deposition rate and can furthermore result in a change in the stoichiometry of the film.

### 4.2.3 Deposition of the Ablated material on Substrate

This stage is important to determine the quality of the deposited films. The highly energetic species ablated from the target bombard the substrate surface and may cause damage to the surface by sputtering off atoms from the surface but also by causing defect formation in the deposited film. The sputtered species from the substrate and the particles emitted from the target form a collision region, which serves as a source for condensation of particles. When the condensation rate is high enough, a thermal equilibrium can be reached and the film grows on the substrate surface at the expense of the direct flow of ablation particles.

### 4.2.4 Nucleation and Growth of Films

The nucleation and growth of crystalline film on a substrate depend on several factors such as the density, energy, ionization degree of the ablated material and temperature, roughness and crystalline properties of the substrate. Al-



Figure 4.1: A plume ejected from  $LiCoO_2$  target during pulsed laser deposition.





Figure 4.2: PLD setup.Excimer laser beam is reflected by mirror and then is focused by converging lens with focal length 75cm.

though PLD has a much lower average deposition rate than other deposition techniques such as Sputtering Deposition (SD) depending on the repetition rate of the laser, it can be demonstrated that the fraction of stable nucleation sites is orders of magnitudes higher for PLD than for SD. This has several implications on the growth mechanism in PLD: the critical nucleus radius is smaller and in the range of 1 or 2 atoms, Since the nucleation rate is proportional to the nucleation site density and the rate of impingement, it is much higher in the case of PLD. Furthermore, the high density of nucleation sites also increases the smoothness of the deposited film.

## 4.3 Experimental Setup

Figure 4.2 shows a schematic diagram of our experimental PLD setup. It consists of an excimer laser, a set of optical components, target holders and a substrate holder sitting inside a vacuum chamber.

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wavelength(nm)	248nm	excitant	KrF
Pulse Energy	600mJ	Max.Rep.Rate	10Hz
Ave Power	5W	Pulse Duration	25ns
Beam Dimension $(mm \times mm)$	$24 \times 6(\text{to12})$	Beam Divergence mrad (V×H)	$3 \times 1$

Chapter 4. Pulsed Laser Deposition (PLD)

Table 4.1: Laser specifications.

### 4.3.1 The Ablation Laser

The laser used in our system is a Lambda Physik Excimer Laser, COMPex201 F-version. Table 4.1 shows the laser specifications.

The COMPex201 uses a combination of (He, Kr and Ne) and the reactive gas  $F_2$  (shown in table 4.3.1) to react under the appropriate conditions of electrical stimulation to form the excited dimer molecule KrF<sup>\*</sup>. Energy is pumped into the gas mixture through avalanche electric discharge excitation. The pumping creates ionic and electronically excited species that react chemically and produce the excimer molecules. Electron-beam excitation and microwave discharge excitation have also been used as a means to pump the gas mixture. The lasing action takes place between a bound upper electronic state and a repulsive or weakly bound ground electronic state of a diatomic molecule. Because the ground state is repulsive, the excimer molecule can dissociate rapidly (on the order of a vibrational period  $10^{-13}$ s) as it emits a photon during transition from upper state to ground state. The high ratio of upper state lifetime to lower state lifetime makes the excimer the perfect laser medium because population inversion and therefore high gain can be easily achieved.

Figure 4.3 shows the cut way drawing of the laser tube. When it works, a high voltage discharge between the electrodes transfers the energy to the excimer gas mixture. In order to obtain a controlled, spark-free discharge, the laser gas has to be preionized. A sufficiently high density of free charged molecules has to be created between the electrodes. This is achieved with preionization pins arranged along the main electrodes. The result is a ho-

Gas	$F_2/{ m He}$	Kr	Ne
Partial Pressure (mbar)	80	100	3120
Pressure(%)	0.10/1.71	3.93	94.26

Table 4.2: Composition of gas mixture required for COMPex201 excimer laser. Total pressure is 3300mbar

mogeneous preionization of the laser gas. The switching of preionization and main discharge in series ensures a perfect synchronization between preionization and main discharge. Between successive laser pulses, the gas volume in the discharge area has to be completely exchanged because of thermal inhomogenities in the laser gas after the high-voltage discharge. The transverse circulation fan is positioned within the laser tube to replace the gas between the main electrodes. And the gas flows through the heat exchangers to be cooled down to the correct operating temperature (approx.30°C). At last, the electrostatic filter integrated in the gas circulation removes the particles created in each discharge pulse which might diminish beam intensity, if they precipitate on the laser window, by scattering and absorption.

The details of the kinetics and chemical reactions leading to the formation of the excimer molecules are quite complex and can consist of many steps. Some of the more important reactions for the case of KrF are listed below where the \* denotes an electronically excited species and X denotes a third body (He,Ne) from the buffer gas[17].

 $Kr + e^{-} \longrightarrow Kr^{+}, Kr^{*}, Kr_{2}^{+}$   $F_{2} + e^{-} \longrightarrow F + F^{+}$   $Kr^{+} + F^{-} + X \longrightarrow KrF^{*} + X$   $Kr_{2}^{+} + F^{-} \longrightarrow KrF^{*} + F$   $Kr^{*} + F_{2} \longrightarrow KrF^{*} + F$ 

(4.1)



Figure 4.3: A cross-sectional view of Lambda Compex201 excimer laser. A-preionizationpin, B-electrodes, C-Laser tube, D-transverse circulation fan, E-the electrostatic filter, F-the heat exchages. Credit from [24].



Figure 4.4: Pulse energy as a function of charging voltage. Credit from [24].

Once the excimer is formed, it will decay via spontaneous emission and collisional deactivation giving the molecule a lifetime of 2.5ns. Moderate output energies of several hundred millijoules per laser pulse dictate an excimer population density requirement on the order of  $10^{15}/cm^3$ . Therefore, in order for lasing action to occur, the formation rate of the ionic and excited precursors must be fast enough to produce excimers at a rate of several  $10^{23}/cm^3/s$ .

A homogeneous uniform laser output is required for good-quality deposition work. This is especially important when working with multicomponent deposition targets. Poor beam quality can result in nonstoichiometric films as well as undesirable droplet formation. Figure 4.4 shows the typical laser output dependence on charging voltage and the image of the real laser beam is shown in Figure 4.5 a). The laser spot is not uniform at the edges. Therefore we position a collimator right behind laser output window to cut the

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uneven edges and get a uniform beam for focusing.

As excimer laser gases age, the pulse energy obtained from a given charging voltage will decrease. Therefore, the laser can run either in the Energy Constant mode or in the High Voltage Constant mode. When running in the Energy constant mode, laser control continuously adjusts the high voltage to achieve laser operation at a preset energy level. Figure 4.3.1(a) shows charging voltage increases as time flies. On the other hand, as shown in Figure 4.3.1(b), the pulse energy decreases with time when laser is running in the voltage constant mode, as excimer laser gases have a limited lifetime. When deposition is in process, laser is usually used in energy constant mode, while the voltage constant mode is primarily used for diagnostic purposes.

### 4.3.2 Optics

Between the laser output port and the laser window of the deposition chamber, optical elements are placed in order to steer and focus the beam. As shown in Figure 4.2, the optical elements that couple the energy from the laser to the target are collimator, rastering mirror, converging lens, and laser window.

#### Mirrors

The mirror used for PLD are dielectric multilayer mirrors and are designed for an optimal reflectance. Dielectric multilayer coating are optimized for the specific wavelength 248nm with a thickness of quarter wavelength. Two motors are connected to the mirror making it possible to tilt the mirror in the two directions perpendicular to the beam path. Therefore the focused beam inside the chamber could be rastered, and scan a relatively large area on the target surface. It would help to reduce the roughness of target surface due to laser ablation and keep congruent vaporization and also average over plume distribution. As shown in figure 4.2, the primary beam out of laser is reflected off by the rastering mirror incident at an angle of 45° with respect to the normal to the mirror.

#### Lenses

The primary function of the lens is to collect laser beam and focus it to a corresponding point on the target to achieve the desired energy density



Figure 4.5: a) Image of laser spot at laser output window. Spot size is  $1.2 \times 2.8 \text{cm} \times \text{cm}$ ; b) Image of focused laser beam inside main chamber. Focused laser spot is of  $4.06 \times 2.05 \text{mm} \times \text{mm}$ 



Figure 4.6: (a) Charging voltage increases in the energy constant mode. (b) Energy decrease in the HV constant mode. Credit from [24]

for ablation. In the pulsed laser deposition of various thin films, one of the most important deposition parameters that controls the film stoichiometry and crystallographic quality is the laser energy density (expressed in  $J/cm^2$ ) incident on the target. In most cases, it has been found that the laser energy density has to be above a minimum threshold value in order to obtain films with the same stoichiometry as the target. Spherical lenses are most widely used in PLD, although cylindrical lenses can also be used. Spherical lenses magnify in two orthogonal planes, and hence a point source is imaged as a point. Cylindrical lenses have magnification only in one plane and can change the the height of an image without changing its width, imaging a point source as a line. In PLD, cylindrical lenses can be used to change the shape of the laser beam.

Considering the range of wavelengths that must be transmitted by the lens material, we chose UV-grade fused-silica lenses for our KrF excimer laser at 248nm. The lens must be free of inclusions and bubbles, mechanical distortions and dust on its surface.

In achieving the optimum energy density at the target surface, it is necessary to take into account the two most common lens aberrations: spherical aberration and coma. In spherical aberration, the bundle of rays parallel and close to the optic axis come to focus at a point different from the bundle of rays parallel and away from the optic axis. Spherical aberration can be reduced by using apertures to attenuate the beam away from the optic axis. This reduces the total energy delivered to the target.

The focusing lens used in our system was shipped together with PLD system. Laser beam can be transmitted through in one way but not the other way. Its focal length is 75cm, which is the exact distance between the focusing lens and target. The lens is positioned with its optical axis  $5^{\circ}$  off the beam path in order to avoid any damages caused by the beam reflected back into the laser. In order to reduce the spherical aberration, we centered the laser beam as much as possible. Figure 4.5 b) shows the image of focused laser spot on the target. The image was captured on a small piece of burn paper which was clapped to the target inside the chamber. It's not uniform with some flares at the edges. The size of the spot except flares is  $4.06 \times 2.05 \text{mm}^2$ . We measured the beam energy right after the focusing lens with the Molectron J50 power meter. It was calibrated with the laser built-in energy meter before use. The responsivity is 1.87 Volt/Joule. Measurements show that only 1/3 of beam energy beam is left right after the converging lens. 2/3 is lost due to the reflection and absorption of the rastering mirror

and both lenses, and 20% of the rest beam intensity was lost because of the laser window and flare. The energy density on target is only  $1.53 \text{J/cm}^2$  when the laser outputs at 600mJ/pulse. It is lower than the values reported in others' PLD system[25]. That's not optimum due to the lens quality and geometry constraint of the lab, but is the best focused beam we could achieve after long time adjustment.

#### Laser Windows

The laser windows through which the laser enters the deposition chamber is made out of laser-quality optical material (fused silica for 248nm), polished to a very high degree of flatness. These windows must be free of defects such as bubbles and inclusions since these defects can deteriorate the beam quality. Since the laser window is UV transparent, the energy loss when passing through it is neglectable.

### 4.3.3 Deposition System

Once the laser beam passes through the optical elements, it enters the deposition chamber. Deposition systems, in general, can become very complex, combining various deposition methods, such as PLD, magnetron sputtering, with load lock, and differential pumping, and analysis equipment. A good foundation for a versatile PLD deposition system is comprised of the following elements: chamber, target manipulation, substrate holder and/or heater, pump, gas flow, and vacuum gauging.

#### Chambers

Figure 4.7 shows the deposition chamber in our system. In addition to the standard ports required on all vacuum chambers (eg. pumping port, gas inlet, pressure gauging and viewports), the PLD chamber also have ports for the targets, substrates, and laser beam. Because sometimes the substrates need to be heated, the chamber will also be heated and be cooled externally. The radiation heater is positioned at the center of the chamber to distribute heat uniformly over the chamber surface, thus to minimize the need for external cooling. In Figure 4.8, five dimensions are indicated: the laser port length, L; working distance, which is the target to substrate distance, S; the substrate port flange-to-substrate distance, Z; distance between target flange



Figure 4.7: Main deposition chamber, 60L, manufactured by Neocera, Inc.



Figure 4.8: Schematic illustration of important parameters in PLD chamber. L=laser port length; S=working distance; T=distance between target flange and target plane; Z=the substrate port flange-to-substrate plane;  $\theta$ =angle between target normal and laser normal.

and target plane, T; and the angle between the target normal and laser beam,  $\theta$ .

In PLD, the deposition is very forward-directed along the target normal. Considerable materials will find their way to all surfaces within the chamber, including the laser window, especially when a background gas is present during deposition. Materials deposited on the window will interact with the laser beam, and the result could be permanent damage to the window. By increasing L, the length of the laser port, the rate of material deposited on the window will be reduced. Making L too long, however, reduces the available area to which the beam may be focused. Thus, to balance these two factors, L in our system is set to be 75cm.

The optimization of S depends on the energy density, chamber pressure, and target morphology. By allowing S to be adjustable, optimized depositions can be obtained. For most cases, S will be in the range 3 to 15cm, although longer distances could be desirable to increase the surface area which is uniformly coated. In our system, however, the location of the substrate plane is fixed because the substrate is sitting at the center of the chamber. We can change S by extending target holding rods over a small range of 2-3cm. Now the working distance S is  $98.37 \pm 0.05$ mm, which is longer than that reported in [25]. Longer working distance means longer path for the plume travelling from target to the substrate. Although particles inside the plume can't reach equilibrium within such a short time, it indeed increases the chance of Li loss. That may make the stoichiometric growth more difficult.

#### Target Manipulation

There are few intrinsic restrictions placed on the targets used in a PLD system. Successful depositions can be made from pressed powders, sintered pellets, cast material, single crystals, and metal foils. The main differences between these different target morphologies is in the nature of the target erosion, and the generation of particulates. Generally speaking, high-density and highly homogeneous targets yield the best films.

In order to get uniform target erosion and consumption, we rotate the targets during deposition. In this fashion, an annular region of the disk-shaped target is ablated. Meanwhile, the laser beam is also be rastered over the surface of the flat target to provide for uniform erosion. Such beam rastering can improve the edge-to-edge thickness and compositional uniformity, when films are deposited on large substrates (significantly larger than 1cm in diameter).

One of the great advantages of PLD over other thin-film fabrication techniques is the ease with which in situ multilayer structures can be formed. A target carousel containing several targets is employed for this application. Our disk-shape targets are firmly silver-painted to target holders, which can be slid onto the supporting rod stretching from the carousel. Six targets can be mounted to the carousel. In deposition, the carousel can be rotated at the same time of each target spins separately. This helps target uniform erosion and facilitate the switching between different targets in one deposition. A shield with a aperture is placed in front of the target plane to minimize target cross-contamination and to protect the carousel mechanism. When laser is firing, only the target right behind the aperture could be ablated, while others are safe under the protection of the shield.

#### Substrate Holders and Heaters

As with most thin-film deposition techniques, the manner in which the substrate is held and its location relative to the target are important parameters. Frequently, the substrate must be heated to produce good adhesion and/or epitaxy. Since the evaporants are ejected as a highly forward-directed plume of material along the target normal, the substrate are held directly opposite the target as shown in 4.8. As the need for temperature uniformity increases, so does the complexity of the substrate heater. Temperature uniformity becomes critical when the formation energy of the desired compound or the need for epitaxy forces the temperature controlled witin a narrow band. Our substrates are bonded to the inconel holder plate with silver paint which provides good thermal conduction to improve temperature uniformity of the substrate. The holder is clipped to the radiation heater with three radial springs (see figure 4.9. During heating or deposition, substrate plate can rotate in order to reach a uniform temperature.

#### Pumps, Gas flow, and Vacuum gauges

One of the advantages of PLD as compared to other film deposition techniques is that it requires very simple, relatively economical pumping and gasflow systems. Although any high vacuum pumping system can be adapted for use on a PLD system, as with most thin-film deposition techniques, maintaining a clean, dust-free, and oil-free environment is important. Depending on the nature of the gas being pumped, corrosion-resistant pumps might be required in order to guarantee the safe operation and long life of the system. For depositing metal oxides and other complex structures, a high gas pressure might be required necessitating the use of high gas throughput and pumps capable of operating at high pressure. In our system, we use a Pfeiffer membranvakuumpumpen diaphragm vacuum pump (Model: MVP 055-3) together with a Pfeiffer turbomolecular drag pump (Model: TMH520). Their specifications are listed in table 4.3.3. The chamber can be pumped down to  $10^{-5}$  Torr in half an hour and down to  $10^{-8}$  Torr in several days when they work together.

Considering the fact that we may deposit various materials with background pressures ranging from several morr to 1Torr, we installed two vacuum gauges. One is a Cap Manometer which is in effect when the pressure is in the range of 1Torr to 6mTorr. The other one is cold cathode type of


Figure 4.9: Substrate when mounted inside the chamber. Si substrates are silver-painted to the inconel plate which is clamped to the heater by three springs.

Pump	Pumping Speed $(L/s)$	Final Pressure (Torr)
MVP055-3	3.3/3.8	2
tmh520	500	<5E-10

Table 4.3: Specifications of pumps

ionization gauge which will be automatically switched to when pressure is below 6mTorr.

### 4.4 Experimental

Substrate temperature and oxygen pressure are two controlling factors in PLD process. Substrate temperature mainly effects the activity of substrate material and dynamics of ejects, while oxygen pressure defines the shape of plume.

In our system, substrate thermal source is the radiation heater behind whose temperature is detected by a thermometer attached. However, the ellipsometric data of Si suggests that the temperature on substrate surface be far below the reading of the thermometer. Substrate was silver-painted to the tantalum holder in good thermal contact. The temperature gradient may explain the temperature difference between substrate surface and heater. A careful temperature recalibration is carried out and shown in Figure 4.10. All temperature values cited afterward are substrate temperatures after calibration.

Oxygen pressure plays an important role in defining the shape of plume. Figure 4.11 shows plume shapes under different oxygen pressure induced by the same laser energy 600 mJ/pulse. Plume under 50mTorr oxygen looks very thin and pale. When oxygen pressure was increasing, plume became longer and stronger and reached its maximum at 150mTorr oxygen. At that point, plume fully occupied the distance between substrate and target, and moved periodically as the laser beam was rastering. When oxygen pressure was 500mTorr, the plume expanded vertically but shrank in longitudinal direction, just like a light bulb. Implanting oxygen to 1000mTorr(the maximum pressure allowed in our chamber), plume continuously shrank in volume, and was only half way to the substrate at last.

Different PLD setup would differently optimize deposition conditions. In [25], their films were grown from phase-pure stoichiometric ceramic LiCoO<sub>2</sub> target in a controlled atmosphere vacuum chamber using a 248nm, 325-415mJ/pulse, excimer laser operating at 10 Hz. Typically one deposition ran 10,000 to 20,000 pulses. Their films were deposited in the oxygen pressure range (50, 3000) mTorr over the substrate temperature range(300°C,700°C). Julien *et al.* added a variable Li<sub>2</sub>O content in the range 5-15 weight percent in order to compensate the Li loss during deposition[32]. Their energy source



Figure 4.10: Temperature calibration of substrate surface

was a Nd:YAG Lumonics laser ( $\lambda$ =532 nm, pulse duration 10 ns). Thin film deposition was performed in 50 mTorr oxygen at different temperature from room temperature to 300°C.

In this work, we chose 3 inch Si wafer from MBE lab in AMPEL as the substrate material, since Si is the best known material that can be precisely characterized by ellipsometry. Si wafer was cut into  $10\text{mm} \times 10\text{mm}$  pieces. They were cleaned to get rid of surface grease and dust before use and were Ag painted to the inconel substrate holder to reach good thermal conduction, as shown in Figure 4.9. Substrates were loaded inside the main chamber through load lock and were attached to the radiation heater by 3 springs at the center of the chamber. Before deposition, the base pressure inside chamber was kept at  $4.8 \times 10^{-8}$  Torr. During growing, the desired oxygen pressure was maintained by balancing an appropriate and actively controlled O<sub>2</sub> flow rate against the pumping speed determined by the evacuation valve opening, set manually before the deposition run. Films were typically grown over the substrate temperature range (room temperature, 600°C) in oxygen pressure range (50, 150) mTorr. During deposition, the excimer laser was fired 10,000 shots at 2 Hz with 600mJ/pulse. The beam was rastering over



Figure 4.11: Different plume shapes under different oxygen pressures with the same laser energy density.

the target surface by the periodical moving of mirror. The substrate was rotating at a constant speed (usually  $60^{\circ}$  /second )to improve film uniformity. Meanwhile, in situ ellipsometry data was taken to trace the deposition.

After deposition, we took *ex situ* ellipsometry data of the films. The films were also characterized by X-ray diffraction and atomic force microscope (AFM). Resistivity and thickness of the films were also measured. Details of characterizations are discussed in Chapter 5 and 6.

# Chapter 5

# Ellipsometer

### 5.1 Ellipsometry Introduction

Ellipsometry is a sensitive measurement technique. It uses polarized light to characterize thin films, surfaces, and material microstructure. Figure 5.1 shows the geometry of ellipsometer. Linearly polarized light is cast onto the sample surface, interacts and then reflects off. The interaction with the sample surface causes changes of light polarization, from linear to elliptical polarization. The polarization change is then detected by analyzing the light reflected from the sample. The measured values are expressed as psi ( $\Psi$ ) and delta ( $\Delta$ ). These values are related to the ratio of Fresnel reflection coefficients  $\widetilde{R_p}$  and  $\widetilde{R_s}$  for p- and s- polarized light, respectively.

$$\rho = \frac{R_p}{R_s} = tan(\Psi)e^{i\Delta} \tag{5.1}$$

Ellipsometry is commonly used to characterize both thin films and bulk materials. The most frequent application is measurement of thin film thickness and optical constants. For many samples, ellipsometry is sensitive to film thickness on a sub-monolayer level. It has also proved to be the primary technique for determining optical constants in the full wavelength ranges, from ultraviolet to infrared. Ellipsometry is very flexible and is sensitive to many microstructural material properties, such as surface roughness, interfacial information, and doping concentration, etc.

Spectroscopic ellipsometry combined with variable angle of incidence is an extremely powerful measurement technique. The combination of variable angle of incidence and spectroscopic measurements allows the user to acquire large amounts of data from a given sample. The spectral acquisition range and angles of incidence may be optimized for the determination of certain sample parameters such as a layer thickness or the optical constants of one of the films. As a result the variable angle of incidence spectroscopic ellip-



Figure 5.1: Geometry of an Ellipsometric measurement. Credit from [27].

someter has the flexibility necessary to handle a very broad range of sample materials and structures, and has the power to characterize many complex structures which single angle and/or single wavelength ellipsometers cannot.

Many simple samples may be characterized by ellipsometric measurements at a single wavelength, while spectroscopic measurements are able to provide much more information about the sample. They can acquire data in spectral regions where the measured data are sensitive to the unknown model parameters, like film thickness. In many cases the dispersion (variation with wavelength) of the optical constants of a given material is known, or the optical constants may be parameterized in such a way as to enforce some type of dispersion on the optical constants (for example, Cauchy, Lorentz, and parametric semiconductor models). In this case, the acquisition of spectroscopic data enables the user to obtain more information from the analysis of spectroscopic data than would be possible by analyzing data from a single wavelength.

Ellipsometry works best for film characterization when the film thickness is not too much smaller or larger than the wavelength of the light used for the measurement. It is relatively difficult to use a probe of 500nm wavelength to characterize a 0.5nm or 10,000nm thick film, whereas films from about 5nm to 1000nm are much simpler to characterize with this wavelength. Also, roughness features on the sample surface or at film interfaces should be less than ~10% of the probe beam wavelength for the ellipsometric analysis to be valid. Larger features can cause non-specular scattering of the incident beam and depolarization of the specularly reflected beam. Finally, a critical factor is the uniformity of a film within the measured spot. It is best if the thickness of the film under study varies by no more than about 10% over the width of the spot on the sample surface. If not, the assumption of parallel interfaces of the film is invalid, and the calculated data cannot be expected to match the experimental data.

Ellipsometric measurements are very precise, because it measures the ratio of two values. Also, if the model used to fit the ellipsometric data is unique (i.e., does not contain any strongly correlated parameters), the results of the modelling of the ellipsometric data will be very precise as well, meaning that many measurements of the same quantity (a layer thickness, for example) will yield the same result to a very high degree of precision.

## 5.2 Relection of polarized Light from Planar Structures

#### 5.2.1 Measurement Geometry

Ellipsometer measures the sample parameters  $\Psi$  and  $\Delta$  by launching a probe beam with a known polarization state onto the sample and then measuring the polarization state of the reflected beam. In Figure 5.1, a linearly polarized input beam is converted to an elliptically polarized reflected beam.

The coordinate system used to describe the ellipse of polarization is the p-s coordinate system. The s-direction is taken to be perpendicular to the direction of propagation and parallel to sample surface. The p-direction is taken to be perpendicular to the direction of propagation and contained in the plane of incidence. The plane of incidence (shaded in Figure 5.1) is defined as the plane containing the input and output beams, and the normal of sample surface.

The incident angle is defined as the angle between the input beam direction and the direction normal to the sample surface. For any angle of incidence greater than 0° and less than 90°, p-polarized light and s-polarized lights will be reflected differently. This means that  $R_p \neq R_s$ .

#### 5.2.2 Optical Constants

Ellipsometry is an optical technique that requires an accurate model of the measurement process to analyze the measured data. The key components of all ellipsometric models are the optical constants of the substrate and sample layers and the thicknesses of the layers. To obtain good model fits to the measured data, highly accurate optical constants are required.

In our case, optical constants are expressed as a complex dielectric function,  $\tilde{\varepsilon} = \varepsilon_1 + i\varepsilon_2$ , or as a complex refractive index,  $\tilde{n} = n + ik = \sqrt{\tilde{\varepsilon}}$ . We consider any optical constants with a positive imaginary part to represent an absorbing material.

With regard to the available published optical constant sets, spectroscopic ellipsometry has had something of an iterative history. First, simple samples were measured and the data analyzed to obtain useful optical constants. Then those optical constants were used in modelling more complicated samples that in turn yielded optical constants for additional materials. In this way, a large base of optical constants has already been accumulated.

Alternatively, some materials do not seem to have intrinsic optical constants, in that the optical constants depend on the deposition process. Materials such as TiN,  $TiO_2$ , and polycrystalline silicon exhibit a range of optical constants depending on how they are deposited. Metal films are also notable because the grain structure and surface morphology greatly impact their apparent optical constants.

The optical constants of real materials have some sort of expected dispersion as a function of wavelength. They are not random functions, but generally smooth functions of wavelength and there is a causality relationship (the Kramers-Kronig relation) between the real and imaginary parts. Because of this, the optical constants for many materials can be very adequately modelled using functional forms.

#### **Bulk Materials**

For bulk materials, assuming it to be optically thick and no coatings or overlayers, we can calculate the Fresel reflection coefficients. The reflected and transmitted beam from the sample surface is described by Jones matrix equations:

$$\begin{bmatrix} \widetilde{E}_p \\ \widetilde{E}_s \end{bmatrix}^{reflected} = \begin{bmatrix} \widetilde{r}_p & 0 \\ 0 & \widetilde{r}_s \end{bmatrix} \cdot \begin{bmatrix} \widetilde{E}_p \\ \widetilde{E}_s \end{bmatrix}^{incident}$$
(5.2)

$$\widetilde{E}_{p} \\
\widetilde{E}_{s} \end{bmatrix}^{transmitted} = \begin{bmatrix} \widetilde{t}_{p} & 0 \\ 0 & \widetilde{t}_{s} \end{bmatrix} \cdot \begin{bmatrix} \widetilde{E}_{p} \\ \widetilde{E}_{s} \end{bmatrix}^{incident}$$
(5.3)

Thus, the Fresnel reflection coefficients are defined as follows:

$$\widetilde{r}_{p} \equiv \frac{\widetilde{E}_{p}^{reflected}}{\widetilde{E}_{p}^{incident}}$$

$$\widetilde{r}_{s} \equiv \frac{\widetilde{E}_{s}^{reflected}}{\widetilde{E}_{s}^{incident}}$$

$$\widetilde{t}_{p} \equiv \frac{\widetilde{E}_{p}^{transmitted}}{\widetilde{E}_{p}^{incident}}$$

$$\widetilde{t}_{s} \equiv \frac{\widetilde{E}_{s}^{transmitted}}{\widetilde{E}_{p}^{incident}}$$
(5.4)

The p- and s- components of the incident, reflected, and transmitted electromagnetic waves may now be written as :

$$\vec{E}_{p,s}^{incident}(\vec{r},t) = \vec{E}_{0p,s}^{incident} exp(\frac{i2\pi\tilde{n}_{0}}{\lambda}\hat{q}_{incident}\cdot\vec{r})exp(-i\omega t)$$
$$\vec{E}_{p,s}^{reflected}(\vec{r},t) = \vec{E}_{0p,s}^{reflected}exp(\frac{i2\pi\tilde{n}_{0}}{\lambda}\hat{q}_{reflected}\cdot\vec{r})exp(-i\omega t)$$
$$\vec{E}_{p,s}^{transmitted}(\vec{r},t) = \vec{E}_{0p,s}^{transmitted}exp(\frac{i2\pi\tilde{n}_{0}}{\lambda}\hat{q}_{transmitted}\cdot\vec{r})exp(-i\omega t)$$
(5.5)

The unit vector  $\hat{q}$  lies along the propagation direction of the beam.

Insert Eqns 5.5 into definition equations 5.4 for the Fresnel reflection and transmission coefficients. Subjected to boundary conditions, the tangential components of  $\vec{E}$  and  $\vec{H}$  are required to be continuous, so are the normal

components of  $\vec{D}$  and  $\vec{B}$ . In addition, the phase quantities to be identical at all points on the interface. Some useful results are yielded:

First, the reflected angle must be equal to the incident angle. That means the beam will be specularly reflected from the sample. Second, the equality of phase at the interface leads to the famous *Snell's* law:

$$\tilde{n}_0 \sin\phi_0 = \tilde{n}_1 \sin\phi_1 \tag{5.6}$$

Third are the expressions for the Fresnel reflection and transmission coefficients for the surface of the bulk sample:

$$\begin{split} \tilde{r}_p &= \frac{\tilde{n}_1 cos\phi_0 - \tilde{n}_0 cos\widetilde{\phi}_1}{\tilde{n}_1 cos\phi_0 + \tilde{n}_0 cos\widetilde{\phi}_1} \\ \tilde{r}_s &= \frac{\tilde{n}_1 cos\phi_0 - \tilde{n}_0 cos\widetilde{\phi}_1}{\tilde{n}_0 cos\phi_0 + \tilde{n}_1 cos\widetilde{\phi}_1} \\ \tilde{t}_p &= \frac{2\tilde{n}_0 cos\phi_0}{\tilde{n}_1 cos\phi_0 + \tilde{n}_0 cos\widetilde{\phi}_1} \\ \tilde{t}_s &= \frac{2\tilde{n}_0 cos\phi_0}{\tilde{n}_0 cos\phi_0 + \tilde{n}_1 cos\widetilde{\phi}_1} \end{split}$$
(5.7)

Now  $\Psi$  and  $\Delta$  can be simply evaluated by inserting equations above into the ellipsometric equation Eqn 5.1. It is instructive to use these equations to examine the behavior of  $\Psi$  and  $\Delta$  as functions of incident angle for different choices of the sample index of refraction. Note that the ambient index is chosen to be one, with no absorption, corresponding to air or free space.

#### Single Films on Thick substrates

Multiple reflections of the incident light beam occur in the film when the beam is cast on to a single film on an optically thick substrate as shown in Figure 5.2. In principle, there are an infinite number of reflected and transmitted beams, but they quickly die out after reflections, because the splitting of the beam into reflected and transmitted components at each reflection quickly reduces the amplitude of the subsequent reflections. In addition, the beam would be more attenuated if any absorption happens in the film.



Figure 5.2: Multiple reflected and transmitted beams for a single film on an optically thick substrate

It is simple to show that propagation of a wave across the film results a wave of the following form:

$$\widetilde{E}_{after} = \widetilde{E}_{before} \cdot e^{-i2\beta} \tag{5.8}$$

where  $\beta$  is the optical thickness of the film for the given wanvelength and incident angle, given by:

$$\beta = 2\pi \tilde{n}_1 \frac{d}{\lambda} \cos \tilde{\phi}_1 = 2\pi \frac{d}{\lambda} \sqrt{\tilde{n}_1^2 - \tilde{n}_0^2 \sin^2 \phi_0}$$
(5.9)

in which d is the film thickness and  $\lambda$  is the wavelength. Quantities relating to the ambient medium have the subscript '0', while film-related quantities are denoted with the subscript '1'. Correspondingly, the subscript '2' labels quantities relating to the substrate. In the following, all Fresnel reflection and transmission coefficients will be given two numbers for a subscript, where the first one denotes the region from which the beam is incident on the interface, and the second one denotes the region on the other side of the interface. Now we can express the successive reflected beams in Figure 5.2 as follows:

$$\widetilde{E}_1^r = \widetilde{r}_{01} \widetilde{E}_{incident} \tag{5.10}$$

$$\widetilde{E}_2^r = \widetilde{t}_{10}\widetilde{t}_{01}\widetilde{r}_{12}e^{-i2\beta}\widetilde{E}_{incident}$$
(5.11)

$$\widetilde{E}_3^r = \widetilde{t}_{10}\widetilde{t}_{01}\widetilde{r}_{10}\widetilde{r}_{12}^2 e^{-i4\beta}\widetilde{E}_{incident}$$
(5.12)

$$\widetilde{E}_4^r = \widetilde{t}_{10}\widetilde{t}_{01}\widetilde{r}_{10}^2\widetilde{r}_{12}^3 e^{-i6\beta}\widetilde{E}_{incident}$$
(5.13)

and so no. The general form for the  $n_{th}$  reflected beam can be written as :

$$\widetilde{E}_n^r = \widetilde{t}_{10}\widetilde{t}_{01}\widetilde{r}_{10}^{n-2}\widetilde{r}_{12}^{n-1}e^{-i(2n-2)\beta}\widetilde{E}_{incident}$$
(5.14)

The summation of the reflected beam using this form is:

$$\widetilde{E}_{total}^{r} = \left[\widetilde{r}_{01} + \widetilde{t}_{10}\widetilde{t}_{01}e^{-i2\beta}\sum_{i=2}^{\infty}\widetilde{r}_{10}^{n-2}\widetilde{r}_{12}^{n-2}e^{-i2n\beta}\right] \cdot \widetilde{E}^{incident}$$
(5.15)

From Eqns 5.7, we can deduce that:

$$\tilde{r}_{01} = -\tilde{r}_{10}\tilde{t}_{10}\tilde{t}_{01} = 1 - \tilde{r}_{01}^2$$
(5.16)

Plugging Eqn 5.16 into 5.15, and evaluating the resulting convergent series,

the total reflected beam can be expressed as follows:

$$\widetilde{E}_{total}^{r} = \left(\frac{\widetilde{r}_{01} + \widetilde{r}_{12}e^{-i2\beta}}{1 + \widetilde{r}_{01}\widetilde{r}_{12}e^{-i2\beta}}\right) \cdot \widetilde{E}^{incident}$$
(5.17)

This equation is valid for p- or s- polarized input beam, provided that the corresponding p- or s- polarized Fresnel reflection coefficients for the interfaces are employed. By using equation 5.17, we find the pseudo-Fresnel reflection coefficient  $\tilde{R}_p$  <sup>1</sup>as follows:

$$\widetilde{R}_{p} \equiv \frac{\widetilde{E}_{total}^{r}}{\widetilde{E}^{incident}} = \frac{\widetilde{r}_{01} + \widetilde{r}_{12}e^{-i2\beta}}{1 + \widetilde{r}_{01}\widetilde{r}_{12}e^{-i2\beta}}$$
(5.18)

We may now calculate  $\Psi$  and  $\Delta$  from a broader definition of the ellipsometric parameters, valid for any sample exhibiting pseudo-Fresnel p- and s-polarized reflection coefficients  $\widetilde{R}_p$  and  $\widetilde{R}_p$ , respectively:

$$\widetilde{o} = \tan \Psi e^{i\Delta} \equiv \frac{\widetilde{R}_p}{\widetilde{R}_s} \tag{5.19}$$

## 5.3 M-2000 Spectroscopic Ellipsometer Configurations

All ellipsometer arrangement start with a light source and end with a detector. It is the arrangement of optical components between the source and detector that defines the type of ellipsometer being used. There are three types of ellipsometers-null, polarization modulation, and rotating element ellipsometers. In our system, M-2000 spectroscopic ellipsometer belongs to the last type with a rotating compensator.

#### 5.3.1 Optical Components used in Ellipsometer

Light source: Spectroscopic ellipsometers require a broad spectral output to match the desired range of measurement. Ideally the light source would

<sup>&</sup>lt;sup>1</sup>Pseudo-Fresnel coefficient is defined in terms of the incident, reflected and transmitted beam. They contain information of both the film and the substrate. The properties of thin film can be extracted from further analysis.

Type	Window Material	Max Avg. Input Power	$\begin{array}{c} \text{Min } \lambda \\ \text{(nm)} \end{array}$	$\max_{(nm)} \lambda$	Avg life(hr)
Xenon	Fused Silica	75W	185 .	2000	2000

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#### Table 5.1: Specifications of Xenon arc lamp.

be very stable (constant intensity vs. time) and exhibit roughly constant output as a function of wavelength over the necessary spectral range. M-2000 spectroscopic ellipsometer uses Xenon arc lamp which can generate beam light from 185nm in deep ultraviolet to 2000nm in infrared. Its specifications are listed in table 5.3.1. However, the range ellipsometry measures is from 248nm to 1892nm.

**Optical Fibers**: Optical fibers are used in M-2000 spectroscopic ellipsometer in order to couple the light beam between optical elements. These fibers typically have a 200-400micron core diameter. Two types of fibers are used. The UV transmitting fibers exhibit good transmission deep into the UV end of the spectrum, but have a strong absorption band around 1340-1450nm such that they cannot be used in this spectral region. The IR fibers do not transmit much light below 300nm, but are transmitting throughout the NIR region.

**Beam modulators**: Two types of devices are commonly used for beam modulation. The first is the simple mechanical chopper to harmonically modulate the intensity of the light beam, for subsequent synchronous detection. Electro-optic or magneto-optic modulators are also commonly used to harmonically perturb either the beam intensity or polarization state for subsequent synchronous detection. These types of modulators can be very difficult to calibrate and maintain, and very sensitive to temperature.

**Polarizers**: The most important optical element for making ellipsometric measurements is the polarizer. An ideal polarizer will transmit light polarized in one direction, but will extinct any light polarized along the perpendicular direction. A polarizer converts any light beam into linearly polarized light oriented along the transmission direction. The Jones matrix for an ideal polarizer will depend on the orientation of the axis of the polarizer. Normalized Jones matrices for several polarizer orientations are shown below: Axis along  $p - direction : \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}$ Axis along  $s - direction : \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix}$ 

Axis 45° between p - and s - directions :  $\frac{1}{2} \begin{vmatrix} 1 \\ 1 \end{vmatrix}$ 

The best way to describe a polarizer of arbitrary orientation is to rotate the coordinate system to match the axis of the polarizer, use the p-direction polarizer matrix shown above, and then rotate the coordinate axes back to the normal p- and s-directions.

1

**Retarders**: A retarder introduces a phase delay between perpendicular linear polarizations (the perpendicular components of the electric field of the beam). They can be constructed from thin plates of birefringent material or from polished crystal rhombs. However, the exact retardation of such element is a strong function of optical alignment and of the light wavelength being used. Retarders are useful but they are harder to work with than polarizer.

Some ellipsometric measurement schemes use a compensator, which can convert linearly polarized light to circularly polarized light. An ideal compensator is an optical retarder that has a retardation of exactly  $90^{\circ}$  (or 1/4wave). A rotatable compensator combined with a rotatable polarizer can convert unpolarized light into any elliptical polarization.

**Detectors**: Three types of detectors are commonly used for ellipsometry: photodiodes, diode-arrays, and photomultiplier tubes. In the M-2000 spectroscopic ellipsometer, a charge-coupled device(CCD) enables simultaneous monitoring of hundreds of spectral components when the light beam disperses across it. Si arrays are used up to 1100nm, but are replaced with InGaAs to cover the near infrared (to 1700nm).

#### 5.3.2 Null ellipsometers

The null ellipsometer configuration is constructed as follows:

Source  $\Rightarrow$  Polarizer  $\Rightarrow$  Compensator  $\Rightarrow$  Sample  $\Rightarrow$  Analyzer  $\Rightarrow$  Detector

To perform a measurement, the orientation of the polarizer, compensator and analyzer are adjusted to "null" the light hitting the detector. Usually performed manually, this measurement technique is slow and it is very difficult to make spectroscopic measurements. Assuming quality optical elements and four zone nulling are used, the null configuration is accurate and has low systematic errors.

#### 5.3.3 Polarization modulation ellipsometers

The polarization modulation ellipsometer configuration:

 $Source \Rightarrow Polarizer \Rightarrow modulator \Rightarrow Sample \Rightarrow Analyzer \Rightarrow Detector$ 

The modulator is typically a time dependent retarder which can run at very high speeds, 50kHz. Theoretically, the high modulation rate allows for very fast data acquisition (10milliseconds per point). However, to achieve satisfactory signal-to-noise levels, either a very intense source, like a laser, or longer integration times are required. To perform spectroscopic measurements, the amplitude of the modulation needs to be adjusted at each wavelength. Constructing an ellipsometer of this type with stable calibration characteristics is difficult, and stable calibrations are necessary for high accuracy measurements, Also polarization modulators tend to exhibit strong sensitivity to the ambient temperature.

#### 5.3.4 Rotating Element Ellipsometers

Before rotating compensator ellipsometers, there are two types of rotating element ellipsometers: rotating polarizer ellipsometers (RPE) and rotating analyzer ellipsometers (RAE). Unlike the null and polarization modulation ellipsometer configurations, they don't include retarding elements after the polarizer, but are constructed with only two polarizers (polarizer and analyzer). However, RPE requires the light source to be totally unpolarized. Any residual polarization in the source will be a source of measurement error unless corrected. Similarly, RAE is susceptible to polarization sensitivity in the detectors. It is most accurate when the beam entering the detector is nearly circularly polarized and less accurate when the beam is nearly polarized. To alleviate these problems, a compensator is introduced into the system and implements the rotating compensator ellipsometer (RCE) configuration. The typical configuration of the rotating analyzer ellipsometer is:

 $Source \Rightarrow Polarizer \Rightarrow Continuously rotating Compensator \Rightarrow Sample \Rightarrow Analyzer \Rightarrow Detector M-2000$ 

There are many advantages to the RCE configuration, including: accurate measurement of the ellipsometric  $\Psi$  and  $\Delta$  parameters over the complete

spectral range( $\Psi = 0 - 90^{\circ}, \Delta = 0 - 360^{\circ}$ ), no residual input or output polarization sensitivity (due to a fixed polarizer on input and a fixed analyzer on output, and the capability to directly measure depolarization effects.

## 5.4 General Procedure for Optical Experiments

All optical experiments follow the same general procedure as outlined in Figure 5.3. Optical experiments never directly measure the sample parameters of interest (thickness, optical constants,etc.); rather they measure some quantity that is a function of the parameters of interest. It is then necessary to solve the inverse problem of modelling the measured data to estimate the values of the sample parameters that yield data predicted from the model which best match the measured data. This procedure may be divided into the following four steps.



Figure 5.3: General procedures used in ellipsometry measurements to determine material properties from experimental data.

First is the sample measurement. Optical experiments measure things like reflected or transmitted beam intensities or polarization states in the hope that these quantities are affected by the physical sample parameters we are interested in. Then by measuring these uninteresting optical quantities  $(R,T,\Psi,\Delta)$  we can somehow infer the values of the physical parameters of interest. Thus, we conduct an optical experiment and measure beam intensities (reflectance and transmittance) or polarization states (ellipsometric  $\Psi$ and  $\Delta$ ), usually as functions of the light beam wavelength, angle of incidence, and/or polarization state.

After measurement, we built a model from which we can accurately predict what we should measure from a sample of known properties. This model should contain some known parameters, such as the wavelengths of the incident light, the incident beam polarization state, and the incidence angle. The model should also contain some unknown physical parameters, such as layer thicknesses or optical constants.

Having developed a model, we can fit model to measured data. We vary the unknown physical parameters and generate data until we find a set of optimized parameters that minimize the differences between calculated data and measured optical data. These parameters are expected to accurately present the true physical structure of the sample under study. The Levenberg-Marquardt nonlinear multivariate regression algorithm is employed for the fitting process.

The last step is to evaluate the best-fit model. We must establish that the best-fit set of parameters are unique, physically reasonable, and not strongly correlated. If these criteria are met, we can conclude that the best-fit model probably represents the physical reality of the sample. We may also calculate a number of statistical quantities that help to evaluate the accuracy and precision of the fit results. The model can be modified if we are unsatisfied with the results; either because statistics show the results are not unique or because the features in the experimental data are not adequately described by the current model.

In the real experiment, what we do basically follows the procedures discussed above. First we took ellipsometry data of Sis substrate before deposition to get the information such as temperature and native oxide thickness. Then we took *in situ* ellipsometric data during the deposition and *ex situ* measurement afterward. After measurement, we built models to fit parameters of interest. The principle of building an effective model is to best describe the physical layers and properties of the film. Since Si is one of the well-studied materials, a good model is easy to build and to fit the data quite well. However, for some "new" materials, LiCoO<sub>2</sub> in our case, their optical data are still unclear and there is no existing optical constant files in built-in library. We have to extract them out. We could vary the optical constants directly at each measured wavelength, which means to fit 672 parameters with 672 data points at the same time. So many unknown parameters would correlate to each other then result in some ununique conclusion, sometimes even unphysical. A better way to avoid this problem is to parameterize the dispersion model. It benefits the modelling process in several ways. First they are inherently continuous, and can't exhibit random noise in the optical constants due to random experimental noise. Second, a constrained parameterization could decrease the number of unknown fitting parameters and then reduce strong correlations in the optical model. General-Oscillator (GesOsc) layer and effective medium approximations (EMA) are two mostly used special layers to model unknown materials' optical properties. Figure 5.4 shows the typical appearance of the GenOsc layer and EMA layer.

GenOsc layer use the summation of several oscillator functions that constrains to obey Kramers-Kronig relations to simulate optical constants. Kramers-Kronig relation is the relation between the real and imaginary parts of complex permittivity  $\epsilon(\omega)$ :

$$Re\{\epsilon(\omega)\} = \epsilon_0 + \frac{2}{\pi} \cdot P \int_0^\infty \frac{\Omega Im\{\epsilon(\Omega)\}}{\Omega^2 - \omega^2} d\Omega$$
$$Im\{\epsilon(\omega)\} = \frac{2\omega}{\pi} \cdot P \int_0^\infty \frac{Re\{\epsilon(\Omega)\} - \epsilon_0}{\Omega^2 - \omega^2} d\Omega$$
(5.20)

where the above integrals are Cauchy integrals and P denotes the Cauchy principal value.

It can be reformed in the following form in terms of refraction index n and extinction coefficient k:

$$n(\omega) = 1 + \frac{c}{\pi} \cdot P \int_0^\infty \frac{\alpha(\Omega)}{\Omega^2 - \omega^2} d\omega$$
 (5.21)

where  $\alpha$  is the intensity absorption coefficient, c is the light speed in vacuum.  $f(\omega)$  is a function to which Kramers-Kronig relations apply. Lorentz, harmonic, Gaussian, Tauc-Lorentz are all supported oscillators in GenOsc





Figure 5.4: Appearance of general oscillator and EMA layer

layer.

The EMA layer is used to calculate the optical constant spectra of mixtures of two or three materials of known optical constants, provided the volume fractions of the constituent materials and the physical geometry of the mixing are known. There are three different EMA mixing methods: simple linear combination, Bruggemean EMA, and Maxwell-Garnet EMA. The linear EMA interpolates between the constituents dielectric functions to get the optical constants of the composite material. The Maxwell-Garnett assumes spherical inclusions of materials two and three exist in a host matrix of material one. The Bruggeman EMA makes the self-consistent choice of the host material. The latter two are more commonly used[29]. EMA layer is very useful for describing surface and interfacial roughness.

When we built the model, we fit it to the measured data. We started with values cited from [30] to fit the data, and evaluated the resulting optical constants by checking their uniqueness and correlations. Then we improved the model and refit the experimental data starting with the newly achieved set of optical constants, and evaluated the new fitting results. We did it iterately until a satisfactory result is achieved.

# Chapter 6

# Other Characterization Techniques

### 6.1 X-ray Diffraction

X-ray diffraction is probably the most widely used technique for investigation of the atomic structure of matter. The scattered X-ray from crystals provide information on the location of atoms within solids. In our experiment, we use XRD to investigate the crystal structures of  $\text{Li}_x\text{CoO}_2$  films and determine their lattice constants.

Bragg's Law is usually applied to explain diffraction peaks' position. In Bragg's model, a crystal is made out of parallel planes of ions separated by a distance d. X-ray will be specularly reflected by any one of the planes. A sharp peak would appear when the "reflected" rays from successive planes interfere constructively (Fig6.1). In other words, the path difference should be an integer number of wavelength,

$$n\lambda = 2dsin\theta \tag{6.1}$$

where  $\theta$  is the diffraction angle, d is the spacing between the planes in the atomic lattice,  $\lambda$  is the wavelength of the x-ray.

In our case,  $LiCoO_2$  crystallizes in a hexagonal lattice, then the spacing d can be expressed as:

$$d = \frac{1}{\sqrt{\frac{4}{3}\frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2}}}$$
(6.2)

where a, c are lattice constant of the hexagonal lattice constants, and h, l, h, k are the Miller indices.

Plugging equation (6.2) into Bragg's Law 6.1, the final equation for the



Figure 6.1: Bragg's law

diffraction angle of hexagonal lattice constants becomes:

$$\sin^2 \theta = \frac{\lambda^2}{4} \left[ \sqrt{\frac{4}{3} \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2}} \right]$$
(6.3)

When more than one atom is contained in the unit cell, the relative position of different atoms in the unit cell changes the phase of the scattered wave from each atom and consequently effect the interference between them. In that case, a new term "structure factor" should be introduced in order to describe the effect:

$$s = \sum_{i} f_i(\vec{K}) e^{i\vec{K}\cdot\vec{R}_i} \tag{6.4}$$

where  $\vec{K}$  is the reciprocal lattice and  $\vec{R_i}$  is the relative position of different atoms in the unit cell.  $f_i(\vec{K})$  is the atomic form factor and is entirely determined by the internal properties of the atoms.

The x-ray diffraction experiment was performed with Rigaku and Simens X'pert diffractometer x-ray facilities in the  $\theta/2\theta$  mode. Figure 6.2 shows the basic components of the Rigaku. X-rays are generated by bombarding a copper target held in vacuum with high energy electrons in the following



Figure 6.2: Scheme of xray setup. The generated X-rays are diffracted by the sample and reflected by the graphite monochromator to filter  $K_{\alpha}$  lines our of the undesirable wavelengths. The monochromator is arranged such that  $\phi$  satisfies Bragg condition for (001) reflection from graphite for  $K_{\alpha}$  lines. Finally, the signals are detected by a conventional detector operating in room temperature.

atomic transition:

$$K_{\alpha 1} : 2p_{3/2} \mapsto 1s_{1/2}, \lambda = 1.540598A \tag{6.5}$$

$$K_{\alpha 2} : 2p_{1/2} \mapsto 1s_{1/2}, \lambda = 1.544418A \tag{6.6}$$

During the scan, we fix the x-ray source, rotate the sample by the Bragg angle  $\theta$  with respect to the incident vector  $\vec{k}$  and rotate the detector by  $2\theta$ with respect to  $\vec{k}$ . This geometry is referred as the  $\theta/2\theta$  mode.

## 6.2 Atomic Force Microscopy(AFM)

The atomic force microscope(AFM) is a very high-resolution type of scanning surface probe microscope. It consists of a microscale cantilever with a sharp tip (probe) at its end that is used to scan the specimen surface. The cantilever is typically silicon or silicon nitride with a tip radius of curvature on the order of nanometers. When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according Hooke's law. Depending on the situation,

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Figure 6.3: Block diagram of AFM. Credit from [28]

forces that are measured in AFM include mechanical contact force, Van der Waals forces, capillary forces, chemical bonding, electrostatic forces, magnetic forces, Casimir forces etc. The deflection is measured using a laser spot reflected from the top of the cantilever into an array of photodiodes.

If the tip were scanned at a constant height, there would be a risk that the tip would collide with the surface, causing damage. Therefore, a feedback mechanism is employed to adjust the tip-to-sample distance to maintain a constant force between the tip and the sample. The sample is mounted on a piezoelectric tube, that can move the sample in the z direction for maintaining a constant force, and the x and y directions for scanning the sample.

The AFM are commonly operated in two modes: contact mode and tapping mode. In contact mode, the force between the tip and the surface is kept constant during scanning by maintaining a constant deflection. In our case, AFM scanning was done in tapping mode. In the tapping mode, the cantilever is externally oscillated at or close to its resonance frequency. It is positioned above the surface so that it only taps the surface for a very small fraction of its oscillation period. The oscillation amplitude, phase and resonance frequency are modified by tip-sample interaction forces; these changes in oscillation with respect to the external reference oscillation provide information about the sample's characteristics.

### 6.3 Thickness and Resistivity Measurements

Apart from the characterization methods discussed above, we made thickness and resistivity measurements via other techniques.

Film thickness measurement is taken with Canon Mask Aligner PLA-501 and alpha step profilometer both located inside AMPEL cleanroom. First a  $2\mu$ m layer of photoresist was spin on top of the film and exposed under mask aligner with half of film surface shielded. Wash away the shielded half of PR after baking, and etch that part film layer away to make a sharp step. At last clean the other half of PR on film surface. The depth of the step was the thickness of the film and was measured with alpha step profilometer. The obtained thickness then is compared with that extracted from ellipsometric data.

Since film resistivity behaves as a function of film Li content, we use the standard 4-wire Kelvin technique to measure the film resistivity and compare it with published result[6].

# Chapter 7

# **Results and Discussions**

After deposition, films were characterized by XRD, ellipsometer and AFM. Their thicknesses and resistivity were also measured. This chapter presents the film structures determined by XRD, optical constants obtained by ellipsometer, film morphology revealed by AFM, thickness measured by alphastep and Li content derived from resistivity.

### 7.1 Film Structure and Lattice Constants

Film structure is strongly related to the substrates. If the substrate lattice constants match those of the film lattice, film may be grown in a preferred direction. Table 7.1 shows lattice mismatching<sup>1</sup> of some substrates we tried. From Table 7.1, we could expect that the films deposited on Si (100) substrate would prefer to grow in (001) orientation, while those on STO and MgO would be oriented off the c-axis. The lattice constants of the film is also a function of deposition condition (substrate temperature, oxygen pressure, etc.). X-ray diffraction allows us to test the expectation based on substrate lattice matching.

Figure 7.1a) shows the XRD pattern of LiCoO<sub>2</sub> powder. All peaks are indexed in hexagonal system. Since it's a powder sample, without preferred orientation, all diffraction peaks should be recorded by the detector through the whole scan. Compared with the XRD pattern of HT-LiCoO<sub>2</sub>, the presence of hexagonal (006) and (012) peaks indicates hexagonal structure of the powder. This is confirmed by the hexagonal (018) and (110) peaks splitting from cubic (440) peak due to hexagonal distortion. Lattice constants calculated from XRD pattern are:  $a = 2.83 \pm 0.01$  Å,  $c = 14.28 \pm 0.02$  Å. Experimental a and c are 0.5% and 1.6% larger than literature values[4][6] respectively.

Figure 7.1 shows the XRD spectrum of the film on Si (100) substrate.

 $<sup>^{1}</sup>$ Mismatching= $\frac{|substrate\ lattice\ constant-film\ lattice\ constant|}{film\ lattice\ constant|}$ 



(b)

Figure 7.1: a) is  $LiCoO_2$  powder XRD pattern labelled in hexagonal lattice. b) is the spectrum of the film deposited on Si substrate. The film was grown at  $450^{\circ}C$  under 150mTorr oxygen. Compared with a), only (00n) peaks are present. The films deposited on Si substrate are thus highly c-axis oriented.

			· · · · · · · · · · · · · · · · · · ·	
material LiCoO <sub>2</sub>	$a(100)(\text{\AA})$ 2.8155		a (104)(Å) 2.003	1/3 of c(001(Å)) 4.77
substrate	$a(100)({ m \AA}) ({ m \AA}) ({ m \AA})$	Mismatching in (100)	Mismatching in (104)	Mismatching in (001)
${ m Si(100)}\ { m MgO(100)}\ { m Ge(100)}$	5.4037 4.216 5.64613	0.919268 0.497425 1.005374	1.6697803 1.104843 1.818837	$\begin{array}{c} 0.132851 \\ 0.11614 \\ 0.311181 \end{array}$

Chapter 7. Results and Discussions

Table 7.1: Mismatching of several substrates in different orientations.

Compared with Figure 7.1, we can see the big difference between the two graphs. As expected from Table 7.1, films on Si are highly c-axis oriented. Except two Si substrate peaks, only (00n) peaks are present. With the information provided by XRD graph, only the lattice constant c can be extracted:  $c = 14.17 \pm 0.06$  Å.

In Figure 7.2, two XRD spectra are presented. These 2 film samples were deposited under exactly the same temperature and oxygen pressure. The only difference is that, for Sample A, a very thin silver layer of 66Å thick was sputtered on top of Si substrate before the film was deposited. Both films are c-axis oriented since (0 0 3) peaks are dominant in both patterns. However, the thin Ag layer on top of Si still makes Sample A different from B. The presence of (101) and (104) peaks indicates that it's less c-oriented than Sample B. The lattice constants are:  $c = 14.15 \pm 0.08$ Å for Sample B, and  $c = 14.15 \pm 0.09$ Å for Sample A. c values of these two samples are consistent within uncertainties.

Figure 7.3 a) shows patterns of thin films on MgO substrate deposited under different conditions. Growing conditions are listed in Table 7.2. Green line is bare Magnesium Oxide substrate in (100) direction. For Sample A, the two non-substrate peaks correspond to peak (104) and (208) of  $\text{LiCoO}_2$ respectively, as we expected that films grown on MgO substrate should oriented in off-c-axis direction. But Sample B and C show a different orientation. The two main non-substrate peaks of these two are diffracted from plane (101) and (202). Deposition temperature is the main factor affecting the structure of the resulting films. Particles arriving at a hotter substrate



Figure 7.2: A) is the x-ray diffraction spectrum of the film deposited on Ag coated Si substrate. B) is the XRD spectrum of the film deposited on Si substrate.

label	Temperature (° $C$ )	Oxygen Pressure(mTorr)
А	530	150
В	room temperature	50
С	238	50

Table 7.2: Growing conditions of films on MgO substrate

surface can anneal and diffuse to their lowest energy configuration and follow the direction it prefers. Comparing Sample B and Sample C, the intensity ratio of LiCoO<sub>2</sub> (101) peak to MgO (200) peak increases from 1.29 to 1.48 as deposition temperature increases from room temperature to  $238^{\circ}C$ . Both of the films were made of the same number of laser shots on the same MgO substrates, therefore they should be about the same thickness. Consequently, thickness difference contributes little to the peak intensity ratio difference, so that different ratios mainly suggest the difference in film crystallization. Now we can conclude that raising temperature also improves film crystallization.

Spectrum of films deposited on Ge substrate (100) is really strange as shown in Figure 7.3 b). Several peaks belonging to different plane families show up in the spectrum and no substrate peaks are detected at all. Ge substrate used is in (100) direction with 6° off to (111). Deposition is processed at 398°C under 100mTorr oxygen, which are normal conditions for other substrates. From table 7.1, we would expect the films on Ge grow in c-axis. However, on the contrary to the expectation, it seems to be polycrystalline without a preferred orientation.

### 7.2 Deposition and Optical Constants

Ellipsometry was used as the *in situ* characterization of the the deposition process. Before deposition, we took ellipsometric data of hot Si substrate, extracted its temperature and native oxide layer thickness from data fitting, and fixed those quantities for subsequent steps. Figure 7.4 shows a very good fitting for Si data. The fitting yields the temperature at Si surface  $593 \pm 2^{\circ}C$  and the thickness of native oxide layer  $15.8 \pm 0.1$ Å thick. Mean Square Error(MSE) is the quantity to characterize the goodness of the fitting. 3.1046 is a very tolerant value. Since Si is one of the best known materials, the model fits data quite well and leads to very precise and reasonable values for temperature and surface morphology which are confirmed by temperature recalibration (refer to Figure 4.10) and AFM scanning.

Ellipsometry is a very sensitive technique. It can pick up the changes in  $\Psi$  and  $\Delta$  within several laser shots. Figure 7.5 a) shows the spectra in successive 4 mins during one deposition process. We can clearly see the changes in  $\Psi$  as the film was being grown. The 4 lines are similar in shape with shift in position of feature. In the growth process, laser was fired at 1Hz







Figure 7.3: a) XRD spectra of films deposited on MgO substrates under different conditions. b) XRD spectrum of the film deposited on Ge substrate.



Figure 7.4: Ellipsometry data fitting for Si(100) substrate.

corresponding to a deposition rate at 14Å per minute. This suggests that ellipsometry has the resolution to detect the changes when film thickness increases by, at least, every 14Å in one minute. Therefore we could take *in situ* ellipsometric data to track the deposition process. In situ data can be presented in 2 ways. Figure 7.5 b) shows  $\Psi$  corresponding to 5 different wavelengths varies as a function of time as the deposition process goes on. We can also show the spectrum of whole wavelength range, as shown in Figure 7.5 c) and d), at different time. The time resolution is 3s in this case. The changes in shape indicate the film optical properties vary as the it grows thicker. With the fitting of *in situ* data , we could fit film final thickness and deposition rate. For this sample, we obtain film thickness (1837±104)Å, and a deposition rate (0.36±0.02)Å per laser shot

After deposition, we took *ex situ* data with multiple incident angles to better analyze our films. Multi-angle data is shown in Figure 7.6 with red fitting lines. Then we built a model to derive film optical constants with a fixed thickness.

The model used to fit data is shown in Figure 7.7. Starting from the bottom, the first layer is Si substrate with a fixed thickness 0.5mm. Next is



Figure 7.5: a) is the spectra of 4 successive minutes in one deposition process. b) is the time spectrum of  $\Psi$  corresponding to 5 wavelengths. c) and d) are spectra of  $\Psi$  and  $\Delta$  respectively at several time slices. The changes in shape indicate the changes in the film optical properties.



Figure 7.6: Spectra of multiple incident angles.

native-oxide layer which is an interface layer between main substrate and film. Its thickness is obtained from data of Si substrate measured before deposition. A third one is  $LiCoO_2$  film layer. Unfortunately, there is no existing optical property files in built-in library, then we have to use a General-Oscillator layer (see details in Chapter 5) instead to extract them as well as the film thickness. Figure 5.4 a) shows the details of the GenOsc layer. In this case, it includes only three oscillators, one Lorentz and two Gaussian. When all the oscillator parameters are selected to be fitting parameters as well as layer thickness, the total number of fitting parameters is only 10, much fewer than 672 if varing the optical constants directly at each measured wavelength. Therefore General-Oscillator layer decreases the risk of correlation between unknown fitting parameters. For films, we always care about surface roughness after deposition. Here we use EMA layer to simulate film surface roughness. As shown in Figure 5.4 b), EMA layer was mixed by 20% void layer and 80% GenOsc layer for LiCoO<sub>2</sub>. Both layer thickness and compositional fraction were open to fit.

The model discussed above reasonably describes physical structure of our film in the absence of interdiffusion or substantial Li loss. After several fitting iterations, it works out the thickness and film optical constants. From Figure 7.6, we can see that the model fits reasonably well with small deviations at the infrared region. The resulting refraction indice and extinction coefficients
3 ema (ge10sc2_11)/06_2)/83.7% vold	0.399 Im
2 ge10sc2_11,06_2	168.452 im
i itue_jaw	2.000 nm
0 \$I	0.5 mm

Figure 7.7: The model used to fit ellipsometric data of  $LiCoO_2$  film.



Figure 7.8: Optical constants of  $\text{Li}_x \text{CoO}_2$  as a function of Li intercalation: a) refraction index and b) extinction coefficient. Credit from [30]

are shown in Figure 7.11 a) and b) respectively.

The optical constants of  $\text{LiCoO}_2$  are not firmly established and they also depend on Li concentration in the film. Slack's group studied the optical indices for  $\text{Li}_x\text{CoO}_2$  for series of lithiated states as shown in Figure 7.8[30]. Their films were deposited by PLD at 50 mTorr and characterized by a variable-angle spectroscopic ellipsometry from 250nm to 1000nm. However, the lithiation on the graph was not well calibrated. We can see from the figure that the optical constants vary as a function of Li concentration, x, of the film. In the extinction coefficient graph, there is only one absorption peak around 500nm in the whole spectrum and it shifts as x varies. Julien *et al.* investigated the FTIR (Fourier Transform Infra Red) spectrum of LiCoO<sub>2</sub> in far IR region upon lithium deintercalation[31]. They observed a decrease of the oscillator strength and a broadening of all the infrared bands as shown in Figure 7.9. They associated that to the disorder induced by the departure of Li ions located between two CoO<sub>2</sub> blocks.



Figure 7.9: FTIR absorption spectra of  $\rm LiCoO_2$  as a function of Li concentration. Credit from [31]



Figure 7.10: Optical constants of LiCoO<sub>2</sub> grown by W.Tian at Oakridge.

We also measured a single crystal grown by W.Tian in the group of D.Mandrus at Oakridge and fit data to the model built above. The result is shown in figure 7.10.

Comparing sets of optical data listed above, it is not surprising that they don't resemble each other. Films of  $0.1 \,\mu\text{m}$  are quite different. Their optical properties depend on deposition techniques and conditions, and also behave as a function of Li content of the film. But we can find some common features between these sets of optical constants. Compared with figure 7.10, 7.11 a) shows the same trend in UV region, but refraction index greatly increases as wavelengths increases in visible light region and decreases to 2.5 as wavelength goes to the IR region. The extinction coefficients are much bigger, meaning that our films are more absorptive in all regions. The absorption peak at 700nm is difficult to understand. Probably it is just because of the defect on sample surface diffracting much of the light at that wavelength.





Figure 7.11: optical constants of film deposited at 150 mTorr  $O_2$  at 410°C: a) refractive index and b) extinction coefficient

#### 7.3 Film surface morphology, thickness and Li content

AFM scanning were usually taken on the sampling area of  $1\mu m \times 1\mu m$  and 500 nm × 500 nm. Surface roughness was measured based on the full image window. The results from two images are consistent within 10% error. Figure 7.12 shows the surface structure of one film deposited on Si substrate. We could see clearly the triangular crystallities of the material. That is the image that we should see exactly along c axis. Therefore the AFM images are consistent with the result concluded from xray diffraction experiments that films deposited on Si are oriented in (00n) direction. They also provide surface roughness information of films deposited under different conditions (Table 7.3). The surface of one film becomes more rough as it grows thicker and under higher gas pressure.

Film thickness measured by alpha-step and fit by ellipsometry are listed in Table7.4, along with deposition conditions for comparison. For Sample A, thicknesses obtained by both techniques agrees within error bars. Its thickness is  $1200 \pm 120$  Å and the deposition rate is 0.24Å per laser pulse.



Figure 7.12: AFM images of film surface of Sample B. a) Scanning area is  $1\mu m \times 1\mu m$ . b) Scanning area  $500nm \times 500nm$ .

sample label	# of laser pulses	Oxygen Pressure (mTorr)	Surface roughness (nm)
• ·	۲1	50	4.050
А	ЪК	50 -	4.058
В	10k	50	4.57
$\mathbf{C}$	10k	150	6.64

Chapter 7. Results and Discussions

Table 7.3: Surface roughness of films deposited under different conditions

sample	number of	O <sub>2</sub> Pressure	thickness1(Å)	thickness2(Å) (from $\alpha$ -step)
label	laser pulse	(mTorr)	(from ellipsomery)	
A	5k	$\frac{50}{150}$	$1106 \pm 70$	$1200 \pm 120$
D	10k		$1673.1 \pm 3$	$2837.5 \pm 95$

Table 7.4: Film thickness comparison. Both sample are grown at the same temperature.

However, for Sample D, two results are quite different. Thickness achieved by alpha-step is more direct and reproducible than that from ellipsometry fitting, which makes itself more reliable. Sample D used as twice as many laser shots to deposit, therefore it's reasonable to expect a doubled thick film compared with Sample A. Oxygen is used to adjust the shape of plume and is not a main factor of deposition rate. So the difference in oxygen pressure should not have much effect on the thickness of the resulting film. The value given by alpha-step is more acceptable as the thickness of Sample B. The reason why ellipsometer's result is so much off is maybe the penetrating depth of ellipsometer beam. As shown in Figure 7.11 b), the film absorbs in all range of the beam with very high extinction coefficients at some wavelengths. That results a relatively short penetrating depth. When the beam light is completely absorbed before it reaches the film bottom, the reflected beam from surface brings back no thickness information. The ellipsometric data now is totally "thickness independent" and thicknesses fit from that data are spurious and sometimes unphysical.

The resistivity of  $\text{LiCoO}_2$  behaves as a function of Li content[6]. According to the resistivity measurement, Li concentration in deposited samples are less than 0.95 but more than 0.9, which means that our films are metallic rather than semiconductive. Some Li is lost during ablation process. It is reasonable because ablated elements are angular-dependently distributed when they form the plume. As the lightest atoms, Li can be easily "knocked" out of the plume. Although rastering laser ablation and rotating the substrate do help to decrease the Li loss, it is impossible to completely avoid it. A better way to solve this problem is to add more Li inside the target before ablation to compensate its loss[32].

## Chapter 8

### Conclusions

We have given an introduction of pulsed laser deposition process and our PLD setup. Its basic setup is easy and user-friendly. Various materials can be deposited in a relatively shorter time compared with other techniques such as MBE. Even multi-layer thin films can be deposited at once by simply switching between different targets inside the chamber.

 $Li_xCoO_2$  thin films were deposited by PLD and *in situ* characterized by ellipsometer. We varied deposition temperature and oxygen pressure, used different substrates, and investigated their effects on the properties of resulting films. Temperature of substrate has a strong effect on film crystallization and lattice structure. The higher the temperature, the more crystallized the film is. Films on MgO are (101) oriented when deposited at low temperature, but grow in (104) direction at higher temperature. Substrate lattice mismatching is also an important factor for film lattice structure. Different substrates result in differently oriented thin films. Films grown on Si (100) substrate are always grown in c axis, while MgO substrates produce off-axis films either oriented in (101) direction or (104) direction, depending on the deposition temperature. Oxygen pressure helps define the shape of ablation plume, and consequently contributes to the variance of film composition. It also relates to the film surface roughness. Generally speaking, the higher pressure, the more rough the surface is.

When deposition was carried out at  $385^{\circ}C$  in 50mTorr oxygen, 5000 shots laser shots with a constant energy 600mJ/pulse produced films of 1200Å thick, corresponding to a deposition rate of 0.24Å/laser pulse. Resistivity measurement shows that Li/Co ratio in the resulting film is be in the range of (0.9, 0.95). It suggests Li loss during the deposition.

Ellipsometry is proved to be a good characterization technique both exsitu and in situ. It is so sensitive that it can detect the changes in  $\Psi$  and  $\Delta$  within several laser shots. Therefore in situ ellipsometric data can be taken to track the deposition process and to record the evolution of pseudo optical constants of whole sample. Film thickness and deposition rate can be attained from data fitting. Ex situ data is shown to be able to provide information on film thickness, optical constants of film layer and surface morphology. We have built a model based on sample physical structure for data fitting, in which general oscillator layer was used as film layer. The thickness fit by ellipsometric data agrees with the value measured by  $\alpha$  step when the thin film is far from "optically thick". It proves that ellipsometry measurement is precise and reliable when ellipsometer can "see through" it. The optical constants extracted from the same data set show a reasonable trend compared with published results.

Some improvement could be done in future work. Compared with normal deposition rate 1Å/laser pulse, 0.24Å/laser pulse is not satisfactory. This low deposition rate can be attributed to two factors: low energy density of focused laser beam on target surface and long working distance. On one hand, a more powerful converging lens is needed along with the readjustment of optics to get more uniform and more focused laser beam shining onto target surface. On the other hand, replace supporting rod on the carousel with longer ones to shorten the working distance between target and substrate. Li loss is inevitable during deposition. One way to lessen the loss is to add more Li inside the target. Usually, people mix 15% Li<sub>2</sub>O with LiCoO<sub>2</sub> to compensate Li loss during the deposition. Extend annealing time at high temperature after deposition to smoothen down film surface, which will help improve ellipsometry measurement. As for ellipsometry, transmission measurement is sometimes useful to help extract optical constants of some unknown material deposited on transparent substrate. A model precisely describing the physical structure of multilayer sample is critical in data fitting. Gathering sample information as much as possible, especially that regarding the unknown film layer, and structuring oscillator layer more physically would greatly enhance fitting quality.

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# Appendix A Polarized Light

Maxwell's equations for a non-conducting, non-dispersive medium appear as follows:

$$\vec{\nabla} \cdot \vec{E} = 0$$
  

$$\vec{\nabla} \cdot \vec{B} = 0$$
  

$$\vec{\nabla} \times \vec{E} + \frac{1}{c} \frac{\partial \vec{B}}{\partial t} = 0$$
  

$$\vec{\nabla} \times \vec{B} - \frac{\mu \epsilon}{c} \frac{\partial \vec{E}}{\partial t} = 0$$
  
(A.1)

where E and B are the electric and magnetic field , c is the light speed, and  $\mu and\varepsilon$  are the the permeability and dielectric function, respectively (assuming the medium of propagation to be isotropic). Any light beam propagating in medium must obey these equations. These equations can be combined to yield the wave equation for the electric field:

$$\vec{\nabla}^2 \vec{E} - \frac{1}{v^2} \frac{\partial^2 \vec{E}}{\partial t^2} = 0 \tag{A.2}$$

where the optical impedance v is defined as

$$v = \frac{c}{\sqrt{\varepsilon\mu}}.\tag{A.3}$$

A solution of the electric field wave equation is the electromagnetic plane wave:

$$\vec{E}(\vec{r},t) = \vec{E}_0 e^{\left(\frac{i2\pi\vec{n}}{\lambda}\vec{q}\cdot\vec{r}\right)} e^{(i\omega t)} \tag{A.4}$$

where  $\vec{q}$  is a unit vector along the direction of wave propagation,  $\tilde{n}$  is the complex index of refraction n+ik,  $\lambda$  is the wavelength of the light in vacuum, w is the angular frequency of the wave, and  $\vec{E}_0$  is a complex vector constant specifying the amplitude and polarization state of the wave. Such a wave propagating in a medium with no absorption (k=0) is shown in Figure A.1



Figure A.1: An electromagnetic plane wave. Credit from [26]

[26]

The E-field and B-field, and the direction of propagation are all orthogonal with respect to each other. Because of the relationship between the fields, only the E-field and the direction of propagation are required to completely define a plane wave.Polarization states are usually defined in terms of the direction and phase of the E-field vector, only.

# Appendix B

## Jones Vectors and Matrices<sup>[27]</sup>

One of Maxwell's equations states that the divergence of the displacement field must equal  $4\pi$  times the local charge density.

$$\vec{\nabla} \cdot \vec{D} = 4\pi\rho \tag{B.1}$$

where  $\overrightarrow{D}$  is the displacement field, and  $\rho$  is the free charge density. In the absence of space charges,  $\rho$  is zero and if we assume the material to be isotropic the above equation reduces to

$$\vec{\nabla} \cdot \vec{E} = 0 \tag{B.2}$$

where  $\vec{E}$  is the electric field. This requires that the components of the polarization vector  $\vec{E}_0$  must lie in the plane of perpendicular to the direction of beam propagation, again assuming the material in which the beam is propagating is isotropic. In this case, we can describe the polarization state of any beam by specifying its components along any two orthogonal axes in the plane perpendicular to the direction of beam propagation.

In ellipsometric experiments it is common to use the so-called p- and sdirections as the two orthogonal basis vectors used to express beam polarization states, as shown in Figure 5.1. The p-direction is defined as lying in the plane of incidence. The plane of incidence contains the incident and reflected beams and the vector normal to the sample surface. The s-direction lies perpendicular to the p-direction such that the p-direction, s-direction, and direction of propagation define a right-handed Cartesian coordinate system.

We can now express a totally polarized beam by specifying the components of the electric field of the beam along the p- and s- directions. These components are complex numbers, which may be conveniently written as a two-component vector, known as a Jones vector.

$$\vec{E} = \begin{bmatrix} \widetilde{E}_p \\ \widetilde{E}_s \end{bmatrix}$$
(B.3)

We may now express the action of any optical component or sample upon the polarization state of the propagating beam very simply, by means of a  $2 \times 2$  transfer matrix, known as a Jones matrix. The diagonal elements of the Jones matrix represent the change of amplitude and phase of the pand s- components of the beam, while the off-diagonal elements describe the transfer of energy from the p-component to the s-component, and vice versa.

The polarization state of a light beam refers to the path its Electric field traces as it propagates through space and time. There are three classifications of polarization used to describe a plane wave: linear, circular, and elliptical.

If one looks at the  $\vec{E}$ -filed vector of linearly polarized light in a plane perpendicular to the direction of propagation (x-y plane), one sees that the E-field lies in one line at all times. Hence the name linearly polarized light. The tip of the E-field vector traces out a line segment as function of time.

This general linear polarization can be described as two component waves propagating in phase, in the same direction, but with orthogonal E-field in the x and y directions. The polarization state is defines with respect to some physical frame of reference. The orientation of the total E-field with respect to the coordinate system is defined by the relative amplitudes of the  $E_x and E_y$  fields. The Jones vector representation of linearly polarized light is  $\begin{bmatrix} E_p e^{i\phi} \\ E_s e^{i\phi} \end{bmatrix}$ , where  $\phi$  is a phase angle, which must be identical for both components. For the special case of p- or s- polarized light, the (normalized) Jones vectors have the particularly simple forms (up to an arbitrary multiplicative complex constant)  $\begin{bmatrix} 1 \\ 0 \end{bmatrix}$  (p-polarized) and  $\begin{bmatrix} 0 \\ 1 \end{bmatrix}$  (s-polarized).

If the  $E_x$  and  $E_y$ -fields are equal in magnitude but 90<sub>o</sub> out of phase, then the polarization state is called circular because in the x-y plane, the tip of the total E-field vector traces out a circle as a function of time.

There are two kinds of circular polarizations. If looking into the propagation beam, the electric field vector is precessing counterclockwise around the circle, the beam is left-circularly polarized, and the normalized Jones vector for the beam(up to an arbitrary multiplicative constant) is  $\frac{1}{\sqrt{2}} \begin{bmatrix} 1\\ i \end{bmatrix}$ . If

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the electric field vector is recessing clockwise around the circle the beam is right-circularly polarized, and the corresponding normalized Jones vector for the beam is  $\frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -i \end{bmatrix}$ .

In general, the  $\vec{E}_x and E_y$  fields do not have to be equal in magnitude, and they could have any phase relationship. For a general polarization state, the tip of the total E-field vector traces out an ellipse as a function of time.

Linear and circular polarizations are just special types of elliptical polarized light. Ellipsometry measures  $\Psi$ andDelta by determining the polarization ellipse of the probe beam after interaction with the sample, hence its name.