Synthesis and Characterisation of Non-Evaporable Getter Films Based on Ti, Zr and V

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Non-evaporable getters (NEG) are widely used in ultra high vacuum (UHV) systems for particle accelerators to assure distributed pumping speed. By heating the NEG to an activation temperature, the oxide layer on the surface dissolves into the material, leaving a clean (activated) surface. The activated NEG surface is capable of chemisorbing most of the residual gases present in a UHV system and will act as a vacuum pump. NEG can be sputter deposited on the inner wall of vacuum chambers, turning the whole wall from a source of gas into a pump. At the largest particle accelerator in the world, the Large Hadron Collider, more than 6 km of beam pipe has been NEG coated.

In this work, a DC magnetron sputtering system dedicated for coating cylindrical vacuum chambers with NEG has been assembled, installed and commissioned. The system has been used to do NEG depositions on inner walls of vacuum chambers. The vacuum performance of the coating has been measured in terms of pumping speed, electron stimulated desorption and activation temperature. In addition, the thin film composition and morphology has been investigated by scanning electron microscopy (SEM).

The work has resulted in an operational DC magnetron sputtering system, which can be used for further studies of NEG materials and compositions.
Abstract

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A Standardised symbols for vacuum technology
Acronyms

CERN  Conseil Européen pour la Recherche Nucléaire (European Organisation for Nuclear Research)
NEG  Non-Evaporable Getter
LHC  Large Hadron Collider
LEP  Large Electron-Positron collider
UHV  Ultra-High-Vacuum
ESD  Electron Stimulated Desorption
EDS  Energy-dispersive X-ray Spectroscopy
SEM  Scanning Electron Microscopy
XPS  X-ray Photoelectron Spectroscopy
CVD  Chemical Vapour Deposition
PVD  Physical Vapour Deposition
DC  Direct Current
RGA  Residual Gas Analyser
DNXX  Nominal Diameter of XX mm
TMP  Turbo Molecular Pump
RVP  Rotary Vane Pump
CFG  Compact Full range ion Gauge
CPG  Compact Process ion Gauge
BAG  Bayard-Alpert Gauge
VLV  Variable Leak Valve
Chapter 1

Introduction

The research in the framework of this Master’s Thesis has been performed at the European Organisation for Nuclear Research (CERN) facilities outside Geneva, Switzerland. The Project has mainly been divided in two parts: the synthesis, and the characterisation of non-evaporable getters (NEG). In the synthesis part, the work has been focusing on the construction of a DC magnetron sputtering system. The system was then used to produce NEG coatings, on which the characterisation measurements were done.

This chapter will give a short introduction to the background of the work, the goals and purpose followed by the research strategy and outline of this thesis.

1.1 Background

1.1.1 CERN

CERN was founded 1954 and is one the largest and most respected scientific laboratories in the world. It is a collaboration between 20 member states with the main focus on particle physics. The instruments used for research are particle accelerators and detectors. Throughout the years, overlapping experimental projects have contributed to a huge complex of accelerators. The speed of a beam of particles is boosted in one accelerator before it is injected to the next one. Eventually, the beam is brought to collision with either fixed targets or head-on to other particles in different experiments, all recorded by detectors. An overview of the huge accelerator complex is shown in Fig. 1.1 [1].

In order to keep the beam life time long enough to perform controlled experiments, the density of the gas molecules must be as low as possible [2]. Therefore, the pressure inside the accelerators is at ultra high vacuum (UHV), in the range of $10^{-10} \text{ mbar}$, which means about 10 billion times lower than atmospheric pressure [3]. The main obstacle for achieving such a low pressure is thermal and beam induced hydrogen outgassing from the inner walls of the vacuum chamber. The
pumping speed in long narrow chambers, like particle accelerators, is strongly conductance limited, which makes it problematic to achieve an evenly distributed UHV with discrete pumping [4]. A tested and proven solution for this problem is ex situ deposition of a non-evaporable getter (NEG) thin film on the inner wall of the beam pipe. When the NEG is heated to an activation temperature, its native oxide layer dissolves into the bulk material, causing a clean surface where most of the residual gas molecules can stick by chemisorption. The NEG transforms the walls from a source of gas into a pump, which, besides maintaining a lower pressure, also provides a uniform pressure profile [5].

1.1.2 Large Hadron Collider

The Large Hadron Collider (LHC) experiment at CERN is currently the largest particle accelerator in the world, with a circumference of 27 km. It is located around 100 m under ground on the border of Switzerland and France outside Geneva (see Fig. 1.2). Inside, beams of protons are circulating in opposite directions through two storage rings with a velocity nearly the speed of light (at maximum 99.9999991% of light-speed). The accelerator is not a perfect circle, it consists of eight straight sections and eight bending arcs. At certain points, the
1.2 Motivation

Getters are materials or alloys of materials capable of chemisorbing most of the gases in an UHV environment. In such a presence, the getter acts as a pump, where the gas molecules react chemically with the getter to form stable compounds. A getter exposed to air will get saturated and lose the ability to chemisorb molecules, since that requires a clean surface [7]. A clean surface can be accomplished in two ways depending on the getter, either by \textit{in situ} sublimation of a new surface (evaporable getters), or by heating (non-evaporable getters, NEG). Evaporable getters are mostly used for lumped pumping (pumping at discrete positions of the vacuum system), and therefore cannot solve the problem of strongly varying pressure profiles in conductance-limited systems like accelerators [8]. Therefore they are not treated in this thesis.

The heating process of the NEG is called the activation process, which makes
the oxygen atoms bound to the surface dissolve into the bulk material, causing a clean activated surface. The getter can be deposited as a thin film on the inner walls of vacuum chambers by sputtering. NEG film coatings are widely used in UHV systems for particle accelerators to assure distributed pumping speed and prevent thermal and beam induced outgassing of the inner walls [5]. An extended explanation of NEG will be given in Chapter 2.

An on going challenge in the research of NEG is the reduction of the activation temperature. A lower activation temperature allows a larger selection of substrate materials, since it reduces the risk of negative thermal effects during the activation process. Previous investigations have shown that films based on Ti, Zr and V have a very low activation temperature (180° C for 24 h of heating). The optimal composition found so far is 30 at.% Ti, 30 at.% Zr and 40 at.% V. TiZrV is currently used in the LHC project [5, 7].

In the framework for further studies in the NEG research, it was desirable to manufacture a small-scale coating system, to produce NEG coatings on the inner wall of cylindrical vacuum chambers. At CERN, two identical coating systems for that particular geometry exists, but in a larger scale used for the long straight section (LSS) chambers of the LHC, where each chamber is in the range of 2 – 5 m long [6]. A smaller system dedicated only for NEG coatings in the length of approximately 50 cm would be more convenient for approaching research.

1.3 Goals and Objectives

This project has the purpose of developing a small-scale coating system, with the primary intention to reproduce a TiZrV coating with the same vacuum performance as former studies. The system will, as in the past, be a DC magnetron sputtering system. The project will comprehend building of the sputtering system, produce coatings and perform measurements of the coatings. When the system is operational, it can be used for studying alloys of other elements as well as varying the composition of the existing ones.

The goal for the coating system was to achieve a small-scale production of thin films coatings on the inner walls of cylindrical vacuum chambers.

The goal for the characterisation part of this work has been to produce NEG coatings with the system, followed by measurements of its vacuum performance. In order to assure accurate behaviour of the coating system, known coatings were produced and characterised. One goal was to reproduce the same or similar properties as done in the past.
1.4 Research strategy

To start with, a rigorous literature study was performed to get acquaintance with vacuum technology and the theory of getters. At the same time as the literature study was carried out, the assembling of the system was started. Once the system was operational, the first coating was made.

The coated sample was then demounted from the system for measurements to verify the pumping ability of the sample. This was done by measuring the sticking probability and electron stimulated desorption (see Chapter 2 and Chapter 4). At the same time, parts of the sample were sent to surface and activation analysis by SEM, EDS and XPS (See Chapter 4). After the vacuum performance of the getter was measured, the system was once again assembled for a new coating to repeat the same procedure.

1.5 Outline

After this introduction chapter, a theoretical chapter (Chapter 2) will follow, with the intention of giving a brief explanation of vacuum theory, pumps and gauges that concern the deposition system. In addition, the chapter will also comprehend an introduction to getters and finally the sputtering technique that will be used. The next chapter (Chapter 3) will explain how the system was assembled and how it is used for coating. Chapter 3 will end the first part of the project in the sense that the rest of the thesis will only concern the produced coatings.

In Chapter 4, all different measurement procedures that were used to investigate the vacuum performance of the coatings will be described. Since the techniques for measuring electron stimulated desorption (ESD) and pumping speed were performed on a system developed at CERN, these procedures will take up a larger part of this chapter. The results from the measurements accompanied by the discussion are presented in Chapter 5 and the conclusions that can be drawn from the work are presented in Chapter 6.
Chapter 2

Theory

This theory chapter has the intention of giving a short introduction to the different aspects of this work. To start with, a section called Vacuum (see Sec. 2.1) will go through some brief introductory vacuum theory, gas flow kinetics and defining some of the fundamental measurable quantities that will be of importance for the evaluation of getters. In following section, the components of the vacuum system belonging to the sputtering system will be introduced (see Sec. 2.2). The chapter will continue with a section devoted to getters (see Sec. 2.3) and end with an introduction to thin film deposition with focus on sputtering (see Sec. 2.4).

2.1 Vacuum

Vacuum is a term with many definitions. A common way of defining vacuum is to say that it is an expression of nothing, a space entirely devoid of matter [9]. A theoretically perfect vacuum, where absolutely no particles exist, cannot be achieved and can be contemplated as an abstract ideal, which is not a very useful definition in practical means. Therefore, in vacuum technology, it is more common to relate vacuum to gas pressure (see Sec. 2.1.1), where gas pressures below the atmospheric pressure is defined as vacuum. This allows a broader interpretation of vacuum: instead of vacuum defined as one absolute "state", it has a wide spectrum of regimes. These regimes are divided into groups of individual pressure ranges (see Table 2.1). Applications or experiments using vacuum technology often demands

<table>
<thead>
<tr>
<th>Rough vacuum</th>
<th>Atmospheric pressure to 1 mbar</th>
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<tr>
<td>Medium vacuum</td>
<td>1 to $10^{-3}$ mbar</td>
</tr>
<tr>
<td>High vacuum (HV)</td>
<td>$10^{-3}$ to $10^{-8}$ mbar</td>
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<tr>
<td>Ultra high vacuum (UHV)</td>
<td>$10^{-8}$ to $10^{-12}$ mbar</td>
</tr>
<tr>
<td>Extreme high vacuum (XHV)</td>
<td>Less than $10^{-12}$ mbar</td>
</tr>
</tbody>
</table>
a certain regime of vacuum. For instance, a rough vacuum can be used when the force created by the atmospheric pressure has to be negligible in an experiment. In particle accelerators such as the LHC, the gas densities must be much lower (at UHV) to avoid interactions between the charged particle beam and the residual atoms in the chamber.

The SI unit for pressure is Pascal ($\text{Pa}$) and is measured in $N/m^2$, while the atmospheric pressure can be expressed as $1\ \text{atm}$. In this thesis, mbar will be used to denote the pressure unit, which is the common unit used in vacuum practice for Europe [10]. These three units have the following relation:

\[ 1\ \text{mbar} = 100\ \text{Pa} = 9.87 \times 10^{-4}\ \text{atm} \]

### 2.1.1 Kinetic theory of an ideal gas

The kinetic theory of gases is essentially based on two fundamental assumptions. The first is that all matter consist of very small particles, which are monoatomic or polyatomic at a gaseous state. When the temperature is increased, the particles dissociate into pure atoms or even ions and electrons to form a plasma (see Sec. 2.1.2). The second assumption is that gas molecules are in constant motion, which can be related to macroscopic quantities such as temperature and pressure. Pressure is defined as the force ($F$) distributed on an area ($A$). The force from a gas with $n$ particles with the same mass $m$ in a cubical container can be calculated as

\[ F = \frac{nm\bar{v}^2}{3L} \]  

where $L$ is the distance between opposite walls in the container and $\bar{v}^2$ is known as the mean square velocity of a particle. This yields a total pressure ($P$) inside the container of

\[ P = \frac{F}{L^2} = \frac{nm\bar{v}^2}{3V} \]  

where $V$ is the total volume of the cubic chamber. To relate the pressure with the temperature inside, the mean square velocity can be used to calculate the total mean translational kinetic energy of the particles. The translational energy expressed in thermal energy is defined as:

\[ \frac{1}{2}mv^2 = \frac{3}{2}k_BT \]  

where $T$ is the temperature in Kelvin and $k_B$ is the universal Boltzmann constant ($k_B = 1.38 \times 10^{-23}\ J/K$). Combining Eq. 2.2 and Eq. 2.3 leads to the equation that unifies pressure and temperature and is called the ideal gas law (see Eq. 2.4), which is applicable for an ideal gas but a good assumption for real gasses as well.

\[ PV = n k_B T \]  

The ideal gas law is a central part in the understanding of gas kinetics and is often written using the universal gas constant, $R_0 = k_B N_A$, where $N_A$ is Avogadro’s
2.1 Vacuum

number \( (N_A = 6.022 \times 10^{23} \text{molecules/mol}) \) [10, 11].

\[ PV = nR_0T/N_A \quad (2.5) \]

2.1.2 Definitions

This section’s aim is to define and explain some of the major concepts and quantities that will be used or discussed later in the thesis.

Mean free path

A mean free path denotes as the mean distance that a molecule will travel before it collides with another molecule in a gas of \( n \) particles inside a volume \( V \).

\[ \lambda_{mfp} = \frac{V}{\sqrt{2\pi d^2 n}} \quad (2.6) \]

where \( d \) is the molecular diameter of the gas [11]

Knudsen ratio and flow regimes

The Knudsen ratio, \( Kn \), is the ratio between the mean free path, \( \lambda_{mfp} \), and the diameter of a vacuum chamber, \( D \).

\[ Kn = \frac{\lambda_{mfp}}{D} \quad (2.7) \]

The Knudsen ratio is an important parameter because it determines in which flow regime a gas is. A gas behaves differently depending on which type of molecular interaction is dominant. The gas flow is divided in three different regimes (See Table 2.2). A large Knudsen ratio \((Kn > 1)\), indicates that the average distance travelled by a molecule between successive collisions with another molecule is greater than the distance between the walls of a vacuum chamber. This regime is called the free molecular flow regime and indicates that the gas molecules has a much higher probability of interacting with the walls than with each other, meaning that the gas have no viscous behaviour. When the Knudsen ratio is very low \((Kn < 0.01)\), the continuum flow regime or viscous flow regime, the molecules interact with each other, causing the gas to behave more like a fluid than independent gas molecules. Between these regimes, there is an overlapping regime called the transitional regime \((1 > Kn > 0.01)\), in which the flow characteristics is dependent on both wall collisions and intermolecular collisions [10, 11].

<table>
<thead>
<tr>
<th>Flow regime</th>
<th>Kn</th>
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<tbody>
<tr>
<td>Free molecular flow</td>
<td>( Kn &gt; 1 )</td>
</tr>
<tr>
<td>Transitional flow</td>
<td>( 1 &gt; Kn &gt; 0.01 )</td>
</tr>
<tr>
<td>Continuum flow</td>
<td>( Kn &lt; 0.01 )</td>
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Conductance, $C$, and throughput, $Q$

As described in section 2.1.1, the product of the pressure by the volume, $PV$, gives a direct measure of a quantity of gas at a constant temperature. When measuring a flowing gas, the volumetric flow rate, $\dot{V}$, is used to define the throughput, $Q$, which is commonly measured in mbar litres per seconds.

$$Q = P \dot{V} \quad [\text{mbar} \text{ l} \text{s}^{-1}]$$  \hfill (2.8)

Since the pressure varies depending on where it is measured (See Fig. 2.1), the quantity *Conductance*, $C$, is defined as the relation between the pressure difference in a feedthrough and the throughput:

$$Q = C(P_1 - P_2) \quad [\text{mbar} \text{ l} \text{s}^{-1}]$$  \hfill (2.9)

![Figure 2.1: Flow through a feedthrough of two chambers.](image)

When assembling a vacuum system, several pipes and vessels with different conductances are often connected in series, which means that the conductance of the whole system has to be summarised. This can be done using Eq. 2.10 for systems connected in series and for parallel pipes using Eq. 2.11.

$$\frac{1}{C_{Sys}} = \frac{1}{C_1} + \frac{1}{C_2} + etc\ldots$$  \hfill (2.10)

$$C_{Sys} = C_1 + C_2 + etc\ldots$$  \hfill (2.11)

The conductance itself depends on the geometry of the aperture. Since NEG (see Sec. 2.3) is pumping through its surface, it is convenient to know the conductance of a surface. The conductance of an orifice (assuming zero wall thickness approximation) is calculated in Eq. 2.12.

$$C = 3.64 \sqrt{\frac{T}{M}} \quad [\text{l} \text{s}^{-1} \text{cm}^{-2}]$$  \hfill (2.12)

where $T$ is the absolute temperature in Kelvin and $M$ is the molecular weight [8, 10, 12].
2.1 Vacuum

Pumping speed, $S$ and sticking probability, $\alpha$

When describing pumps of any kind, one important factor is the pumping speed ($S$) since it is defined as the ability to move a certain volume of gas per time unit.

$$S = \dot{V} = \frac{dV}{dt} \, [l \, s^{-1}]$$

(2.13)

The pumping speed has the same dimensions as the conductance and is often measured in litres per second.

The pumping speed of a getter is defined through the sticking probability, $\alpha$. The sticking probability is the probability that a particle impinging on a surface will be trapped:

$$0 \leq \alpha \leq 1$$

(2.14)

When measuring the pumping speed of a getter, it is common to extract the sticking probability from a pressure drop by means of a Monte Carlo simulation. Together with the conductance, the pumping speed per unit area can be defined as [8, 7]:

$$S = \alpha C \, [l \, s^{-1} \, cm^{-2}]$$

(2.15)

All pumping speed investigations in this thesis will be presented with sticking probability measurements.

Bake out

A vacuum system that has been vented to air will have a lot of gases adsorbed on the inner walls when pumping down the system to UHV. Of the atmospheric gases, there will be a relatively large amount of water vapour trapped on the surface and also in microscopic cracks in the vacuum chamber surface. When pumping down from atmospheric pressure, the desorption of these gases will start to contribute to the gas load when the pressure inside has reached $10^{-1}$ mbar. When the pressure continues to fall, the increasing gas load will slow down the pumping of the system. Gas molecules that are loosely bound to surfaces will quickly get pumped away, and tightly bound molecules will have a very slow desorption rate and do not contribute significantly to the total gas load. The amount of water vapour trapped is very high, and will take long time to desorb since the desorption rate is decreasing slowly.

One solution to the problem of reducing the pump down time is to perform a bake out on the system after pumping down to high vacuum. The system is heated to temperatures of $150 - 250^\circ C$ in the order of 10 $h$ with continuous pumping. The desorption rate of the adsorbed gas will increase significantly causing a higher pressure, but when cooling back to room temperature the outgassing rate of the water vapour will be decreased by a factor of $\sim 10^3$ or more. When achieving UHV conditions in a laboratory environment, the experiment is often limited in the order of hours. In order to finish the pump down cycle within a reasonable amount of time, a bake out is required [10].
Plasma

The term plasma is used to describe an ionised gas. A plasma differs so much in behaviour from condensed liquid and solid states of matter that it was first called the "rare fourth state of matter" when discovered. As it later turned out, 99% of the Universe is considered to consist of plasma, which would make the other three states the rare ones.

A plasma consists of a number of positively charged ions, \(n_i\), electrons, \(n_e\), and neutral molecules, \(n_0\) where the number of charged particles are over a large volume equal, i.e. \(n_i = n_e = n\). This makes the plasma electrically quasi-neutral, meaning that it is overall neutral, but considering a small confined area of plasma, it might have a charge due to inhomogeneous distribution of the charged particles.

Since it contains charged particles, it is capable of transporting electricity. A plasma is often used in thin film deposition where it is used as a discharge medium (See Section 2.4) [12].

2.2 Components of a vacuum system

The exact setup for the vacuum system will be described in Chapter 3, but a basic theoretical description of each part will be described in this section. In a vacuum system, there are generally two different categories of devices: pumps and gauges. A general description will be given of pumps and gauges followed by a short explanation of the parts included in this project.

2.2.1 Pumps

There are numerous different pumps to be used in a vacuum system. Which ones to used are correlated to which application and which pressure range is to be dealt with. In general, there are three different types of pumps, divided after which kind of action on the gas molecules is taking place:

- Positive displacement pumps
- Momentum transfer pumps
- Capture pumps

The first one, the \textit{Positive displacement pump}, is used to pump down a system from atmospheric pressure, so called primary pumping or 'rough' pumping. The gas will be in the viscous flow regime, with the main interaction between molecules, causing a fluidic behaviour due to the low mean free path. By repetitive mechanical movement, the pump displaces a load of gas at the time, until almost all of the initial present gas is removed. As the gas density decreases, the mean free path grows larger and the flow regime is slowly turning to molecular flow and the gas is losing its fluidic behaviour. The mechanical movement can be achieved in many ways; either by rotating vanes or movement of diaphragms, claws, pistons or scrolls.
2.2 Components of a vacuum system

When the rough vacuum is pumped, a secondary *momentum transfer pump* is used. Once the molecular flow regime is reached, the main interaction is randomised molecule-surface collisions, i.e. Knudsen ratio of $Kn > 1$. Due to this, there is no way that more gas molecules can be "sucked" in to the pump. Kinetic energy is instead transferred in order to further affect the residual gas molecules. This can either be done by collision with fast-moving solids or interaction with high-velocity stream fluids. The momentum transfer pumping is usually done in steps, where each step transfers the molecules toward an outlet. It should be stressed that there is always a small probability of the molecule going back to the previous step. Examples of momentum transfer pumps are diffusion pumps (vapour jet), turbo molecular pumps and drag pumps. These secondary pumps can not function in atmospheric pressure, which requires a backing primary pump mounted in series by the exhaust outlet.

*Capture pumps* are often used when the system is already pumped with a primary and secondary pump. In this state, the pressure is so low that outgassing of the inner walls is the main obstacle for achieving higher vacuum. By trapping the remaining gas molecules on the walls with either chemical or physical means, they are removed from the gas phase. This can be done either by cryogenics, where the temperature is decreased and the molecules condensate on the wall, or by adsorption through chemical bonding. The latter is one of the features in an ion pump, and the main application for getters (See Section 2.3) [10, 11].

**Rotary Vane Pump**

A rotary vane pump is often employed as primary pump in a vacuum system. It consists of a precisely placed rotor, containing movable sliding vanes that are attached to each other by a compressed spring (See Fig. 2.2). The spring presses

![Figure 2.2: Cross section of a rotary vane pump.](image)

the vanes outwards, making them follow the interior of the vacuum pump while rotating. A quantity of gas from the vacuum system is sucked in through the inlet, compressed and discharged through the exhaust valve to the atmosphere [12]. The
The rotary vane pump is a positive displacement pump, which main purpose is to back the secondary pump. Therefore, it is of importance to know the requirements of the secondary pump when choosing the primary pump. Typical pressures reached with the rotary vane pump are $10^{-1} \text{ mbar}$, or $10^{-3} \text{ mbar}$ for a two stage pump. In this initial rough pumping, most of the ambient air inside the chamber is removed (about 99.99% at $10^{-1} \text{ mbar}$) [10, 11].

**Turbo Molecular Pump**

A turbo molecular pump (TMP) was used in this project as a secondary pump. The TMP is a momentum transfer pump and consists of rotating blades with different angles mounted on a spinning axis, with stationary stator blades in the slots between the rotor blades (See Fig. 2.3). In order to achieve a pumping effect in the molecular flow regime, the blades are spinning around the rotational axis with the velocity of the molecules to be pumped. The tilting angle of the blades is in direction towards the outlet of the TMP, forcing the particles down to the next level where the stator blades are located. Each time the flat blade hits a molecule, a short interaction followed by a random desorption will take place. The desorption will have a cosine distribution, but since the blade is tilted downwards, most of the molecules will continue to the next level. Due to the random desorption, there is always a probability of the molecule going back to where it came from, which will eventually prevent the pump from reaching a higher vacuum [10]. Ultimate pressures that can be attained using a TMP are in the range of $10^{-10} \text{ mbar}$. TMPs are widely used in the pump down sequence of
the LHC and in its pre-accelerator chain.

## 2.2.2 Gauges

There are a lot of different vacuum gauges, where none are capable of measuring the whole range of pressures from ambient pressure down to UHV. Below, the ones used in this project will be mentioned, together with a brief explanation.

### Pirani Gauge

The Pirani gauge is a thermal conductivity gauge and consists of a thin metal filament with an applied heating current (See Fig. 2.4). The pressure in a system is determined by measuring the thermal energy loss of a thin filament. A heated wire in a gaseous environment will lose heat in three different ways: through radiation ($W_R$), through conduction to supports ($W_C$) and by gas transport ($W_G$). The total energy loss of the wire can be written as the sum of all three energy losses (Eq. 2.16).

$$W_T = W_R + W_C + W_G \quad (2.16)$$

The energy loss due to radiation and conduction to supports is considered pressure independent and can viewed as a constant background loss. If $W_R + W_C$ is known (and can thereby be taken into account), the heat lost in the wire will be dependant on the amount of gas in the system [11]. By measuring the heat loss, the pressure can be determined for a calibrated system. In order to calibrate the gauge, high vacuum is used where the energy loss by gas transport is negligible (slightly less than $10^{-3}$ mbar), which means that only the background heat loss ($W_R + W_C$) is measured and can be determined. On the other hand, when the pressure is increased and the mean free path of the gas is comparable to the width of the filament, the gas will form a sheath around the wire, which inhibits further heat...
transfer. This implies that a Pirani gauge is suitable for measuring in the range of $10^{-3} \text{ mbar} - 10 \text{ mbar}$.

**Ionisation gauges**

In a higher vacuum than previously discussed, ionisation gauges are the only practical option at the present time. The concept of the ionisation gauge is to ionise the residual gas molecules inside the vacuum chamber, and measure the current induced by the charged particles. The number of positive ions produced in the gauge is directly proportional to the molecule density in the gas.

There is two different types of ionisation gauges: the hot cathode and the cold cathode ionisation gauge. They mainly differ from each other in their way of ionising the gases [10].

**Hot cathode gauge**

The hot cathode gauge is using a thermionic source (cathode) to emit electrons. A grid is set to a positive potential relative to the cathode ($\sim 200 \text{ V}$), forcing the emitted electrons to accelerate towards the grid due to the electrostatic field. On the opposite side of the grid, an anode is placed with a negative potential relative to the cathode ($\sim -20 \text{ V}$). Since the grid is made of thin wire, the electrons will pass through it, and eventually reach a point where the potential is the same as that of the cathode. The electrons will turn back towards the grid, to continue oscillating back and forth until it is finally trapped on the grid. On the way, there is a probability that the electron hits a gas molecule, which will be ionised by the collision. The positive ion is then attracted to the ion collector (anode), where it is registered as an ion current. The ion current is directly proportional to the molecule density of the gas inside and can be measured.

When the electron finally strikes the grid, soft X-rays are produced. These X-rays will affect the lower pressure limit of the ionisation gauge. X-rays with sufficient energy will cause a photoelectric effect when reaching the ion collector, with an emitted electron as the result. An emitted electron is equal to a captured positive ion in the registered current, leading to a higher measured ion current. The photocurrent is the same order of magnitude as an ion current of a gas pressure of $10^{-8} \text{ mbar}$. The upper limit of the gauge is around $10^{-3} \text{ mbar}$ and is due to that at higher pressures the electron-ion or positive-negative ion recombination is too high, making the sensitivity of the gauge decrease.

There are many different variations of hot cathode gauges, and one of the most common hot cathode gauges is the Bayard-Alpert gauge (BAG) (see Fig. 2.5). The BAG consists of a helical shaped grid set at a high potential with a thin ion collector in the middle. The thermionic cathode is place outside the grid. The setup with a thin ion collector in the middle reduces the area for the X-rays to produce a photocurrent, which means that the lower pressure limit can be decreased to $10^{-11} \text{ mbar}$ [11, 14].
Cold cathode gauge

A cold cathode gauge is a ionisation gauge with an absence of electron-emitting filament. Among different cold cathode gauges, the Penning gauge and the inverted magnetron are the most common ones [10].

The Penning gauge consists of two cathode plates with an anode in form of a looped metal wire placed in between the plates. A potential difference is applied between the cathodes and the anode together with a magnetic field in the direction of the planes, achieved by an external permanent magnet. Electrons on the surface of the cathodes will accelerate towards the anode, but due the presence of the magnetic field, the trajectory of the electrons will be helical instead of straight. Once the electron passes the plane of the anode loop, it will decelerate and eventually go back in the reversed way, due to the electric field caused by the opposite cathode. This will make the path of the electron very long, with an increasing probability to ionise a the background gas on the way. Once the gas is ionised, it is collected by the surface of the cathode and the ion current is measured. This gauge operates in the range between $10^{-6} \text{ mbar}$ and $10^{-3} \text{ mbar}$. At the high pressure end, glow discharge becomes dominant and at the lower end the ionisation rate is insufficient to sustain the discharge.

In the case of the inverted magnetron gauge (also called the Hobson-Redhead gauge), the geometry is cylindrical, where the inner cylinder is the anode. The anode is an inner cylinder inside a larger cathode cylinder. Outside the cathode, an extra, auxiliary cathode is placed (See Fig. 2.6). The external magnetic field is employed in the direction of the axis, orthogonal to the electric field, which is radial. This configuration gives the electron path a cycloidal path in a circumferential movement around the axis. The auxiliary cathode acts as an electrostatic shield and attracts the field emission current while the inner cathode collects the
ion current. This configuration avoids spurious addition to the true ion current and further decreases the range of the measurable pressure down to the range $10^{-10} \text{mbar}$ [10, 14].

2.2.3 Residual Gas Analyser (RGA)

A partial pressure analyser, or a residual gas analyser (RGA), is a very useful part of a vacuum system. The RGA makes it possible to study which types of gasses are present in the system, and also quantify the amount of each gas. The three main components of an RGA is described in Fig. 2.7. In the first step, the residual gas is ionised and is sent to the filter. The filter separates the gas according to their mass-to-charge ratios ($m/e$). A common filter is the quadrupole mass filter, which separate the different masses by bending the trajectory of the ions in an electromagnetic field. The ions will have different trajectories depending on which mass they possess. Finally, the ions with the selected mass-to-charge ratio is sent to the detector where the produced current is registered. In this way, it is possible to follow the partial pressure for each type of gas with the same mass inside a vacuum system [10].

![Figure 2.7: The main three components of an RGA](image)

2.3 Getters

A molecule can be bound to a surface by adsorption. If the mean time that the molecule is adsorbed, $\tau$, is longer than a given experiment, the surface material can be used as a pump [8], or as previously described, a capture pump. There are fundamentally two kinds of adsorption; physisorption and chemisorption. Physisorption is characterised by electrostatic van der Waals bonds, with binding energy of less than $50 \text{kJ/mol}$. A particle bound by chemical bonding
2.3 Getters

(metallic, covalent or ionic) has normally a binding energy significantly higher than 50 kJ/mol. The mean time the particle stays on a surface, \( \tau \), is given by Frenkel’s law (Eq. 2.17)

\[
\tau = \tau_0 \cdot e^{\frac{E}{R_0 T}}
\]  

(2.17)

where \( E \) is the binding energy, \( R_0 \) is the universal gas constant, \( T \) is the temperature in Kelvin and \( \tau_0 \) is the period of the particle vibration. For physisorbed molecules, the mean sojourn time at room temperature is typically \( \tau = 10^{-11} \, \text{s} \), which means that in order to achieve useful pumping, the temperature must be decreased. Capturing molecules by decreasing the temperature is called cryopumping, and is used in all the bending sections of the LHC.

If instead the binding energy becomes higher, as in the case of chemisorption, \( \tau \) increases drastically. Ultra high vacuum at the range \( 10^{-8} \, \text{mbar} \) to \( 10^{-12} \, \text{mbar} \) can then be achieved and maintained at room temperature [6, 7].

Solid materials that can chemisorb molecules and form stable compounds are called getters. Getters are divided into two families; evaporable getters and non-evaporable getters (NEG). In order for the getter to pump, the surface of the getter must be clean. This can be achieved in two ways, either by "in situ" deposition of a new clean getter or by heating the getter to an activation temperature. The getters that demand a fresh layer are called evaporable getters and the ones that can be reactivated by heating are called NEG.

The first example is mostly used for lumped pumping (pumping at discrete positions of the vacuum system), and therefore cannot solve the problem of strongly varying pressure profiles in conductance-limited systems like accelerators. Since this project is investigating non-evaporable getters for particle accelerators, evaporable getters will not be further investigated here [8].

2.3.1 Non-evaporable getters

Non-evaporable getters have been used as a solution for linear pumping in modern particle accelerators at CERN the last decades. In the former particle accelerator, the Large Electron Positron collider (LEP), a NEG coated strip was integrated along the particle accelerator, covering about 23 km out of the 27 km tunnel (See Fig. 2.8) [15]. One problem with this solution however, was that \( H_2, CO, CO_2 \) were extracted from vacuum chamber walls by synchrotron radiation, resulting in much higher pressures and in a progressive decrease of the pumping speed due to gas coverage on the NEG surface. For the LHC, the NEG was instead coated on the inner wall, covering all surface and preventing further outgassing [15].

An important factor for NEG material is to have a low activation temperature. The NEG with the lowest activation temperature found so far is a combination of Ti(30 at. %), Zr(30 at. %) and V(40 at. %), which has proven to be fully activated after a 24 h heating at 180° C. A low activation temperature allows a wider range of substrate materials to be used, since it must not exceed the baking temperature
of the substrate. For instance, a stainless steel vacuum chamber should not be baked at a temperature higher than 400 °C, while copper and aluminium chambers should not exceed a baking temperature of 200 °C [16].

Another feature that is of great importance for the NEG is the surface roughness. A rough surface allows a higher area of pumping, contributing to a higher surface pumping capacity, i.e. the amount of gas that can be captured by the NEG before it stops sorbing gas. When the NEG surface is rough, it is possible for the molecule to collide with the surface several times in the same impingement. These multiple collisions will enhance the sticking probability. So, a rough surface both increases the pumping speed and the surface pumping capacity [5, 7].

A thin film of activated NEG is able to pump most of the residual gases in a UHV system, i.e. $H_2$, $CO$, $CO_2$, $H_2O$ and $O_2$ in case of leaks. NEG cannot pump chemically inert gases and the pumping for $CH_4$ is also negligible. The dissociation energy for $CH_4$ is too high at metal surfaces, which causes an upper limit sticking probability of $10^{-6}$ at room temperature [5].

2.3.2 Choice of NEG materials

When choosing getter material, some different aspects are worth taking into consideration. Due to the oxide layer on the surface before activation, materials with a high oxygen diffusivity are favourable since high diffusivity implies lower activation temperature. In order to be able to vent the NEG to air between each pump down cycle, a high oxygen solubility limit is also desirable. As an example, if the film is in the order of 1 μm and the oxide layer is 2 – 3 nm, venting the film 10 times would provide a solubility limit of around 3%. A reasonable lifetime of the NEG requires a limit of at least 10%. As a third aspect, a large enthalpy for adsorption of usual residual gases in an UHV environment is important, i.e. $H_2$, $CO$, $CO_2$ and $N_2$. In addition to these aspects which concerns the vacuum, it is also desirable that the material has a good adhesion to the substrate, high melting point and mechanical resistance, non-toxic or non-flammable, non-magnetic and low photoelectric and secondary electron yield [4].

In the periodic table, the 4th group, Ti, Zr and Hf, fulfil these requirements.
2.4 Thin film deposition

In this project, the NEG was deposited as a thin film on the inside wall of a vacuum chamber. The deposition technique used was DC magnetron sputtering, which is a physical vapour deposition technique (PVD). In general, there are two families of deposition techniques: chemical vapour deposition (CVD) and physical vapour deposition (PVD).

In CVD, a volatile compound (precursor) of the material to be deposited reacts with other gases in order to form a solid film on a substrate. The reaction byproducts are transferred away by the pumping system. The chemical reactions during CVD are commonly triggered by high temperature, therefore this process does not necessarily require the use of high voltage components and high vacuum and therefore it is convenient for industrial applications. However, the precursors usually also contain elements other than the constituents of the film to be deposited (e.g. Br, Cl, C etc.) which may cause film contamination and deteriorate its properties. Therefore CVD is not a suitable solution for growth of NEG films. [10, 12].

The other method, PVD, the source of material to be deposited as a coating, is a solid of the material itself, often called a "target". By transferring energy to the solid, either by thermal, electrical or by physical means, the material will start to vaporise. If a substrate is placed in front of the vaporised material, the atoms will condense on the surface and eventually form a film. This requires high vacuum, to prevent unwanted interactions on the way to reach the substrate (see Fig. 2.10).
Figure 2.10: General PVD.

The transfer of thermal energy is called thermal evaporation, and uses an increase in temperature to evaporate the material. In the method called arc-deposition, a high density electron beam is focused on the target, causing it to melt and vaporise. In addition, multivalent ions are also emitted from the surface, which will help sustain the vacuum plasma [12]. Both these methods are widely used but hard to implement in the cylindrical environment that will be used in this project (see Chapter 3). In sputtering deposition, momentum and energy are transferred to the target using ions, causing the target molecules to eject from the surface and form a layer on the substrate. This will be further discussed below.

### 2.4.1 Direct Current (DC) Sputtering (Diode sputtering)

Sputtering is a technique where ions are accelerated to bombard a target surface and, if the ion energy is high enough, eventually knock out an atom of the target, i.e. a sputtered atom.

When an ion hit a surface, multiple reactions can occur: the ion can reflect, stick (be adsorbed) or get implanted in underlying layers (ion implantation). In addition to this, the transfer of momentum and energy in the collision can sputter or displace surface atoms, and eject electrons and photons. The knocked out atoms will start to grow a new layer on a substrate that is usually placed in front of the target. The efficiency of the sputtering process is called the Sputtering yield ($S$) and is defined in Eq. 2.18.

\[
S = \frac{\text{Number of sputtered atoms}}{\text{Incident particle}} \quad (2.18)
\]

The process of Direct Current (DC) sputtering, or diode sputtering, is described in Fig. 2.11. To start with two electrodes, a target (cathode) and a substrate (anode), are normally placed opposite to each other. The target and substrate are situated in a vacuum chamber, where the pressure is pumped down to a high vacuum environment. This pressure is called the base pressure, and is achieved to assure a clean process. When base pressure is reached, a noble gas is injected to the vacuum chamber until the operating pressure is attained. In addition, a
negative potential, $-V$, is applied to the cathode (see Fig. 2.11a). The operating pressure, or working pressure, is normally the lowest pressure that can be used but still have enough particles to produce a plasma.

The negative potential on the cathode causes the acceleration of intrinsically existing ions of the noble gas towards the target. In the collision with the target surface, momentum and energy will be transferred, ejecting sputtered atoms and secondary electrons (See Fig. 2.11b). The secondary electrons will continue the process, causing an avalanche of ionisation events that create and sustain a plasma (See Fig. 2.11c). Each ionising collision will provide another free electron, which contributes to the ionisation process of the noble gas. The sputtered atoms travel until they reach the substrate, where eventually a thin film growth will occur (See Fig. 2.11d) [12].

### 2.4.2 DC Magnetron sputtering

To further increase the efficiency of the sputtering yield, a magnet is adapted to the system. In the planar setup, permanent magnets are placed on the backside of the target, either ellipse-like or circular rings depending on the geometry of the target. The generated magnetic field from the magnet, together with the electric
field have the following effect on a charged particle, known as the Lorentz force:

$$
F = q(E + (v \times B))
$$

(2.19)

where \( F \) is the force acting on the particle, \( q \) the charge of the particle, \( E \) the electric field, \( v \) the velocity of the particle and \( B \) is the magnetic field. Due to its low mass, this will mostly affect the electron motion, where the added magnetic field will increase the trajectory length. In the case of the electric and magnetic field being parallel, the electrons will have a helical path as long as the velocity vector \( v \) is not parallel to \( B \) (See Fig. 2.12a) and where the magnetic and electrical field lines are orthogonal, the motion will be cycloidal (see Fig. 2.12b) [17].

![Electron motion diagram](image)

Figure 2.12: Electron motion according to the Lorentz-force

As a result, the probability of ionising the inert gas increases drastically.

The benefit of a higher ionisation degree is that operating pressure can be maintained lower and while still achieving a self-sustained plasma. The lower operating pressure causes less scattering of the sputtered atoms on the way to the substrate since the molecule density is lower. The sputtered atoms will arrive at the substrate with a higher energy, and at a higher deposition rate since more atoms will reach the substrate [12].

### 2.4.3 Cylindrical-post magnetron

So far the described setup has been a planar target and substrate. When coating the inside wall of a vacuum tube, the geometry has to be cylindrical (See Fig. 2.13). The target is the inner cylinder, given a negative potential and placed inside the chamber to be coated. The chamber (the substrate) is grounded and surrounds the cathode, causing a radial electric field. A coaxial solenoid is employed to establish a uniform magnetic field parallel to the cathode. When an electron is emitted from the cathode, instead of accelerating towards the anode, it will be trapped in a cycloidal orbit around the circumference of the cathode. This movement is due to the force on the particle created when the electrical field and the magnetic field is perpendicular to each other [12].
Figure 2.13: Cylindrical sputtering setup.
Chapter 3

Coating system

3.1 System configuration

The setup of the coating system is a cylindrical-post magnetron sputtering system (described in Chapter 2). It is basically divided in two parts: a vacuum system for the pump down process and discharge gas injection, and a part where the actual coating process takes place. These parts are connected by a bellow. This chapter will describe in detail the setup of each part, and describe the coating procedure.

Drawings describing the system were made using the standardised symbols from ISO document 10 628 [18] and DIN document 28 401 [19] for vacuum technology. The symbols used in this particular system can be found in Appendix A. Since the coating dome had no standardised parts, a general picture of a cross-section was made.

A general image of the entire sputtering system configuration is shown in Fig. 3.1 with the vacuum system on the right side and the coating part to the left. The vacuum part is, except for a pumping station, equipped with an RGA, a vacuum gauge, a main gate valve and valve for the bypass line. In addition, a variable leak valve (VLV) is mounted for injection of the process gas used for coating. The coating part has a solenoid, a target cathode and a process gauge.

A more detailed description of the parts will be given in following sections, where flanges, reductions and the nominal diameter is also included. The nominal diameter in mm of each flange is denoted with DNXX, or DNXX BF where a blind flange is mounted.

3.1.1 Vacuum system

The vacuum system is the part that pumps the whole system down to UHV (See Fig 3.2). The pumping station comprises of a rotary vane pump as a primary pump, and a TMP as secondary. The TMP is connected to the main pumping
Figure 3.1: A general description of the entire sputtering, with the coating part to the left and the vacuum part to the right.

Figure 3.2: Vacuum System.
dome, which is equipped with an RGA and a compact full range ion gauge (CFG). The CFG has two gauge heads, a Pirani and an inverted magnetron, which gives the combined gauge a measurable range of $5 \times 10^{-9} - 1000 \text{ mbar}$. This gauge is used during pumping down the system to UHV. After pump down, the RGA can be used to discover possible leaks or contaminations. It can also be used to measure the gas composition of the process gas.

Above the dome the main gate valve of the system is connected, which is open during pump down to allow faster pumping. During the coating process, the main gate valve is closed and the system is only pumped through the bypass line. The bypass line has a very low conductance due to its small diameter, which means that the pumping speed of the system is very small when pumping through the bypass line, allowing a stable operating pressure during coating.

The process gas for the system is injected through a variable leak valve (VLV). The VLV makes it possible to keep a very precise rate of the injected gas. Due to this, the pressure of the injected gas can be kept constant at the required rate during the coating process.

As process gas for the coatings produced for this work, Krypton is used. Krypton is a heavy noble gas, which due to its high mass will strike the target with a high kinetic energy. This gives both an increased sputtering yield and a deeper implantation in the target [12], preventing back sputtering of loosely implanted ions in the target.

### 3.1.2 Coating system

The sputtering deposition part of the system, where the actual coating takes place, is shown in Fig. 3.3. A cylindrical coating chamber is mounted on a base dome, which is connected to the vacuum system. In addition, a compact process ion gauge (CPG) is also connected to the dome. The CPG is a combination of a Pirani and a hot cathode ion gauge. The measurable range of the CPG is $2 \times 10^{-6} - 1000 \text{ mbar}$. It is placed closed to the coating dome in order to get an accurate measurement of the injected gas pressure during coating.

The cathode is centrally placed inside the chamber in the axial direction. It consists of the sputter material, i.e. in the case of this project, a combination of $Ti \ Zr$ and $V$ that is made by three inter-twisted wires (See Fig 3.4). On top of the tubes, an electrical feedthrough is mounted where the target cathode are connected. The chamber is connected to earth, and the cathode is insulated with ceramics both on top and the bottom to keep it insulated from the vacuum chamber walls. On the other side of the feedthrough, a high voltage connection is adapted.

Once the system is assembled, a $2.5 \text{ m}$ solenoid is winched down over the sample by a manual handle. The solenoid creates a magnetic field in the axial direction of the vacuum tubes, perpendicular to the electrical field, which is radial.
3.2 Calculation of deposition duration

To estimate how long a coating should proceed until a certain thickness was reached, a thickness approximation was made. Since the accuracy of the film thickness calculation had to be within the correct order of magnitude, a couple of assumptions were made.
Eq. 2.18 from Chapter 2 defines the sputtering yield $S$ as the number of sputtered atoms per incident particle. This is rewritten in Eq. 3.1, stating that the number of incoming particles per second is the discharge current ($I$) divided by the elementary charge ($e = 1.602 \times 10^{-19} \text{C}$), i.e. the same as the number of incident charges. This multiplied with the sputtering yield results in the number of sputtered atoms per second, $n_s$.

$$n_s = \frac{I}{e} \cdot S$$

(3.1)

Since the measurable quantities during coating were the discharge current and voltage, the sputtering yield was calculated using a report by Yasunori Yamamura and Hiro Tawara [20], where the yield is approximated depending on sputtering gas, target material and discharge voltage.

Assuming that all sputtered particles ($n_s$) reach the substrate and stick to it, results in a total number of particles in the coated layer of $n_{\text{total}}$:

$$n_{\text{total}} = n_s \cdot \Delta t$$

(3.2)

where $\Delta t$ is the time that the same conditions has been kept.

The tube to be coated has an inner radius of $r$, a length of $l$ and a targeted coating layer thickness of $\delta(t)$ which will increase with time. To calculate the volume of the sputtered layer, $V_{\text{layer}}$, the following calculations were made:

$$V_{\text{layer}}(\delta) = V_{\text{tube}} - V_{\text{tube with layer}}(\delta)$$

$$= \pi l r^2 - \pi l (r - \delta)^2$$

$$= \pi l (2r\delta - \delta^2)$$

$$\Leftrightarrow$$

$$\delta = r - \sqrt{r^2 - \frac{V_{\text{layer}}}{\pi l}}$$

(3.4)

Since the target cathode was an equal combination of $Ti$, $Zr$ and $V$, the average particle leaving were assumed to be an equal combination of these three. Hence, the values used for the particle parameters were estimated to have the mean values of $Ti$, $Zr$ and $V$. The total number of TiZrV particles ($n_{\text{total}}$) in the sputtered layer could be determined using Eq. 3.5

$$n_{\text{total}} = \frac{V_{\text{layer}} \rho_m N_A}{M_{\text{TiZrV}}}$$

(3.5)

where $\rho_m$ is the mean density at room temperature, $N_A$ the Avogadro’s number and $M_{\text{TiZrV}}$ is the mean atomic weight. Combining this with Eq. 3.2 yield the following time dependant equation for the volume of the sputtered layer:

$$V_{\text{layer}} = \frac{M_{\text{TiZrV}} n_s \Delta t}{\rho_m N_A}$$

(3.6)
Eq. 3.6 together with Eq. 3.4 gives the final equation of the coated layer thickness, Eq. 3.7:

\[ \delta = r - \sqrt{r^2 - \frac{M_{TiZrV}n_s\Delta t}{\rho_mN_A\pi l}} \]  

(3.7)

This formula can be used to derive the coating duration, by solving \( \Delta t \):

\[ \Delta t = \frac{\rho_mN_A\pi l(2\delta r - \delta^2)}{M_{TiZrV}n_s} \]  

(3.8)

### 3.3 Deposition procedure

The deposition procedure starts with mounting the system as described above. The cylindrical coating chamber consists of vacuum tubes with an individual length of 50 cm and an inside diameter of 10 cm. All of the chambers are to be coated, where one of the tubes is the sample. The sample is preferably chosen to be in the middle, where the magnetic field is most uniform. In addition to the tubes, stainless steel strips are put inside the sample (See Fig. 3.5), for further measurements where a cylindrical tube geometry can not be adapted in the measurement equipment (See Chapter 4). When the sample is mounted, the system is ready for pump down (See Fig. 3.6a), which is made with all valves left open. The system is pumped down and a bake out is performed over night at a temperature of 150°C for the vacuum part, and at 250°C for the tubes to be coated. After cooling down to room temperature and the pressure is stabilised at the system base pressure \((< 5 \times 10^{-9} \text{ mbar})\), all valves are closed except the bypass line, through which the whole system is now pumped.

The solenoid is lowered over the system (See Fig. 3.6b), which provides a magnetic

![Figure 3.5: A cross section of three mounted tubes and the position of the stainless steel strips.](image)
3.3 Deposition procedure

Field of $\sim 220$ Gauss. Krypton is then injected to the system through the variable leak valve. When a working pressure of $\sim 10^{-2}$ mbar is reached, the cathode is given a negative potential of $-500\, V$. The working pressure is adjusted until the discharge current is stabilised. In order to keep track of the thickness, notes of the discharge current and volt are taken during the entire coating process. When the targeted thickness is reached, the system is shut down, and the tubes are dismounted for measurements.

During this project, three different coatings were made with the sputtering system. The first coating was produced in diode sputtering mode, since the solenoid necessary for magnetron sputtering mode was not assembled to the system at that point, hence a higher working pressure had to be adapted. The last two coatings were made in magnetron sputtering mode. The parameters used during the different coatings are presented in Table 3.1.
Table 3.1: Average parameters used for the NEG coating

<table>
<thead>
<tr>
<th>Parameter</th>
<th>1&lt;sup&gt;st&lt;/sup&gt; (diode)</th>
<th>2&lt;sup&gt;nd&lt;/sup&gt;</th>
<th>3&lt;sup&gt;rd&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base pressure [mbar]</td>
<td>$5 \times 10^{-9}$</td>
<td>$5 \times 10^{-9}$</td>
<td>$5 \times 10^{-9}$</td>
</tr>
<tr>
<td>Cathode diameter [mm]</td>
<td>3</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Cathode length [m]</td>
<td>2.0</td>
<td>1.5</td>
<td>1.4</td>
</tr>
<tr>
<td>Cathode cooling</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Discharge gas</td>
<td>Kr</td>
<td>Kr</td>
<td>Kr</td>
</tr>
<tr>
<td>Discharge gas pressure [mbar]</td>
<td>$1.2 \times 10^{-1}$</td>
<td>$9 \times 10^{-3}$</td>
<td>$1.0 \times 10^{-2}$</td>
</tr>
<tr>
<td>Deposition rate [nm s&lt;sup&gt;-1&lt;/sup&gt;]</td>
<td>0.004</td>
<td>0.014</td>
<td>0.04</td>
</tr>
<tr>
<td>Discharge voltage [V]</td>
<td>460</td>
<td>400</td>
<td>500</td>
</tr>
<tr>
<td>Discharge current [mA]</td>
<td>200 per m</td>
<td>75 per m</td>
<td>270 per m</td>
</tr>
<tr>
<td>Magnetic field [Gauss]</td>
<td>-</td>
<td>$\sim 220$</td>
<td>$\sim 220$</td>
</tr>
<tr>
<td>Power [W]</td>
<td>$\sim 90$ per m</td>
<td>$\sim 30$ per m</td>
<td>$\sim 140$ per m</td>
</tr>
</tbody>
</table>
Chapter 4

Measurements

The coated samples were investigated by several measurement methods. To study the properties of the NEG, sticking probability and electron stimulated desorption (ESD) were measured in lab with an ESD system. Morphology and thickness observations were made with a scanning electron microscope (SEM), and the composition of the thin film was investigated with energy-dispersive X-ray spectroscopy (EDS). Activation temperature was analysed with X-ray photoelectron spectroscopy (XPS), where the dissolution of oxygen was studied with respect to increasing temperature. This chapter will give a brief introduction to the different techniques, with more focus on the ESD system since the system built at CERN.

4.1 Electron stimulated desorption (ESD) and sticking probability

Electron stimulated desorption is a technique to measure the surface outgassing induced by electron bombardment. The ESD decreases with decreasing gas surface coverage, which makes ESD measurement an indication of how clean a surface is. A clean NEG surface however, is an activated surface, which means that the measured yield in reality is further decreased by additional surface pumping [15, 4].

4.1.1 Experimental setup

The ESD system that was used for measuring was built at CERN and is schematically described in Fig. 4.1. This system was used both for sticking probability and ESD measurement. The tube formed sample is attached to the ESD system to one side of the system (right side in Fig. 4.1), containing an electron source (ES). The ES can be moved out of the sample, by two contractible bellows mounted on the other side of the system. In the middle of the system, a gate valve is placed, which is used to separate the two sides from each other once the ES is retracted from the sample.
Figure 4.1: ESD system (picture taken from [21] where the Fischer-Mommsen dome displayed in publication is no longer installed on the system).

A general cross section image of the whole system with the electron source retracted is shown in Fig. 4.2. This figure shows how the parts are mounted together. Both sides are connected to a TMP pumping station through two pneumatic valves, $V_1$ and $V_2$, which can be controlled electrically to allow pumping
where it is required. On the sample side, a Bayard-Alpert gauge (BAG 1) and 
$V_1$ are connected. The sample is also insulated from the system by a ceramic 
feedthrough. On the bellow side, an RGA, a Bayard-Alpert gauge (BAG 2), and 
a NEG coated vessel is installed. In addition a penning gauge is placed near the 
TMP pumping station.

When the sample is to be replaced, the main gate valve is closed to protect the ES 
from being vented to air (as in Fig 4.2). $V_2$ is also closed, meaning that only the 
NEG vessel maintains the vacuum on the bellow side. After replacing the sample, 
the right hand side is pumped down by the TMP and baked before the main gate 
valve can be opened for measurement.

Together with the electron source, a deflector is mounted (See Fig. 4.3). During 

![Figure 4.3: The electron source together with the deflector on top.](image)

sticking probability measurement, a potential difference of 500 V is set between 
the deflector and electron source. When the deflector is bombarded with electrons, 
desorption of gas molecules causes a pressure increase.

### 4.1.2 Measurement procedure for sticking probability and ESD

Both sticking probability and ESD were measured with respect to activation tem-
perature. The values were measured in a heating cycle containing the temperatures 
$120° C$, $160° C$, $200° C$ and $250° C$. The sample was activated for $2 h$ for each 
temperature, followed by immediate measurement after cooling down below $30° C$. 
If a second measurement cycle were to be done, the sample would be vented for 
$1 h$ before it is mounted back to the system. Unfortunately, there was no time for 
a second cycle due to the time limit of this project.

For each temperature, sticking probability and ESD were measured, starting with 
sticking probability. The measurement procedure was carried out at an initial 
pressure in the low $10^{-10} mbar$ range.
Sticking probability

During this measurement, the electron source was kept on the bellow side of the system as shown in Fig. 4.2. The RGA was used to follow the mass of $H_2$ with respect to time. In the initial starting condition, the main gate valve and $V2$ was opened, with $V1$ and the NEG vessel closed. That configuration assures that all gases pass the RGA when being pumped.

The actual measurement was carried out in 5 steps, where data points were taken. The theoretical pressure curve extracted from the RGA is shown in Fig. 4.4 with the following explanation of each step, remembering that the RGA follows the pressures on the bellow side.

![Figure 4.4: Measurement procedure curve.](image)

1. **Initial condition**
   Starting with the main gate valve opened and the system only pumped by the turbo through the second valve. With this configuration, the pumped molecules had to pass by the RGA.

2. **Closing the gate valve**
   After closing the gate valve, there are two possibilities. Either the residual pressure increases, or decreases. If the NEG had been activated and was pumping, the pressure should increase since the contribution from the NEG sample was shut of. If the NEG had not been activated during heating, the pressure should decrease due to the smaller degassing surface when one side is blocked.

3. **Turning on emission current on ES**
   The emission current on electron source was set to $1 \text{ mA}$, causing a pressure increase due to the degassing of the deflector. This pressure rise would immediately start to decrease, due to the pumping from the TMP, giving the curve a negative slope.

4. **Opening the main gate valve**
   With the electron source still at $1 \text{ mA}$, the main gate valve was opened. With
4.1 Electron stimulated desorption (ESD) and sticking probability

a pumping NEG sample on the other side of the gate valve, the pressure should go down as the NEG starts contributing to the pumping.

5. Closing the main gate valve
A last data point was taken with the gate valve closed in order to determine measurement point 4′ by regression.

To extract the pumping rate of the sample, a regression line was made to figure out measurement point 4′. The ratio between the pressure difference with respect to the initial value at point 4 and point 4′ were then calculated and related to a sticking probability via a Monte-Carlo simulation.

ESD

Directly after measuring the sticking probability, the ES was inserted to the sample by the contractible bellow (See. Fig 4.1). In this setup, a standardised potential difference of 500 V was set between the ES and the sample to achieve electron bombardment on the inner sample wall. With the RGA following the masses, an emission current of 1 mA was applied to bombard the surface for 100 s. The pressure increase, ΔP was recorded for calculation of the effective desorption yield.

The effective desorption yield, η, i.e. the number of molecules leaving per impinging electron was calculated using the following formula.

\[ \eta = \frac{S_{eff} \Delta P \cdot n_{PV}}{I_e/e} \]  

(4.1)

Where \( I_e \) is the emission current and \( e \) is the elementary charge. \( S_{eff} \) is the effective pumping speed by the RGA, calculated by adding all aperture conductances until the RGA together with the pumping speed of the turbo:

\[ \frac{1}{C} = \sum_{i=1}^{n} \frac{1}{C_i} \]

\[ \frac{1}{S_{eff}} = \frac{1}{S_{pump}} + \frac{1}{C} \]  

(4.2)

and \( n_{PV} \) is the number of moles per pressure-volume unit, extracted from the ideal gas law:

\[ PV = nk_BT \]

\[ n_{PV} = \frac{n}{PV} \]

\[ \implies \]

\[ n_{PV} = \frac{1}{k_BT} \left[ \frac{mol}{mbar\,l} \right] \]  

(4.3)

Once the ESD measurement was done, the ES was retracted and the gate valve was closed to start heating the sample to next activation temperature in the cycle. The procedure was then repeated for the next temperature.
4.2 Scanning electron microscopy (SEM) and Energy dispersive X-ray spectroscopy (EDS)

In order to measure the thickness and metallic composition of the coated thin film, a scanning electron microscope (SEM) was employed. A SEM uses a beam of high-energy electrons to scan over the sample to be investigated. The electrons impingement on the surface causes secondary electrons close to the surface to emit. Continuous random scattering events inside the material will also cause so-called back scattered electrons to leave the sample. In addition, characteristic X-rays from atoms will be produced. The electrons are detected and used to produce a high resolution image of the surface topology of the sample, while the X-rays will reveal the metallic composition of the film (EDS) [12].

SEM images and EDS spectrum was measured on the coated stainless steel strips described in Chapter 3 using a SEM Sigma ZEISS microscope.

4.2.1 SEM procedure

A 10 mm × 30 mm peace of NEG coated stainless steel was mounted in the SEM vacuum chamber. After pumping down to high vacuum, the sample was bombarded with electrons with an energy of 20 eV. Images were first made from a top view to get a picture of the surface morphology. In order to achieve a cross sectional view of the film, it was bent 180° to peel of the coating. The film was then scanned from the side, where the thickness could be measured at several places. An average value was extracted from the different measured values when deciding the thickness. The SEM pictures were taken using SmartSEM software.

4.2.2 EDS

Three EDS measurements were made on the same sample using INCA software to investigate the metallic composition of the film. X-rays intensity peaks from the interactions in the film were plotted versus the energy of the incoming beam. The quantitative analysis from the raw data was done using the ZAF method. The ZAF method is using a correction factor for the atomic masses (Z), the adsorption (A) and the fluorescence (F) to correct the raw data from the analysis according to the considered elements, i.e. Ti, Zr and V.

4.3 X-ray photoelectron spectroscopy (XPS)

XPS is a technique to analyse the chemical composition of a material surface. The sample to be investigated is subjected to X-ray radiation, causing the material to emit electrons via the photoelectric effect. By measuring the electron energies, the chemical composition of the surface layers can be analysed. XPS is a true surface analytical technique since the detected electrons are emitted from the surface layers less than ∼15 Å deep.
The theory behind the method is that a photon hits an electron, transferring enough energy to emit the electron from the atom via the photoelectric effect. The kinetic energy of the photoelectron, \( E_k \), can be measured by a detector. A modified version of the Einstein equation for the photoelectric effect can be expressed as

\[ E_k + \phi = h\nu - E_B \]

\[ \Rightarrow E_B = h\nu - (E_k + \phi) \]

where \( h\nu \) is the energy of the impinging photon, \( \phi \) is the work function of the material and \( E_B \) is the energy of the bound electron state. Since each element has specific binding energy values, atomic identification can be made through measuring the photoelectron energies. The technique is performed under UHV conditions, to avoid contaminations and keep a long electron mean free path [12].

In this project, XPS was employed to observe activation properties of the film, following the oxygen peak from the surface of the coating while heating to various well-defined temperatures. In the activation process, the oxygen layer on the NEG surface diffuses into the bulk material, causing a decrease in the XPS spectra. The magnitude of the decrease was then evaluated through comparing the results with a standardised quality control EDMS document [22]. In addition, possible contaminations on the thin film could be discovered by XPS.

### 4.3.1 Measurement procedure

A small sample (about 10\,mm \times 20\,mm) from the coated stainless steel strips was monitored by following the changes in the surface chemical composition with respect to temperature. XPS spectra were first taken at room temperature, and then in steps after heating the sample to 160° C, 200° C and 250° C. Each heating of the sample was done for 1 h. The XPS data acquisition was started immediately after each heating, and the sample was kept under constant temperature during the whole scan procedure.
Chapter 5

Results and Discussion

Three different coatings were made during this project, the first one in diode sputtering mode and the last two made in magnetron sputtering mode. The last coating satisfied the desired properties, while on the first two coatings, contaminations were detected. The system was completely dismounted and cleaned between the second and the third coating.

The results from the measurements will be presented in this chapter. Influence of the coating contamination and the difference between coating in diode and with a magnetron will be dealt with and presented in the discussion part.

5.1 Results

5.1.1 Thickness and composition measurements

SEM pictures where taken from the coatings to investigate the thickness of the film. Cross section images of the three different coatings can be seen in Fig. 5.1. The average value of various different points taken from four different pictures was then calculated for the magnetron mode coatings. For the coating made in diode mode, three values where extracted. The different values are displayed in Table 5.1. All three coatings were made with the aim to achieve a thickness of 1 \( \mu m \). Due to the lower sputtering rate in diode mode, the first coating ended up about 10 times thinner than the ones done in magnetron mode.

Images were also taken from a top view of the samples to observe the surface roughness. The SEM pictures reveals a very smooth homogeneous surface on all three samples (see Fig. 5.2). A smooth surface is not in favour for the NEG pumping performance since it provides a lower area for molecules to stick to, and thereby a lower surface pumping capacity [7]. The cracks in the pictures are due to the substrate material morphology.

Quantitative analysis of the films was made with EDS. Since the film coated
Results and Discussion

(a) Diode mode with contamination

(b) Magnetron mode with contamination

(c) Magnetron mode, without contamination

Figure 5.1: Cross sectional SEM pictures of the three different coatings.

Table 5.1: SEM thickness measurements.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Thickness [$\mu m$]</th>
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<tbody>
<tr>
<td></td>
<td>1$^{st}$ (diode)</td>
</tr>
<tr>
<td>1</td>
<td>0.11</td>
</tr>
<tr>
<td>2</td>
<td>0.11</td>
</tr>
<tr>
<td>3</td>
<td>0.10</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>Average</td>
<td>0.11</td>
</tr>
</tbody>
</table>

in diode mode was too thin, the EDS spectra contained a signal from the substate material, causing an inaccurate result of the composition. However, software approximations yielded that the film was made of Ti, Zr and V with a larger quantity of V followed by Zr and finally Ti.

For the second film, no EDS spectra were made since knowledge about the contamination led to no further measurements at that point. The third NEG coating measurement resulted in a plot (see Fig. 5.3) and the quantitative analysis was done using the ZAF method. Table 5.2 shows the percentile composition of the third NEG thin film, as a result from the EDS measurement. The aim for the
5.1 Results

(a) Diode mode with Na contamination

(b) Magnetron mode with Na contamination

(c) Magnetron mode, without Na contamination

Figure 5.2: Cross sectional SEM pictures of the three different coatings.

Figure 5.3: EDS analysis spectra

Table 5.2: EDS quantitative analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic %</th>
</tr>
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<tbody>
<tr>
<td>Ti</td>
<td>28.4 ± 0.4</td>
</tr>
<tr>
<td>Zr</td>
<td>30.5 ± 0.9</td>
</tr>
<tr>
<td>V</td>
<td>41.1 ± 0.6</td>
</tr>
</tbody>
</table>

coating was to achieve Ti 30 at.%, Zr 30 at.% and V 40 at.% of the produced film.
5.1.2 Sticking probability

The sticking probability for $H_2$ was measured on the ESD system described in Chapter 4, and is presented in Fig. 5.4. Before each measurement point in the graphs, the samples were activated for 2h (according to Chapter 4) and cooled down to below 30 °C. The sticking probability for the first two contaminated samples are shown as the blue and red line in Fig. 5.4 and the green line shows the results from the uncontaminated sample.

The diode coated film (blue line Fig. 5.4) does not show any sign of pumping, except from a small negligible sticking probability rise at 120 °C and 250 °C. These small increases are however likely to be due to measurement uncertainties since the film could not have been activated at 120 °C.

For the samples coated in magnetron mode, the NEG does not show any measurable pumping below 160 °C, thereafter the sticking probability starts to increase (activation). The third coating (green line Fig. 5.4) keeps a higher sticking probability value than the second coating (red line). The highest value of slightly over $1 \times 10^{-2}$ was obtained after heating to 250 °C in the last of the three coatings.

5.1.3 Electron stimulated desorption measurement (ESD)

The ESD result is presented in Fig. 5.5 and shows that the measured effective desorption yield curve for $H_2$ decreases drastically once the NEG is activated. Even though the sticking probability measurement of the diode mode coating did not show any signs of activation, a total decrease of two orders of magnitude can be seen in the ESD result graph from the same film (blue line Fig. 5.5).

According to the sticking probability measurement for the other two coatings,
5.1 Results

Figure 5.5: Effective desorption yield of $H_2$ for the TiZrV coatings. The electron are impinging on the NEG surface with an energy of $500\,eV$ and the electron current of $1\,mA$.

the film should have been activated between $160\,^\circ C - 200\,^\circ C$, in which range the desorption yield drops by two orders of magnitude (red and green line Fig. 5.5). The effective desorption yield refers to the net desorption per impinging electron, i.e. the amount of molecules ejected from the surface per incoming electron. This result gives an indication of how the pumping ability of the NEG effects the surface degassing. The desorption yield was measured directly after the sticking factor measurement, i.e. using the same cycle of heating.

The lowest ESD value was below $1 \times 10^{-5}$ molecules per impinging electron, achieved with the third coating (green line Fig. 5.5). This corresponds well with the sticking probability measurements, where the third coating showed the highest pumping ability in terms of sticking probability.

5.1.4 Activation measurement

Since XPS measurement reflects the atomic composition on the surface, possible surface contamination can be detected. It was shown that all NEG coatings had a Fluorine ($F$) surface contamination of $\sim 2\,at.\%$ on the samples. In previous measurement, a small amount of $F$ (around $1 - 2\,at.\%$) has always been present and is believed to be due to the cleaning process of the vacuum chambers [22].

In addition to $F$, Sodium ($Na$) was found on the first two coatings. For the first coating in diode, $Na$ contamination of $4.6\,at\.%$ was found, and for the second coating $9.6\,at\.%$ was measured.

In the activation measurement, all NEG coatings were measured, following the decrease of the oxygen intensity peak on the surface with respect to temperature. None of the first two coatings activated correctly according to the standardised
EDMS document. The EDMS standards are based on the series of LSS chamber coatings, and has the acceptance limit of a total decrease over 66% for oxygen $O$ [22].

Fig. 5.6 shows the oxygen ($O1s$) peak area for the coating made in diode (Blue line), and the contaminated coating produced in magnetron sputtering mode (Red line) as a function of the heating temperature in the cycle. The data point for 160 °C of the red line in Fig. 5.6 was not measured due to a storage mistake. The green line shows the oxygen ($O1s$) peak area for the third coating where the decrease is above 75%. A reference curve [22] was also plotted (dashed line) in the same graphs.

Figure 5.6: XPS for oxygen. The dashed purple line represents the reference curve and the blue curve represents the oxygen ($O1s$) peak for the NEG.

5.2 Discussion

According to literature, a NEG coating of $Ti_{30}Zr_{30}V_{40}$ should be fully activated at 180 °C after 24 of heating or correspondingly at 200 °C after 2h [4, 7]. The results in Fig. 5.4 indicates that the NEG reaches its maximum sticking probability value at 250 °C.

One explanation for this could that the amount of $F$ on the surface was too high. $F$ has in previous investigations been proven to have a negative effect on the NEG, since it bonds with the surface to form stable compounds that do not dissolve into the bulk material. The $F$ contamination will therefore prevent gettering of residual gases on the NEG surface, destroying its pumping capability. [23]. Due to the system contamination of the first two coatings, the whole system was dismounted, cleaned and taken to a furnace for a high-temperature bake out over night before the last coating.
In contrast to the sticking probability measurement, the largest decrease of the desorption yield is between 160 – 200 °C, which would correspond to a high increase in pumping in this interval, while the slope levels of after 200 °C. With respect to previous results, the effective desorption yield for the second and the third coating is somewhat lower than the typical value that is expected to reach a yield of $2 \times 10^{-4}$ molecules per electron at full activation [5].

The investigated thin film shows a smooth surface, which is expected for NEG coated on stainless steel substrate. This has been taken into account when evaluating the results, where the sticking factor and electron stimulated desorption measurement are compared to former results from smooth NEG surfaces. The surface roughness plays an important role since it affects the surface capacity. A rougher surface gives a larger area for pumping and it gives rise to multiple different reflections when a molecule strikes the surface.

There has been shown several ways in the past how to achieve a high surface roughness. One way is to vary the substrate material. While NEG coatings on stainless steel and copper has been proven to exhibit a smooth surface, coatings on aluminium and beryllium forms a 'cauliflower' structure [16]. Another way is to roughen the surface prior to coating or to increase the temperature of the substrate during coating. It has been shown when depositing NEG on copper, that when the substrate temperature exceeds 200 °C, the film roughness increases significant [7].

The behaviour of the third sample corresponds to the standardised acceptance limit for proper activation. The oxygen decrease should exceed 66 % for normal activation. A total drop of 75 % (Fig. 5.6) is observed for the third coated sample, which is enough for normal activation, i.e. the oxygen decrease agrees or even exceeds the standardised EDMS document [22]. The first two did not reach the acceptance limit for normal activation.

Except for a 4 at.% impurity of Cu, there are no acceptance levels for impurities since their effect on functional performance is not known. But since the presence of F can be deleterious for the NEG performance, it is expected to stay under 1 at.% [22] which is not fulfilled in these coatings. However, previous coatings has often exhibit an impurity of somewhat higher than 1 at.% and have still shown good pumping properties. As previously discussed, a F contamination of 2 at.% can be the reason for the lower sticking probability increase that was shown in Fig. 5.4. F is believed to originate from the cleaning process of the vacuum chambers, where the chambers are stripped from previous coatings in favour for new ones.

### 5.2.1 Contamination influences

The surface contamination obtained in the first two coatings was F and Na. Since the second coating was done in magnetron sputtering with similar conditions as
the third, that one will be discussed here in terms of difference in vacuum performance. The quantity of the contamination was a small amount of F (2.3 at.%) on the second coating and F (2.1 at.%) for the third. A large amount of Na (9.6 at.%) was found on the second coating. F, as previous discussed, has a deleterious effect on the NEG. What effect Na has is not known, neither has it been observed before at CERN for these type of coatings.

XPS results from the contaminated coating showed that the NEG did not activate properly. This does also coincide with the results from the sticking probability measurement (see Fig. 5.7), where the probability curve stays constantly lower than of the curve obtained without contamination. In the point of view of the ESD measurement for the second coating, the drop of the desorption yield is smaller but within acceptable range according to literature [5]. It was, in the

![Figure 5.7: Variations of the $H_2$ sticking probability as a function of activation (2 h) temperature. The above lines are the same as the red and green line presented in Fig. 5.4.](image)

time of this project, unknown if the difference in performance of the NEGs was a result of the somewhat higher concentration of F or if the Na was causing the behaviour. F is known to affect the vacuum performance of the NEG negatively, but the quantity difference of the F is not significant between the coatings (0.2 at.%). The main difference between the coatings were the surface contamination of Na, almost 10%. To draw a conclusion of its influence, more measurements have to be done.

### 5.2.2 Growth mode difference between diode and magnetron coating

All coatings during this project were investigated with the same techniques. That made it possible to study the difference between the coatings made in diode sputtering mode and the coating in magnetron sputtering mode.

One big difference in coating parameters were that the coating in diode had to be done using a higher pressure to achieve a self-sustained plasma. The pressure used
for DC sputtering was just above $1 \times 10^{-1}$ mbar. This decreases the mean free path of the ions, forcing more collisions between the ions and the gas atoms. The high energy of the ions will be lost in these collisions due to charge transfer and energy exchange, causing lower kinetic energies of the sputtered atoms [12]. Due to the lower kinetic energy, the film exhibits a columnar structure (see Fig. 5.8a), while the magnetron sputtered film is more dense (see Fig. 5.8b).

Another remark about sputtering in diode mode is that the deposition rate is much lower in than in magnetron mode. Due to the shorter electron trajectory, the ionisation yield is lower which causes less sputtered atoms. The pressure has to be increased in order to produce a self-sustainable plasma, which will cause more gas scattering and in addition a higher contaminant level of $O_2$ and $H_2O$. These contaminants can form an insulating layer on the target, which further reduces the current and deposition rate [12]. In the thickness calculations for the sputtered layers, this was not taken into account. This explains why the diode sputtered film is about 10 times thinner than the magnetron sputtered film.
Chapter 6

Summary and conclusions

Non-evaporable getters are widely used in ultra high vacuum systems such as particle accelerator, as vacuum pumps. The NEG pumps through chemisorption of the residual gas molecules in the vacuum system. The chemisorption process requires a clean surface, which is obtained by heating to an activation temperature. The activation makes gases adsorbed onto the surface of the NEG diffuse into the bulk.

NEG can be sputter deposited on the inner walls of vacuum chambers, turning the whole wall into a pump that is evenly distributed over the coated surface. In the largest particle accelerator in the world, the Large Hadron Collider, a total of 6 km beam pipe has been coated with NEG.

An ongoing challenge in NEG research is to lower the activation temperature. A lower activation temperature provides a wider spectrum of substrate materials to be used in a vacuum system. At present, the NEG with the lowest proven activation temperature is a ternary alloy of $Ti(30\,\text{at.\%})$, $Zr(30\,\text{at.\%})$ and $V(40\,\text{at.\%})$. The $Ti_{30}Zr_{30}V_{40}$ has proven to be fully activated after heating to 180$^\circ$C for 24 h and was discovered at CERN after a very focused development during 1995 – 2002 in the framework of the LHC [4, 16, 5].

In the framework for further studies in the NEG research, this master thesis has been part of developing a small-scale cylindrical sputtering system for vacuum chambers. In the course of the work, a coating system dedicated to the investigation of various NEG parameters has been assembled, installed and commissioned. This thesis has also shown which parameters are important for the process, and also some of the challenges.

In total, three coatings has been done with the assembled system. All three coatings had surface contamination of $F$ ($\sim 2\,\text{at.\%}$) that was believed to be due to the cleaning process of the system parts where $F$ is employed. In addition, the first two coatings had Na contamination (between 6 – 10 at.%), whose origin was not discovered. However, after dismounting the system and performing another
standard cleaning procedure, the $Na$ contamination disappeared.

None of the $Na$ contaminated NEG coatings showed vacuum performance comparable to reference standards. The third coating however, was comparable to the reference standard, thereby proving that the system works as required. It should be mentioned that more coatings have to be done to reproduce the same results as achieved in the third coating.

Even though the system managed to produce a coating comparable to the reference standards, the pumping ability in terms of sticking probability was somewhat slowly (fully activated at $250^\circ C$ instead of $200^\circ C$) which contradicts the other measurements which suggest that the sample is fully activated at $200^\circ C$ with respect to reference standards. The reason for this could not be concluded.

### 6.1 Future work

The next step is to produce more coatings with exactly the same composition, to prove the reproducibility of the system. Since the origin of the $Na$ source was not found, it cannot be entirely concluded that the problem has vanished. The origin of why the sticking probability and activation measurement is not coinciding also has to be determined.

This project was limited in time, to 20 weeks. All the work done in this thesis was performed during that time. Various obstacles (contamination etc.) have been overcome, and the next step is to ensure the reproducibility. After establishing a stable system with good reproducibility, the system should be used for what it was built: coatings of different compositions as well as trying new material combinations.
Bibliography


## Appendix A

### Standardised symbols for vacuum technology

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<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
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<td><img src="image1" alt="Symbol" /></td>
<td>Rotary vane pump (RVP)</td>
</tr>
<tr>
<td><img src="image2" alt="Symbol" /></td>
<td>Turbo molecular pump (TMP)</td>
</tr>
<tr>
<td><img src="image3" alt="Symbol" /></td>
<td>NEG pump</td>
</tr>
<tr>
<td><img src="image4" alt="Symbol" /></td>
<td>General flange</td>
</tr>
<tr>
<td><img src="image5" alt="Symbol" /></td>
<td>Manual operation valve</td>
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<td><img src="image6" alt="Symbol" /></td>
<td>Pneumatic valve</td>
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<td><img src="image7" alt="Symbol" /></td>
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<td><img src="image8" alt="Symbol" /></td>
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<td><img src="image9" alt="Symbol" /></td>
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<td><img src="image10" alt="Symbol" /></td>
<td>Reducer</td>
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<td><img src="image11" alt="Symbol" /></td>
<td>General gauge</td>
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<td>Gauge with digital indicator</td>
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<tr>
<td><img src="image13" alt="Symbol" /></td>
<td>Residual gas analyser (RGA)</td>
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Table A.1: Standardised symbols for different parts