Doctoral Thesis

Analysis of Laser-Induced Plasmas Utilizing $^{18}\text{O}_2$ as Oxygen Tracer

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Analysis of Laser-Induced Plasmas Utilizing $^{18}\text{O}_2$ as Oxygen Tracer

A dissertation submitted to

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for the degree of

Doctor of Sciences

presented by

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2014
The true sign of intelligence is not knowledge but imagination.
Strive not to be a success, but rather to be of value.

Albert Einstein
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Abstract

In this dissertation, the correlation between the background gas as well as ablation PLD conditions and the corresponding plasma / film properties during pulsed laser deposition has been investigated. Combinational plasma analysis approaches, such as kinetic energy resolved mass spectrometry, emission wavelength and time resolved plasma imaging and Langmuir probe measurements have been used to analyse the plasma properties over a large variety of material types using different PLD conditions, such as background pressure, background type, ablation fluence, ablation photon energy. Rutherford back scattering (RBS) and elastic recoil detection analysis (ERDA) have been used to characterize the composition of the deposited thin films.

From the physical interaction aspect, background interactions have been observed to vary the metallic plasma / film composition, apart from reducing the plasma kinetic energy. A congruent, elemental transfer during pulsed laser deposition of target metal species for as grown, non-annealed films is achieved in two constant pressure windows: below $10^{-3}$ mbar (quasi-vacuum plasma expansion) and the low $10^{-1}$ mbar range (shockwave plasma expansion). When using pressures in the $10^{-2}$ mbar range or pulsed reactive crossed-beam laser ablation (PRCLA), a cation deficiency for light metallic element has been observed as a result of pronounced elastic scattering effects as well as the less effective confinement of the plasma species due to the lack of the formation of a shockwave front. Time and emission wavelength resolved plasma imaging results confirm these observations. For using $10^{-2}$ mbar constant pressure or PRCLA a narrower spatial distribution has been observed for excited La as compared to Mn, while same spatial distribution for La and Mn has been observed using $10^{-1}$ mbar pressure. This insight will provide guidance how to approach successfully oxide thin film growth of complex materials, implying that the pressure window to obtain
films with a desired composition is narrow requiring careful adjustment.

From the chemical reaction aspect, the positive metal-oxygen ions have been observed as the main product from the oxidization of metallic species by background gas molecules. From a systematic investigation of the relative amount of positive metal-oxygen ion (MO⁺) compared to the metallic ion (M⁺) over a large variety of metallic elements and O₂ / N₂O background pressures, it has been shown that the chemical stability of MO⁺ largely influence the oxidization probability of the metallic species by the background molecules. For MO⁺ with dissociation energy larger than that of the background molecule, the MO⁺ / (M⁺ + MO⁺) ratio significantly increases with the used O₂ or N₂O pressure and exceeds 90% at the low 10⁻¹ mbar pressure range. In contrast, when the dissociation energy of MO⁺ is smaller than that of the background molecules, a large MO⁺ / (M⁺ + MO⁺) ratio is not achievable even at the largest used pressure, and the metallic elements arrive at the substrate as metallic atoms or ions rather than as metal-oxygen species.

By labelling the target material or substrate with ¹⁸O isotope, a quantitative characterization has been carried out to determine the origin of oxygen for plasma species and thin films. Background molecules have been shown to be the most important oxygen source for plasma species and thin films when using a pressure of 10⁻¹ mbar O₂ or N₂O as well as using PRCLA (O₂) for a La₀.₆Sr₀.₄MnO₃ deposition.

From a fundamental aspect, a better understanding of how plasma / background interactions influence the plasma / deposition properties during PLD has been presented in this dissertation. From the practical application aspect, some guidance for designing deposition strategies, i.e. how to choose the background gas, deposition pressure, ablation fluence and wavelength, are also provided.
Zusammenfassung


Von dem Standpunkt der chemischen Reaktion werden positiv geladenen Metalloxidionen als Hauptprodukt der Oxidation metallischer Spezies durch
Hintergrundgasmoleküle beobachtet. Die relative Menge an positiven Metalloxidionen (MO^+) verglichen mit dem entsprechenden metallischen Ion (M^+), wurde für eine Vielfalt metallischer Elemente und O\textsubscript{2} / N\textsubscript{2}O Hintergrunddrücke systematisch untersucht. Es hat sich gezeigt, dass die chemische Stabilität von MO^+ die Oxidationswahrscheinlichkeit der metallischen Spezies durch Hintergrundgasmoleküle weitgehend beeinflusst. Für MO^+ mit grösserer Dissoziationsenergie als die der Hintergrundmoleküle nimmt das MO^+ / (M^+ + MO^+) Verhältnis signifikant mit dem verwendeten O\textsubscript{2} oder N\textsubscript{2}O Druck zu und übersteigt 90\% im unteren Bereich von 10\textsuperscript{-1} mbar. Wenn die Dissoziationsenergie von MO^+ hingegen kleiner ist als die der Hintergrundmoleküle kann ein hohes MO^+ / (M^+ + MO^+) Verhältnis nicht erreicht werden, auch nicht für die höchsten verwendeten O\textsubscript{2} oder N\textsubscript{2}O Drücke (10\textsuperscript{-1} mbar Bereich): Das metallische Element kommt in der Regel unoxidiert beim Substrat an.

Durch Markieren des Substrates mit dem \textsuperscript{18}O Isotop kann eine quantitative Charakterisierung durchgeführt werden um den Ursprung des Sauerstoffs in Plasma und Film zu bestimmen. Wechselwirkungen mit dem Hintergrund haben sich als die wichtigste Sauerstoffquelle für das Plasma sowie den Film erweisen. Hierfür wurde ein O\textsubscript{2} or N\textsubscript{2}O Druck von 10\textsuperscript{-1} mbar verwendet, beziehungsweise PRCLA mit O\textsubscript{2} für eine Fallstudie an LSMO Abscheidungen.

Es wird erwartet, dass diese Beiträge zur Forschung zu einem besseren Verständnis der fundamentalen physikalischen und chemischen Prozesse im Plasma während des PLD Prozesses führen. Ausserdem werden aus einem anwendungsorientierten Blickwinkel einige Richtlinien für den Entwurf von PLD Strategien für neue Materialien vorgestellt.
1. Introduction

1.1 Pulsed laser deposition

The main questions to address when growing high quality multi-elemental oxide thin films are how to achieve the required anion and cation stoichiometry combined with a good crystallinity in order to gain the expected physical properties. To prepare such films, pulsed laser deposition (PLD) is at present the main tool for oxide thin film growth of materials with a complex composition. Its relative ease of handling, flexibility in laser wavelength and power allow a wide variety of materials combinations to be deposited [1-4].

In table 1.1, the characteristics of several vacuum deposition techniques are compared with PLD. PLD can be operated in a pressure range from $10^{-7}$ to 1 mbar which permits to adjust the composition, kinetic energies of plasma species, $E_k$, and, hence, the growth mode of a film. This is unlike other deposition techniques (sputtering [5, 6], physical vapour deposition, molecular beam epitaxy [7, 8], chemical vapour deposition [9]) where the deposition pressure and the variety of materials which can be deposited within one deposition system are often limited. The most prominent examples where PLD had a major impact are cuprate superconductors [10-11], doped manganates [12-15], oxides ion conductors [16], and diamond like carbon (DLC) [2, 17]. The deposition process can be monitored using in situ techniques such as reflection high-energy electron diffraction (RHEED), or by a multi-beam optical stress sensor (MOSS) during the PLD process. With this precise monitoring of the film growth process the quality of oxide interfaces became comparable to interfaces prepared by molecular beam epitaxy, and the physics related to oxide interfaces more widely accessible [18-20].
<table>
<thead>
<tr>
<th>Deposition Approach</th>
<th>Pressure (mbar)</th>
<th>Species $E_K$ (eV)</th>
<th>Deposition Rate</th>
<th>Deposition type of thin films</th>
<th>Comments (pros and cons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulsed laser deposition (PLD)</td>
<td>$10^{-7}$ - 1</td>
<td>1-1000</td>
<td>~0.1 nm/s</td>
<td>oxides, nitrides, carbon, metals, alloy</td>
<td>Easy handling, suitable for a large variety of materials, largely maintains the same stoichiometry of film to target material; Difficult to achieve commercial scale production</td>
</tr>
<tr>
<td>Thermal Evaporation</td>
<td>$10^{-2}$-10^{-2}</td>
<td>~0.1</td>
<td>1-10 nm/s</td>
<td>metal, chalcogenides, alloy</td>
<td>Easy handling, large deposition speed, suitable for commercial production; Not for the deposition of materials with a high melting-point</td>
</tr>
<tr>
<td>Molecular beam epitaxy (MBE)</td>
<td>$&lt;10^{-9}$</td>
<td>~0.1</td>
<td>&lt;1 nm/s</td>
<td>oxides, nitrides, chalcogenides, III-V compounds</td>
<td>Achieve good epitaxial growth and high purity of the film; low deposition rate, complex deposition facility, require high or ultra high vacuum</td>
</tr>
<tr>
<td>Sputtering or magnetic sputtering</td>
<td>$10^{-3}$-10</td>
<td>1-500</td>
<td>0.1-1 nm/s</td>
<td>Si, metal, alloy, oxides, nitrides, chalcogenides</td>
<td>Easy handling, relatively large deposition speed; more complicated to achieve a stoichiometric transfer compared to PLD due to variation in sputter rate for elements with different atomic weight</td>
</tr>
<tr>
<td>Chemical vapor deposition (CVD; or MOCVD, PECVD)</td>
<td>$10^{-3}$-10</td>
<td>~0.1</td>
<td>1-10</td>
<td>Si, chalcogenides, III-V compounds, oxides, nitrides</td>
<td>Easy handling, large deposition speed, suitable for commercial scale production; Often requires poisonous or explosive precursors; Achieves a precise control of the film thickness by reaction cycles; low deposition rate, complex deposition facility.</td>
</tr>
<tr>
<td>Atomic layer deposition (ALD)</td>
<td>$&lt;10^{-9}$</td>
<td>~0.1</td>
<td>~0.1 Å/cycle</td>
<td>oxides, nitrides, metals, metal sulfides</td>
<td></td>
</tr>
</tbody>
</table>

Table 1.1. Characteristics of various deposition approaches by vacuum process [1-20, 101, 139-154]

Although it is assumed that a congruent elemental transfer of elements from a target to a thin film is easily achieved by PLD, a clear knowledge and control over the film composition vs. the used PLD conditions are actually absent [19, 20]. Contrary to commonly conveyed knowledge, PLD is not a technique intrinsically linked to a congruent transfer of target species and the often quoted congruent transfer from the target to the substrate is not necessarily correct [21-28]. Instead it often depends on
the atomic mass of the ejected species [29], background gas/pressure respectively the interaction between these species generated by scattering events in the plasma plume, and/or changes of the target surface composition [28].

1.2. Plasma dynamics for PLD

During PLD, the material transfer from a bulk target to a substrate to form a film is achieved by a laser induced plasma plume [1-4, 15-17]. When using a nanosecond laser pulse to remove material from a solid, the laser energy is absorbed by the surface region of the target material. This process strongly heats and excites the irradiated volume. The material from the heated volume is ejected from the solid but continues to absorb laser photon energy forming a partially ionized thin vapour layer near the target surface. At the termination of the laser pulse, these initial plasma species expands adiabatically in three dimensions [2, 15, 16].

The plasma plume directly generated from laser / solid interactions usually consists of fast species with a kinetic energy up to a few hundreds of eV [15], which does not favour the film deposition in many cases. Therefore, a background atmosphere is usually used to interact with the plasma species and to adjust its properties for the deposition.

Figure 1.1a shows the schematic illustration of the chamber for a standard PLD using a constant background pressure, while Figure 1.1b illustrates the chamber for pulsed reactive crossed-beam laser ablation (PRCLA) where a pulsed reactive gas crossed beam is used to interact with the plasma. When using a constant background pressure, the collision mean free path between the plasma species and background molecule is controlled by the magnitude of background pressure, roughly estimated as

$$\lambda \approx \frac{kT}{P\pi(R_1 + R_2)^3}$$

(with $\lambda$ the collision mean free path, $R_1$, $R_2$ the radius of plasma species and background molecule, $P$, $k$ and $T$ the background pressure, Boltzmann constant and temperature, respectively). An alternative approach is to inject a pulsed
gas beam to interact with the initial plasma species at their early propagation stage (see illustration in Figure 1.1b). It is well known that the physical interaction of the ablated species with a background gas is leading to a thermalization of the plasma plume with a change in the kinetic energy from a couple of 10 to 100 eV in vacuum down to a few eV [15]. Equally important are chemical reactions between plasma and background species to adjust the plasma composition for the depositions.

![Figure 1.1](image.png)

**Figure 1.1.** Schematic illustration of the chambers for (a) a common PLD and (b) a PRCLA [16, 17]

### 1.3. Film deposition

Although the PLD process is considered to be rather simple, it has been realized that in many cases a desired deposition is only achieved within a narrow range of deposition conditions, limited by the background gas and pressure, ablation photon energy and fluence, target to substrate distance, substrate type and deposition temperature, or laser ablation frequency [1-4, 15-17]. These phenomena reveal complex correlations between the PLD conditions, plasma and film properties.

The substrate has been considered to largely determine the nucleation as well as crystal growth of the arriving species as a film. For example, depending on film / substrate lattice mismatch and the difference in the binding energy between film and
substrate, three fundamental modes for film growth have been established: (1) Volmer-Weber (3D island growth), Frank-van der Merwe (2D layer by layer growth) and Stranski-Krastanov (2D growth followed by 3D growth), see Figure 1.2a [1-4, 15-17]. The substrate temperature influences the surface diffusion of arriving species, and also varies the dynamics between nuclei and crystal growth of the film material.

![Figure 1.2](image)

**Figure 1.2.** (a) Illustration of the three fundamental modes for film growth; (b) Illustration of the atomic processes occur on the substrate surface during deposition [15, 16].

Equally important is the composition and kinetic energy of the arriving plasma species, which are influenced by the laser ablation processes as well as background conditions. Figure 1.2b illustrates the possible processes considered to occur when plasma species arrive at the surface of the substrate. Kinetic energies below 10 eV are generally considered to be favourable for a deposition, while species with larger kinetic energy may disturb the film growth via processes such as defect generation, implantation, and re-sputtering [2, 15, 16]. Apart from the plasma $E_K$, the film composition is expected to be largely affected by the plasma composition, which usually varies as a result of chemical reactions between plasma species and
background molecules [15, 32]. Also, the background scattering events can vary the plasma propagation and spatial distribution [27-29].

1.4. Analysing the plasma properties for PLD

For many examples, the explorations of the appropriate PLD conditions are very dependant on expertise and experimental tries, which is time consuming. Therefore, establishing a general correlation between PLD conditions, laser induced plasma and film properties are beneficial for the exploration of PLD conditions for the deposition of the new materials. Meanwhile, it also improves the understanding of PLD from a fundamental point of view. To achieve these goals, in previous investigations the PLD plasma properties have been investigated by plasma analytical techniques such as Langmuir probe measurements [33, 34], plasma imaging [27-29, 41], emission/absorption spectroscopy [38-40] and quadrupole or time of flight (TOF) mass spectrometry [32, 35-37].

In Table 1.2, the functions of several plasma analysis approaches are summarized and compared. Each approach possesses specific functions in analyzing certain aspects of the plasma. For example, when using mass spectrometry, it is possible to distinguish the mass to charge ratio in order to analyze the ionic plasma compositions [15, 32, 35-37]. By combining the mass spectrometer with a kinetic energy selector, it is possible to analyze also the kinetic energy of the respective plasma species. In addition, it is also possible to detect neutral species by introducing an ionization region before the quadrupole / TOF mass analyzer. There the neutral species are ionized through processes such as electron impact [15]. The mass spectrometer usually possesses a complicated construction and is costly [15]. For comparison, a much cheaper technique, e.g. Langmuir probe detection, has been also used to investigate the plasma properties. A metal probe with variable bias voltage is used to detect the charged plasma species as a function of the plasma propagation time, which gives information of the plasma velocity. In addition, from the correlation between the
magnitude of detected current and the used bias voltages, the electron temperature and density can be derived [33, 34]. Apart from the direct detection of species, the plasma composition can be also detected by looking at the light emission from excited species using emission spectroscopy, or by looking at the light absorption from species at the ground state using absorption spectroscopy [27-29, 38-41]. Also, time-resolved plasma imaging techniques have been also used to investigate the propagation dynamics of the plasma plume by observing the temporal dependence of the spatial distribution of excited species [27-29].

<table>
<thead>
<tr>
<th>Approach</th>
<th>What can be detected</th>
<th>What information can be acquired</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_k$-resolved Mass</td>
<td>* Ionic species;</td>
<td>* Plasma composition;</td>
</tr>
<tr>
<td>spectrometry (in this work)</td>
<td>* Neutral species;</td>
<td>* $E_k$ of plasma species;</td>
</tr>
<tr>
<td></td>
<td>* Plasma velocity;</td>
<td></td>
</tr>
<tr>
<td>Langmuir probe</td>
<td>* Ionic species;</td>
<td>* Plasma velocity;</td>
</tr>
<tr>
<td></td>
<td>* Electrons;</td>
<td>* Electron temperature;</td>
</tr>
<tr>
<td></td>
<td>* Plasma composition;</td>
<td>* Electron density;</td>
</tr>
<tr>
<td>Emission spectroscopy</td>
<td>* Light emission from the excited species (ions or neutrals);</td>
<td>* Plasma composition;</td>
</tr>
<tr>
<td></td>
<td>* Plasma composition;</td>
<td>* Electron density;</td>
</tr>
<tr>
<td>Absorption spectroscopy</td>
<td>* Light absorption by plasma</td>
<td>* Plasma composition;</td>
</tr>
<tr>
<td></td>
<td>species (ions or neutrals);</td>
<td>* Species excitation dynamics</td>
</tr>
<tr>
<td>Time-resolved plasma imaging</td>
<td>* Light emission from the excited species;</td>
<td>* Spatial distribution of excited species;</td>
</tr>
<tr>
<td></td>
<td>species;</td>
<td>* Plasma velocity;</td>
</tr>
</tbody>
</table>

Table 1.2. Characteristics of various plasma analysis approaches for film deposition

In general, most of the previous investigations about PLD plasma are mainly focused on physical aspects, such as plasma propagation dynamics, velocity, electron temperature and density [2, 15, 30-41]. A more quantitative approach to capture the simultaneously ongoing chemical aspects, in particular the reaction of plasma species with a background gas and reliably determine the film composition, is still missing.
Important questions are, e.g. how is the anion and cation composition in a film affected by the background gas type / pressure or laser ablation conditions? Which oxygen source (target, background, or substrate) finally determines the composition of the deposited thin film? This is vital information since answers to these questions influence the strategy how to approach oxide thin film growth in general.

1.5. Aim of this work

In this dissertation, the laser induced plasma properties were analysed using $E_K$-resolved mass spectrometry, time-resolved plasma imaging, and Langmuir probe measurement over a large variety of PLD conditions and target materials. Correlating the plasma properties to the as-deposited film composition and crystalline structures allows to establish a correlation between PLD conditions and plasma / film properties.

Chapter 2 describes the experimental conditions for the plasma analysis as well as film deposition and characterization in more details. Chapter 3 reports the plasma / film properties vs. $O_2$ background pressure as well as ablation fluence during the deposition of $La_{0.6}Sr_{0.4}MnO_3$. By using $^{18}O_2$ isotope labelling of the target or substrate, the proportion of the film oxygen composition, from target, background or substrate can be distinguished and quantified. A kinetic energy resolved mass spectrometry was used to analyse the plasma properties. In order to gain a more thorough understanding, the investigations are extended to a large variety of oxide target materials, which reveals the variety in plasma / background oxidization reactions due to the bond energy of the metal-oxygen species compared to the dissociation energy of the background molecules.

In Chapter 4, the PLD process of $Ca_3Co_4O_9$ and 3-YSZ are selected as two representative cases to further expand the correlation of the plasma / film properties and $O_2$ background pressure developed in Chapter 3. For $Ca_3Co_4O_9$ the dissociation energy of Ca-O and Co-O are all smaller than the dissociation energy of $O_2$, while for 3-YSZ the dissociation energy of Y-O and Zr-O are all larger than the dissociation
energy of O₂. These studies strengthen the conclusions drawn in Chapter 3 and result in a better understanding with respect to the chemical reactions between laser induced plasma species and the background molecules.

In Chapter 5, two other laser wavelengths (193 nm and 308 nm) are used for the plasma analysis and film deposition of La₀.₆Sr₀.₄MnO₃, in order to further explore the influence coming from the photon energy to the PLD process. The plasma / film properties when using 308 nm and 193 nm laser ablations are systematically investigated as a function of O₂ background pressure, which are compared with the results using the 248 nm laser described in Chapter 3.

Chapter 6 describes what will happen to the plasma and film properties if a pulsed reactive crossed beam is used as an alternative approach to involve plasma / background interactions. The plasma / film properties are investigated for the deposition of La₀.₆Sr₀.₄MnO₃ when using an O₂ gas pulse. The results are compared to the ablation results when using a constant background pressures as presented in Chapter 3.

Chapter 7 describes why in many cases a N₂O background is beneficial for the deposition of specific materials. The ¹⁸O labelled La₀.₆Sr₀.₄MnO₃ has been used for plasma analysis by mass spectrometry as well as plasma imaging and also for film deposition under various N₂O pressures. The mass spectrometry plasma investigations are extended to a large variety of oxide target materials in the pressure range between 10⁻² and 10⁻¹ mbar N₂O. The presented results are compared to the results observed in Chapter 3 thereby addressing the question when the implementation of a N₂O background is useful for deposition.

Chapter 8 compares the results of ionic plasma species properties detected by Eₖ-resolved mass spectrometry and Langmuir probe measurements. The La₀.₄Ca₀.₆MnO₃ target was ablated using a 308 nm laser at different fluences. The Eₖ distributions for the main ionic species detected by mass spectrometry are converted to their time of arrival (TOA) distributions and compared with the result directly measured by the Langmuir probe. Combining the results from both techniques, the temporal dependence of the negative ion density was derived.
In Chapter 9, the main conclusions of the thesis are presented. Overall, correlating the background dependence of film composition, described in Chapter 3, 4 (vs. $p\text{O}_2$) and 7 (vs. $p\text{N}_2\text{O}$), arrives at an improved understanding of plasma / background interactions. Correlating the background dependence of plasma composition described in Chapter 3-7 arrives at an improved understanding of plasma / background reactions from a chemical point of view.
2. Experimental

2.1. Plasma generation

For these studies, excimer lasers with nanosecond pulse lengths at 3 wavelengths have been used: 1) KrF (248 nm), 2) XeCl (308 nm) and 3) ArF (193 nm). The laser beam profile was imaged by a rectangular aperture onto the target inside a multifunctional ultra high vacuum (UHV) chamber. The spot size has been fixed to 1.4 mm$^2$ and the ablation fluence is controlled by varying the incoming laser energy. The maximum ablation fluences which can be achieved are $\sim$10 J/cm$^2$, 2.6 J/cm$^2$ and 3 J/cm$^2$ for using the KrF (248 nm), XeCl (308 nm) and ArF (193 nm) excimer lasers, respectively. The target to substrate (or detector) distance has been fixed at 4 cm.

For the investigation of plasma species interacting with a background gas (O$_2$, N$_2$O, Ar and N$_2$), a constant background pressure from $\sim$10$^{-8}$ mbar to 5 x 10$^{-1}$ mbar was used. Alternatively, plasma species can also interact with a synchronized O$_2$ or N$_2$O gas pulse, a technique also known as reactive crossed-beam laser ablation (PRCLA).

2.2. Plasma probe set-up

The laser induced plasma properties are analyzed using kinetic energy ($E_K$) resolved mass spectrometry, time and emission wavelength resolved plasma imaging, and Langmuir probe measurement. As-illustrated in Figure 2.1, the plasma properties can be analyzed in the UHV chamber at the same time by mass spectrometry and plasma imaging. Both setups are triggered by a photodiode, which detects the incoming laser beam. The center of the plasma points towards the mass spectrometer for the detection of the signal from plasma species. Meanwhile, the emission light of the plasma is
detected by the camera for plasma imaging. For Langmuir probe detection, a disk
shaped target is used. The target is rotated anticlockwise by 90° as compared to the
position illustration in Fig 2.1. Therefore, the Langmuir probe points to the center of
the incoming plasma plume. The circulated numbers in purple in Figure 2.1 illustrate
the specific processes in detail for mass spectrometry, plasma imaging and Langmuir
probe detections.

**Figure 2.1** Schematic illustration of the working principle of plasma analysis by mass
spectrometry, plasma imaging and Langmuir probe measurement for common PLD

**Mass spectrometry:** The laser beam is detected by the photodiode. The photodiode
sends a starting signal to the delay generator (process 1). By receiving the start signal
from the photodiode, the delay generator generates a time window of 0.5 ms and
sends it to the mass spectrometer to detect the plasma species (process 2).

**Plasma imaging:** The laser beam is detected by the photodiode. The photodiode
sends a starting signal to the camera for plasma imaging (process 1). The plasma
imaging camera starts working after receiving the starting signal from the photodiode. The delay generator and gate width controller for the image acquisition is integrated in the camera.

**Langmuir probe detection:** The target as illustrated in Figure 2.1 needs to rotate 90 degrees anticlockwise to make the probe pointing to the center of the plasma. The laser beam is detected by the photodiode. The photodiode sends a starting signal to the Langmuir probe as well as the oscilloscope, which is used as the zero point for the time (process 1). The Langmuir probe with appropriate bias voltage detects the temporal current signal from the plasma, which is detected by an oscilloscope (process 3).

Apart from the plasma analysis for a standard PLD process, it is also possible to analyse the plasma properties by using mass spectrometry or plasma imaging for PRCLA as illustrated in Figure 2.2. O₂ or N₂O has been used for the gas pulse. The pressure at the piezo valve is around 2 bar. The circulated numbers in purple shown in Figure 2.2 illustrate the specific processes in detail for PRCLA and plasma analysis.

An additional gas pulse controller is used in order to give the starting signal for the injection of the gas pulse (process 1) and also to send a starting signal to the oscilloscope as the zero point for the time. The gas pulse controller sends a starting signal to the laser as well as the oscilloscope (process 2) after an adjustable delay time from 100 – 900 μs is set at the gas pulse controller. The photodiode detects the laser beam and afterwards sends a starting signal to the plasma imaging camera, the oscilloscope as well as the delay generator for controlling the mass spectrometer controller (process 3). The delay generator generates a time window of 0.5 ms and sends it to the mass spectrometer to detect the plasma species (4).
2.2a. Kinetic energy resolved mass spectrometry plasma analysis

An electrostatic quadrupole mass spectrometer (Hiden analytical EQS) with a high-transmission $45^\circ$ sector field ion kinetic energy analyzer was used as illustrated in Figure 2.3a. The incoming ions are first filtered by the high-transmission $45^\circ$ sector field ion kinetic energy selector, which allows species with specific $E_K$ to pass through. The incoming ions are affected by the electric field force perpendicular to its velocity by turning $45^\circ$, which can be described as $F = qE = \frac{mv^2}{R} = \frac{2E_K}{R}$ ($E$ is the variable electric field strength, $R$ the radius of the circular motion fixed by the geometry and $q$ is the electric charge of the ion). Therefore, a specific kinetic energy.
is selected by the added electric field. Afterwards, a quadrupole mass selector is used to separate ions with a specific mass to charge ratio to pass through. During the detection, the pressure inside the mass spectrometer has to be kept lower than $10^{-4}$ mbar. Therefore, when analysing the plasma in a background gas, a small aperture ($\phi=0.06$ mm) has been used for the ions to enter and the mass spectrometer which is differentially pumped.

![Figure 2.3](http://www.hidenanalytical.com)

(a) Schematic illustration of the kinetic energy resolved mass spectrometer (source: [http://www.hidenanalytical.com](http://www.hidenanalytical.com)); (b) An example of the $E_K$ distribution of La$^+$, La$^{16}$O$^+$ and La$^{18}$O$^+$ detected from 308 nm laser induced La$_{0.6}$Sr$_{0.4}$Mn$_{16/18}$O$_3$ plasma at 1 x $10^{-2}$ mbar O$_2$.

For the detection of ionic plasma species, the amount of species with specific mass to charge ratio is scanned as a function of their kinetic energy. Other electro-optical parameters are further optimized at the most probable kinetic energy. Using the appropriate electro-optical parameters, the amount of ionic species is detected as a function of their kinetic energy, called a kinetic energy distribution ($dN/dE_K$). Figure 2.3b shows an example of the $E_K$ distribution of La$^+$, La$^{16}$O$^+$ and La$^{18}$O$^+$ detected from 308 nm laser induced La$_{0.6}$Sr$_{0.4}$Mn$_{16/18}$O$_3$ plasma at 1 x $10^{-2}$ mbar O$_2$. The total amount of a specific ionic species ($N$) is obtained by

$$N = \int_{0(E_K)}^{100(E_K)} dN dE_K,$$

while its average kinetic energy ($E_{K,\text{Avr.}}$) is estimated by

$$E_{K,\text{Avr.}} = \frac{\int_{0(E_K)}^{100(E_K)} E_K dN dE_K}{N}.$$
In order to gain a better understanding for plasma / background interactions vs. target metallic type, various oxides, i.e. La_{0.6}Sr_{0.4}MnO_3, La_{0.4}Ca_{0.6}MnO_3, YBa_2Cu_3O_7, TmMnO_3, SrTiO_3, SrMoO_4, TbMnO_3, LuMnO_3, TmMnO_3 and La_{0.8}Ca_{0.2}CoO_3, 8-YSZ (8 mol% Y_2O_3 doped ZrO_2), Al_2O_3 and ZnO were ablated at a fixed O_2 or N_2O pressure and fixed fluence for mass spectrometric plasma analysis. In order to evaluate the background oxidization probability for various metallic species, the relative amount of the positive metal-oxygen (MO^+) ions are compared to the metallic ions (M^+), using MO^+ / (M^+ + MnO^+) or MO^+ / M^+ to evaluate the proportion of the oxidized metallic ions into metal-oxygen ions as compared to the remaining metallic ions.

Apart from measuring ionic species, neutral species can also be detected by using an ionization region before the kinetic energy analyzer. In that case, a reversed extractor voltage is used in order to expulse the ionic species. The entered neutral species are ionized by the electron ionization filament installed at the entrance of the mass spectrometer, which make them detectable by the kinetic energy analyzer as well as the quadrupole mass analyzer [15]. However, a quantitative detection of neutral species can not be achieved due to the unknown ionization efficiency of the incoming species. For example, different ionization efficiencies are expected for different types of incoming neutral species. In addition, the amount and kinetic energy of the incoming neutral species may also influence the ionization efficiency. The current work therefore is mainly focused on the detection of ionic species.

2.2b. Time-resolved plasma imaging combined with an acousto-optical tunable filter

Time resolved plasma imaging (Andor Solis USB iStar) combined with an acousto-optical tunable filter (AOTF) (Brimrose VA210-.40-.65-H, detection range of 400 - 650 nm, resolution: 0.8 nm - 2.1 nm) has been used in this work in order to observe the spatial distribution of specific excited state species. Figure 2.4a shows the image of the plasma imaging setup. The incoming light can be transmitted through the AOTF and imaged on to the charge coupled device (CCD) chip.
Figure 2.4. (a) Image of the used time-resolved plasma imaging set up combined with AOTF; (b) Working principle illustration of the acousto-optical tunable filter (source: http://en.wikipedia.org/wiki/Acousto-optic_modulator).

Figure 2.4b illustrates the construction of the AOTF. In response to an oscillating radio frequency (RF) electric signal, a piezo-electric transducer generates a high frequency vibration wave inside a crystal, such as TeO$_2$ or quartz. As a result, a high frequency acoustic wave (wavelength $\Lambda$) is generated inside the crystal, which causes the periodic redistribution of the refractive index through the crystal. This principle has been used for a transmission diffraction grating or a Bragg diffracter. For example, in the case of the AOTF, the incoming light is perpendicular to the acoustic wave. Whether a diffracted beam emerges at an angle $\theta$ depends on the wavelength of the light wavelength $\lambda$ relative to the sound wavelength $\Lambda$, as $\sin(\theta) = \frac{m\lambda}{2\Lambda}$ (m: order of diffraction, usually m=1 is used). Therefore, whether the light wavelength can be diffracted at the angle $\theta$ is determined by the acoustic wavelength, which makes it possible to control the transmitted light wavelength by using the frequency of the piezo-electric transducer. When using only one piezo-electric transducer, the output light frequency ($f_{\text{out}}$) is shifted as compared to the input frequency ($f_{\text{in}}$) by $f_{\text{out}} = f_{\text{in}} + mF$ (F represents for the acoustic frequency) due to processes such as Doppler-shift. The AOTF setup used in this work has two transducers to generate a standing wave in the crystal. Therefore, there is no shift of the transmitted light frequencies before and
after the AOTF [164].

To distinguish different species using an AOTF, the characteristic emission wavelength for the experiment needs to be selected with the best compromise between intensity and resolution. In this work, the plasma imaging experiments were mainly carried out for La$_{0.6}$Sr$_{0.4}$MnO$_3$. Therefore, it is important to choose strong and well-distinguished emission wavelength among elements of La, Sr, Mn and O as well as metal-oxygen species, such as LaO, SrO and MnO. The emission wavelengths for all involved elements have been looked up from the National Institute of Standards and Technology (NIST) data base, and several lines are selected for further investigation. Table 2.1 summarizes their emission wavelength as compared to their closest emission wavelengths from other elements or molecules and the detection resolution of the AOTF. It can be seen that the emission wavelength for e.g. MnI is well distinguishable, while those for the other lines show a small overlap with their nearest species.

<table>
<thead>
<tr>
<th>Interested specie (wavelength / nm)</th>
<th>Nearest Species (wavelength / nm)</th>
<th>Nearest Species (wavelength / nm)</th>
<th>Resolution / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaI (563.1)</td>
<td>SrII (562.3)</td>
<td>SrII (565.1)</td>
<td>~1.5</td>
</tr>
<tr>
<td>MnI (450.2)</td>
<td>OII (449.1)</td>
<td>LaII (452.2)</td>
<td>~1</td>
</tr>
<tr>
<td>SrI (496.2)</td>
<td>OII (495.6)</td>
<td>MnI (496.6)</td>
<td>~1.2</td>
</tr>
<tr>
<td>SrO (440)</td>
<td>OII (439.6)</td>
<td>OII (440.5)</td>
<td>~1</td>
</tr>
<tr>
<td>OII (495.6)</td>
<td>MnO (494.4)</td>
<td>SrI (496.2)</td>
<td>~1.2</td>
</tr>
</tbody>
</table>

Table 2.1. Emission characteristic wavelength used for this research as compared for their closest emission wavelength from the other involved elements from NIST.

Due to the complexity of the target composition, the emission spectrums from different elements strongly overlap and it is nearly impossible to select clearly separated emission lines for all species considering the resolution of the AOTF. In order to better distinguish the selected emission wavelength from probable
overlapping ones, a high resolution monochromator (ARC Action Research Cooperation, Spectrapro-500) was used for detecting the emission spectrum at this wavelength window. Figure 2.5 gives two examples of the emission spectroscopy measurements around 496 nm (Figure 2.5a) and 440 nm (Figure 2.5b). The processes such as the electric charge and velocity of the plasma species could broaden the width of the emission lines and therefore the practical distinguishability is lower than the theoretical resolution. From Figure 2.5a (image acquisition in vacuum), the intensity of the selected SrI emission wavelength is clearly seen from the emission spectrum, despite there could be overlapping with the nearest MnI with much lower intensity. From Figure 2.6b (image acquisition at 3 x 10^{-2} mbar pO$_2$), the intensity of the selected SrO emission wavelength is clearly seen, despite there could be an overlap with the nearby OII. Compared to the selected SrO which partially overlap with OII, nearly all the emission wavelength for LaO and MnO strongly overlaps with those for La and Mn (from NIST) and hence cannot be used for element selective plasma imaging.

![Figure 2.5: Emission spectrum detected for laser induced LSMO plasma at (a) 490 nm in vacuum and (b) 440 nm at 3 x 10^{-2} mbar pO$_2$ using high resolution monochromator.](image)

### 2.2c. Plasma analysis by Langmuir probe

Langmuir probe detection is perhaps the most simple and direct plasma analysis approach. A metal probe with a variable bias voltage is used to detect the positive or negative current signal from the plasma as a function of time. Two properties of the
plasma can be obtained from Langmuir probe detection: 1) The plasma velocity, which is estimated by the arrival time of the detected current signal as compared to the laser ablation; 2) The electron temperature, which is derived from the relationship between the magnitude of the detected current signal and used bias voltage. Figure 2.6a shows the illustration for a typical Langmuir probe experiment.

![Illustration of the detection principle of the Langmuir probe](image1)
![Image of the used Langmuir probe](image2)
![Simplified electric circuit for the working principle of a Langmuir probe](image3)

**Figure 2.6 (a)** Illustration of the detection principle of the Langmuir probe [15]; **(b)** Image of the used Langmuir probe; **(c)** Simplified electric circuit for the working principle of a Langmuir probe.

Figure 2.6a shows the illustration of the working principle of the Langmuir probe measurement, while in Figure 2.6b the image of the probe used for this investigation is shown. In this work, a rod-shaped Langmuir probe of 3 mm diameter and 36 mm length has been placed in front of the target at a distance which can be varied from 6 to 14 cm. The probe points towards the laser ablation spot and was kept parallel to the normal of the target surface during the ablation experiment. The current drawn by the
probe was found by measuring the voltage across a load resistor, which had values of 10, 50 and 100 Ω, depending on the signal to be measured. Figure 2.6c illustrates the simplified circuit for Langmuir probe measurement. The probe signals were averaged over 40 laser shots. For the calculation of the practical load resistance, the load resistance of the cable connected with the oscilloscope should be considered in parallel to the variable load resistance.

2.3. Determination of the origin of oxygen by isotope exchanging technique

The oxygen of the thin film material may come from the following three origins: 1) target material, 2) backgrounds and 3) substrate. In order to distinguish the origin of the oxygen for plasma species as well as film, a hollow cylindrical ceramic La$_{0.6}$Sr$_{0.4}$MnO$_3$ targets was cut into two parts, with one half partially $^{18}$O exchanged to a fixed $^{16}$O/$^{18}$O isotope ratio of ~0.9 as measured by Rutherford back scattering (RBS) and elastic recoil detection analysis (ERDA). This ratio is distinct enough to discriminate chemical processes occurring between the oxygen background with its natural oxygen isotope ratio, and plasma species from the target. The other half of the La$_{0.6}$Sr$_{0.4}$MnO$_3$ target has a natural oxygen isotope ratio.

For separating the oxygen coming from the target and background, the La$_{0.6}$Sr$_{0.4}$Mn$^{16/18}$O$_3$ target was ablated in a $^{16}$O$_2$ or N$_2$$^{16}$O background. Plasma species measured from a vacuum ablation consist of species originating from the target only. The amount of $^{16}$O and $^{18}$O species ($A_{^{16}OVac}$; $A_{^{18}OVac}$) was measured and the concentration $c$ of $^{18}$O from the target ($c_{^{18}OTarg}$) was calculated as $c_{^{18}OTarg} = A_{^{18}OVac} / (A_{^{18}OVac} + A_{^{16}OVac})$, which is around 52%. Correspondingly, $c_{^{16}OTarg} = 1 - c_{^{18}OTarg}$, which is around 48%. In an $^{16}$O$_2$ background, the detected amount of $^{18}$O species ($A_{^{18}OBac}$) represents $c_{^{18}OTarg}$ fraction of oxygen coming from target, while the detected amount of $^{16}$O containing species ($A_{^{16}OBac}$) consists of $c_{^{16}OTarg}$ fraction of oxygen coming from target plus the total contribution from the background. Therefore the total number of oxygen species with respect to the $^{18}$O
isotope can be expressed as follows:

\[ A_{\text{Targ}} = \frac{A_{18\text{OBac}}}{c_{18\text{OTarg}}}; \]

\[ A_{BG} = A_{16\text{OBac}} - A_{\text{Targ}} \cdot (1 - c_{18\text{OTarg}}) = A_{16\text{O}_2\text{Bac}} - (\frac{A_{18\text{OBac}}}{c_{18\text{OTarg}}}) \cdot (1 - c_{18\text{OTarg}}) \]

\[ = (A_{16\text{OBac}} + A_{18\text{OBac}}) - A_{18\text{OBac}} / c_{18\text{OTarg}}. \]

In order to separate the oxygen in the film coming from the substrate diffusion, the films on an \(^{18}\)O labeled SrTiO\(_3\) substrate were deposited using the La\(_{0.6}\)Sr\(_{0.4}\)Mn\(_{16}\)O\(_3\) target and \(^{16}\)O\(_2\) background. The \(^{18}\)O exchange for the non-terminated SrTiO\(_3\) substrates has been conducted at 1100°C for 48h to exchange the substrates on average to an \(^{18}\)O content larger than 60%. The surface \(^{18}\)O concentration (\(C_{18\text{OSub}}\)) of the STO substrate was between 70 and 80%, measured by ERDA. After the deposition, the \(^{18}\)O concentration of the film (\(C_{18\text{OFilm}}\)) is measured by ERDA. Therefore, the proportion of oxygen from substrate is calculated as \(C_{18\text{OFilm}} / C_{18\text{OSub}}\).

**2.4. Film deposition and characterization**

The film depositions were conducted using comparable ablation / background conditions to plasma analysis. For the deposition of La\(_{0.6}\)Sr\(_{0.4}\)Mn\(_3\)O\(_3\), all three laser wavelength (248 nm, 308 nm and 193 nm) were used for an ablation at 5 Hz. The laser spot size was fixed to 1.4 \(\text{mm}^2\), and the ablation fluence was controlled by the laser energy. The target to substrate distance is fixed at 4 cm. The (001) Si substrate was used for the deposition at room temperature and the (001) SrTiO\(_3\) was used for the deposition at 650 °C. A pyrometer is used to measure the temperature on the surface of the substrate in order to control the deposition temperature.

The crystal structure of the film is determined by X-ray diffraction using a Siemens D500 powder diffractometer. To better distinguish the film peaks close to the substrate peak, the thin film X-ray diffraction was also performed using a Seifert 3003 PTS four-circle diffractometer, which uses monochromatic Cu Kα1 radiation to achieve a better resolution.
Figure 2.6. Schematic illustration for the RBS and ERDA measurements

RBS is used for measuring the film composition, while ERDA is used to separate the light elements, i.e. $^{16}\text{O}$ and $^{18}\text{O}$, $^{14}\text{N}$ and $^{16}\text{O}$. Figure 2.7 illustrates the working principle for RBS and ERDA. In brief, a incident beam with kinetic energy around several MeV is used to interact with the film, which causes the elastic backscattering of the incident beam (detected in RBS) and the elastic recoil of the film atoms (detected in ERDA). The elastic interaction of the incident beam with the film can be described as follows:

$$m_1v_0 = m_1v_1 \cos \theta + m_2v_2 \cos \phi$$  \hspace{1cm} (1.1) \\
$$0 = m_1v_1 \sin \theta - m_2v_2 \sin \phi$$  \hspace{1cm} (1.2) \\
$$m_1v_0 = m_1v_1 \cos \theta - m_2v_2 \cos \phi$$  \hspace{1cm} (1.3)

In these formulas, $m_1$ and $m_2$ represent the mass of the atoms for the incident beam and film. $v_0$ represents the velocity of $m_1$ before collision, while $v_1$ and $v_2$ are the velocity of $m_1$ and $m_2$ after collision. $\theta$ and $\phi$ represent the angle of the $v_1$ and $v_2$ as compared for $v_0$. Solving (1.1) – (1.3), the following relations are obtained:

$$v_1 = \frac{m_1 \cos \theta - \sqrt{m_2^2 - m_2^2 \sin^2 \theta}}{m_1 + m_2} v_0$$  \hspace{1cm} (1.4) \\
$$v_2 = \frac{2m_1 \cos \phi}{m_1 + m_2} v_0$$  \hspace{1cm} (1.5)

From the calculated $v_1$ and $v_2$, the kinetic energy of the incident atom and film atom after the collision ($E_1$ and $E_2$) can be calculated. Formula 1.6 and 1.7 show the ratio of $E_1$ and $E_2$ as compared for $E_0$, which has been named as kinematic factor.
\[
\frac{E_1}{E_0} = \left[ \frac{1 - (m_1 / m_2)^2 \sin^2 \theta}{1 + m_1 / m_2} \left( \frac{m_1 / m_2 \cos \theta}{1 + m_1 / m_2} \right)^2 \right]^{1/2} \quad (1.6) \quad \text{(RBS)}
\]

\[
\frac{E_2}{E_0} = \left[ \frac{4m_1 m_2}{(m_1 + m_2)^2} \right] \cos^2 \varphi \quad (1.7) \quad \text{(ERDA)}
\]

At a fixed detection angle, the \( E_1/E_0 \) ratio is determined by the atomic mass of the film atoms, as shown in formula (1.6). This correlation has been used for RBS measurements. During the RBS measurement, the number of backscattered incident atom is plotted vs. \( E_1 \). An example of a RBS spectrum of a LSMO film grown on (100) SrTiO\(_3\) at \( T = 650^\circ\) C and \( pO_2 = 5 \times 10^{-1}\) mbar is given in Figure 2.7. From the raw data (black circles) the known substrate contribution has been subtracted (red circles) and fitted using the RUMP software. The fitting curve matches well with the measured spectrum, and a nominal composition of La\(_{0.59}\)Sr\(_{0.41}\)Mn\(_{1.03}\)O\(_{2.70}\) can be deduced. The film thickness is reflected by the width of the RBS peaks. Since RBS cannot well separate light elements with small difference in atomic weight (i.e. O and N), the amount and kinetic energy of the sputtered film atom is also detected in ERDA measurements. Using the correlation given in formula 1.7, the light element can be better distinguished in ERDA.
Figure 2.7. An example of the RBS spectrum of a LSMO film grown on a (100) SrTiO$_3$ substrate at $T = 650^\circ$ C and $pO_2 = 5 \times 10^{-1}$ mbar with a nominal composition of $La_{0.59}Sr_{0.41}Mn_{1.03}O_{2.70}$. From the raw data (black circles) the known substrate contribution has been subtracted (red circles) and fitted using the RUMP software.

In this work, the RBS measurements were performed using a 2 MeV $^4$He beam and a silicon PIN diode detector at $\theta = 168^\circ$. The collected RBS data were simulated using the RUMP software. Depending on sample quality, the determined error for the composition is typically $\sim 3\%$, at most 5%. For the ERDA analysis a 13 MeV $^{127}$I beam was used at $\phi = 18^\circ$ incidence angle. The scattered recoils were identified by the combination of a time-of-flight spectrometer with a gas ionization chamber.
2.5. Experiments for deposition and laser induced forward transfer of Ca$_3$Co$_4$O$_9$

Target fabrication of Ca$_3$Co$_4$O$_9$: The target fabrication of Ca$_3$Co$_4$O$_9$ was achieved via solid reaction of high purity CaCO$_3$ and Co$_2$O$_3$ powders. After numerous experimental tries, the following strategy is used in order to obtain phase pure Ca$_3$Co$_4$O$_9$. The CaCO$_3$ and Co$_2$O$_3$ powders were stoichiometrically mixed by planetary ball milling with high rotation speed. The mixed powders were afterwards cold pressed into pellets and calcinated at 900 °C for 20 h in air. Intermediate grinding and ball milling was repeated at least five times to obtain phase pure Ca$_3$Co$_4$O$_9$. The final powder was spark plasma sintered into a disk shape at 600 °C and 20 MPa.

Deposition of Ca$_3$Co$_4$O$_9$: Ablation of the Ca$_3$Co$_4$O$_9$ target was done using a KrF excimer laser (λ = 248 nm, τ= 25 - 30 ns, repetition rate = 3 Hz) at a fixed laser fluence of 1.2 J/cm$^2$ in vacuum or O$_2$ background at a substrate-target distance of 3 and 4.5 cm, respectively. Thin films of Ca$_3$Co$_4$O$_9$ were deposited onto single-crystal Si (100) wafers and Pt sputter coated (40 nm) or uncoated quartz substrates at a substrate temperature of 650°C.

Electrical properties measurement: The in plan electrical conductivity and Seebeck coefficient of the films were measured in temperature range from 300 K to 500 K in air (RZ2001i–h system from Ozawa Science, Japan) The electrical conductivity was determined using a four-point probe method with four electrical Pt contacts directly pushed against the film.

Laser induced forward transfer of Ca$_3$Co$_4$O$_9$: Figure 2.8 illustrates the LIFT process for using a sacrificial layer (Figure 2.8a) or without using a sacrificial layer (Figure 2.8b). As illustrated in Figure 2.8a, a sacrificial layer, i.e. polymers or thin metal layer, are used for many materials transfers to interact with the laser beam and push forward the material to be transferred. Using the sacrificial layer shields the material of interest from a direct laser interaction, which benefits the transfer of materials such as polymers or tissues [95, 97, 98]. Instead, it is also possible to
directly shoot the laser beam onto the material to be transferred as illustrated in Figure 2.8b, which is the case for the transfer of materials such as metals or alloys [96].

![Figure 2.8](image)

**Figure 2.8.** Schematic illustration the LIFT process: (a) with sacrificial laser and (b) without sacrificial laser

In this work, the LIFT setup consists of the pulsed XeCl laser beam (\(\lambda = 308\) nm, 30 ns pulse length, 1 Hz repetition rate) which is imaged with an optical system onto the donor substrate to transfer micro-pixels (500 × 500 µm) from the donor substrate to the receiving surface. Two types of donor substrates were used: i) \(\text{Ca}_3\text{Co}_4\text{O}_9\) thin films directly deposited onto quartz substrates, and ii) \(\text{Ca}_3\text{Co}_4\text{O}_9\) thin films deposited onto quartz substrates previously coated with a Pt layer (40 nm thick). The intermediate Pt layer is introduced as a sacrificial layer, and is added to protect the oxide layer from direct laser radiation. As receiver substrates polydimethylsiloxane (PDMS) polymer films (2 mm thick) are used. The laser fluence is varied from 400 mJ/cm² to 700 mJ/cm². A computer-controlled xyz translation stage allows the displacement of both donor and receptor substrates with respect to the laser beam. The donor and the receiver are kept in contact while the laser irradiates the donor from the backside. For each laser pulse single \(\text{Ca}_3\text{Co}_4\text{O}_9\) micro-pixels are obtained. All experiments are carried out at ambient pressure and room temperature.
Morphological characterization of the micro-pixels: The donor surface and the micro-pixels deposited onto PDMS were investigated by scanning electron microscopy (SEM). The images were obtained from top view SEM and were acquired with a Zeiss Supra VP55 FE-SEM operating at a voltage of 5kV and an in-lens detector.
3. Plasma / film properties vs. $pO_2$ and ablation fluence

For the preparation of oxide thin films by PLD, $O_2$ is the most commonly used background gas. Depending on the background pressure and respective plasma-background interactions with the plasma, consisting of ions, neutrals and electrons, the physical as well as growth properties of the oxide film largely varies. The diversity of plasma properties as a result of interactions at different $pO_2$ influences the composition as well as structural and physical properties of as-grown films. This chapter reports on the relationship between film composition, background conditions and plasma species using a semi-quantitative plasma analysis approach combined with a quantitative composition analysis shown exemplarily for the deposition of $La_{0.6}Sr_{0.4}MnO_3$ (LSMO) in $^{16}O_2$ using PLD. The oxygen content in the plasma and films is traced by an $^{18}O$ isotope labelled $La_{0.6}Sr_{0.4}Mn^{16/18}O_3$ target and $SrTi^{16/18}O_3$ substrates to determine the origin of the oxygen in as-grown thin films for different background conditions.

According to previous research [15, 27, 28] pronounced plasma / background interactions are expected to occur around $10^{-2}$ mbar, at which pressure the collision mean free paths of most species are shorter than 20 mm as compared to the 40 mm propagation distance of the plasma. In our case, this can be directly observed in the optical images of the laser induced plasma shown in Fig. 3.1a where distinct changes in the color and shape of the plume at various $O_2$ pressures and constant fluence are observed starting at $1 \times 10^{-2}$ mbar. These variations in luminosity, confinement of the plume and changes in the emission colors are clear indications of the changes in the plasma properties as a result of an increase in the number of scattering events, which leads to an increase in the chemical activity.
Figure 3.1. (a) Appearance of the laser induced LSMO plasma in vacuum as well as various $pO_2$ background; (b) Mass spectra of positive and negative ionic plasma species from a La$_{0.6}$Sr$_{0.4}$Mn$_{16/18}$O$_3$ target measured at four different $^{16}$O$_2$ pressures.

Comparing the PLD plasma composition for charged species in vacuum and various $pO_2$ from a La$_{0.6}$Sr$_{0.4}$Mn$_{16/18}$O$_3$ target (Figure 3.1b), it can be concluded from the respective mass spectra that for a vacuum ablation the relative amount of $^{16}$O and $^{18}$O containing positive and negative species is in agreement with the oxygen isotope ratio of the target. Introducing $^{16}$O$_2$ as a background gas the isotope ratio is starting to shift towards $^{16}$O containing species due to a collisional dissociation as a consequence of scattering events between plasma species and $^{16}$O$_2$. As a result positively charged diatomic metal-oxygen species, e.g. of manganese and strontium, are detected. These
are absent in vacuum and created via chemical reactions between the metallic species and the oxygen background. LaO$^+$ ions are present for all pressures since they are the species with the largest bond energy (8.9 eV) which cannot be easily dissociated by the laser photons (248 nm $\leq$ 4.99 eV) or scattering. For negatively charged species and at the highest pressure measured, O$^-$ ions are found only. In addition, the total number of species arriving at the mass spectrometer decreases with increasing $p_{O_2}$ indicating a significant variation in the momentum and/or direction of species due to physical scattering, in particular at the highest pressure used.

To investigate the influence of the target on the film stoichiometry, the LSMO thin films were grown on SrTiO$_3$ at a substrate temperature of 650 °C using the $^{18}$O labelled La$_{0.6}$Sr$_{0.4}$Mn$_{16/18}$O$_3$ target. For all pressures, the target-substrate distance was fixed at a distance of 4 cm, the same distance used for the aperture for the mass spectrometer to collect the plasma species. The target material was chosen because it is composed of elements with very different masses, sizes, and stability of the metal-oxygen species. Analyzing the film composition by RBS and ERDA [42] it is possible to determine the average film composition vs. $p_{O_2}$ (Figure 3.2a shows the Sr and Mn content vs. $p_{O_2}$ for La$_{0.6}$Sr$_x$Mn$_{y}$O$_{3.6}$, fixing La to be 0.6 as the reference). The composition analysis for epitaxially grown films has been repeated for most pressures at least twice at different times and found to vary within the error bar of 5%. This thickness averaged composition should also be a more reliable number than the composition determined using surface sensitive techniques [28, 43] since a variation in the composition near a surface for oxides has been noted [44] and hence could lead to misleading results. Only films deposited at $2 \times 10^{-3}$ and $2 \times 10^{-1}$ mbar O$_2$ showed a cation composition corresponding to the target, for vacuum and within the $10^{-2}$ mbar range a loss of the lighter elements Mn and Sr is noted. The oxygen composition for LSMO films, however, shows an unexpected and opposite variation. At a low background pressure the oxygen content is $\sim$2.7 with a sudden increase to $\sim$2.9 at $10^{-2}$ mbar, subsequently decreasing to $\sim$2.75 with further increasing $p_{O_2}$. Hence, the oxygen content has the largest deviation for the optimal cation composition.
Figure 3.2: (a) Sr, Mn and O stoichiometry of La\textsubscript{0.6}Sr\textsubscript{x}Mn\textsubscript{y}O\textsubscript{3−x} thin films deposited on (001) SrTiO\textsubscript{3} substrate as a function of the O\textsubscript{2} background pressure. The error to determine the composition with RBS combined with ERDA is at most 5%. (b) X-ray diffraction patterns of as grown La\textsubscript{0.6}Sr\textsubscript{x}Mn\textsubscript{y}O\textsubscript{3−x} films on (001) SrTiO\textsubscript{3}.

The difference in the oxygen content with $p$O\textsubscript{2} reveals the diversity of the ongoing chemistry from background interactions as well as on the hot substrate surface while the film constituents assemble themselves to form the crystalline structure. Nevertheless, in almost all pressure regimes, films with a good crystalline quality can be grown as shown by the XRD spectra taken for (00l) oriented LSMO films grown under different background conditions (see Figure 3.2b) despite the differences in composition. The LSMO films cover a range of lattice parameters depending on the
specific anion to cation composition as can be seen from the different 2Θ values for the (004) film Bragg peak depending on the deposition pressure. A good crystalline structure does not necessarily imply that the physical properties are correctly represented since one would expect in Mn-deficient films e.g. the magnetic moment to be significantly smaller than the expected \( \mu_B/\text{Mn} \approx 3.6 \) for this nominal doping level.

Another interesting feature in the XRD spectrum is the broad shoulder on the left hand side of the STO (002) Bragg peak which is related to a gradient in oxygen deficient STO near the substrate surface.

To understand the change in film composition vs. \( p_{O_2} \) the pressure dependence of metal-oxygen species (Figure 3.3a) was investigated, in particular of LaO\(^+\) since it is the most abundant species in vacuum as well as in an O\(_2\) background. The number of La\(^{16}\)O\(^+\) increases with increasing \( p_{O_2} \) until reaching a maximum at 1 x 10\(^{-2}\) mbar with a subsequent decrease towards 1 x 10\(^{-1}\) mbar. In contrast, La\(^{18}\)O\(^+\), originating from the target, and La\(^+\) decrease monotonically up to 1 x 10\(^{-2}\) mbar before decreasing more strongly. Plotting the ratio of LaO\(^+\)/La\(^+\) vs. \( p_{O_2} \), a revealing tendency in particular for pressures above 1 x 10\(^{-2}\) mbar (Figure 3.3c) was observed. The very pronounced changes in LaO\(^+\)/La\(^+\) vs. \( p_{O_2} \) imply two competing processes are taking place at the same time. On the one side the increase of La\(^{16}\)O\(^+\) is caused by an enhanced oxidization of atomic lanthanum with increasing pressure. At the same time, the simultaneous decrease of La\(^{18}\)O\(^+\) is direct evidence that LaO\(^+\) is dissociated or scattered through collisions in particular at elevated \( p_{O_2} \). As a consequence, the balance between the competing reactions is shifted towards the generation of La\(^{16}\)O\(^+\) species in an oxidizing background with increasing \( p_{O_2} \). The pressure dependence for MnO\(^+\) and SrO\(^+\) is similar compared to LaO\(^+\) but with smaller numbers of species (see Figure 3.3b), with MnO\(^+\) and SrO\(^+\) at high \( p_{O_2} \) being generated due to O\(_2\) background interactions only. Even at the highest \( p_{O_2} \) the relative amount of MnO\(^+\) and SrO\(^+\) is \(~10\) times smaller compared to their metallic ions (Figure 3.3c).
Figure 3.3: (a) Number of La$^+$, La$^{16}$O$^-$ and La$^{18}$O$^-$ vs. $p_{O2}$; (b) Number of Mn$^{16}$O$^+$, Mn$^{18}$O$^+$, Sr$^{16}$O$^+$ and Sr$^{18}$O$^+$ vs. $p_{O2}$; (c) Ratio of MO$^-$ to M$^+$ for La, Mn and Sr vs. $p_{O2}$; (d) Number of Mn$^{16}$O$^-$, Mn$^{18}$O$^-$, Mn$^{16}$O$_2^-$ and Mn$^{16,18}$O$_2^-$ vs. $p_{O2}$.

Looking at negatively ionized oxidized species in vacuum, MnO$_2^-$ and MnO$^-$ have the largest abundance (Figure 3.3d). With increasing pressure the amount of negative oxide ions decreases significantly, in particular species associated with the target, except for Mn$^{16}$O$^-$ which shows a maximum around 6 x $10^{-3}$ mbar. This maximum is most likely the result of a shift in the reaction equilibrium between its dissociation and generation. Nevertheless, these metal-oxygen negative ions are not detected at $10^{-1}$ mbar $p_{O2}$, which indicates their low stability when experiencing intensive background interactions due to low electron affinities (see Table 3.1). Therefore, MO$^+$ is considered to be more important than MO$^-$ at the most interesting PLD pressure range.
<table>
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<th>Element (M)</th>
<th>Ionization Energy of M (eV)</th>
<th>Ionization Energy of MO (eV)</th>
<th>Electron Affinity of MO (eV)</th>
<th>$E_{\text{dissoc.}}$ of MO (eV)</th>
<th>Calculated $E_{\text{dissoc.}}$ of MO$^+$ (eV)</th>
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Table 3.1. Summary of the ionization energy of metal atoms ($\Delta E_{\text{IE. M}}$) [50], the electron affinity ($\Delta E_{\text{EA. MO}}$) [46, 52-57] as well as the ionization energy ($\Delta E_{\text{IE. MO}}$) [58-67] of metal-oxygen species, and also the bonding energy of the neutral metal-oxygen species ($\Delta E_{\text{(M-O)}}$) [68], for all the investigated metallic elements. The dissociation energies of the positive metal-oxides ions have been calculated by: $\Delta E_{\text{(M-O pos.)}}$ are deducted by $\Delta E_{\text{(M-O pos.)}} = \Delta E_{\text{IE. M}} - \Delta E_{\text{IE. MO}} + \Delta E_{\text{(M-O)}}$. In addition, some experimentally measured $E_{\text{dissoc.}}$ for MO$^+$ have also been listed [166-170].

The dissociation energies of MO have been presented in the literature for all the investigated metallic elements [68]. For comparison, a limited number of dissociation energies for MO$^+$ has been published determined either by calculation or by experimental measurements [166-170]. For a known ionization energy of the metal atoms ($\Delta E_{\text{IE. M}}$), ionization energy of MO ($\Delta E_{\text{IE. MO}}$) and the the bonding energy of the neutral metal-oxygen species ($\Delta E_{\text{(M-O)}}$), the dissociation energies of the positive metal-oxides ions can be calculated using $\Delta E_{\text{(M-O pos.)}} = \Delta E_{\text{IE. M}} - \Delta E_{\text{IE. MO}} + \Delta E_{\text{(M-O)}}$ [167]. In addition, the dissociation energy of MO$^+$ has also been measured for some
elements using ICP-MS to ionize both M and MO based on the interaction with noble gas molecule [166-170]. In order to keep consistency for all the investigated elements, the calculated MO$^+$ ($E_{\text{dissoc.}}$) values as presented in Table 3.1 are used for plotting Figure 3.4.

When comparing MO$^+$/$M^+$ for the different plasma species, it is found to be largest for La followed by Sr and Mn. This matches well with the respective dissociation energies of LaO$^+$, MnO$^+$ and SrO$^+$ (8.9, 2.9 and 3.8 eV). To further confirm this trend for other metallic species, oxides such as YBa$_2$Cu$_3$O$_7$, SrTiO$_3$, SrMoO$_4$, TbMnO$_3$, LuMnO$_3$, TmMnO$_3$ Al$_2$O$_3$, 8-YSZ (8 mol% Y$_2$O$_3$ doped ZrO$_2$), La$_{0.4}$Ca$_{0.6}$MnO$_3$, La$_{0.8}$Ca$_{0.2}$CoO$_3$, or ZnO were ablated in vacuum as well as 2 x 10$^{-3}$, 1 x 10$^{-2}$ and 1.5 x 10$^{-1}$ mbar O$_2$ and a fluence of 1.8 J/cm$^2$ to cover a larger variety of metallic elements for different crystallographic compounds. In Figure 3.4, the MO$^+/(M^+ + MO^+)$ ratios are plotted vs. the dissociation energy of MO$^+$ ($E_{\text{dissoc.}}$) for vacuum as well as the three O$_2$ pressures of 2 x 10$^{-3}$ mbar, 1 x 10$^{-2}$ mbar and 1.5 x 10$^{-1}$ mbar. It is found that MO$^+/(M^+ + MO^+)$ ratios are comparable for one metallic element when ablated from different oxide targets using the same ablation and background conditions. The MO$^+/(M^+ + MO^+)$ ratio for the different MO$^+$ species increases significantly with increasing $E_{\text{dissoc.}}$ at ~5 eV, an energy which corresponds to $E_{\text{dissoc.}}$(O$_2$) (red dashed line at 5.12eV, Figure 3.4). Although the photon energy of 248 nm laser is also around 5 eV, the observed results are more probable to be determined by $E_{\text{dissoc.}}$(O$_2$) rather than $E_{\text{phot.}}$, since at 10$^{-2}$ mbar or higher pO$_2$, the plasma properties are more influenced by collisions with background gas molecules. As a confirmation, the MO$^+/(M^+ + MO^+)$ ratio vs. $E_{\text{dissoc.}}$(MO$^+$) shares similar dependence for using 308 nm and 193 nm lasers in 1 x 10$^{-2}$ mbar pO$_2$ as compared for using 248 nm.
Figure 3.4. Ratio of MO+/M+ vs. dissociation energy of MO+ as determined in (a) vacuum (248 nm laser) as well as at pO₂ of (b) 2 x 10⁻³ mbar (248 nm laser), (c) 1 x 10⁻² mbar (248 nm laser), (d) 1.5 x 10⁻¹ mbar (248 nm laser) and (e) 1.5 x 10⁻³ mbar (308 nm laser). As shown MO+/M+ for a metallic element is the average value from different oxide targets, while the error bar represents their standard derivation. The red dashed line represents the dissociation energy of O₂ (5.12 eV), while the black dotted line represents the laser photon energy (5 eV).
Figure 3.4 demonstrates for vacuum as well as the three pressures that the chemical stability of MO\(^+\) plasma species is reflected by its relative amount in the plasma. It also suggests that atomic oxygen from dissociated O\(_2\) enables a shift in the balance of the continuous formation and dissociation of MO\(^+\) species towards the formation of MO\(^+\). For MO\(^+\) species with \(E_{\text{dissoc}}(\text{MO}^+) > E_{\text{dissoc}}(\text{O}_2)\) the formation of MO\(^+\) from M\(^+\) and O\(_2\) would probably be favored. However, the exothermicity of this reaction is not taken into account since the energy released is of the order of the dissociation energy. For \(E_{\text{dissoc}}(\text{MO}^+) < E_{\text{dissoc}}(\text{O}_2)\) the dissociation into M\(^+\) and O due to scattering is very effective (\(E_k > \text{several eV}\)) and the formation of MO\(^+\) via atomic oxygen seems more probable. For a vacuum ablation, a comparable tendency was found that MO\(^+\) species with \(E_{\text{dissoc}}(\text{MO}^+) > E_{\text{Photon}}\) 248 nm \(\approx 4.99 \text{ eV}\) are detected in the mass spectrum while others are absent (Figure 3.1).

Although the photon energy of the 248 nm laser is also 5.0 eV (the dark line in Figure 3.4a), the laser wavelength is considered to be an unlikely reason to determine the MO\(^+\)/\((\text{M}^+ + \text{MO}^+)\) ratio at the \(10^{-1} \text{ mbar } p_{\text{O}_2}\), since at this high pressure range the plasma propagation is dominated by the interactions with background gas. A direct prove to this understanding is shown in Figure 3.4e the MO\(^+\)/\((\text{M}^+ + \text{MO}^+)\) vs. \(E_{\text{dissoc}}(\text{MO}^+)\) at \(1.5 \times 10^{-1} \text{ mbar } p_{\text{O}_2}\) when using 308 nm laser (photon energy: 4 eV) at 1.8 J/cm\(^2\). Similar results have been observed as compared to that shown in Figure 3.4d for using the same condition but 248 nm laser. For MO\(^+\) species with \(E_{\text{dissoc}}(\text{MO}^+) > E_{\text{dissoc}}(\text{O}_2)\) the M\(^+\) is able to be fully oxidized by O\(_2\). For \(E_{\text{dissoc}}(\text{MO}^+) < E_{\text{dissoc}}(\text{O}_2)\) the plasma species arrives as atomic rather than metal-oxygen species.

The situation for MO\(^-\) species is different. As an example, in Fig 3.5a the relative amount of MO\(^-\) compared to MO\(^+\) (MO\(^-\)/MO\(^+\)) is plotted for Mn as a function of \(p_{\text{O}_2}\). A decrease in the relative amount of MnO\(^-\) is clearly observed with increasing \(p_{\text{O}_2}\) as a result of an increase in plasma / background interactions. In Fig 3.5b, the MO\(^-\)/MO\(^+\) ratio is plotted as a function of the metallic atomic radius for a range of ionic MO species for \(1 \times 10^{-2} \text{ mbar } p_{\text{O}_2}\). A decrease of the MO\(^-\)/MO\(^+\) is observed with an
increasing metallic radius. Since a larger atomic radius is usually correlated with a larger scattering cross section, this result reveals a possible influence of collision cross-sections during background interactions to the stability of MO'. These negative metal-oxygen ions are most likely formed directly of the ejected species and electrons by electron attachment but are less stable than MO⁺ due to their small electron affinity (0.5-1.8 eV). However, due to their smaller chemical stabilities, an increase of scattering events at higher $pO_2$ is more likely to dissociate these MO⁻ or detach their electron. Consequently, MO⁺ species are expected to contribute more to the final oxygen composition of a film, in particular at elevated oxygen partial pressures due to their larger proportion in the plasma compared to metallic ions. In addition, films containing elements with large M-O⁺ dissociation energies e.g. La are expected to be prepared more reliably with respect to the nominal film composition.

The role of the oxygen background during the ablation of an oxide target is threefold: moderation of $E_K$, oxidization of metallic species, and directly contributing to the oxygen content of the as-grown, not annealed film. The question is how to quantify the target and background contributions to the oxygen content in a film for the various pressure regimes. In Figure 3.6, as-measured $E_K$ distributions for O⁻, O⁺
and O are shown at various $pO_2$. It is interesting to note that during a vacuum or low pressure ($2 \times 10^{-3}$ mbar) ablation the plasma contains $O^+$ species with larger $E_k$ (40 – 80 eV) compared to $O^-$ and O (<30 eV). When increasing $pO_2$ to $10^{-2}$ mbar or higher, $E_k$ of $O^-$ was dramatically decreased to around 5 eV.

**Figure 3.6.** Kinetic energy distributions of positive ($^{16}O^+$ and $^{18}O^+$), negative ($^{16}O^-$ and $^{18}O^-$) and neutral ($^{16}O$ and $^{18}O$) atomic oxygen species in various $O_2$ background pressures.

By integrating the amount of species over the measured $E_k$ range, the total amount of the selected species is obtained. In Figure 3.7 the species amounts are plotted for $O^-$, $O^+$, O and $O_2^-$, containing $^{16}O$ or $^{18}O$ isotopes, vs. $pO_2$. In addition, the blue dashed lines show the $pO_2$ dependence of the $^{16}O/^{18}O$ isotope ratios.
Below an O₂ pressure of 2 x 10⁻³ mbar, the amounts of positive, negative and neutral atomic oxygen species have similar magnitudes, a scenario which is comparable to the ablation in vacuum. A faster increase in the amount of diatomic ¹⁶O₂⁻ has been observed below 2 x 10⁻³ mbar (see Figure 3.7 b), compared to the atomic ¹⁶O⁻ (see Figure 3.7 a), due to the electron attachment to the O₂ molecules from the background. By further increasing the background pressure to 6 x 10⁻³ mbar, a dramatic decrease of both, ¹⁶O⁺ and ¹⁸O⁺, was observed (see Figure 3.7 c) while the total number of ¹⁶O⁻ and ¹⁸O⁻ show a corresponding increase. With further increasing the background pressure, the ¹⁶O⁺ signal increases while the other three ¹⁶O containing species decrease, which indicates that O⁺ species originate from background interactions. In addition, a stronger scattering of the ¹⁸O containing atomic oxygen species occur. As a result, the ¹⁶O/¹⁸O ratios for all oxygen-containing
species decrease dramatically with increasing oxygen background pressure. The amount of the neutral atomic oxygen species shares a similar pressure dependence of the negative atomic oxygen ions.

Knowing the measured amount of oxygen species for various oxygen pressures and the numbers estimated from the $^{18}$O-exchanged target, oxygen species from the two sources can be discriminated. In Figure 3.8a and 3.8b, the pressure dependence of the ionic oxygen species ($O^-$, $O^+$ and $O_2^-$) from the target and background is presented. With increasing $pO_2$ the number of $O^+$ originating from the target dramatically decreases while $O^-$ shows an increase up to $10^{-2}$ mbar before decreasing (Figure 3.8a) due to a rise in scattering events taking place in this pressure regime. The small number of $O_2^-$ species steadily decreases with increasing $pO_2$. As for the oxygen species created during background interactions, $O^-$ shows a maximum at around $10^{-2}$ mbar before decreasing in numbers with increasing $pO_2$, whereas $O^+$ steadily increases up to $3 \times 10^{-2}$ mbar before decreasing, and $O_2^-$ gives a noticeable signal up to $10^{-2}$ mbar originating from the background. The distinction between oxygen from the target and background highlights several processes: The presence of $O_2^-$, $O^-$ and $O^+$ at elevated pressures clearly indicates that these species are generated through $O_2$ dissociation ($O_2 + 5.12$ eV $\rightarrow 2O$) or electron attachment ($O_2 + e^- \rightarrow O_2^- + 0.44$ eV) whereas the pronounced existence of negative oxygen is favoured via an electron attachment process due to its low formation energy ($O + e^- \rightarrow O^- + 1.46$ eV) compared to an ionization process ($O + 13.6$ eV $\rightarrow e^- + O^+$) as a result of the interaction processes with plasma species [45, 46]. With increasing $pO_2$ the dissociation process of $O_2$ seems to be more favourable than ionization in particular above $10^{-2}$ mbar, which is the pressure range where the intensive background interaction becomes noticeable. Comparing the pressure dependence of $O^+$ to $O^-$ and $O$ also suggests a partial conversion of $O^+$ from the target into $O^-$ or $O$ through an electron attaching process. With increasing $pO_2$ from $10^{-2}$ to $10^{-1}$ mbar, a continuous reduction in the total number of oxygen species was observed due to stronger physical scattering as well as the oxidization of the metallic species. At the low $10^{-2}$ mbar pressure range, the most significant amount of $O^-$ with a small kinetic energy was
observed, which may correlate with the highest film oxygen composition achieved at the same pressure range [15, 32], as shown in Figure 3.2 a.

![Figure 3.8](image)

Figure 3.8. Total number of ionic atomic oxygen as a function of the O₂ background pressure originating from (a) the target and (b) O₂ background.

As demonstrated, due to the large variation in plasma properties at different pressure regimes, the LSMO film composition and crystalline structure undergoes significant changes. Nevertheless, for a film with the correct cation composition showing also the expected physical and structural properties, the largest possible oxygen content is not necessarily to be obtained during the growth since oxygen can be subsequently supplied after the deposition by an *in situ* annealing step as often done routinely for such films. This strongly suggests that the pressure window for a congruent target-substrate transfer for optimal film properties is very narrow. A further indication of a narrow deposition parameter window is taken from the target-substrate distance or laser fluence dependence reported e.g. for the preparation of nominal stoichiometric SrTiO₃ [43]. The composition of the plume including the number of species is different as a function of expansion distance due to the number of scattering events and hence the optimal deposition window will be different for each parameter set comprising fluence, distance, $pO_2$ and substrate temperature. However, the observed cation deficiency vs. $pO_2$ is considered to be a general feature for the oxide deposition using PLD since similar results were also observed for other background gases or target materials (see Chapter 4.1 and Chapter 7).
To further pin down the origin of the oxygen contribution in an as grown film from the three potential oxygen sources target, background gas and the substrate [47, 48], two kinds of experiments have been conducted: LSMO films were grown on $^{18}$O exchanged STO substrates ablated from a La$_{0.6}$Sr$_{0.4}$Mn$_{16}$O$_3$ target in $^{16}$O$_2$, and films prepared from La$_{0.6}$Sr$_{0.4}$Mn$_{16/18}$O$_3$ in $^{16}$O$_2$ onto non-exchanged STO substrates.

![Figure 3.9](image)

**Figure 3.9.** (a) Depth profile of the oxygen percentage from substrate diffusion in vacuum, deduced by measuring $^{18}$O/$^{16}$O ratio of LSM$^{16}$O film grown on ST$^{18,16}$O substrate using ERDA; (b) $^{18}$O isotope concentration of the LSMO films grown on ST$^{16,18}$O substrate in vacuum, 2 $\times$ 10$^{-3}$ mbar and 1 $\times$ 10$^{-2}$ mbar $O_2$ detected by ERDA.

Figure 3.9 shows the $^{18}$O concentration of the films material grown on the ST$^{16,18}$O substrate, which indicates the oxygen diffusion from the substrate. Figure 3.9a gives an example of the depth profile of the $^{18}$O ERDA signal of LSMO on ST$^{16,18}$O for a deposition at 650°C in vacuum. Figure 3.9b shows the average $^{18}$O concentration of the film materials grown in vacuum as well as 2 $\times$ 10$^{-3}$ mbar and 1 $\times$ 10$^{-2}$ mbar $pO_2$ background. It can be seen that the STO substrate contribution to the total oxygen content in a LSMO films is limited to $\sim$3% in vacuum, < 1% at 2 $\times$ 10$^{-3}$ mbar, and none at higher oxygen partial pressures.
Knowing the substrate contribution to the film oxygen content, the next step is to further determine the contribution from the target and background. Therefore, the LSMO films were prepared using the La$_{0.6}$Sr$_{0.4}$Mn$_{16/18}$O$_3$ target in O$_2$ on non-exchanged STO substrates at different O$_2$ background pressures. The $^{18}$O/$^{16}$O isotope ratios of these films are detected by ERDA, and the percentage of oxygen coming from target material is estimated accordingly (see more detail about the estimation in chapter 2). Figure 3.10a shows the estimated contribution from background, target material and substrate to the film oxygen composition. It can be seen that the background contribution is enhanced with increasing $p$O$_2$, while a corresponding decrease is observed for the oxygen contribution from the target to the film. Oxygen transferred from the target to the film is $\sim$44% and 29% at 2x10$^{-3}$ and 1 x 10$^{-2}$ mbar and decreases down to $\sim$1% for 2 x 10$^{-1}$ mbar. This suggests that for a deposition at a high $p$O$_2$, the oxygen content of a target is not an important parameter for the deposition. Figure 3.10b compares the relative amount of oxygen coming from the background for the main oxygen containing plasma species. Correlating the results presented in Figure 3.10a and 3.10b indicates that the background contribution to the film is between those to atomic oxygen (the black line with square dots and red line with round dots as shown in Figure 3.10b) and metal-oxygen ions (the blue line with
triangle dots as shown in Figure 3.10b). This result also implies the significant contribution from the generation of MO$^+$ with large $E_{\text{dissoc.}}$ to the oxygen content of the film.

Apart from the influence coming from the O$_2$ background pressure, the ablation fluence is also considered to be an important deposition parameter to influence the deposition. Therefore, the properties of some ionic plasma species are examined vs. ablation fluence. Similar to the investigations above, the oxygen and metal-oxygen ions are mainly studied.

![Image of kinetic energy distributions](image)

**Figure 3.11.** Kinetic energy distributions of (a) O$^-$ and (b) O$^+$ from 248 nm laser induced LSM$^{16}$O in vacuum at various ablation fluences.

Figure 3.11 shows the $E_K$ distributions of O$^-$ and O$^+$ in vacuum using various ablation fluences when ablating LSM$^{16}$O. For O$^-$, $E_K$ is observed to be smaller than 40 eV for all fluences and the most probable $E_K$ value is lower than 10 eV for most fluences. For O$^+$, $E_K$ extends up to a couple of 100 eV with the most probable distribution around 50 eV for small fluences and up to 125 eV for the largest fluence of 5.8 J/cm$^2$.

Figure 3.12 shows the $E_K$ distribution of O$^-$ and O$^+$ at 1.5 x $10^{-1}$ mbar $\rho$O$_2$ using different ablation fluences. Through strong plasma / background interactions, $E_K$ of O$^-$ and O$^+$ are effectively reduced to less than 20 eV. No significant variation is observed for $E_K$ for different ablation fluences.
However, it is noted that the amount of O⁻ as compared to O⁺ is enhanced with increasing ablation fluence, in particular for a fluence > 2 J/cm². This is shown in Figure 3.13 where the O⁻/O⁺ ratio vs. ablation fluence at 1.5 x 10⁻¹ mbar O₂ is plotted. Correlating this result with the previous observation vs. pO₂, O⁻ was observed to possess the largest relative amount as compared to O⁺ at 10⁻² mbar when using a fluence of 1.8 J/cm². For comparison, a smaller O⁻/O⁺ ratio has been observed at 10⁻¹ mbar due to the low electron affinity energy of O⁻ making O⁻ not very stable during the very intensive interactions with background molecules. Using a fixed pO₂ of 1.5 x 10⁻¹ mbar and increasing the ablation fluence, the total amount of plasma species increased. This is expected to be less effective to be stopped through background interactions using the same pressure. Therefore, the plasma plume is able to propagate further and contains more O⁻.
Figure 3.13. O\(^{-}/\)O\(^{+}\) ratio at 1.5 x 10\(^{-1}\) mbar O\(_2\) vs. ablation fluence. The used O\(^{-}\) and O\(^{+}\) amounts are deduced by the integration over their \(E_K\) distributions.

Figure 3.14 shows the \(E_K\) distribution of Mn\(^{+}\), Sr\(^{+}\), La\(^{+}\) and LaO\(^{+}\) at various ablation fluence and 1.5 x 10\(^{-1}\) mbar O\(_2\), the pressure which results in a stoichiometric metallic transfer. Due to the strong background interactions, \(E_K\) of these positive metal or metal-oxygen ions are observed to be lower than 20 eV. A larger amount of species is observed with increasing fluence which could be attributed to the larger amount of material ablated with increasing fluence. Nevertheless, the most probable \(E_K\) values for these species are not observed to vary much.
Figure 3.14. Kinetic energy distributions of (a) \(\text{Mn}^+\), (b) \(\text{Sr}^+\), (c) \(\text{La}^+\) and (d) \(\text{LaO}^+\) from 248 nm laser induced LSM\(^{16}\text{O}\) at 1.5 \(\times\) 10\(^{-1}\) mbar \(\text{O}_2\) and various ablation fluences.

Figure 3.15a shows the \(\text{LaO}^+ / (\text{La}^+ + \text{LaO}^+)\) ratio vs. ablation fluence in vacuum, 1 \(\times\) 10\(^{-2}\) mbar and 1.5 \(\times\) 10\(^{-1}\) mbar \(\rho\text{O}_2\). As has been presented in Figure 3.4, much larger \(\text{MO}^+ / (\text{M}^+ + \text{MO}^+)\) ratio has been observed for La as compared for Sr and Mn at 10\(^{-1}\) mbar \(\rho\text{O}_2\). At all used fluences the \(\text{LaO}^+ / (\text{La}^+ + \text{LaO}^+)\) ratio is the largest at 1.5 \(\times\) 10\(^{-1}\) mbar (> 90%), followed by 1 \(\times\) 10\(^{-2}\) mbar (40%–60%) and smallest in vacuum (< 10%). At 1 \(\times\) 10\(^{-2}\) mbar, a small decrease in the \(\text{LaO}^+ / (\text{La}^+ + \text{LaO}^+)\) ratio with ablation fluence was observed. This decrease could be caused by the less effective oxidization of La or \(\text{La}^+\) species due to their increasing ablation amount with fluence. However, compared to the ablation fluence, the background pressure has a more significant influence on the oxidization reaction of metallic species during plasma / background interactions. In Figure 3.15b, the \(\text{SrO}^+ / (\text{Sr}^+ + \text{SrO}^+)\) and \(\text{MnO}^+ / (\text{Mn}^+ + \text{MnO}^+)\) ratio vs. ablation fluence at 1.5 \(\times\) 10\(^{-1}\) mbar \(\rho\text{O}_2\) are shown. Compared to that
of La at the same pressure, the $\text{MO}^+ / (\text{M}^+ + \text{MO}^+)$ ratios for Sr and Mn are observed to be much smaller, i.e., around 10%.

![Diagram](image)

**Figure 3.15.** (a) $\text{LaO}^+ / (\text{La}^+ + \text{LaO}^+)$ ratio in vacuum as well as $1 \times 10^{-2}$ mbar and $1.5 \times 10^{-1}$ mbar O$_2$ vs. ablation fluence; (b) $\text{MO}^+ / (\text{M}^+ + \text{MO}^+)$ ratios for Sr and Mn at $1.5 \times 10^{-1}$ mbar O$_2$ vs. ablation fluence.

In order to further investigate the metallic film composition vs. ablation fluence, the LSMO thin films were grown on Si(001) at room temperature as a function of the O$_2$ background pressure using $F=1.8$ J/cm$^2$ and also as a function of ablation fluence at $1.5 \times 10^{-1}$ mbar O$_2$. The metallic composition of these films are detected using RBS and shown as a function of $p$O$_2$ and ablation fluence in Figure 3.16a and 3.16b, respectively.
Figure 3.16: Sr, Mn and O stoichiometry of La$_{0.6}$Sr$_x$Mn$_y$O$_{3-\Delta}$ thin films deposited on Si(001) substrate at room temperature: (a) as a function of the O$_2$ background pressure using 1.8 J/cm$^2$ ablation fluence; (b) as a function of ablation fluence at 1.5 x 10$^{-1}$ mbar O$_2$.

When using the fixed ablation fluence, the Mn and Sr composition show a non-monotonic variation vs. $p_{O_2}$, similar to the situation when growing LSMO films on STO at 650 °C. An almost stoichiometric cation transfer is achieved in the pressure range at 10$^{-3}$ mbar or lower and for the low 10$^{-1}$ mbar range, while films grown ~10$^{-2}$ mbar show a loss of the lighter elements of Mn and Sr compared to La. The possible reason for this observation has been explained earlier in this chapter. A pressure of 10$^{-3}$ mbar or lower is not high enough to reduce the collision mean free path below the plasma propagation distance, and no intensive plasma / background interactions are expected to occur. At the low 10$^{-1}$ mbar range, the plasma propagation transformed into the previous described shock wave expansion and the formation of a relative condensed shockwave front largely confines the spatial distribution of species with various atomic weights into the same region. In both cases a stoichiometric cation transfer can be achieved. For comparison, in the 10$^{-2}$ mbar range there are already pronounced plasma/background interactions but they are not strong enough to cause the formation of a relatively condensed shock wave front to confine the plasma plume.
Therefore, a loss of lighter composition is expected through elastic collisions with the background molecules.

When fixing the O₂ pressure to 1.5 x 10⁻¹ mbar and varying the fluence, a decrease in the Mn and Sr content compared to La is observed. This phenomenon supports the understanding of the previously observed variation of the film composition vs. pO₂. At 1.5 x 10⁻¹ mbar, the plasma species pushes the background molecules forward due to their multiple collisions, and compress them into a relatively condensed shockwave front that strongly confines the spatial distribution of the species [27, 28, 129-131, 137, 138]. At the fixed pressure, the confinement of all species is expected to become less effective due to an increase in the number of ablated species. Therefore, a loss of lighter element is expected. To further verify this point experimentally in chapter 6 emission spectroscopy and time resolved plasma imaging results will be discussed. The oxygen contents of these films are not discussed since a hydrogen signal for these LSMO films grown at room temperature is observed from ERDA. This indicates that these amorphous films absorb a considerable amount of water.

It is undeniable that several intrinsic reasons may also cause the compositional variations of the film, i.e. compositional changes of the target surface and morphology due to the long time ablation of the target or laser plume alignment errors have been reported to cause the compositional variations during PLD [28, 43]. However, this seems unlikely since the film composition of epitaxially grown five films in vacuum over a time window of one year changed very little (see Figure 3.17).
To summarize, in this chapter plasma analysis of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Mn}^{16/18}\text{O}_3$ reveals significant variations in plasma/background interactions as a function of the $\text{O}_2$ background pressure. A congruent transfer of the target composition has been achieved in a pressure window around $10^{-3} \text{ mbar}$ and again for a narrow window in the $10^{-1} \text{ mbar}$ range. In the intermediate pressure range the film stoichiometry is cation deficient. In the pressure range of $10^{-2} \text{ mbar}$ plasma/background interactions are not sufficient for the formation of a shockwave front to confine the plasma species. As a result, lighter elements are scattered more by elastic interactions with the background molecule causing the loss of the lighter elements in the cation composition of the film. At the same time the oxygen content in epitaxial films is significantly higher. This is related to chemical reactions with the background oxygen during the LSMO formation on the hot substrate surface, and also with the presence of a large number of metal-oxygen and $\text{O}^-$ species. It is further found that with increasing $p\text{O}_2$ metal-oxygen species with large dissociation energies are preferentially formed in the plasma as a consequence of plasma interactions with the oxygen background. This suggests that at a high partial oxygen pressure, the oxygen contribution to the final LSMO composition is strongly administered from these
metal-oxygen species, atomic oxygen, and the oxygen background. At the same time these species influence the cation composition. In addition, the origin of oxygen in the plasma as well as in the film material was traced by $^{18}$O labelling of the target as well as substrate. At low pressures, most of the oxygen is provided by the target whereas at high pressures the background molecules and respective interactions are the main oxygen source.
4. Comparing two representative cases: Ca$_3$Co$_4$O$_9$ and 3-YSZ

In this chapter, two representative oxides materials, Ca$_3$Co$_4$O$_9$ and 3-YSZ (3 mol% Y$_2$O$_3$ doped ZrO$_2$), are selected to further develop the correlation between the O$_2$ background pressure and plasma/film properties. From the observation in Chapter 3, the chemical stability of the metal-oxygen species largely determines whether the arriving composition are metallic or metal-oxygen species when using $10^{-2}$ or $10^{-1}$ mbar $p$O$_2$. For Ca$_3$Co$_4$O$_9$, the bond energy of both CaO$^+$ (4.2 eV) and CoO$^+$ (2.8 eV) are smaller than the bond energy of O$_2$ molecules. The opposite situation is for 3-YSZ, where the dissociation energies of YO$^+$ (7.6 eV) and ZrO$^+$ (8.3 eV) are both larger than that of O$_2$. Therefore, a dramatic difference is expected in the respective plasma properties vs. $p$O$_2$ during the deposition of the two materials.

4.1. Deposition, plasma analysis and laser induced forward transfer of Ca$_3$Co$_4$O$_9$

The Ca$_3$Co$_4$O$_9$ (also denoted as [Ca$_2$CoO$_3$]$^{RS}$[CoO$_2$]$_{1.62}$) is one of the most promising $p$-type thermoelectric (TE) oxides with prospective applications such as a solid-state electric power generator from temperature gradients or the operation as heat pumps for solid state refrigeration [69-85]. Apart from the traditional metal-alloy TE materials oxides TE materials received considerable attention due to their lower cost.

This chapter is summarized by the following publication:
as well as reduced toxicity and larger tolerance to an oxidizing atmosphere [69].
Ca$_3$Co$_4$O$_9$ has a layered structure: stacked CdI$_2$-type CoO$_2$ layers are alternating with
a rock-salt-type Ca$_2$CoO$_3$ layer along the c-axis as illustrated in Figure 4.1a [86-89].
In order to achieve a good TE performance, which is evaluated by a figure of merit $ZT$
($ZT = S^2\sigma T/\kappa$; with $S$ as the Seebeck coefficient, $\sigma$ and $\kappa$ as the electrical and thermal
conductivity), the correct composition and crystal structure is required [69-71].
Nevertheless, the complexity in the chemical composition and crystal structure of
Ca$_3$Co$_4$O$_9$ brings considerable difficulties to the preparations of the bulk materials as
well as thin films depositions. For example, the phase purity of
[Ca$_2$CoO$_3$]$^{RS}_{\text{CoO}_2}$.62 bulk material is achieved via long-term and repetitive solid
state reaction procedures at appropriated annealing temperatures. When fabricating
Ca$_3$Co$_4$O$_9$ thin films by PLD, the crystal structure of as-deposited thin film is reported
to be rather sensitive to the deposition conditions [86-88] such as background pressure,
substrate temperature and laser frequency. Therefore, a detailed study of the plasma
properties is necessary in order to correlate them with the respective deposition
conditions as well as structural and electrical transport properties. As a case study, the
plasma / film properties vs. background conditions are investigated and compared
with the data in Chapter 3.

Another important reason why Ca$_3$Co$_4$O$_9$ is interesting is that it can be deposited
on substrates, such as Si, glass or quartz. Therefore, it provides an opportunity to
firstly deposit Ca$_3$Co$_4$O$_9$ on UV transparent substrates and subsequently pattern the
film directly via a laser induced forward transfer (LIFT) process for the further
fabrication of TE micro-devices. For a micro-scaled TE device, a subsequent
patternning step is required to define the shape of the $p$-$n$-type TE films onto the same
plane which can be achieved by micro-fabrication techniques, such as lithography and
etching [74-79], or micromachining [80]. These processes often require complex
facilities involving high costs along with a reduced flexibility in device design [92].
An alternative approach is laser-induced forward transfer [93], a direct printing
technique in which a laser beam is shaped and imaged onto the backside of a
transparent support plate coated with the material to be transferred (also named donor).
The laser partially vaporizes and subsequently transfers the donor material onto a receiver substrate which is usually in close proximity. The dimensions (e.g. length and width) and hence shape of the transferred material (also called pixel) is controlled by the imaged incident laser beam with a high spatial resolution of a few μm. LIFT has been successfully applied for patterning a wide range of materials for micro-devices such as organic light-emitting diodes (OLEDs), or chemical sensors [93-99]. Recently, $p$- and $n$-doped chalcogenide thin films have successfully been laser transferred by directly imaging the beam onto the donor [96]. The as-transferred large area pixels showed some signs of thermal damage but remained largely intact in terms of their morphology, structure and composition showing reduced but still reasonable thermoelectric properties as compared to the donor material.

Figure 4.1. (a) Schematic illustration of the crystal structure of the Ca$_3$Co$_4$O$_9$ and Ca$_x$CoO$_2$ [88]; (b)-(e) $E_K$ distributions of Ca$^+$, Co$^+$, O$^+$ and O$^-$ in vacuum as well as 0.08 and 0.25 mbar O$_2$
Figure 4.1b-e shows some examples of the $E_K$ distributions of some of the main existing ionic plasma species when ablating Ca$_3$Co$_4$O$_9$ in vacuum as well as O$_2$ backgrounds. From Figure 4.1b-d it can be seen that $E_K$ of O$^+$, Ca$^+$ and Co$^+$ decreases with $p$O$_2$. In comparison, O$^-$ shows a larger $E_K$ at 0.08 mbar O$_2$ as compared to in vacuum as well as at 0.25 mbar. According to the understanding in Chapter 3, this result could be caused by the charge conversion from O$^+$, originating from ablation of target and possessing large $E_K$, to O$^-$ through background interactions.

Figure 4.2. Total detected amount of the ionic plasma species in laser induced Ca$_3$Co$_4$O$_9$ plasmas for the PLD process in four different background conditions. The average kinetic energies are marked for the principle ions in blue.

The numbers of the total detected ionic species as well as their average kinetic
energies for different background pressures and substrate-target distances are summarized in Figure 4.2 showing a large variation in the ionic plasma composition and $E_{K,av}$. The variations in plasma composition, kinetic energy are expected to influence the crystal structures as well as electrical transport properties of the deposited thin films.

Figure 4.3. (a) Photos of laser-induced plasma plume from a Ca$_3$Co$_4$O$_9$ target at various background conditions. (b) XRD patterns and compositions of the as-deposited Ca$_3$Co$_4$O$_9$ films in various background conditions. (c) Electric conductivity and Seebeck coefficient of the as-deposited Ca$_3$Co$_4$O$_9$ films in various background conditions. (d) XRD of the Ca$_3$Co$_4$O$_9$ donor film grown on Pt/quartz prior to LIFT.

In vacuum, the plasma consists mainly of charged atomic species (Ca$^+$, Co$^+$, O$^+$ and O$^-$) with large $E_{K,av}$ between 20 and 40 eV. The deposited films showed no pronounced film Bragg peaks in the XRD pattern and the film composition has the lowest oxygen content as determined by RBS. Potential reasons why the crystalline structure in the growing film was not obtained are re-sputtering effects due to the
large $E_K$ of the plasma species or too little oxygen was supplied from the target during the deposition and hence prevented the correct crystalline phase to be formed.

At 0.08 mbar $pO_2$, the emission intensity of the plasma plume is stronger compared to in vacuum (see Figure 4.3a), which imply the re-excitation of the plasma species due to background interactions. As a result, $E_{K,Avr}$ for the lighter Ca$^+$ and O$^+$ ions is reduced to $\sim$12 eV, while $E_{K,Avr}$ for Co$^+$ was effectively unchanged. The plasma shows now a strong increase in CaO$^+$ and CoO$^+$ metal-oxygen ions due to the oxidization of the metallic species as a result of background reactions. In addition, the relative amount of O$^-$ compared to O$^+$ ($O^-/O^+$: $\sim$2) is strongly enhanced when compared to a vacuum deposition ($O^-/O^+$: $\sim$0.2). This can be attributed to either (1) an enhanced background formation of O$^-$ species or (2) a conversion of O$^-$ to O or O$^+$ respectively, originating from electron attaching processes (see Chapter 3). The first process, the formation of O$^-$, requires a much lower formation energy ($O_2 + e + 3.66$ eV $\rightarrow$ O + O$^-$) compared to the formation of O$^+$ ($O + 13.6$ eV $\rightarrow$ e$^-$ + O$^+$). In addition, the electron attaching of O$^+$ ($O^+ + e \rightarrow O + 13.6$ eV) or O ($O + e \rightarrow O^- + 1.46$ eV) also release energy. With these plasma conditions, the prepared films shows a Ca$_x$CoO$_2$ structure instead of the desired [Ca$_2$CoO$_3$]$_{RS}$[CoO$_2$]$_{1.62}$ where the Ca cation directly intercalates into the CoO$_2$ layer without the formation of the rock-salt-type Ca$_2$CoO$_3$ layer. Compared to the desired [Ca$_2$CoO$_3$]$_{RS}$[CoO$_2$]$_{1.62}$, the Ca$_x$CoO$_2$ structure is thermodynamically less stable but dynamically easier to form due to its smaller lattice parameter (5.4 Å for Ca$_x$CoO$_2$, and 10.8 Å for Ca$_3$Co$_4$O$_9$) and the larger tolerance in composition [88].

When enhancing $pO_2$ to 0.25 mbar and keeping the target-substrate distance at 3 cm, the plasma plume just reaches the substrate position with the strongest confinement and emission intensity (Figure 4.3a). In this pressure range, the shockwave plasma propagation is expected that effectively stops the plasma species [27]. Mass spectrometry reveals that $E_{K,Avr}$ of the ionic species is further reduced ($< 10$ eV) while the relative amount of O$^-$ compared to O$^+$ is largest ($O^-/O^+$ $\sim$6). Under such plasma conditions, the desired [Ca$_2$CoO$_3$]$_{RS}$[CoO$_2$]$_{1.62}$ phase and correct film composition (Ca$_{2.9}$Co$_{4}$O$_{9.0}$) were observed for epitaxially grown films on Si and
Pt-coated quartz. The XRD pattern for a Ca$_3$Co$_4$O$_9$ film on Pt-coated quartz (Fig 4.3d) shows a well (00l) oriented growth of the correct Ca$_3$Co$_4$O$_{9.0}$ phase. Subsequent electrical transport measurements (Figure 4.3c) show a similar resistance and Seebeck coefficient as reported in [86-88]. This proves that with the selected plasma conditions, Ca$_3$Co$_4$O$_9$ films with a proper composition and electrical properties can be prepared at a deposition temperature of 650 °C.

By increasing the target-substrate distance to 4.5 cm at 0.25 mbar $p_{O_2}$, the plasma plume is not reaching the substrate and the lowest amount of species as well as a further reduced $E_{K,Avr}$ is observed. Atomic oxygen is almost absent and the very low concentration is attributed to the fact that light elements are scattered more strongly than heavier metallic species and are therefore lost from the plasma cloud reaching the substrate. These films show again a Ca$_3$Co$_4$O$_2$ phase instead of the desired structure despite being almost fully stoichiometric (Ca$_{2.9}$Co$_{4.8}$O$_{8.8}$). This leads to the conclusion that the correct crystalline structure of Ca$_3$Co$_4$O$_9$ is very sensitive to the correct oxygen content and a high concentration of O$^-$ is necessary to support the formation of the proper crystalline modification.

Knowing the optimum deposition condition for Ca$_3$Co$_4$O$_9$ films, the following option have been considered to derive a strategy in order to directly patterning the film material using LIFT. A similar LIFT procedure to as described in ref. [96] for transferring Bi$_2$Te$_3$/Bi$_2$Se$_3$ was firstly tried. The Ca$_3$Co$_4$O$_9$ film was directly deposited onto a UV transparent quartz substrate. Afterwards, a XeCl laser beam ($\lambda = 308$ nm, 30 ns pulse length, 1 Hz repetition rate) was imaged with an optical system through the transparent back side of the quartz substrate onto the film. The laser beam evaporates the illuminated film and transferred it forward. However, due to the higher mechanical hardness and brittleness of Ca$_3$Co$_4$O$_9$ as compared to the Bi$_2$Te$_3$/Sb$_2$Te$_3$ [96], a LIFT procedure as described in ref. 96 turns the as-transferred continuous oxide film into powder.

Therefore, the LIFT procedure was further optimized by introducing a Pt interlayer between the quartz substrate and Ca$_3$Co$_4$O$_9$ film material to serve as a sacrificial layer for the LIFT process, instead of a direct laser interaction with the
Ca$_3$Co$_4$O$_9$ film. As illustrated in Figure 4.4, the Ca$_3$Co$_4$O$_9$ film was firstly grown onto a transparent quartz substrate coated with a sputtered Pt interlayer (40 nm) by PLD (Figure 4.4 left). In the second step, the Ca$_3$Co$_4$O$_9$ film is transferred with the desired shape and size using LIFT onto a soft polymer receiver substrate (Figure 4.4 right).

The LIFT procedure was therefore optimized to avoid a direct laser interaction by introducing a thin Pt film as a sacrificial layer to absorb the laser light in order to enable a damage-free transfer of the Ca$_3$Co$_4$O$_9$ pixel onto the receiver substrate. In addition, a soft substrate, i.e. polydimethylsiloxane (PDMS), was used in order to reduce the stress on the pixel upon transfer [96, 97]. The use of PDMS as a soft receiver substrate is very attractive: it is biocompatibility, and can be used in challenging environmental, processing and operating conditions. In addition it is widely used in lab-on-a-chip devices [100]. For µ-TE applications, PDMS has potential to be used in medical but also in sensor applications.

The laser ablation fluence for transfer is further optimized over a broad range from 0.2-1 J/cm$^2$ for a laser wavelength of 308 nm. The optical images of Ca$_3$Co$_4$O$_9$ micro-pixels obtained immediately after transfer at different laser fluences are displayed in Fig. 4.5a-d. For low laser fluences, i.e., below 0.45 J/cm$^2$, no transfer occurs. At 0.45 J/cm$^2$ a pixel from the donor is transferred onto the receiving substrate as seen in Fig. 4.5a. However, the pixels transferred at this laser fluence have an inhomogeneous shape and are laterally not well resolved. For the fabrication of a
micro-device it is very important to control both the size and the shape of the transferred spot. In Fig. 4.5 b, c, and d micro-pixels transferred with different laser fluences (500 – 600 mJ/cm²) are shown. All the pixels present a similar size of about (500 × 500) μm² but in some cases the edges are less uniform, e.g. the left bottom corner at 500 mJ/cm². This is probably due to a pulse to pulse energy variation of the laser. All transferred pixels are regularly arranged. In the case of bismuth telluride pixels obtained by LIFT [96], the optimal laser fluence for the transfer of intact pixels is ~100 mJ/cm². The difference in fluence is related to the hardness of the transferred materials and the energy required to evaporate the sacrificial layer in order to move the brittle layer. With this approach, layers with a thickness of 0.5μm are possible to be transferred.

Figure 4.5. Ca₃Co₄O₉ micro-pixels deposited onto PDMS substrate at different laser fluences a) 450 mJ cm⁻², b) 500 mJ cm⁻², c) 550 mJ cm⁻², d) 600 mJ cm⁻². SEM image of e) a Ca₃Co₄O₉ micro-pixel deposited at 600 mJ cm⁻² laser fluence, f) the edge of the pixel shown in e), and g) the middle part of the pixel shown in e).

In order to assess any modifications of the micro-pixel morphology due to the absorption of the laser pulse, scanning electron microscopy (SEM) images were acquired. A SEM image of a transferred pixel (at 600 mJ/cm²) is shown in Fig. 4.5 e. The SEM images with higher magnification of the middle part and edge of the same pixel (shown in Fig. 4.5 f and g) reveal that the Ca₃Co₄O₉ is immobilized on the PDMS substrate. The transferred micro-pixel is homogeneous, with well defined edges (see
The micro-pixel has a clean surface with no visible changes in the morphology or debris from the Pt interlayer (see Fig. 4.5 g).

The following question to address is whether there is an influence on structure and composition of the Ca$_3$Co$_4$O$_9$ micro-pixels caused by a possible heat-transfer during the LIFT process. A composition of the pixel after the LIFT transfer of Ca$_{3.2\pm0.3}$Co$_4$O$_9$ has been measured for single pixels which compares well to the cation composition of the donor film (Ca$_{3.0\pm0.15}$Co$_4$O$_9$) before material transfer. The oxygen content has a major influence on the thermoelectric properties of misfit cobaltites but is difficult to determine due to the small pixel size and small amount of pixel material available. Some Pt is also detected in the RBS spectrum. From the position in the spectrum it can be concluded that the Pt forms a discontinuous layer on the surface of the pixel as verified by SEM. Due to the evaporation of Pt as a sacrificial layer, nano-sized metallic droplets on the transferred pixel has been found indicating that Pt has coalesced to small particles after the transfer and thus should not have a negative influence on the TE properties of Ca$_3$Co$_4$O$_9$ micro-pixels. Both (001) and (002) diffraction peaks have been observed for the XRD pattern of as-transferred pixels (see Figure 4.6). This is a direct indication that the crystal structure was preserved during and after the LIFT process.

![Figure 4.6. XRD spectra of the Ca$_3$Co$_4$O$_9$ pixel transferred at 600 mJ/cm$^2$.](image)

To summarize, through $E_k$-resolved mass spectrometry, the correlation between
$pO_2$, plasma properties and film properties is established for the deposition of Ca$_3$Co$_4$O$_9$ by PLD. The variations in both plasma and film properties vs. $pO_2$ well support the observations shown in Chapter 3: 1) a stoichiometrical transfer of Ca and Co during PLD is achieved in either quasi-vacuum or low $10^{-1}$ mbar $pO_2$ range, while a loss of the lighter Ca film composition is observed at $10^{-2}$ mbar range. 2) the relative amount of O$^-$ compared to O$^+$ enhances with $pO_2$ until the optimum deposition pressure where O$^-$/O$^+$ reaches a maximum value. 3) Since the dissociation energies of CaO$^+$ and CoO$^+$ are smaller than that of the O$_2$ molecule, the Ca and Co containing species mainly arrive at the substrate as atoms or atomic ions.

In addition, a combined process of PLD and LIFT has been used for direct patterning of Ca$_3$Co$_4$O$_9$ TE micro-scaled pixels for potential applications in TE micro-devices. For the transfer of Ca$_3$Co$_4$O$_9$ as a micro-pixel, a Pt sacrificing layer is introduced to avoid the direct laser interaction with the TE material thereby preserving composition, structure and shape of the transferred pixel. This is unlike directly transferred pixels where a structural and compositional change can occur due to the intense laser-matter interaction. Compared to conventional patterning processes, e.g. optical lithography or micro-machining, the LIFT procedure simplifies the fabrication of complex TE micro-scaled devices. In addition, the aspect ratio of as-transferred patterns can be conveniently adjusted via the laser beam shape. The demonstrated approach for the direct patterning of the $p$-doped TE Ca$_3$Co$_4$O$_9$ can be extended to other materials in order to fabricate fully functional thermoelectric micro-devices on soft, biocompatible substrates.
4.2. Plasma analysis of 3-YSZ

Yttria stabilized zirconia (YSZ) is a well-known oxygen ion conductor and has been commonly used as electrolyte material for solid oxide fuel cells (SOFC) [101-106]. The substitution of Zr with Y in the ZrO$_2$ lattice generates oxygen vacancies enabling an oxygen ion transport ($Y_2O_3 \rightarrow 2Y^\prime_{Zr} + 3O^X_{O} + V_{O}^{\cdot\cdot}$) and stabilizing the structure [101, 102]. Compared to the Ca$_3$Co$_4$O$_9$ deposition, the oxidization of metallic species is considered to be much more pronounced for the deposition of YSZ in an O$_2$ background. As already described, the chemical stability of YO$^+$ (7.6 eV) and ZrO$^+$ (8.3 eV) are larger than for O$_2$ molecules (5.12 eV) while the opposite situation is for CaO$^+$ (4.2 eV) and CoO$^+$ (2.8 eV). Therefore, a much more significant enhancement in the MO$^+$ / (M$^+$ + MO$^+$) ratio with the increasing O$_2$ background pressure is expected for the deposition of YSZ as compared for Ca$_3$Co$_4$O$_9$.

Fig 4.7 compares the ionic plasma compositions of the laser induced plasma detected for various O$_2$ background pressure using a fixed ablation fluence of 1.5 J/cm$^2$. Even at the lowest pressure of 1 x 10$^{-3}$ mbar, the plasma consists of a certain amount of YO$^+$ and ZrO$^+$ species, similar to the La described in Chapter 3. By increasing $p_{O_2}$, the relative amount of YO$^+$ and ZrO$^+$ increases compared to their metallic ions. O$^-$ is observed as the main negative ion. Although some negative metal-oxygen ions such as YO$^-$, YO$_2^-$, ZrO$^-$ and ZrO$_2^-$ are also observed, their amount is much smaller compared to O$^-$. At the highest used pressure of 10$^{-1}$ mbar, negative ions are almost absent, a result which agrees with the observations reported in Chapter 3.
Figure 4.7. Ionic plasma composition of 248 nm laser induced 3-YSZ in various O₂ pressures with fixed ablation fluence at 1.5 J/cm²

In Figure 4.8 (a) and (b), the pressure dependence of the YO⁺, Y⁺, ZrO⁺ and Zr⁺ is shown, while in Figure 4.8 (c) the MO⁺/M⁺ ratio is plotted vs. pO₂. With an increasing O₂ pressure from $10^{-3}$ to $10^{-2}$ mbar, the amount of YO⁺ and ZrO⁺ increases while the amount of Y⁺ and Zr⁺ decreases, which indicates the oxidization of metallic species to metal-oxygen species. By further enhancing $pO_2$ to $10^{-1}$ mbar, the amount for YO⁺, Y⁺, ZrO⁺ and Zr⁺ is reduced due to the stronger background scattering. However, their MO⁺/M⁺ ratio shows a significant enhancement. These results are similar to the observations for La described in Chapter 3. The positive metal-oxygen ions are expected to be more important for the deposition, since their amount are more than 10 times larger than the negative metal-oxygen ions.
Figure 4.8. (a) YO$^+$ and Y$^+$ amount; (b) ZrO$^+$ and Zr$^+$ amount; (c) YO$^+$/Y$^+$ and ZrO$^+$/Zr$^+$ ratios in 248 nm laser induced 3-YSZ plasma vs. $p_{O_2}$ at fixed ablation fluence at 1.5 J/cm$^2$

In Figure 4.9 (a) and (b), the average $E_{K,Avr.}$ of positive metallic as well as metal-oxygen ions are plotted vs. $p_{O_2}$. A more significant decrease in $E_K$ with increasing $p_{O_2}$ is observed for the metallic ions than the positive metal-oxygen ions. In Figure 4.9 (c), $E_{K,Avr.}$ of O$^+$ and O$^-$ are plot vs. $p_{O_2}$. A clear decrease of $E_{K,Avr.}$ with increasing fluence has been observed for O$^+$, while $E_{K,Avr.}$ for O$^-$ stays nearly constant.
Figure 4.9. Average kinetic energies of (a) YO\(^+\) and Y\(^+\); (b) ZrO\(^+\) and Zr\(^+\); (c) O\(^+\) and O\(^-\) in 248 nm laser induced 3-YSZ plasma vs. \(p_{O_2}\) at fixed ablation fluence at 1.5 J/cm\(^2\)

The fluence dependences of species amount as well as \(E_{K,\text{Avr.}}\) are also studied for YO\(^+\), Y\(^+\), ZrO\(^+\), Zr\(^+\), O\(^+\) and O\(^-\). Figure 4.10 (a) and (b) show the amount of YO\(^+\), Y\(^+\), ZrO\(^+\) and Zr\(^+\) vs. the ablation fluence at 1.6 x 10\(^{-2}\) mbar O\(_2\), while Figure 4.10 (c) shows the MO\(^+\)/M\(^+\) ratio vs. fluence. When increasing the fluence from 0.8 to 1.5 J/cm\(^2\), a significant increase in the amount of Y\(^+\) and Zr\(^+\) is observed, while YO\(^+\) and ZrO\(^+\) only increase slightly. Increasing the fluence towards 4 J/cm\(^2\), the amounts of Y\(^+\) and Zr\(^+\) slightly increases, while YO\(^+\) and ZrO\(^+\) show a decrease. The MO\(^+\)/M\(^+\) ratio decreases with increasing fluence which indicates a reduction of the arrival metal-oxygen species as compared to metallic species. The observations for Zr and Y agree with the observation for La as described in Chapter 3.
In Figure 4.11 (a) and (b), the $E_{K,Avr}$ of positive metallic as well as metal-oxygen ions are plotted vs. ablation fluence, while the data for O$^-$ and O$^-$ are shown in Fig 4.11 (c). At the used pressure, the collision mean free path is considered to be smaller than the plasma propagation distance and therefore pronounced plasma / background interactions are expected. The $E_{K,Avr}$ for the metallic species such as Y$^+$, Zr$^+$, and O$^+$, increases with increasing fluence while those for YO$^+$, ZrO$^+$ and O$^-$ do not show pronounced variations.

Figure 4.10. (a) YO$^+$ and Y$^+$ amounts; (b) ZrO$^+$ and Zr$^+$ amount; (c) YO$^+/Y^+$ and ZrO$^+/Zr^+$ ratios in 248 nm laser induced 3-YSZ plasma vs. ablation fluence at 1.6 x 10$^{-2}$ mbar O$_2$. 

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Figure 4.11. Average kinetic energies of (a) YO\(^+\) and Y\(^+\); (b) ZrO\(^+\) and Zr\(^+\); and (c) O\(^+\) and O\(^-\) average kinetic energies in 248 nm laser induced 3-YSZ plasma vs. ablation fluence at 1.6 \(\times\) 10\(^{-2}\) mbar O\(_2\).

According to the previous description in Chapter 3, MO\(^+\) and O\(^-\) are more likely to be formed through the background reactions as compared for M\(^+\) and O\(^+\). With an increasing O\(_2\) pressure, \(E_K\) of species such as Zr\(^+\), Y\(^+\) and O\(^+\) decreases due to the increase in physical collisions with background molecules. For comparison, \(E_K\) of species such as ZrO\(^+\), YO\(^+\) and O\(^-\) are observed to be smaller at a low pressure (10\(^{-3}\) mbar or vacuum). When increasing \(p_{O2}\), to 10\(^{-2}\) mbar or higher, these species are mainly formed through plasma / background reactions and the measured \(E_K\) remains unchanged.

The plasma properties shown in Figure 4.8 - 4.11 reveal the following correlations between deposition pressures and film properties of YSZ. Due to the similar atomic weight of Y and Zr, the film composition is not expected to vary significantly with respect to the target composition as a function of the deposition pressure, which has been confirmed in [16]. Nevertheless, the film morphology can vary significantly at
different deposition pressures and temperatures. For example, in ref [16], when depositing YSZ at the low $10^{-2}$ mbar or lower pressure at 600 °C, a densed film is achievable, which favors the application of YSZ as electrolyte in solid state fuel cells [16, 103, 101]. For comparison, when depositing YSZ at the high $10^{-2}$ mbar or $10^{-1}$ mbar pressure range the films were observed to be more porous due to the largely reduced $E_K$ of the plasma species that makes the atom mobility on the substrate insufficient.

To summarize, the laser induced YSZ plasma properties vs. $pO_2$ pressure as well as ablation fluence is well supported by the conclusion drawn in Chapter 3. The behavior of Y and Zr are quite similar to La in background atmosphere, since they all possess a large bond energy with oxygen. The MO+/M$^+$ ratio is enhanced dramatically with increasing $pO_2$ due to the high stability of both ZrO$^+$ and YO$^+$. At a fixed pressure, the MO$^+/M^+$ ratio decreases with an increasing fluence. Compared to the ablation fluence, the oxygen background pressure is observed to have a more significant influence on the composition as well as the kinetic energy of the plasma species.
5. Plasma/film properties vs. laser photon energy for the deposition of La$_{0.6}$Sr$_{0.4}$MnO$_3$

Apart from the typically used KrF excimer laser ($\lambda$=248 nm) for PLD other lasers such as XeCl excimer ($\lambda$=308 nm) [107-111], ArF excimer ($\lambda$=193 nm) [107-115], or a Nd-YAG lasers ($\lambda$: 266 nm, 355 nm, 532 nm or 1064 nm) [110, 111, 116] have also been used for PLD. Table 5.1 summarizes the wavelength as well as photon energy of these lasers. The variation in photon energy is expected to influence the ionization / dissociation of the illuminated target material [107, 110, 111, 115, 116] and therefore vary the initial plasma properties and compositions. However, only a limited number of studies have been carried out to investigate the influence of the photon energy with respect to plasma / film properties [110, 111, 115, 116]. In this chapter, the plasma as well as deposition properties for La$_{0.6}$Sr$_{0.4}$MnO$_3$ are investigated when using a XeCl or ArF laser. The results are compared to the data presented in Chapter 3 for using a KrF laser.

<table>
<thead>
<tr>
<th>Laser Type</th>
<th>Laser wavelength (nm)</th>
<th>Photon energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KrF excimer</td>
<td>248</td>
<td>5.0</td>
</tr>
<tr>
<td>XeCl excimer</td>
<td>308</td>
<td>4.0</td>
</tr>
<tr>
<td>ArF excimer</td>
<td>193</td>
<td>6.4</td>
</tr>
<tr>
<td>Nd-YAG (fundamental)</td>
<td>1064</td>
<td>1.2</td>
</tr>
<tr>
<td>Nd-YAG (freq. doubled)</td>
<td>532</td>
<td>2.3</td>
</tr>
<tr>
<td>Nd-YAG (freq. tripled)</td>
<td>355</td>
<td>3.5</td>
</tr>
<tr>
<td>Nd-YAG (freq. quadruple)</td>
<td>266</td>
<td>4.6</td>
</tr>
</tbody>
</table>

Table 5.1 Summery of the wavelength as well as photon energies for various lasers.
Figure 5.1a shows the XRD patterns of LSMO films deposited on (100) STO at 650 °C in vacuum using laser wavelengths of 308 nm, 248 nm or 193 nm with F = 1.8 J/cm². A strong diffraction peak from the crystallized film was obtained only when the 308 nm laser was used. The film composition was determined as La$_{0.60}$Sr$_{0.42}$Mn$_{0.95}$O$_{3.0}$ by RBS as compared to La$_{0.60}$Sr$_{0.38}$Mn$_{0.93}$O$_{2.7}$ (λ=248 nm) and La$_{0.60}$Sr$_{0.38}$Mn$_{0.98}$O$_{2.8}$ (λ=193 nm). Reciprocal lattice mapping shown in Fig. 5.1b illustrates that the film was in-plane-locked as often reported for LSMO growth on SrTiO$_3$ substrates [117]. However, no pronounced film peaks were observed from films made by using the other lasers. Epitaxial LSMO thin films were obtained at $p$O$_2$ = 2 x 10$^{-3}$ mbar and 2 x 10$^{-1}$ mbar (Figure 5.2), typical growth conditions for LSMO using a 248 nm laser. Therefore, when using a 308 nm laser for a LSMO deposition, it is not necessary to involve a background which is different from the reported deposition conditions when using a 248 nm or 193 nm laser.
Figure 5.2 X-ray diffraction patterns of as-deposited LSMO films at $2 \times 10^{-3}$ mbar and $2 \times 10^{-1}$ mbar O$_2$ using 308 nm laser at 1.8 J/cm$^2$.

The variations in the vacuum deposition properties when using the three laser wavelengths are expected to be reflected in the respective plasma properties. Therefore, these variations in the ionic plasma composition as well as $E_K$ are further investigated using the $E_K$ resolved mass spectrometry.

Figure 5.3: Ionic plasma compositions of LSMO plasmas in vacuum as well as various $pO_2$ backgrounds using $\lambda=308$ nm and F=1.8J/cm$^2$. 
Figure 5.3 shows the ionic plasma composition of a $\lambda=308$ nm laser induced plasma in vacuum as well as at $2 \times 10^{-3}$ mbar, $1 \times 10^{-2}$ mbar and $1.5 \times 10^{-1}$ mbar $p_{O_2}$ with a fixed fluence of 1.8 J/cm$^2$. These results are comparable to the data presented in Figure 3.1b using $\lambda=248$ nm. Similar to Figure 3.1b, the plasma for a vacuum ablation with $\lambda=308$ nm consists mainly of atomic ions, such as O$^-$, Mn$^+$, Sr$^+$ and La$^+$. LaO$^+$ is the main observed positive metal-oxygen ion whose amount far exceeds the observed negative metal-oxygen ions, such as MnO$^-$, MnO$_2^-$ and LaO$_2^-$. Looking at the oxygen isotopes the relative amount of $^{16}$O and $^{18}$O containing species are similar which agrees with the oxygen isotope ratio of the target ($^{18}$O concentration $\sim$52%). In vacuum or $10^{-3}$ mbar O$_2$, the amount of O$^+$ for using the 308 nm laser is much smaller as compared to O$^-$. This observation differs from the situation for using a 248 nm laser for ablation, where O$^+$ has been observed to possess a similar amount to O$^-$ in vacuum. When increasing $p_{O_2}$ to $1 \times 10^{-2}$ mbar, positive metal-oxygen ions of MnO$^+$ and SrO$^+$, absent in vacuum, are observed. Also, the relative number of LaO$^+$ as compared for La$^+$ increases due to the oxidization of the metallic species. The $^{16}$O/$^{18}$O ratio of oxygen containing species is dramatically enhanced due to the increasing background reactions. At the highest investigated pressure of $1.5 \times 10^{-1}$ mbar negative ions are almost not observe any more, which could be attributed to their low electron affinity and not being stable during the multiple scattering with background molecules as presented in chapter 3. Looking at the positive ions at this highest pressure used, the amount of LaO$^+$ far exceeds La$^+$ while the amount of MnO$^+$ and SrO$^+$ are much smaller as compared to Mn$^+$ and Sr$^+$, respectively. This result supports the observation and understanding in Chapter 3 and has been explained by the differences in the dissociation energies for MO$^+$ and O$_2$. 
Figure 5.4: (a) Ionic oxygen average kinetic energy and species amount in vacuum when using 308 nm, 248 nm and 193 nm laser ablation at 1.8 J/cm². (b) Ratio of MO⁺/(M⁺ + MO⁺) vs. dissociation energy of MO⁺ as determined in vacuum for 308 nm, 248 nm and 193 nm lasers, respectively. The solid-line in red, dash-line in black and dash-dot line in blue represent the photon energy of 308 nm (4.0 eV), 248 nm (5.0 eV) and 193 nm (6.4 eV) lasers, respectively.

Comparing the ionic plasma composition for using 308 nm laser ablation to 248 nm indicates the most prominent variation for the relative amount of O⁺ compared to O⁻ in vacuum or at low pO₂ (~ 10⁻³ mbar). Figure 5.4a shows the amount of species of O⁻ and O⁺ using lasers with λ=308 nm, 248 nm, and 193 nm at the same fluence in vacuum. The amount of O⁺ is much smaller compared to O⁻ for using a 308 nm laser than a 248 nm or a 193 nm laser. The photon energies for 193 nm, 248 nm and 308 nm laser are 6.4 eV, 5.0 eV and 4.0 eV, respectively, which is much smaller compared to the first ionization energy of atomic oxygen (O → O⁺ + e⁻). Therefore, the ionization of O to O⁺ is a 3-photon process for a 193 and a 248 laser while it is a 4-photon process for a 308 laser, a process which is less likely to occur. In this experiment, the lowest amount of O⁺ was observed in 308 nm laser generated plasma (O⁺/O⁻: 0.03) compared to the plasma for 248 nm (O⁺/O⁻: 0.6) and 193 nm (O⁺/O⁻: 1.1).

The influence of photon energy to the relative amount of metal-oxygen ions (MO⁺) as compared to metallic ions (M⁺) were investigated in vacuum. In order to gain a thorough understanding, a large variety of targets, such as SrTiO₃,
La$_{0.8}$Ca$_{0.2}$CoO$_3$, SrMoO$_4$, TbMnO$_3$, TmMnO$_3$, La$_{0.4}$Ca$_{0.6}$MnO$_3$, La$_{0.6}$Sr$_{0.4}$MnO$_3$, or Al$_2$O$_3$, have been ablated at the same fluence of 1.8 J/cm$^2$ using 308 nm, 248 nm and 193 nm lasers. In Figure 5.4b, the detected MO$^+/(M^+ + MO^+)$ ratios were plotted vs. $E_{\text{dissoc.}}$ of MO$^+$ for all the involved metallic elements. In general, the detected MO$^+/(M^+ + MO^+)$ ratio is much small in vacuum as compared to data as presented in Figure 3.4. In particular, for MO$^+$ with a dissociation energy $< 6$ eV MO$^+$ is not detected in vacuum. This result indicates an effective photon or thermal dissociation of the target material into atomic species during the initial laser ablation processes. For comparison, elements with a larger $E_{\text{dissoc.}}$, i.e., Tb or La, there is only a small amount of MO$^+$ detected as compared to M$^+$. The $E_{\text{dissoc.}}$ of TbO$^+$ is 7.2 eV, which requires a 2-photon process to dissociate TbO$^+$ for all three used laser wavelengths. The TbO$^+/(Tb^+ + TbO^+)$ ratio is observed to be smallest for using the 308 nm laser, followed by 248 nm and the highest for 193 nm lasers. This observation could be attributed to the largest number of 308 nm photons, followed by 248 nm and smallest for 193 nm photons at the fixed ablation fluence. For comparison, $E_{\text{dissoc.}}$ of LaO$^+$ is 8.9 eV which indicate a 2-photon process to dissociate LaO$^+$ for using 248 nm or 193 nm photons and a 3-photon process for using 308 nm photons. Due to the lower probability for a 3-photon process as compared for a 2-photon process, the LaO$^+/(La^+ + LaO^+)$ ratio is observed to be much larger for using 308 nm as compared to 248 nm or 193 nm lasers. The occurrence of a N-photon process ($P$) has been proven to be enhanced with the phonon intensity ($I$) by: $\log_{10}P \propto N*\log_{10}I$ [165]. The current results when using a laser fluence of 1.8 J/cm$^2$ indicates an effective 2-photon process, through which MO$^+$ are effectively dissociated. For example, above a fluence of 1.2 J/cm$^2$ when using the 248 nm laser, the LaO$^+/(La^+ + LaO^+)$ is smaller than 5% (see Figure 3.15a). For comparison, when using the 308 nm laser at the same fluence, a 3-photon process is required to dissociate LaO$^+$, which explains the larger LaO$^+$ proportion (around 16%).

The variation of metal-oxygen species vs. $pO_2$ has been also investigated for $\lambda=308$ nm as shown in Figure 5.5. The amounts of La$^+$, La$^{16}$O$^+$ and La$^{18}$O$^+$ vs. $pO_2$ shown in Figure 5.5a are observed to be similar compared to the ones when using the
248 nm laser (see Figure 3.3a). Figure 5.5b-d shows the MO+ / (M+ + MO+) ratio vs. pO2 with λ=308 nm and 248 nm lasers for La, Sr and Mn. In agreement with the data shown in Chapter 3, the LaO+ / (La+ + LaO+) ratio shows a significant increase from <20% to more than 90% when increasing pO2 from vacuum to 10^-1 mbar, while the SrO+ / (Sr+ + SrO+) and MnO+ / (Mn+ + MnO+) ratios are smaller than 15% even at the highest used pO2. The decrease in the SrO+ / (Sr+ + SrO+) ratio when increasing pO2 from 1 x 10^-1 mbar to 1.5 x 10^-1 mbar, could be caused by a more pronounced dissociation of SrO+ due to the intensive background collisions, since Sr possesses a larger atomic radii than Mn. Comparing the LaO+ / (La+ + LaO+) ratio at 10^-1 mbar indicates very similar numbers for λ=248 nm and 308 nm lasers.

Figure 5.5. (a) Number of La+, La^{16}O+ and La^{18}O+ vs. pO2 for using 308 nm as well as 248 nm lasers at 1.8 J/cm²; (b)-(d) MO+ / (M+ + MO+) ratios for (b) La, (c) Sr and (d) Mn vs. pO2 using 308 nm as well as 248 nm lasers at 1.8 J/cm².
Table 5.2 Average kinetic energy ($E_{K,\text{Avr.}}$) and their corresponding time of arrival (TOA) of the main ionic plasma species when ablating LSMO in vacuum using 308 nm, 248 nm and 193 nm lasers at 1.8 J/cm². The target/substrate (detector) distance is 4 cm.

Knowing the major variations in the ionic plasma composition for plasmas created using lasers with $\lambda=308$, 248 and 193 nm, the next question comes to how does the ablation wavelength influences the $E_K$ of the plasma species. In Table 5.2 the average kinetic energy of the main existing ionic species as well as their estimated arrival time to the substrate position are summarized. The $E_K$ of O$^+$ has been observed to be larger than O$^-$ in vacuum for using 248 nm lasers, which is also the case when using $\lambda=308$ nm or 193 nm. The influence of the laser ablation wavelength on $E_K$ of plasma species in vacuum has been observed to be rather complex [110, 111]. For example, both photon energy and intensities are expected to influence $E_K$ of species [110], and a larger $E_K$ is likely when using a smaller photon energy [111]. The $E_{K,\text{Avr.}}$ for O$^+$ species is observed to be much smaller for 308 nm plasma compared to 248 nm or 193 nm. In contrast, the $E_{K,\text{Avr.}}$ is observed to decrease with the increasing photon energy, which agrees with the observations reported in ref. 111. However, a confirmative explanation for this observation has not been provided so far. The much less effective positive ionization of atomic oxygen when using a 308 nm laser could be an important reason. In that case the photon energy could be converted more to the kinetic energy for metallic species by maintaining a constant ablation fluence.

From the results presented in Table 5.2, it also implies that the high $E_K$ of the metallic ions may not be the main reason for the low film crystallinity when using a 248 nm or 193 nm laser as compared to the 308 nm. The fast O$^+$ species could be a
problem which disturbs the crystallization process of the LSMO films due to their much earlier arrival time compared to the metallic species. When using 248 nm or 193 nm lasers, a considerable amount of O\(^+\) reaches the substrate around two to four times earlier than the metallic ions (see Table 5.2). For the ablation with \(\lambda=308\) nm in vacuum, the fast positive oxygen ions account for only 3% of all ionic oxygen species, and most of the negative oxygen ions arrive at the substrate between the arrival of Mn\(^+\) and La\(^+\). This seems to favour the crystallization of the film inducing a larger oxygen content.

To summarize, the plasma / film properties for the deposition of LSMO when using a 308 nm laser ablation has been investigated and compared to the results of an ablation with \(\lambda=248\) nm. In addition, a successful film growth of La\(_{0.6}\)Sr\(_{0.4}\)MnO\(_3\) in vacuum using a 308 nm laser has been demonstrated which cannot be achieved by using \(\lambda=248\) nm or 193 nm. The mass spectrometry analysis indicates that the plasma generated by a 308 nm laser consists of a much lower amount of O\(^+\) ions which reaches the substrate earlier than other species compared to O\(^+\) generated by a 248 nm and a 193 nm laser. Therefore, the smaller variation in arrival time between negative oxygen and metallic ions could be a reason for the successful vacuum deposition of the LSMO film when using \(\lambda=308\) nm.
An alternative approach to PLD with a constant background pressure is pulsed reactive crossed-beam laser ablation (PRCLA), a well-established and effective method to enhance the plasma chemical reactions during the deposition of thin films [2, 118-128]. When using PRCLA, instead of setting a constant background pressure in the vacuum chamber, as for standard PLD, a secondary gas pulse is injected through a piezo valve near the laser ablation area of the target [2, 118, 119]. By triggering the laser pulse with an appropriate delay time with respect to the gas pulse, it is possible to set at the origin of the ablated plasma core a local high partial pressure. As a result, significantly enhanced physicochemical interactions between the ablated plasma and the gaseous environment can be achieved. The secondary gas pulse can be used in vacuum or in combination with a constant background pressure with a variety of gases for the background environment and for the gas pulse.

Due to the pulsed nature of the secondary gas jet and the short distance between the target and the gas pulse valve, a relatively small amount of gas is sufficient to locally increase significantly the background pressure in the region immediately above the ablation area. Therefore PRCLA is using very efficiently a relatively high (local) partial pressure of strongly reactive gases, such as NH₃, which would be not possible in a standard PLD set up.

Several successful applications of PRCLA have been reported in the literature over the last two decades. For example, pulsed reactive gases, such as O₂, N₂O, NH₃, N₂ and CH₄, were used to directly react with the laser-induced plasma to fabricate thin films of CuO, AlN, GaN, Ti:Al₂O₃, TiC₃N₉, and SiC [2, 120-122]. Furthermore, the
PRCLA technique was also used to complement the standard PLD method in order to enhance the oxygen content [123-126] or achieve elemental doping, such as nitrogen doping of oxides thin films [127, 128]. Nevertheless, there is still very limited information available on the chemical and physical interactions between the reactive gas pulse and the ablated plasma plume [119].

This chapter reports on the chemical and physical interactions in the plasma during the pulsed oxygen crossed-beam laser ablation of the oxygen isotope labeled \( \text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3 \) target using kinetic energy resolved mass spectrometry and time resolved plasma imaging. High purity oxygen with the natural isotopic ratio was used for the gas pulse, as well as to set the constant background pressure under standard PLD conditions. The relative content of the different ionic species detected in the plasma during the PRCLA has been compared with the results obtained with standard PLD in vacuum as well as in different oxygen static background pressures. In addition, by time-resolved plasma imaging, it was possible to investigate the plasma propagation during PRCLA. By depositing \( \text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3 \) films using \(^{18}\text{O}\) labeled target and \(^{16}\text{O}_2\) gas pulse makes it possible to distinguish the origin of oxygen for using PRCLA (\(\text{O}_2\)).

The most distinguished feature of PRCLA is the relatively large pressure gradient of the background gas into the vacuum chamber in contrast to the uniform and static background pressure in which the standard PLD process takes place [118]. With our experimental set up, the average velocity of the oxygen molecules of the gas pulse ejected near the target surface is about 160 m/s [119]. With a target to substrate distance of 4 cm, the gas pulse will reach the substrate position after about 250 \(\mu s\) giving rise to a large (negative) pressure gradient along the direction of the propagation of the plasma [2, 119]. As a consequence, the ablated plasma will go through a very high local partial pressure near the target, while regions with gradually lower background pressure will be crossed by approaching the substrate surface.

The plasma species have a much higher propagation velocity (about \(5 \times 10^3\) m/s, estimated by Langmuir probe measurements) and will arrive at the substrate (or at the mass spectrometer placed in the same position) within a few \(\mu s\). Such a time of arrival
is about two orders of magnitude smaller than the time required for the gas pulse to expand and set the dynamic pressure gradient described above.

For this reason, to achieve the most effective interaction between the plasma and the gas pulse the laser should hit the target material with the appropriate delay time, allowing the gas pulse to expand and set a suitable pressure background along the direction of the plasma propagation. Moreover, the duration of the gas pulse should be long enough to maintain a high local density of molecules near the target region with a continuous gas supply during the ablation process.

These general considerations are indeed well supported by the plasma imaging results shown in Figure 6.1 where the spatial distributions of excited O$^+$ (OII, emission line: 495.57 nm) are compared for various delay times (200 μs - 700 μs) between the oxygen gas pulse injection and the laser ablation pulse. Each frame in Figure 6.1 was recorded with an exposure time of 200 μs for each single laser pulse ablation and 100 accumulations of exposures using the laser pulse as triggering signal. It can be seen that the largest re-excitation of the plasma species, due to interaction with the gas pulse molecules, appears when using delay times between 400 μs and 500 μs.

**Figure 6.1:** Plasma imaging of OII (emission line: 495.57 nm, using a 200 μs gate for the image acquisition with no delay time) when using various delay times between the pulsed O$_2$ injection and the laser ablation.

The investigation of the plasma composition obtained with the optimized delay time is reported in Figure 6.2 that shows the amount of detected ionic species in the plasma measured by kinetic energy resolved mass spectrometry. The total amount for
each species was calculated by integration over the kinetic energy distribution. In particular, Figure 6.2a and 6.2b show the detected positive and negative ionic species, respectively, during PRCLA of the $^{18}\text{O}$ labeled LSMO target using oxygen as gas pulse and no static background pressure. As can be seen, the metallic species are largely oxidized by the oxygen gas pulse into positively charged diatomic metal-oxygen ions.

![Figure 6.2: (a), (b) Overview of the amounts of the ionic plasma species with positive (a) and negative (b) electrical charges in laser induced La$_{0.6}$Sr$_{0.4}$Mn$_{16.18}$O$_3$ plasmas when using the O$_2$ gas pulse. (b) inset: separation of ionic oxygen species originating from the target as well as from the pulsed O$_2$.](image)

The isotope substitution allows to discriminate between the ionic oxygen species originating from the target and from the gaseous environment. As shown in the inset of Fig. 6.2b, the ionic oxygen species in the plasma originate mostly from the gas pulse and the dissociation of the oxygen molecules into ionic oxygen is much more effective than their ionization into O$_2^-$.

The distinguishing effect on the plasma composition of the PRCLA with respect to the standard PLD process is summarized in Figure 6.3a and 6.3b. Here the total amount of the different metal-oxygen ions in the plasma is compared between PLD in vacuum, in three different static oxygen background pressures, and for PRCLA. As can be seen, the largest amount of metal-oxygen ions in the plasma was detected in the case of PRCLA suggesting an enhanced interaction between the plasma and the
oxygen background gas. In addition, the initial plasma species still largely remain in their excited states [2], which enhances the reaction cross-section and promotes their chemical reactions with the \( \text{O}_2 \) molecules [2, 119]. As a result, mainly positive metal-oxygen ions were found (Figure 6.2a and 6.2b) due to the much higher chemical stability than their negatively charged counterpart.

**Figure 6.3:** Comparison of the total amount of the metal-oxygen species during PRCLA using oxygen as gas pulse and during standard PLD with constant oxygen background pressures or in vacuum: (a) \( \text{La}^+, \text{La}^{16}\text{O}^+, \text{La}^{18}\text{O}^+ \); (b) \( \text{Mn}^+, \text{Sr}^+, \text{Mn}^{16}\text{O}^+, \text{Sr}^{16}\text{O}^+ \).

Comparing the content of \( \text{La}^{18}\text{O}^+ \) shown in Figure 6.3a for different ablation conditions, it can be seen that in the case of PRCLA this value is surprisingly larger than in the case of standard PLD in vacuum, while only at a high static oxygen background pressure the \( \text{La}^{18}\text{O}^+ \) content in the plasma is significantly reduced. Whereas the latter is expected, the very large content in the PRCLA plasma of metal-\( ^{18}\text{O} \) ions may seem counter intuitive, yet can be explained by taking into account the significantly enhanced physicochemical interaction between the plasma and the pulsed gas jet at the very early stage of the plasma propagation. The locally high oxygen pressure significantly reduces the kinetic energy of the ablated species, providing the possibility for the metallic ions to effectively react with the oxygen species even originated from the target material. Thus, the balance of rival reactions of dissociation and generation of the positive metal-oxygen ions are shifted towards
their generation. Moreover, moving away from the region near the target surface, the oxygen partial pressure dramatically drops thereby reducing the probability of further collisions. As a consequence, the dissociation probability of multi-atomic species is largely reduced.

All these observations confirm that the most important advantage of PRLCA over standard PLD is the greatly enhanced number of chemical reactions in the plasma in the region near the ablation area. Here, the very high local density of oxygen molecules at the origin of the plasma core strongly favors the physical interactions and the chemical reactions (oxidation) between the initial plasma species and the gaseous environment [2].

An additional important aspect which must be taken into account while using PRCLA is the potential influence on the spatial distribution of the plasma species due to the very different environment through which the ablated plasma propagates and the expansion takes place. Time resolved plasma imaging provides the possibility to observe the plasma / background interactions indirectly by looking at the spatial distribution of the excited plasma species [27, 129-131]. It is undeniable that during the PLD process complex species excitation / de-excitation mechanisms [1-3, 45]. For example, processes [45] such as photon excitation, the initial heating effects or collisional electron / background molecule excitations during the plasma propagation and chemical reactions are taking place. A quantitative comparison via the absolute emission intensities requires an integral consideration of all possible excitation processes and potential emission line broadening mechanisms (Stark broadening, Doppler effects, instrumental effects) [132-136]. For plasma imaging, one is mostly interested in the plasma plume shape by looking at the spatial distribution of the relative emission intensities rather than comparing the absolute emission intensity [27, 129-131].

Figure 6.4 shows the time-resolved plasma imaging results for excited Mn I (450.22 nm) and La I (563.12 nm) when using PRCLA (Figure 6.4a) compared to a constant $pO_2$ of 3 x $10^{-2}$ mbar (Figure 6.4b) and 1.5 x $10^{-1}$ mbar (Figure 6.4c). By comparing all possible existing emission lines for all relevant elements and molecules,
it is found that the two selected characteristic emission lines for La and Mn are well distinguishable within the detection resolution of the AOTF. The different images were recorded with increasing delay time from 0.6 to 3.6 μs with a constant exposure time of 200 ns and 100 accumulations for each exposure. Similar to the typical way to show the imaging results in previous reports, the as-shown white color in each picture represents 50% of the largest pixel intensity detected by the CCD chip, while the shown black color represents the detected lowest pixel intensity.

**Figure 6.4.** Time-resolved plasma imaging results for excited MnI (450.22 nm) and LaI (563.12 nm) when using (a) PRCLA compared to constant $pO_2$ of (b) $3 \times 10^{-2}$ mbar and (c) $1.5 \times 10^{1}$ mbar

At the early plasma propagation stage ($t < 1.2$ µs) when using PRCLA as
compared to the two constant $pO_2$, the spatial distributions for both wavelength show a longer shape along the propagation direction, which could be associated to the large pressure drop for using PRCLA. In contrast, at a later plasma propagation time ($t > 2.4 \mu s$), the density of background molecule are much smaller for PRCLA than for a constant $pO_2$ due to the dramatically reduced local pressure (around high $10^{-4}$ mbar) for PRCLA. A further comparison of the spatial distributions between LaI and MnI indicates their similar shape when using $1.5 \times 10^{-1}$ mbar at a later propagation time ($t > 2.4 \mu s$), while using PRCLA as well as $3 \times 10^{-2}$ mbar $pO_2$ a narrower spatial distribution (perpendicular to the plasma propagation) is observed for LaI than MnI.

Considering a center to center elastic collision situation between plasma species and a static O$_2$ molecule, the species velocity after the collision is written as

$$v_1 = \frac{m_{\text{species}} - m_{O_2}}{m_{\text{species}} + m_{O_2}} v_0,$$

($v_0$ and $v_1$ represent the velocity of the plasma species before and after the collision, respectively). Larger momentum losses are expected for lighter species after elastic interactions with O$_2$ (the momentum loss in percentage is estimated to be 37%, 53% and 74% for La, Sr and Mn, respectively). During a practical PLD process, where multiple collisions occur, similar effects were also reported from both experimental and simulation aspects [138]. Compared to La, the more spherical spatial distribution of Mn observed at $3 \times 10^{-2}$ mbar O$_2$ (Figure 6.4b) as well as for PRCLA (Figure 6.4a) supports the argument that the light element (Mn) is scattered more. In comparison, when using $1.5 \times 10^{-1}$ mbar O$_2$ (Figure 6.4c), the plasma propagation transform to the shock-wave expansion, where the plasma species compresses and pushes the background molecules forward to form a relatively condensed shockwave front region [27, 129-131]. This region confines the spatial distribution of species with various atomic weights. As a result, a similar spatial distribution of La and Mn has been observed.

From the plasma imaging result it can be seen that when using PRCLA, the plasma / O$_2$ interaction differs from the situations when using a constant $pO_2$ at all interesting ranges for PLD. As already pointed out, during PRCLA the plasma propagation occurs through a dramatically dropping pressure gradient from the locally
high pressure region near the ablation area to the relatively low pressure region near the substrate surface. In this case, the formation of a shockwave front is impossible and a loss of light metallic species is expected via elastic interactions with O₂ molecules.

To study the preservation of the composition between the target and the deposited film using PRCLA, the LSMO thin films were grown at room temperature on Si substrates and at 650°C on (001) SrTiO₃ substrates under the same experimental condition used for the mass spectrometry analysis reported in Figure 6.2a and 6.2b. The composition as well as oxygen isotope ratio of these films were detected by RBS and ERDA, and the results are summarized in Table 6.1. In both cases, a deviation from the nominal composition of the target was observed.

<table>
<thead>
<tr>
<th>Element</th>
<th>Target</th>
<th>Film on Si at RT</th>
<th>Film on STO at 650 °C</th>
</tr>
</thead>
<tbody>
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<td>0.60±0.03</td>
<td>0.60±0.03</td>
</tr>
<tr>
<td>Sr</td>
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<td>0.35±0.02</td>
<td>0.37±0.02</td>
</tr>
<tr>
<td>Mn</td>
<td>1.10±0.06</td>
<td>0.80±0.04</td>
<td>0.82±0.04</td>
</tr>
<tr>
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<td>1.50±0.08</td>
<td>2.48±0.12</td>
<td>2.61±0.13</td>
</tr>
<tr>
<td>¹⁸O</td>
<td>1.63±0.08</td>
<td>0.29±0.01</td>
<td>0.26±0.01</td>
</tr>
</tbody>
</table>

Table 6.1: Chemical compositions of films grown by PRCLA on Si at room temperature and on STO at 650°C, with respect to the composition of the target.

Both films have relatively high oxygen contents, close to the stoichiometric value. Based on the ¹⁶O to ¹⁸O isotope ratio, it is possible to estimate that the oxygen from the gas pulse contributes for about the 78 and 81% of the total oxygen content of the film on Si and STO, respectively. Table I also shows that a loss of the light metallic elements (Sr and Mn) takes place. Similar losses of light elements in the film composition were also observed for thin films of La₀.₆Ca₀.₄CoO₃ and La₀.₆₆Ca₀.₃₄MnO₃ grown by PRCLA using O₂ or N₂O for the gas pulse in either vacuum or in the presence of background pressure [124-126]. Correlating above results to the observations in Chapter 3, it can be seen that the film composition of LSMO deposited using O₂ gas pulse is close to the one deposited using a constant pO₂.
of $3 \times 10^{-2}$ mbar. When using the PRCLA, it is possible to achieve a similar plasma/film composition by using a much smaller amount of reactive gases as compared for the deposition using a constant background pressure of $10^{-2} - 10^{-1}$ mbar. This is more important when the reactive gas is aggressive or corrosive.

To summarize, plasma analysis by mass spectrometry and plasma imaging were used to identify the main differences in the physicochemical interactions occurring during the plasma propagation when using PRCLA and standard PLD. These measurements confirm that during PRCLA the chemical reactivity of the plasma is significantly enhanced due to the presence of a local high density of reactive gas near the target surface. As a result, the molecules of a reactive gas (oxygen in this study) are effectively dissociated and positively charged metal-oxygen ions are generated in large number, which are not achievable by plasma interactions with a constant background pressure. Moreover, the rapidly decreasing pressure along the direction of the plasma propagation preserves the existence of the as-generated metal-oxygen species, as revealed by the significantly enhanced content in the plasma of oxygen species originated from the target and identified in this study by $^{18}$O isotope substitution. When no static background pressure is used the plasma evolution during PRCLA can be divided into two different regimes, near the target and near the substrate. In the first region, time-resolved plasma imaging showed a plasma evolution similar to that observed during standard PLD in a high static background pressure. In the second region the plasma evolves like in the case of standard PLD in vacuum but with the presence of metal-oxygen ions whose generation cannot be achieved in vacuum. When using PRCLA without a static background pressure, the strong negative pressure gradient from the target to the substrate prevents the formation of a condensed shockwave front that confines the plasma during its expansion. This effect is most probably the origin of the loss in the lighter elements which are more scattered. Concerning the preservation of the correct composition between target and film, it must be emphasized that this is not necessarily a drawback of PRCLA, since depending on deposition parameters this is very often an issue also for standard PLD at $10^{-2}$ mbar as described in Chapter 3.
7. \( \text{N}_2\text{O}: \) an alternative background gas for PLD

Although \( \text{O}_2 \) is the most used background gas for thin film deposition, alternative background gases are also used in order to achieve specific film properties. For example, a \( \text{N}_2\text{O} \) background has been extensively used for the thin film deposition for a large variety of oxide materials using PLD [32, 139-144], sputtering [145-147], or plasma-enhanced chemical vapor deposition (PE-CVD) [148-154] in order to create a more oxidizing atmosphere. Compared to \( \text{O}_2 \) (\( E_{\text{Dissoc.}}: 5.12 \text{ eV} \)), \( \text{N}_2\text{O} \) is easier dissociated (\( \text{N}_2\text{O} + 1.6 \text{ eV} \rightarrow \text{N}_2 + \text{O} \)) through interactions with plasma species in either PLD or sputtering. It is therefore expected that \( \text{N}_2\text{O} \) provides a more reactive environment compared to \( \text{O}_2 \) [155-157]. Although \( \text{N}_2\text{O} \) is a better oxidant than \( \text{O}_2 \), it is more toxic, environmentally damaging and expensive than \( \text{O}_2 \). For which situation it is advisable or desirable to use a \( \text{N}_2\text{O} \) background instead of \( \text{O}_2 \) and what pressures to use is at present unclear.

To gain a better understanding about the use of \( \text{N}_2\text{O} \) as a background gas, the ionic composition of the laser induced \( \text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3 \) plasma has been investigated at various \( p\text{N}_2\text{O} \) using kinetic energy resolved mass spectrometry. The time resolved plasma imaging was used to observe the spatial distribution of the excited species as a function of their propagation time. As already presented in Chapter 3, since the \( \text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3 \) target was labeled with \( \sim 52\% \text{^{18}O} \) isotope it is possible to separate the origin of the oxygen for plasma and film. Similar to Chapter 3, the \( \text{MO}^+/(\text{M}^+ + \text{MO}^+) \) ratio was investigated for a large variety of metallic elements at \( 1 \times 10^{-2} \text{ mbar} \) and \( 1.5 \times 10^{-1} \text{ mbar} \) \( \text{N}_2\text{O} \) with fixed laser ablation condition. The obtained results are compared with data acquired with an \( \text{O}_2 \) background presented in Chapter 3.

One of the most important reason to use \( \text{O}_2 \) or \( \text{N}_2\text{O} \) as background is to enhance
the oxidization of the metallic plasma species, therefore to enhance the oxygen composition of the film material. From the results presented in previous chapters, positive metal-oxygen ions have been observed to be the main ionic product from the background oxidization of metallic species, in particular, at the most commonly used pressure range for PLD \( \sim 10^{-1} \) mbar. In Figure 7.1, the \( \text{MO}^+ / (\text{MO}^+ + \text{M}^+) \) ratios are summarized for ablating a large variety of targets at \( 1 \times 10^{-2} \) mbar (Figure 7.1a) and \( 1.5 \times 10^{-1} \) mbar (Figure 7.1b) \( \text{N}_2\text{O} \) using fixed ablation condition. These results are comparable to those as shown in Figure 3.4c and 3.4d where \( \text{O}_2 \) is used. Comparing Figure 7.1a to 7.1b indicates a significant enhancement of the \( \text{MO}^+ / (\text{MO}^+ + \text{M}^+) \) ratio for all metallic elements at \( p\text{N}_2\text{O} \) of \( 1.5 \times 10^{-1} \) mbar as compared for \( 1 \times 10^{-2} \) mbar.

Figure 7.1 Ratio of \( \text{MO}^+/(\text{M}^+ + \text{MO}^+) \) vs. dissociation energy of \( \text{MO}^+ \) species as determined at \( p\text{N}_2\text{O} \) of (a) \( 1 \times 10^{-2} \) mbar and (b) \( 1.5 \times 10^{-1} \) mbar, over a large variety of laser induced plasma species elements. As shown \( \text{MO}^+/(\text{M}^+ + \text{MO}^+) \) for a metallic element is the average value from different oxide targets, while the error bar represents their standard derivation.

Similar to the observation in Chapter 3, a larger \( \text{MO}^+ / (\text{MO}^+ + \text{M}^+) \) ratio is observed for metallic element with a bond energy larger than oxygen and larger atomic radius. For example, Ti and Mn have similar atomic radii, but TiO\(^+\) has a much larger dissociation energy than MnO\(^+\). As a result, a larger TiO\(^+\) / (TiO\(^+\) + Ti\(^+)\) ratio is observed as compared to MnO\(^+\) / (MnO\(^+\) + Mn\(^+)\). The dissociation energy of TiO\(^+\) is similar to LuO\(^+\) or TbO\(^+\), but the atomic radius of Ti is around 40% smaller than Lu or
Therefore, the TiO$^+$ / (TiO$^+$ + Ti$^+$) ratio is observed to be smaller than that for Lu and Tb. Also, Ba and Sr are larger than Ca, which explains why the oxidization probability of Ca is smaller than Ba and Sr. By further correlating the difference between N$_2$O (Figure 7.1a) as compared for O$_2$ (Figure 3.4c and d), the most significant difference is the significantly enhanced MO$^+$ / (MO$^+$ + M$^+$) ratio for metallic elements such as Ca, Sr and Ba when using N$_2$O instead of O$_2$ for both pressure ranges. The dissociation energies of CaO$^+$, SrO$^+$ and BaO$^+$ are between 3 - 5 eV which was covered by the bond energies of N$_2$O (1.6 eV between N$_2$ and O; 4.99 eV between NO and N) [155-157]. As compared to the results when using O$_2$ as presented in Chapter 3, the ‘cut off’ dissociation energy of MO$^+$ that can cause an effective oxidization of metallic species using a high background partial pressure is reduced from $\sim$5 eV for O$_2$ corresponding approximately to the dissociation energy of O$_2$ to $\sim$3.5 eV when using N$_2$O. However, due to the complexity in interactions with N$_2$O, it is not clear yet why the cut off energy is $\sim$3.5 eV. For MO$^+$ with a dissociation energy > 5 eV, the MO$^+$ / (M$^+$ + MO$^+$) ratio is observed to be somewhat smaller when using N$_2$O as compared to O$_2$ at the same nominal pressure.

To extend these studies for a larger range of background pressures, the LSM$^{16/18}$O target has been uses for plasma analysis as well as film deposition. In Figure 7.2, the ionic plasma compositions are compared for the ablation of LSMO in vacuum as well as various $\rho$N$_2$O. Like in an O$_2$ background when introducing N$_2$O as a background gas the oxygen isotope ratio is starting to shift towards the $^{16}$O containing side due to the chemical reactions between plasma species and the background gas. As a result, predominantly positive diatomic metal-oxygen ions were formed. Diatomic positive metal-nitrogen ions (MN$^+$) are also detected. Nevertheless, their amounts are generally much smaller compared to the positive metal-oxygen ions. The amount of MnN$^+$ is comparable to MnO$^+$ at 1 x $10^{-2}$ mbar or at a higher pressure, while those for SrN$^+$ and LaN$^+$ are more than one order of magnitude smaller than their positive metal-oxygen ions. This result could be associated with the dissociation energy of these metal-oxygen or metal-nitrogen species. However, due to the limited information about metal-nitrogen bond energy, the dissociation energies of LaN$^+$,
SrN⁺ and MnN⁺ are not available. Among the negatively charged species the largest abundance of O⁻ is observed for all used pressures. In addition, the negative metal-oxygen ions, such as MnO⁻ and MnO₂⁻, are also observed below 10⁻² mbar, while at the highest pressure measured these species are not observed anymore. In contrast, negative metal-nitrogen ions are not observed for all pressures used. It is also interesting to note that a dramatic drop in all detected species appears when increasing \( p \text{N}_2\text{O} \) from 1 x 10⁻² mbar to 1.5 x 10⁻¹ mbar due to the strongest background scattering.

In order to further compare the plasma composition in \( \text{N}_2\text{O} \) to \( \text{O}_2 \), in Figure 7.3a, the \( \text{MO}^+ / (\text{MO}^+ + \text{M}^+) \) ratios are compared at various \( p\text{O}_2 \) and \( p\text{N}_2\text{O} \) as well as the situation using PRCLA for ablating LSMO at a fixed fluence. A generally increased \( \text{MO}^+ / (\text{MO}^+ + \text{M}^+) \) ratio is observed for all metallic elements with increasing \( p\text{N}_2\text{O} \)

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**Figure 7.2** Mass spectra of positive and negative ionic plasma species from a \( \text{La}_{0.6}\text{Sr}_{0.4}\text{Mn}_{16,18}\text{O}_3 \) target measured at vacuum and three different \( \text{N}_2\text{O} \) pressures.
and $pO_2$. Nevertheless, large variations have been observed for different metallic elements. For example, the oxidation probability is much larger for La compared to Sr and Mn at the same pressure. A further comparison indicates that La is slightly more oxidized when using $O_2$ compared to $N_2O$ while the oxidation probability for Sr in $N_2O$ far exceeds the one in $O_2$. In the case of PRCLA, the $MO^+/(MO^+ + M^+)$ ratios are between the number obtained for $10^{-2}$ mbar and $10^{-1}$ mbar. Also the oxidization of Sr when using $N_2O$ far exceeds $O_2$ when using PRCLA.

![Figure 7.3. (a) $MO^+/(M^+ + MO^+)$ ratio of laser induced $La_{0.6}Sr_{0.4}MnO_3$ plasma species in various $N_2O$ and $O_2$ backgrounds conditions. (b) $^{18}O$ concentration as well as the background contributions to LSMO films grown at various $pN_2O$ and $pO_2$.](image)

Apart from oxidizing metallic species into metal-oxygen species, the background gas is expected to provide oxygen to the film composition through other ways during the film deposition. For example, the background molecule can be dissociated and generate atomic oxygen species and contribute to the film oxygen composition. In addition, when using a high deposition temperature it is possible for the film to directly acquire oxygen by annealing in the background during the whole deposition period. In order to understand the origin of the oxygen composition in these films, several LSMO films were grown using the $^{18}O$ labeled target in $^{16}O_2$ and $N_2^{16}O$ background on Si at room temperature as well as on (001) STO at 650 °C. Figure 7.3b shows the $^{18}O$ concentration of as-grown LSMO films as detected by ERDA, and
also the corresponding background contribution to the oxygen composition of these films. In general, a larger background contribution has been observed for N$_2$O than for O$_2$. Interestingly, comparing the depositions at 1 x 10$^{-2}$ mbar indicates a similar background contribution to the film deposited using O$_2$ at 650 °C, O$_2$ at room temperature, and N$_2$O at room temperature, whereas a film deposited using N$_2$O at 650 °C shows a much larger background contribution to the oxygen content in the film. The substrate diffusion has proven to be not effective for the deposition of LSMO on STO, i.e. the STO substrate contributes only a few percent to the film oxygen composition for a vacuum deposition and has nearly no contributions for depositions at 10$^{-2}$ mbar or higher. Therefore, this observation could be explained by a more effective oxygen acquisition from annealing in N$_2$O than O$_2$ during the film deposition, since N$_2$O is more reactive.

Apart from the influence on the plasma composition, interactions with N$_2$O or O$_2$ may also alter the spatial distribution of the plasma plume differently. In Figure 7.4a, the time resolved spatial distributions of excited OII (495.6 nm), SrI (496.2 nm) and SrO (400.0 nm) are shown in vacuum and also for using O$_2$ and N$_2$O at 10$^{-2}$ mbar as well as 10$^{-1}$ mbar.

**Figure 7.4** Time resolved plasma imaging of OII (495.6 nm), SrI (496.23 nm) and SrO (439.96nm) in vacuum and N$_2$O as well as O$_2$.

In vacuum, the plasma species expand freely and the emission intensities of as-shown plasma species decreases with propagation time due to their emission life
time. At $1 \times 10^{-2}$ mbar O$_2$ and N$_2$O, a pronounced re-excitation of plasma species has been observed due to the smaller collision mean free path compared to the plasma propagation distance [129-131]. Comparing the shape of the plasma plume indicates a cone shaped and more elongated spatial distribution of the species along the propagation direction in N$_2$O as compared to a spherical-shaped plume in O$_2$. In addition, a much larger emission intensity at the wavelength of SrO is observed when using N$_2$O compared to O$_2$, while that for Sr is more reduced. The largest emission intensities for SrO appears at the front of the plasma plume, which indicates that the oxidization of the metallic species into metal-oxygen species takes place via background interactions. By further increasing the pressure to $1.5 \times 10^{-1}$ mbar, smaller variations in the plasma shape are observed for O$_2$ and N$_2$O. The strongest emission intensities for all the three species have been observed for this pressure, which implies a strong re-excitation processes via multiple collisions.

Figure 7.5 shows the kinetic energy distributions for O$^-$ and O$^+$ from both target and background at constant $p$N$_2$O and $p$O$_2$. The separation procedure between background and target species has been described in Chapter 2. At $1 \times 10^{-2}$ mbar N$_2$O as compared to O$_2$, O$^-$ associated with the target is observed to possess a larger amount as well as $E_K$. For comparison, O$^-$ from the background and O$^+$ from both target and background show a similar $E_K$ distribution in N$_2$O and O$_2$. These results support the plasma imaging observations at the same pressure. The larger amount of O$^-$ could be attributed to the larger density of atomic species as well as the electrons at the tip of the cone-shaped plasma, which enhances the density of atomic oxygen as well as the electrons. Therefore, the electron attaching process is further improved ($O^+ + e^- \rightarrow O + 13.6$ eV; O $+ e^- \rightarrow O^- + 1.4$ eV). Enhancing the background pressure to $3 \times 10^{-2}$ mbar and further up to $1.5 \times 10^{-1}$ mbar reduces $E_K$ of atomic oxygen species and also their target contribution. At all these pressures, the relative amount of O$^-$ as compared to O$^+$ is observed to be larger is N$_2$O than in O$_2$ at the same nominal pressure.
Figure 7.5. Kinetic energy distribution of O- and O+ species originating from target and background interactions at various $p_{O_2}$ or $p_{N_2O}$.

To confirm these observations, Figure 7.6 shows the amount of O- and O+ when extending the investigation to a large variety of oxide material using N$_2$O and O$_2$ around the most commonly used PLD pressure range (1.5 x 10$^{-1}$ mbar). For all used target materials a larger amount of O- is observed in N$_2$O compared to O$_2$, while a larger amount of O+ is observed in O$_2$ compared to N$_2$O.
Figure 7.6 Comparison of the O\textsuperscript{-} and O\textsuperscript{+} species amount when ablating various targets in 1.5 x 10\textsuperscript{-1} mbar N\textsubscript{2}O and O\textsubscript{2}, with an ablation fluence of 1.8 J/cm\textsuperscript{2} for perovskites and 2.5 J/cm\textsuperscript{2} for other oxides.

Apart from the variations observed in the plasma composition and spatial distribution, $E_K$ of the plasma species can be also different for using N\textsubscript{2}O to O\textsubscript{2}. In Figure 7.7, the kinetic energy of Mn\textsuperscript{+}, Sr\textsuperscript{+}, La\textsuperscript{+} MnO\textsuperscript{+}, SrO\textsuperscript{+}, and LaO\textsuperscript{+} are compared at 1.5 x 10\textsuperscript{-1} mbar O\textsubscript{2} and N\textsubscript{2}O. It can be seen that the kinetic energy of these species are larger in N\textsubscript{2}O compared to O\textsubscript{2}.
In Table 7.1, $E_{k,Avr.}$ of the main ionic species are compared for LSMO plasma in $1.5 \times 10^{-1}$ mbar N$_2$O and O$_2$. A larger $E_k$ of the plasma species has been observed for using N$_2$O compared to O$_2$, which seems to contradict the conventional understanding for elastic collisions. Since N$_2$O molecules possess a larger molecular weight as well as a larger collision cross section compared to O$_2$ [158, 159], this should result in a larger momentum loss of the plasma species after elastic interactions. These observations imply a possible influence coming from inelastic interaction processes associated with background dissociation. Since the easier dissociation of N$_2$O as
compared to O₂ may decrease the probability for the occurrence of an elastic collision, a process in which the plasma species lose more momentum. This effect could result in a smaller $E_K$ loss of the plasma species after collision. A simplified modeling for the elastic and inelastic collision processes between species of La, Sr, Mn and O with O₂ or N₂O background molecule is still in progress.

<table>
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<th>Sr⁺</th>
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<td></td>
</tr>
</tbody>
</table>

Table 7.1 The average kinetic energies of main existing metallic and metal-oxygen ions at 1.5 x $10^{-1}$ mbar N₂O and O₂ from the laser ablation of LSMO at 1.8 J/cm².

![Figure 7.8](image)

Figure 7.8 Composition of La₃Sr₂Mn₄O₁₂ thin films deposited on (001) SrTiO₃ substrate as a function of the N₂O and O₂ background pressure. The error to determine the composition with RBS combined with ERDA is at most 5%.
Finally, how plasma properties influence the film composition is investigated. Figure 7.8 shows the composition of La$_6$Sr$_6$Mn$_6$O$_{16}$ films grown on (001) STO at 650 °C at different N$_2$O as well as O$_2$ background pressures. Like the films grown in O$_2$, a loss of the lighter metallic elements Sr and Mn was observed for the $10^{-2}$ mbar $p$N$_2$O range. Comparing the oxygen content of these films indicates a surprising drop when increasing $p$N$_2$O from $2 \times 10^{-3}$ mbar to $10^{-2}$ mbar. By further increasing $p$N$_2$O to $10^{-1}$ mbar, the oxygen content monotonically increases. This observation of the oxygen content vs. $p$N$_2$O is different from the one reported vs. $p$O$_2$ in Chapter 3 where the largest oxygen content is achieved at $10^{-2}$ mbar $p$O$_2$. The smaller oxygen content for $10^{-2}$ mbar $p$N$_2$O could be associated with the variation in the spatial plasma distributions as observed by plasma imaging. However, at the most interesting pressure range for PLD at $\sim 10^{-1}$ mbar, a larger oxygen content is achieved when depositing LSMO using a N$_2$O background instead of O$_2$. Although there are some positive metal-nitrogen plasma ions detected by mass spectrometry (see Figure 7.2), the ERDA results indicate a very low nitrogen film content (below 0.5 at% compared to O, see Table 7.2).

<table>
<thead>
<tr>
<th>Pressure (mbar)</th>
<th>N content</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2 \times 10^{-3}$ (650 °C)</td>
<td>$\sim 0.003 \pm 0.002$</td>
</tr>
<tr>
<td>$1 \times 10^{-2}$ (650 °C)</td>
<td>&lt;0.002</td>
</tr>
<tr>
<td>$1 \times 10^{-2}$ (RT)</td>
<td>$\sim 0.014 \pm 0.007$</td>
</tr>
<tr>
<td>$3 \times 10^{-2}$ (650 °C)</td>
<td>$\sim 0.005 \pm 0.003$</td>
</tr>
<tr>
<td>$2 \times 10^{-1}$ (650 °C)</td>
<td>&lt;0.003</td>
</tr>
</tbody>
</table>

*Table 7.2.* Nitrogen composition of the La$_6$Sr$_6$Mn$_6$O$_{16}$ films grown at various $p$N$_2$O

To summarize, with the combination of kinetic energy resolved mass spectrometry, time and emission wavelength resolved plasma imaging, this chapter addresses the issue why in some cases using N$_2$O for pulsed laser deposition is better than O$_2$. It is possible to achieve a more effective oxidization of Ca, Sr and Ba by using N$_2$O instead of O$_2$. A larger oxygen content of the film material is achieved in N$_2$O as
compared to O$_2$ at 10$^{-1}$ mbar pressure range. At the same time, the 10$^{-1}$ mbar N$_2$O also maintains a congruent cation transfer.
8. Mass spectrometry vs. Langmuir probe, a comparison

In Chapter 3-7, mass spectrometry was mainly used to investigate the properties of ionic plasma species. However, mass spectrometry has not yet been very commonly used for the plasma analysis of PLD processes due to its complex construction and high cost. Therefore, it will be helpful to compare mass spectrometry results with data obtained by other plasma analytical techniques to gain a better understanding on a broader experimental basis. Among all the used plasma analytical approaches to investigate the PLD plasma, Langmuir probe and mass spectrometry detect charged species, while exited state species are detected in emission spectroscopy and plasma imaging.

Langmuir probe is a relatively simple and direct plasma diagnostic technique [33, 34, 160-163]. It uses a small metal probe with a tunable bias voltage to detect the signal coming for charged plasma species. Depending on the polarity of the bias, an electron or positive ion current is collected as the plasma flows past the probe leading to a time-of-arrival (TOA) distribution. When the probe is biased negatively to reject electrons, the TOA distribution can be used to find the ion velocity and kinetic energy distributions associated with the plasma flow. The bias on a Langmuir probe can also be varied to measure the IV-characteristic and hence determine the electron temperature [33, 34, 160-163]. Langmuir probe analysis is most suitable when one ionic species is dominant in the plasma plume, like the ablation of elemental metal targets [160]. However, for many PLD applications targets with a complex chemical composition are used, and there may be several different ionic species in the plasma, all of which contribute to the ion current signal in a Langmuir probe measurement. On
the contrary, mass spectroscopy has the capability to distinguish different ion masses and charges, though, of course, the instrumentation is substantially more complicated. Since Langmuir probe analysis and mass spectrometry have different advantages and limitations, it of interest to explore what can be learned of using a combination of the two techniques, and to determine the extent to which the two measurements can be reconciled.

In this chapter, Langmuir probe analysis and mass spectrometry were used to investigate the plasma produced by laser ablation of La$_{0.4}$Ca$_{0.6}$MnO$_3$ (LCMO) using an excimer laser at $\lambda=308$ nm and various values of laser fluence. The Langmuir probe was used to measure the TOA distribution of positive ion species and the electron temperature. The quadrupole mass spectrometer, combined with an electrostatic kinetic energy analyzer, was used to measure the $E_K$ distributions of the different ionic species distinguished according to mass-to-charge ratio. The measured distributions were used to calculate a TOA for each ion species, and these were combined to yield an overall TOA distribution, which was compared with that measured by the Langmuir probe.

The Langmuir probe and mass spectrometry plasma analysis experiments were carried out in the ultra-high vacuum chamber at $\sim10^{-8}$ mbar. The PLD plasma was generated using a XeCl excimer laser beam ($\lambda = 308$ nm, $\tau = 25$ - 30 ns, freq. = 5 Hz) imaged onto a rotating ceramic disc target of La$_{0.4}$Ca$_{0.6}$MnO$_3$ (LCMO) placed at the centre of the chamber. The angle of incidence was 45º and fluences of 0.8, 1.3 and 1.9 J cm$^{-2}$ were used. The target could be rotated to face either the Langmuir probe or the mass spectrometer, as shown in Fig 8.1. A rod-shaped Langmuir probe of 3 mm diameter and 36 mm length was placed in front of the target at a distance which could be varied from 6 to 14 cm. The probe pointed towards the laser ablation spot and was parallel to the normal of the target surface during the ablation experiment. The current drawn by the probe was found by measuring the voltage across a load resistor, which had values of 10 $\Omega$ or 50 $\Omega$, depending on the signal to be measured. The probe signals were averaged over 40 laser shots. Using the same ablation conditions, the mass spectrometry investigations were also carried out to measure the $E_K$ distribution.
of existing ionic species ($dN/dE_k$).

Figure 8.1. Illustration of the alternation between mass spectrometry and Langmuir probe experiment inside the UHV chamber.

Figure 8.2 shows the TOA distributions recorded for probe bias voltages of -10 V (Fig. 8.2a) and 10V (Fig. 8.2b) with the Langmuir probe at 6 cm for various values of laser fluence. As expected, with a negative bias the electron flow to the probe is suppressed and positive ions extracted from the plasma gives rise to a positive current to the probe, though any negative ions reaching the probe surface would decrease the net current recorded. With positive bias, electrons can reach the probe surface, giving rise to a negative current, the value depending on both the magnitude of the bias voltage and the TOA. As has been observed before, the magnitude of the detected negative current signals exceeds by far the positive signals due to the much lower electron mass [160-163]. With decreasing laser fluence both the positive and negative current signals decreased while their arrival times are delayed, indicating a decrease in both amount and expansion velocity of the laser ablation plume. It can be noted that for laser fluences higher than 1.6 J cm$^{-2}$, both the negative and positive TOA distributions show a single sharp peak, while for fluence values below 1.3 J cm$^{-2}$ a double peak is observed in the negative TOA distributions, though the cause of this double peak is not clear at this stage.
Figure 8.2. Time of arrival curves of the ionic plasma species at various laser ablation fluences detected by Langmuir probe with a distance of 6 cm between the target and the probe. (a) Positive species under -10 V probe bias voltage; (b) Negative species detected under 10 V probe bias voltage.

Laser fluence values of 0.8 J cm$^{-2}$ and 1.9 J cm$^{-2}$ were selected for more extensive Langmuir probe investigation. Fig. 8.3 shows the TOA distributions for several values of bias voltage for these two fluence values. For 0.8 J cm$^{-2}$ the double peak is observed for positive bias above 3V; the relative amplitude of second maximum grows with increasing bias, becoming larger than the first peak for bias greater than 10V. In contrast, at 1.9 J cm$^{-2}$ the negative TOA distribution is single-peaked. Increasing the bias voltage up to 30 V leads to a pronounced growth of the current amplitude at the late times up to 20 µs after the laser pulse.
Figure 8.3. Time of arrival curves of the ionic plasma species with 6 cm distance between the target and the probe under various probe bias voltages from 30V to -30 V. (a) 0.8 J/cm² laser ablation fluence; (b) 1.9 J/cm² laser ablation fluence.

The expansion velocity of the plasma plume was determined by changing the target-probe distance, from 6 to 14 cm in 2 cm steps, and recording the positive ion signals for 10 V bias at each position. These signals are shown in Fig. 8.4. As the probe-target distance is increased the current peaks move to later time, are reduced in amplitude and are broadened. For each fluence value the plasma velocities were found by making a linear fit to a plot of the distance vs. peak TOA. The values obtained were 1 x 10⁴ m/s for 0.8 J cm⁻², and 1.5 x 10⁴ m/s for 1.9 J cm⁻².
Figure 8.4. Time of arrival curves of the positive plasma species under -10 V probe bias voltage with various distances between the target and the probe. (a) 0.8 J/cm² laser ablation fluence; (b) 1.9 J/cm² laser ablation fluence.

Figure 8.5 shows the kinetic energy distributions, as measured with the mass spectrometer system, of the positive atomic ions Ca⁺, Mn⁺ and La⁺, the molecular ion LaO⁺ and the negative ion O⁰, which are the main ionic species detected in the plume. The energy distributions are shown for fluence values of 0.8, 1.3 and 1.9 J cm⁻². By integrating these distributions over energy, the relative abundance of each species was determined; the results are shown in Fig. 8.6. This figure also shows the values for several other low-abundance negative ions.

Figure 8.5. Kinetic energy distributions of the Ca⁺, Mn⁺, La⁺, LaO⁺, O⁺ and LaO⁺ ionic species at 0.8 J/cm², 1.3 J/cm² and 1.9 J/cm² laser ablation fluences detected by mass spectrometry.
Figure 8.6. The amounts of the ionic plasma species at 0.8 J/cm², 1.3 J/cm² and 1.9 J/cm² laser ablation fluences detected by mass spectrometry. The amount of each species is obtained by the integration of its $E_k$ distributions, as some further shown in figure 8.5.

While the energy spectra are quite complex, some particular features and fluence dependences can be discerned. The energy distributions of Ca⁺ and Mn⁺ are relatively broad, and extend out to higher energies as the laser fluence is increased. In contrast, the heavier La⁺ ion shows a strong peak around 10 eV, which does not change with fluence. There is a weak tail on the La⁺ distribution, which extends to higher energy as the fluence is increased, reaching ~100 eV at 1.9 J cm⁻². LaO⁺ is the main oxygen species detected, which may be attributed to its relatively high dissociation energy, estimated to be ~8.9 eV (see Chapter 3). Its distribution also shows a strong peak around 10 eV which decreases as the fluence is increased from 1.3 to 1.9 J cm⁻², perhaps indicating the increasing influence of dissociation as more laser energy is coupled to the ablation plume. Both O⁺ and O⁻ are clearly observed in the mass spectra, and the strength of both signals grows with laser fluence. At 1.9 J cm⁻² the O⁺ ion shows a 10 eV wide kinetic energy distribution centered at 30 eV, but this is not seen at lower fluence. O⁻ shows a relatively broad distribution in the 0 - 10 eV region.
which grows in strength with fluence.

It is of interest to see the extent to which the ion TOA recorded by the Langmuir probe can be reconciled with the ion energy distributions measured by the mass spectrometer. This was done by using the energy distribution \( (dN/dE_k) \) for each positive ion to calculate the TOA signal \( (dN/dt) \) due to that ion at the position \( d = 6 \) cm of the Langmuir probe, thus:

\[
\frac{dN}{dt} = \frac{(2E_k)^{3/2}}{m_j^{1/2}d} \times \frac{dN}{dE_k}.
\]

Figure 8.7 (a – e) shows the TOA signals at 6 cm, derived from the measured energy distributions, for the ions \( O^+, \ Ca^+, \ Mn^+ \) and \( La^+ \) and \( LaO^+ \), respectively. Note that the abscissa scale is different in each plot. The strongest signals are due to \( Ca^+ \) and \( Mn^+ \). Here it is worth noting the close correspondence between the features seen at late time \((14 – 20 \mu s)\) in the TOA distributions of \( La^+ \) and \( LaO^+ \). The data clearly suggest that the molecular species \( LaO^+ \) is found in the rear of the ablation plume towards the target, and the late feature the \( La^+ \) distribution is derived from dissociation of \( LaO^+ \) as it transits from the place of production to the aperture of the spectrometer.

**Figure 8.7. (a) - (e)** Time of arrival distribution of \( O^+, \ Ca^+, \ Mn^+, \ La^+ \) and \( LaO^+ \) ions converted from their kinetic energy distributions by mass spectrometry that shown in figure 8.5.
The overall derived positive ion TOA signal was obtained by adding together the individual derived ion TOA signals in Fig. 8.7(a – e). The result is shown is Fig. 8.8(a) for the three fluence values of interest. For comparison, Figure 8.8(b) shows the overall positive ion signal recorded by the Langmuir probe at 6 cm for the same fluence values. It is clear that there is quite good agreement between the net positive ion TOA distributions obtained by these two techniques, giving confidence that they are providing reliable diagnosis of the plasma plume formed by laser ablation of LCMO.

Figure 8.8. (a) Time of arrival distributions of the positive ions obtained by summing up those of the main ionic species converted from their $E_k$ distributions for three used fluences; (b) Time of arrival distributions of the positive current signal detected by Langmuir probe using bias voltage of -10 V; (c) Time of arrival distributions of O$^-$ converted from its $E_k$ distributions for three used fluences; (d) Time of arrival distributions of the negative current signal detected by Langmuir probe using bias voltage of 10 V

The TOA distributions of O$^-$ at the probe position were obtained in the same manner from the energy distributions, and it is plotted in Fig. 8.8(c). For all three fluences, the arrival times of O$^-$ species at the probe position are significantly later.
than the arrival on the positive ions, indicating that those negative ions are found behind the plasma front where the positive ions are mainly found. Figure 8.8(d) shows the Langmuir probe TOA signal for 10 V positive bias. By noting the relative magnitudes of the signals in Fig. 8.8 (a) and (b) and then (c) and (d) it can be concluded the negative ions make a negligible contribution to the signal when the Langmuir probe is under positive bias, rather the signal is dominated by the much lighter electrons.

The electron temperature and density in the ablation plume were measured at a range of time delays by plotting the logarithm of the electron current vs probe bias. The electron temperature, $T_e$, is given by the slope of the graph in the electron-retarding region. Figure 8.9(a) shows the IV-characteristic at 8 μs, where the value of $T_e$ is 0.9 eV. The IV-characteristic can also be used to find the electron density by noting the current values at the knee in the curve, which corresponds to the plasma potential, is given by: $I_{e,sat} = \frac{1}{4} ev_e A n_e$, where $v_e$ is the thermal velocity given by $\left(\frac{8kT_e}{\pi m_e}\right)^{\frac{3}{2}}$. 
Figure 8.9. (a) IV-characterization of the negative current signal detected by Langmuir probe at 8 μs for laser ablation of LCMO ablation at 0.8 J/cm²; (b) Temporal dependence of electron temperature and the probe position (ablation fluence: 0.8 J/cm²); (c) Temporal dependence of electron temperature and the probe position (ablation fluence: 0.8 J/cm²); (d) Temporal dependence of estimated O\(^{-}\) density (ablation fluence: 0.8 J/cm²);

The value obtained from the IV-characteristic in Fig. 8.9(a) is 3.4 x 10\(^{14}\) m\(^{-3}\). Figure 8.9(b) shows the temporal dependence of the electron temperature and the probe position, and Fig. 8.9(c) the temporal dependence of the electron density. Assuming the positive ion density (D\(\text{PI}\)) roughly equals to the sum of the electron density (D\(\text{e}\)) and negative ion density (D\(\text{NI}\)). From Fig 8.8(a) and (c), the amount of ion is already known from mass spectrometry at each arrival time (written as A\(\text{PI}\) and A\(\text{NI}\) for positive and negative ion, respectively). Therefore, the negative ion density (D\(\text{NI}\)) can be estimated by: D\(\text{NI}\) = A\(\text{NI}\) / ( A\(\text{NI}\) + A\(\text{PI}\) ) * D\(\text{e}\). In Fig 8.9d, the temporal dependence of the density of the main negative ion species of O\(^{-}\) is shown. The largest
O\textsuperscript{-} density is observed around 12 \( \mu \)s, which is later than the largest electron density observed around 6\( \mu \)s or earlier. Even at the peak value at 12 \( \mu \)s, the O\textsuperscript{-} density was observed to be more than one order of magnitude smaller than the electron density.

To summarize, the 308 nm laser induced LCMO plasma was analyzed using both Langmuir probe and energy-resolved mass spectroscopy at various ablation fluences. From the Langmuir probe results, the time of arrival current signal was detected from the overall plasma ions. From the mass spectrometry results, the \( E_k \) distributions of the main ionic plasma species of O\textsuperscript{+}, Ca\textsuperscript{+}, Mn\textsuperscript{+}, La\textsuperscript{+}, LaO\textsuperscript{+} and O\textsuperscript{-} were detected which were further converted into their corresponding TOA distributions. Adding these TOA distribution of the main ions converted from each \( E_k \) distribution, the overall TOA distribution of ionic species was obtained from mass spectrometry detection, which agrees well with the one directly detected by Langmuir probe. Combining the results obtained from both plasma analysis approaches, the temporal dependence of the negative ion density was estimated.
9. Conclusion and Outlook

9.1. Conclusion

In this dissertation, the correlation between the used PLD condition and \textit{as-deposited} film composition / structures has been established by investigating the laser induced plasma properties using a combination of several plasma analytical techniques. A better understanding of the physical / chemical plasma processes as well as some guidance for deposition strategies has been developed.

The background pressure has been identified to be one of the most important parameters that varies the plasma propagation from the quasi-free expansion (below $10^{-3}$ mbar) to the shockwave expansion (the low $10^{-1}$ mbar). For both depositions of La$_{0.6}$Sr$_{0.4}$MnO$_3$ and Ca$_3$Co$_4$O$_9$, a congruent transfer of the target composition has been achieved in a pressure window around $10^{-3}$ mbar and again for a narrow window in the $10^{-1}$ mbar range, while in the intermediate $10^{-2}$ mbar pressure range a cation deficiency for lighter metallic composition is observed. These results support the current understanding of plasma properties that light species are more easily lost as a result of elastic scattering inside the plasma, which well explains the results when using a background pressure at $10^{-2}$ mbar. The most interesting results observed in this dissertation is that by increasing the number of collisions when enhancing the background pressure from $10^{-2}$ mbar to the low $10^{-1}$ mbar range, the light metallic composition recovers. This effect is attributed to the formation of a relative condensed shockwave front from highly compressed and mixed plasma species and background molecules that effectively stops the plasma species and confines their spatial distribution to the same region at the shockwave front. This understanding is well supported by time and emission wavelength resolved- plasma imaging results of excited state species which indicate the same spatial distribution of excited Mn and La.
when using $1.5 \times 10^{-1}$ mbar O$_2$ while a narrower distribution for La is observed than for Mn at $3 \times 10^{-2}$ mbar O$_2$.

Positive metal-oxygen ions have been observed as the main product from the oxidization of metallic species by background gas molecules. A systematic investigation about the relative amount of positive metal-oxygen ions compared to its metallic ion has been carried out for a large variety of metallic elements and background pressures. It has been shown that the metallic oxidization probability is largely influenced by the chemical stability of the metal-oxygen ions as compared to the background gas molecule. For metal-oxygen species with a bond energy larger than the dissociation energy of the background molecule, their oxidization probability is significantly enhanced by increasing the background pressure. For example, the oxidization probability of metallic elements such as La, Y, Zr, Lu or Tb exceeds 90% when using $1.5 \times 10^{-1}$ mbar O$_2$. In contrast, for metal-oxygen species with a bond energy smaller than the dissociation energy of the background gas molecule, such as Mn, Ca, Co or Cu, their oxidization probabilities do not exceed 20% even at the largest investigated pressure. These results indicate that at high background pressures, whether the metallic species arrives at the substrate as atomic or metal-oxygen species is not only determined by the background pressure but also by the metallic element.

Compared to the background pressure the influences from the laser photon energy or ablation fluence to the plasma properties are observed to be smaller. With an increase in laser fluence a decrease in the relative amount of positive metal-oxygen ions compared to the metallic ions has been observed. This indicates a more effective dissociation of these metal-oxygen species. Similar effects have been also observed when increasing the laser photon energy at a fixed fluence of 1.8 J/cm$^2$. As compared for the case when using an O$_2$ background pressure in the $10^{-2} - 10^{-1}$ mbar range, a larger variation in plasma composition and kinetic energies vs. ablation conditions has been observed for a vacuum or low pressure ($10^{-3}$ mbar range) deposition, e.g., a smaller relative amount of O$^+$ as compared to O$^-$ has been observed at lower photon energies or smaller ablation fluences.
Two special background cases were also investigated: 1) using pulsed reactive crossed-beam laser ablation instead of a constant background pressure, and 2) using N$_2$O instead of O$_2$.

PRCLA improves the chemical reactions between plasma species and the pulsed gas molecule and achieves the largest amount of metal-oxygen species arriving at the substrate, which cannot be obtained using a constant pressure. The plasma propagates across a dramatically dropping pressure gradient, which improves the plasma / gas pulse interaction at the early stage but is not able to form a shockwave front to confine the species with various atomic weights during the plasma propagation. Therefore, a loss in the light metallic composition is expected when using PRCLA in vacuum.

Using N$_2$O instead of O$_2$ as background gas largely enhances the oxidization probability of some metallic species, such as Ca, Sr and Ba, since the chemical stability of their metal-oxygen ions are between those for N$_2$O and O$_2$. In addition, a larger relative amount of O$^-$ compared to O$^+$ is obtained by using N$_2$O instead of O$_2$, which is expected to benefit the deposition process. Similar to the situation when using O$_2$ a congruent metallic transfer is achieved for two pressure regions at low 10$^{-3}$ mbar and low 10$^{-1}$ mbar. The LSMO films grown at 10$^{-2}$ mbar N$_2$O show a loss in the lighter metallic elements as well as low oxygen composition.

By using $^{18}$O isotope labelling of the target or substrate, the origin of oxygen in the plasma as well as in the deposited films has been traced and quantified as shown for the deposition of LSMO films in a constant O$_2$ or N$_2$O background as well as for PRCLA. The substrate (SrTiO$_3$) contribution to the oxygen composition of the films is only a few percent for films deposited in vacuum or 10$^{-3}$ mbar O$_2$. When using a $p$O$_2$ of 10$^{-2}$ mbar or higher, nearly no oxygen from the STO substrate was observed in the LSMO film. The target contribution to the oxygen content of the film decreases from more than 95% for a vacuum deposition down to only a few percent when using 10$^{-1}$ mbar for the deposition.
9.2. Outlook

A systematic study has been performed in the current dissertation and an improved understanding about plasma / background interactions and the corresponding influence to film composition and crystalline structures during pulsed laser deposition has been achieved. The following three open questions could be addressed when continuing this work:

1) **Quantification of the ionization probability by emission spectroscopy:**

   The plasma also consists of a large amount of neutral species with an amount probably being larger than their ionic counterparts. Therefore, how to quantify the amount of the neutral species becomes an interesting question. The following investigation is expected to show a way to determine the relative amount of neutral plasma species compared to its corresponding positive ion using a combined plasma analysis approach of emission spectroscopy, plasma imaging and mass spectroscopy.

   A possible strategy could be by detecting the plasma composition using emission spectroscopy looking at the characteristic emission intensity coming from both neutral species and the corresponding positive ion. The relative amount between the neutral and positive ion can be deduced from the integration of the emission intensities by taking into account broadening mechanisms such as Doppler or Stark effects as well as instrumental effects. Also, the lift-time of the emission line should be taken into consideration. It is suggested to choose a group of emission lines for both positive ion and neutral species into investigation and plot their emission intensity after calibration (in log scale) vs. the emission photon energy. The slope of this curve correlated to the electron temperature while the interception should correlate to the relative amount between positive ions and neutral species.

   Estimating the relative number of species at the ground state (invisible by emission spectroscopy) compared to the excited could be more complex. This relative amount could be correlated with electron temperature and density, which can be detected by emission spectroscopy or Langmuir probe measurements. Neutral species
can also be measured directly using the mass spectrometer via internal ionization of
the neutral species, and a calibration or correlation is expected to be derived by
comparing results between emission and mass spectroscopy. As a starting point, single
 elemental target such as Ag, Al, Cu, Pt or Au can be used.

2) How to adjust the ionization probability:

After the first step, the following procedure is to work out the correlation between
the ionization probability and PLD parameters, and also think about how to actively
adjust the relative amount between ionic and neutral species. The laser ablation
conditions (i.e. photon energy, ablation fluence, etc) as well as background conditions
(i.e. background pressures, background types, etc) are expected to influence the
ionization probability. Also, the ionization probability is expected to be influenced by
the target composition due to the diversity in the first ionization energy for different
elements. The investigation is expected to cover a large range of elemental types and
compositions by using different ablation and background conditions.

3) How to control the plasma / film properties by using external field

The final aim is to gain a maximum control over the plasma properties by using an
external electric or magnetic field to e.g. control the ionization probability of plasma
species or to selectively remove certain plasma species. A possible implementation to
control the ionic species arriving at the substrate is by inserting an electrostatic filter
into the solid angle segment of the expanding plasma, like an iris where an electric
field with positive or negative potential can be applied. The electric field influence
the plasma ions or electrons, which should also varies the growth properties of the
films. Using the emission spectroscopy, plasma imaging and mass spectroscopy, it is
possible to monitor the changes for ionic / neutral species. Compared to the ionic
species, the electrons are expected to react more strongly in the external field, due to
their much smaller mass. Langmuir probe measurements could be an effective
approach for monitoring the variation in electron temperature, group velocity and
density vs. the external field. All these outlined steps should further improve the understanding of the PLD plasma properties.
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Publications and Conferences

Publications:

Oral presentations

1. **J. Chen**, X. Gui and T. Lippert. Preliminary study on laser induced plasma from ultra low-density sponge-like carbon nanotube block. 2013 Conference of Laser Ablation (COLA), Ischia, Italy;


Posters presentations

1. **J. Chen** and T. Lippert. Influence of an O2 background gas on the kinetic energy distributions of species in laser induced plasmas. 2012 EMRS spring conference, Strasburg, France (*best poster award*)

2. **J. Chen** and T. Lippert. Semi-quantitative analysis of laser induced La$_x$Ca$_{1-x}$MnO$_3$ plasma in Ar by mass spectrometry. 2013 Conference of Laser Ablation (COLA), Ischia, Italy;
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