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Broad Band Anti-Reflection 2-16 μm Coatings on Diamond and
ZnSe

School of Aerospace Transport and Manufacturing
Ultra-Precision Engineering (Manufacturing)

MRes
Academic Year: 2017 - 2018

Supervisor: Dr Glenn Leighton
Associate Supervisor: Prof Jose Endrino
August 2018

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ABSTRACT

In this project, Thin Metal Films an optical coating company is requiring the upgrade of a desktop research type radio frequency magnetron sputtering machine which was custom made for a European funded project and was gifted to it after the project completion. As the machine had no usage history, it had to be investigated and its capabilities and characteristics identified.

The first part of the project, focused on restoring the machine using a systematic approach by utilising a technique called Plan Do Check Act, where a continuous feedback loop is used to identify problems and finding solution to them. Within the restoration process the aim was to improve the coating uniformity and machine's repeatability. The restoration of the machine consumed almost the entire project duration leaving a little time for second part of the project.

The second part was to use the restored machine, to develop single and multilayer Broad Band Anti-Reflective Coatings for Zinc Selenide and diamond optics. The optics are to be used in Attenuated Total Reflectance accessory units for Infrared spectroscopy.

Based on the literature review and multiple decision criteria, yttria and ytterbia were showing promising results in adhering very well to a diamond surface and improving its transmission. Therefore, using Macleod software, a single layer quarter wavelength coating was designed and theoretically examined. It was found that a quarter wavelength yttria at 5000 nm and a quarter wavelength ytterbia at 3370 nm can increase the transmission on both ZnSe and diamond optics to maximum of 98% and 95% accordingly.

The coatings have not actually been deposited on the optics due to both targets breaking before conducting the actual experiments.

Keywords:

Anti-Reflective Coatings, Diamond prism, Zinc Selenide optics, Yttrium, Ytterbia, Infrared, RF PVD sputtering, Thickness Uniformity

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LIST OF ABBREVIATIONS

AR	Anti-Reflection
ATR	Attenuated Total Reflection
BBAR	Broad Band Anti-Reflection
CVD	Chemical Vapour Deposition
DAR	Dual Wavelength Band Anti Reflective Coating
Ge	Germanium
IR	Infrared
LWIR	Long Wave Infrared
MWIR	Mid Wave Infrared
PVD	Physical Vapour Deposition
RF	Radio Frequency
SAR	Single Layer Anti Reflective Coating
SWIR	Short Wave Infrared
VAR	Multilayer Anti Reflective Coating
VIS	Visible
WAR	Broadband Multilayer Anti Reflective Coating
XRD	X-Ray Diffraction
YF ₃	Yttrium Fluoride
Y ₂ O ₃	Yttria
Yb ₂ O ₃	Ytterbia
ZnSe	Zinc Selenide
ZnS	Zinc Sulfide

1 INTRODUCTION

1.1 Overview

As the application of radio frequency (RF) magnetron sputtering is increasing, many optical coating businesses are focusing on the opportunities that this technique offers. In this project, Thin Metal Films, TMF, an optical coating company is requiring the upgrade of a desktop research type RF magnetron sputtering machine. The machine, a custom made for a European funded project, was gifted to TMF after the project completion. As the machine had no usage history, it was up to the company to establish the machine's capabilities and its features by rapid testing and continuous improvement.

The first part of the project focuses on the restoration of the machine. Being able to restore it, it will be used in development of single and multilayer Anti-Reflective Coatings (ARC) for Zinc Selenide (ZnSe) and diamond optics. The optics are to be used in Attenuated Total Reflectance (ATR) accessory units for Infrared (IR) spectroscopy. The restored machine will have a capability to repeatedly deposit ARC on 150 optics at a time, with dimensions of 2.4mm diameter and 1.25 mm height, in a single run and within acceptable tolerances and deposition rate.

The restoration of the sputtering machine and the ability to coat such small optics in a mass production will help in the development of a new capability which creates a great business opportunity for TMF to give them a competitive edge over other local and regional companies.

The second part of the project focuses on designing Broad Band Anti-Reflective, BBAR, 2-16 μm wavelength coatings for the ZnSe and diamond optics. Based on the literature review, only handful of studies have been conducted for developing ARC for diamond optics. And none of them have investigated the coatings performance for a broader wavelength of 2-16 μm .

Therefore, the project took the following approach to solve the addressed problems. Firstly, a systematic approach was used to restore and upgrade the RF magnetron sputtering machine. Secondly, ARCs were designed using Macloed software to enhance the transmission for the optics. Based on the

designed coating specifications, the restored machine was used to deposit the coating on the optics.

1.2 Aims and Objectives:

The aim and objectives of the project are as follows:

1. Restore and upgrade the RF Magnetron Sputtering machine by:
 - a. Standardising its process
 - b. Automating it
 - c. Improving its coating uniformity
 - d. Enhancing its vacuum performance and repeatability
2. Use the restored machine to manufacture Physical Vapour Deposition, PVD, coating on ZnSe and diamond optics by:
 - a. Designing a jig to hold the substrates
 - b. Researching and selecting the best material for the coating structure
 - c. Design a coating structure using Macloed software to enhance the performance of ZnSe and diamond optics for the use in ATR accessory unit
 - d. Applying the coating on the optics using the restored machine
3. Investigate the developed coatings on ZnSe and diamond optics by:
 - a. Reflection and Transmission tests using spectroscopy
 - b. Comparing the performance of the coated and uncoated optics in terms of improvement in transmission and reduction in reflectance.

2 LITERATURE REVIEW AND BACKGROUND THEORY

2.1 Anti-Reflective Coatings (ARC)

Optical coatings or Thin-Film Optical Filters are the two phrases used interchangeably in literature to describe materials applied to surfaces in order to modify the reflection or transmission of light at those surfaces [1]. In simple terms, the function of optical filters is to pass some wavelengths of light, within the electromagnetic spectrum, and reflect or absorb all other wavelengths that are detected. Even though the aim of the project was to design and develop a BBAR ARC; other type of coatings including High-Reflective Coatings, HRC, Bandpass Filters and Beam Splitters, BS, were also briefly covered to appreciate the variety of applications of optical coatings in the industry. Different types of the optical coatings are put together in Figure 1.

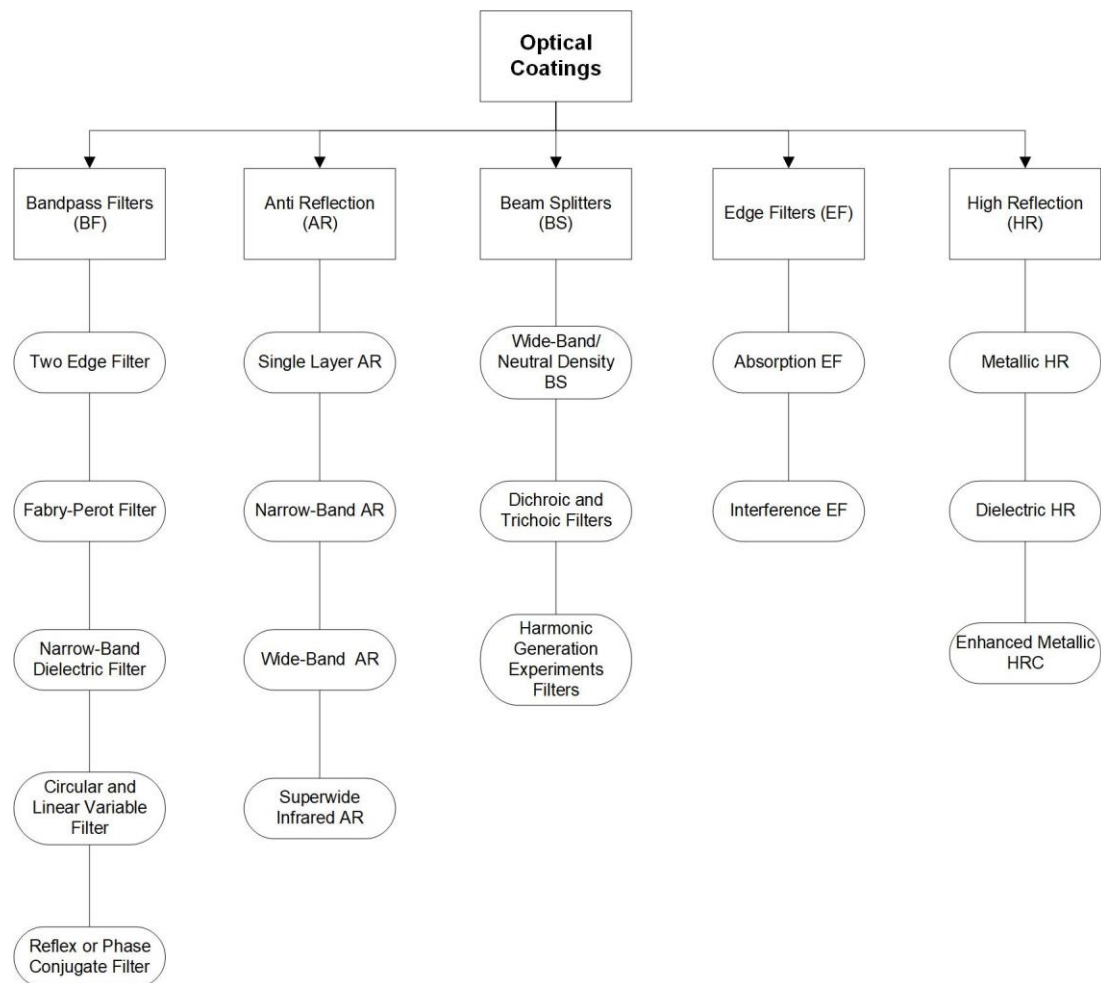


Figure 1: Overview of Optical Coatings in the industry [2][3].

ARCs are the most used coatings in the optical industry and they are designed and produced in many ways and through different techniques. The demand for optical systems that are used in a broader IR wavelength range, such as ATR accessory units, made it necessary to understand the optical and physical limitations of the optical thin films coatings [4]. To make it simpler to follow, the ARCs were divided into the following four categories taken from Hiroyuki, Shigenori and Tetsuro, 1977: 1. Single Layer ARC, SAR, 2. Multilayer ARC, VAR, 3. Broadband Multilayer ARC, WAR, and 4. Dual Wavelength Band ARC, DAR [5].

2.1.1 Single Layer ARC

The most commonly used material in developing Single Layer ARC, SAR, in industry is Magnesium Fluoride (MgF_2) [3]. MgF_2 has excellent performance in the Short Wave IR Range, SWIR, 1-3 μm and in the Mid Wave IR Range, MWIR, 3-5 μm but it's performance decreases in the Long Wave IR Range, LWIR, 8-12 μm [6]. Therefore, it would not be the best option for BBAR coating.

To achieve a good SAR, ideally a compound is used that has a refractive index that is midway between the indices for air and the optical substrate. And the optical thickness of the SAR layer should be chosen to be quarter of the desired wavelength [7]. The quarter wave optical thickness, $QWOT$, is defined as

$$QWOT = \frac{4nd}{\lambda} \quad (2-1)$$

where nd is the optical thickness which is a product of n , refractive index, and d , the physical thickness of the coating. And λ is the wavelength at which the $QWOT$ occurs [3].

The reflectance of a single quarter wave thick film can be calculated by:

$$R = \left[\frac{n_f^2 - n_0 n_s}{n_f^2 + n_0 n_s} \right]^2 \quad (2-2)$$

where n_f is the index of the film, n_0 is the index of the medium and n_s is the index of the substrate [3].

In absorbing thin films, the transmission, reflection and absorption of light can be summarised in a basic formula that is:

$$R + T + A = 1 \quad (2-3)$$

where, R is the intensity reflection, T is transmission ratio and A is the absorption in the filter. For more information on basic concept of lights and optics including Angle of Incidence, Critical Angle and Polarisation please refer to [2,3].

As mentioned earlier, very few studies have been conducted for developing ARCs used for diamond optics. The main reason for the lack of research in the area could be due to the high cost of diamond and its limited applications. Reinhard, et al., 2012, used a Silica (SiO_2) as an ARC material for single crystal diamond optic for a specific wavelength of $1.6 \mu\text{m}$ which is classified as SWIR in the spectral range of between $1\text{-}3 \mu\text{m}$. They coated the SiO_2 on diamond using the Plasma Enhanced Chemical Vapour Deposition, PECVD, with Nitrous oxide (N_2O) and Silane (SiH_4) feed gases. They concluded that a single layer SiO_2 with a thickness of 280 nm on both side of the diamond optic can increase the transmission to 98.7% [8].

Yeung, et al., 2012, also applied a single layer quarter wavelength of SiO_2 on two planar diamond substrates using magnetron sputtering with target wavelength being $0.5\text{-}0.6 \mu\text{m}$. The thickness of the silica layer was measured to be $(95 \pm 5 \text{ nm})$. They claimed that the silica layer adhered robustly to the diamond and managed to reduce the reflection from 17% to nearly 2% [9].

Lu, et al., 2009, performed set of experiments on diamond film IR windows to increase its AR performance using single layer hafnium dioxide (HfO_2) and yttria (Y_2O_3). They prepared the thin films using reactive magnetron sputtering using pure hafnium (Hf) and yttrium (Y) metal targets in reaction with a mixture of argon and oxygen (Ar/O_2) gases. The targeted spectral range was the $3\text{-}5 \mu\text{m}$ and $8\text{-}12 \mu\text{m}$. After applying a quarter wavelength coating of HfO_2 and Y_2O_3 , the IR

transmission of the coated diamond film in the LWIR has increased to 88% and 88.2% respectively. And on the MWIR the IR transmission has increased to 66.8 and 64.9% for both HfO_2 and Y_2O_3 , respectively, Figure 2 [10].

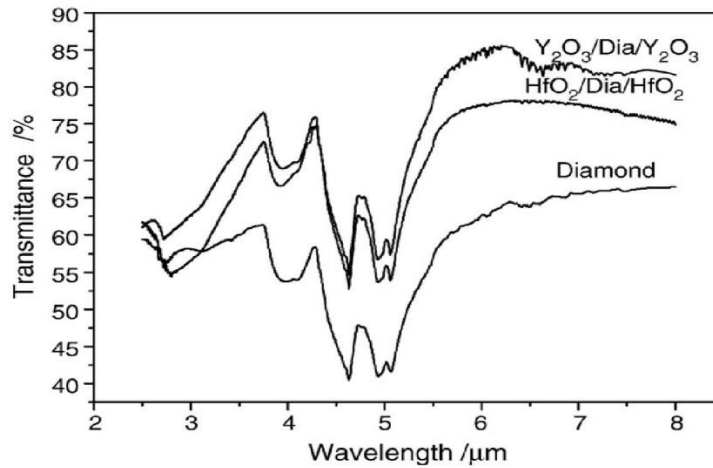


Figure 2: FTIR spectra of diamond coated with SAR HfO_2 and Y_2O_3 at the mid-wave IR range [10].

Even though the SAR coating can reduce the reflection at a specific wavelength to near zero, it can actually increase reflection at wavelengths other than that for which the coating is optimised [7]. Therefore, to produce a high performance BBAR, SAR coating can never be the ideal solution as it will not produce the desired results.

2.1.2 Broadband Multilayer

Broadband Multilayer ARC, WAR or BBAR, have been examined by Kruschwitz and Pawlewicz, 1997. They have examined 14 oxide/ fluoride thin films in the wavelength range of 0.6-12 μm and tested them for adhesion, abrasion and humidity absorption, too. The materials were coated using electron beam evaporation on Fused Silica, Zinc Selenide and Gallium Arsenide substrates. Bismuth Oxide (Bi_2O_3), Cerium Fluoride (CeF_3) and Neodymium Fluoride (NdF_3) provided good IR transmittance but yttrium (Y_2O_3) performed best overall [4].

A few years later, Mollart and Lewis, 2001, tried to develop a coating that can be used on Chemical Vapour Deposition, CVD, diamond optics that are used in airborne imaging applications in the range of 8-12 μm . The materials used were

ytterbium (Yb_2O_3), Zirconium (ZrO_2), Y_2O_3 and HfO_2 . They deposited Y_2O_3 in two different ways. Firstly, using an amorphous silicon layer to adhere the coatings to diamond optics and then deposited the yttrium coating layers. In the second method, they deposited the Y_2O_3 layers without applying an adhesion layer. Based on the multiple impact jet apparatus, MIJA, characterisation test, it was found that the coating layers started to strip when the Damage Threshold Velocity, DTV, was in the range of $220\text{--}248\text{ ms}^{-1}$. That implied the diamond silicon interface had poor adhesion and was not strong enough to hold the coatings together. The Y_2O_3 coatings, on the other hand, had a good adhesion to the diamond surface and boosted the diamond optic transmission by 7-9% [11].

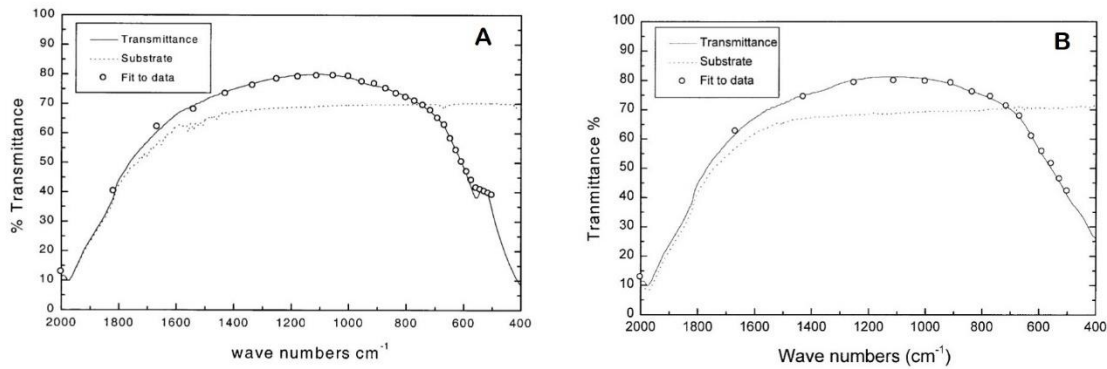


Figure 3: A, Transmission spectrum of diamond coated with $\text{Si}/\text{Y}_2\text{O}_3$. B, Transmission spectrum of diamond coated with $\text{Si}/\text{Yb}_2\text{O}_3$ [11].

In 2007 Child, et al., decided to use oxidised metals, Y_2O_3 and ZrO_2 , for ARC on diamond due to their simplicity to produce using reactive sputtering and are resistant to high temperature in oxidising environment. They also argued that both Y_2O_3 and ZrO_2 have a suitable refractive index for AR on diamond and display low loss in the IR wavebands. Even though ZrO_2 coating displayed a poor performance due to optical loss at longer wavelengths ($>10\text{ }\mu\text{m}$), Y_2O_3 showed much better results. They claimed that by using a thin QinetiQ proprietary layer followed by a quarter-wave of Y_2O_3 a robust AR coating can be achieved to be used on diamond at elevated temperatures [12].

2.1.3 Multilayer ARC

Yan, et al., 2011, have used a combination of Aluminium Nitride (AlN) and Y_2O_3 as coating materials on diamond optics. They used the AlN as an interlayer to enhance the adhesion between the diamond surface and the Y_2O_3 coating layers. The coating layers were designed to increase the transmission and the anti-oxidation characteristics of diamond optics. The target waveband for the experiment was set for LWIR, 8-10 μm where diamond has a good transmission [13]. They managed to design a coating system that increased the VAR effect by 28% when applied in the form of Y_2O_3 /AlN//diamond//AlN/ Y_2O_3 [13].

Komlenok, et al. 2018, have also designed a LWIR VAR that covers a spectral range of 8-12 μm and can withstand radiation loads with high intensity laser beam of $3MW\ cm^{-2}$ in a continuous mode laser exposure [14]. Using an ion-beam assisted evaporation technique they have deposited an uneven seven-layers structure of zinc sulphide (ZnS)/ZnSe and Lead(II) Fluoride (PbF_2) on both sides of CVD diamond plates. The total physical thickness of the structure was 5.8 μm and the deposited VAR achieved a transmission of 94% over the spectral range of 8-12 μm , Figure 4 [14].

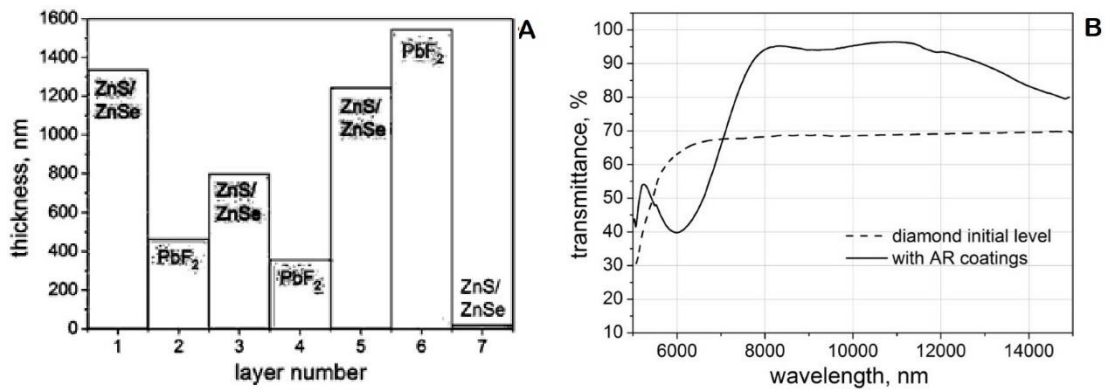


Figure 4: A, Coating structure of VAR type coating for CVD diamond plates. B, Transmission spectrum of the coated and uncoated diamond with VAR [14].

2.1.4 Dual Wavelength Band

Some of the ARCs recently developed were to function in two distinctive bands of the electromagnetic spectrum. Such coatings are called dual-band ARC, DAR,

which are constructed in a multilayer stack structure. Vapenka, Vaclavik and Mokry., 2013, designed and fabricated DAR coating on three substrates including ZnSe for visible, VIS, and IR applications. They have used ZnS and yttrium fluoride (YF_3) as target materials to create their multilayer structure coating for optical bands between 0.8-0.9 μm and between 9.5-10.5 μm using a thermal evaporation method. By laying six alternating ZnS and YF_3 layers on ZnSe substrate they managed to improve the transmittance in both VIS and IR wavebands by up to 40% [15].

Rahmlow, et al., 2013, also developed a DAR coating for application in the IR region of 3.5-5 μm and 7.8-10.5 μm wavelength. They designed their multilayer coating system with ZnS and YF_3 material on ZnSe substrate. They compared the transmission on ZnSe substrate by applying three systems of 8, 15 and 27 layers of ZnS and YF_3 . They concluded that even though the “design performance improves with an initial increase in film thickness and the number of layers, the improvement in film performance becomes increasingly small and the slope of the trend changes from nearly horizontal to nearly vertical” [16]. And in their set of experiments, they concluded that 15 layers coating system had the best transmission of 98% in the range 3.5-5 μm and 97.6% in the range of 7.8-10.5 μm wavelength at zero angle of incidence given the complexity of the designed coating systems, Figure 5 [16].

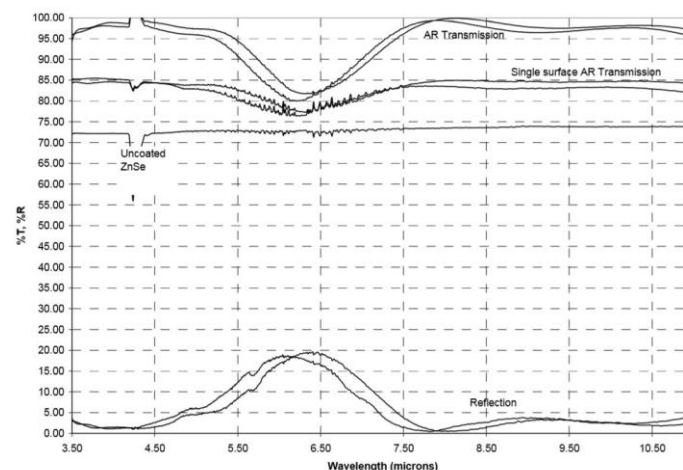


Figure 5: Transmission and reflection spectrum for DAR coated ZnSe [16].

Some other researchers have taken a similar route to design DAR coatings like [16] but with the aim to have them with low reflectance at specific wavelengths like 546nm, 1060 nm and 11000 nm. Zhupanov, et al., 2015, have used ZnSe as substrate and ZnS/YbF₃ as coating layer materials for developing a triple band ARC. They used computational manufacturing experiments to simulate the runs in order to find the optimum number of layers required to achieve high performance DAR. Based on their calculations they came up with a 9-layer structure of ZnS and YbF₃. Even though the maximum transmission was measured as 85% it has been concluded that it was still in an acceptable level [17]. The only challenge they faced was the monitoring of the refractive index of each layer during the deposition and they had to use a combination of different modern design techniques to choose the most practical design for their application [17].

2.2 Other Types of Optical Coatings

2.2.1 High Reflective Coatings

High Reflective Coatings', HRCs, function is exactly opposite to the ARCs where their main function is "to reflect a major portion of the incident light" [2]. In general, there are two types of HRCs: Metallic and Dielectric. The Metallic thin films, MTF, have been used for many centuries. The main materials used for MTF are silver, gold and aluminium. Even though the aim is always to achieve the highest possible reflection in HRC but in some cases, those coatings should also be accompanied by an extremely low absorption feature which leads to another area of HRCs, the Dielectric HRC [3].

The dielectric coatings are normally produced by stacking number of quarter-wave layers with alternating high and low RI. In such type of coatings, the higher the number of the layers the greater the reflectance. And the absorption can be made very small by using a transparent material [2].

2.2.2 Bandpass Filters

Bandpass Filters, BPS, are described by Macleod as filters that "possess a region of transmission bounded on either side by regions of rejection" [2]. The BPS are

broadly divided into broadband and narrowband filters. The main types of BPS are two edge filters in series, Farby-Perot filters, narrow-band dielectric filters, circular and linear variable filters and Phase Conjugate filters which are described in more details in reference books [1–3].

2.2.3 Beam Splitters

The main function of Beam splitters, BS, is to “divide the ray of light into two beams” [3]. The main types of BS are the Wide-Band BS, the Dichroic and the Trichroic filters. Rancourt, 1987, separates the wide-band BS into two categories: the Slab BS and the Cube SB [3]. More information about the BS can also be found in the reference books [1–3].

2.3 Substrates Materials

There are many substrates used in the optical industry; however, the material choices are normally driven by the specific wavelength region over which an optic must function. They can be classified as flexible or rigid, even though high quality optics are made of rigid materials. The below table shows number of substrate materials used for optical filters taken from [3].

Table 1: A list of substrate materials used for optical filters and their short and long wave limits [3].

Material	Short wave limit (μm)	Long-wave limit (μm)
SiO ₂	0.12	4.5
Al ₂ O ₃	0.14	6.5
MgF ₂	0.11	7.5
CaF ₂	0.13	12.0
GaAs	1.0	15.0
Si	1.2	15.0
BaF ₂	0.25	15.0
Ge	1.8	23.0
C (diamond)	0.25	80.0+
ZnSe (CVD)*	0.5	22.0
IRTRAN – 1 (MgF ₂)	0.5	7.5
IRTRAN – 2 (ZnS)	0.4	14.5
IRTRAN – 3 (CaF ₂)	0.13†	11.5
IRTRAN – 4 (ZnSe)	0.5	22.0
IRTRAN – 5 (MgO)	0.23†	9.0
IRTRAN – 6 (CdTe)	0.9	33.0

Notes: Transmission limits include surface reflections and are for a T = 10 percent level and for a sample thickness of 2 mm. IRTRAN data from Kodak Publication U-72, unless otherwise indicated. IRTRAN is an Eastman Kodak Company trademark.

*CVD Incorporated brochure.

As mentioned earlier, the aim of the project was to design a BBAR coating for ZnSe and diamond optics which covers the wavelength of 2-16 μm . Table 1, shows the ranges over which some materials are transparent. Both diamond and ZnSe cover the specified range of 2-16 μm where diamond covers the range of 0.25-80 μm and ZnSe covers the range of 0.5-22 μm .

2.3.1 Zinc Selenide (ZnSe)

ZnSe is microcrystalline in structure. Even though single crystal ZnSe is available, it is not common. It is produced using CVD by synthesis from Zinc vapour and H₂Se gas, forming as sheets on Graphite susceptors. ZnSe is normally used for high power CO₂ lasers due to its low absorption, at their 10.6 μm characteristic wavelength. It is one of the commonly used material for lenses, windows and spectroscopic ATR prism for its low absorptivity at IR wavelengths, where transmission is in the range 0.63 - 18 μm , Figure 6. As it has high refractive index of approximately 2.4 at 10.6 μm , ZnSe requires ARC if high transmission is required [18–20]. It is also used as coating material in the BBAR application in specialised wavelength bands within 0.6-18 μm spectral range [18,19].

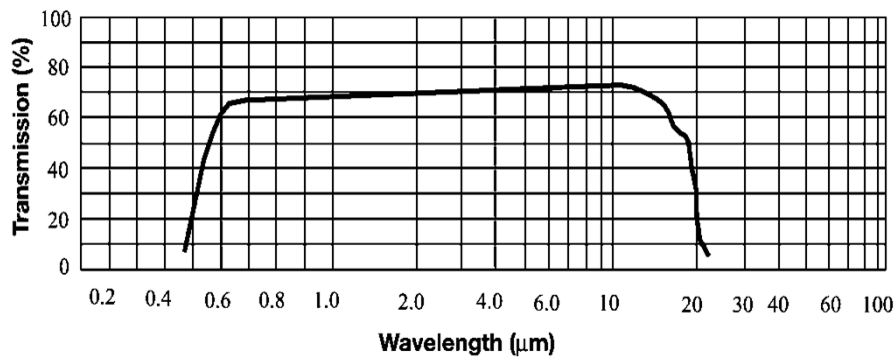


Figure 6: ZnSe IR transmission graph [18].

Different substrate thicknesses results in different transmission spectrums [21,22]. As shown in Figure 7, the transmission spectrum of ZnSe with thickness of 1 mm is much better compare with 2 & 4 mm thickness substrates.

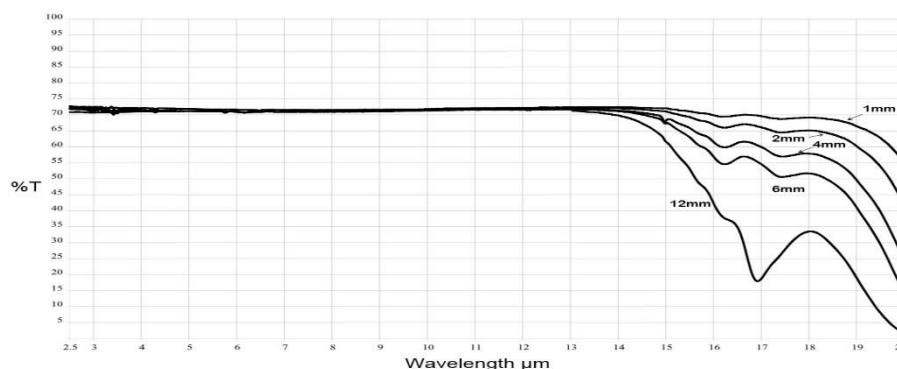


Figure 7: IR transmission graph for various thickness ZnSe substrates [20].

The ZnSe substrates which were used in this project as witness samples were IR polished optical windows with a diameter of Ø25 mm and thickness of 1 mm, Table 2.

Table 2: Specification and characteristics of the used ZnSe taken from the original data sheet [20].

Specification	Range
Transmission Range	0.6 to 21.0μm
Refractive Index	2.4028 at 10.6μm
Reflection Loss	29.1% at 10.6μm (2 surfaces)
Absorption Coefficient	0.0005 cm ⁻¹ at 10.6μm
Reststrahlen Peak	45.7μm
dn/dT	+61 x 10 ⁻⁶ K ⁻¹ at 10.6μm at 298K
dn/dμ = 0	5.5μm
Density	5.27 g/cc
Melting Point	1525°C *See notes below
Thermal Conductivity	18 W m ⁻¹ K ⁻¹ at 298K
Thermal Expansion	7.1 x 10 ⁻⁶ K ⁻¹ at 273K
Hardness	Knoop 120 with 50g indenter
Specific Heat Capacity	339 J Kg ⁻¹ K ⁻¹
Dielectric Constant	n/a
Youngs Modulus (E)	67.2 GPa
Shear Modulus (G)	n/a
Bulk Modulus (K)	40 GPa
Elastic Coefficients	Not Available
Apparent Elastic Limit	55.1 MPa (8000 psi) (1)
Poisson Ratio	0.28
Solubility	0.001g/100g water
Molecular Weight	144.33
Class/Structure	HIP polycrystalline cubic, ZnS, F43m

2.3.2 Diamond

CVD can be used to grow diamond, too. Over the last few decades, this technique has evolved dramatically and now it is possible to grow diamond by CVD in a

range of material grades with diverse characteristics that could be used for specific applications. It is broadly produced into two categories: polycrystalline and monocrystalline [23].

In general, monocrystalline CVD diamond has lower absorption and scattering compare with polycrystalline CVD diamond which makes it a better choice for BBAR applications. Both mono and polycrystalline diamonds offer extreme hardness and strength, excellent transparency, lower thermal expansion and high thermal conductivity compared with other optical materials such as ZnSe and ZnS [23,24].

The transmission spectrum of the CVD diamond is shown in Figure 8. There is a drop in the transmission in the region of the 2.5-7 μm which has been investigated in details in references [11,25–27].

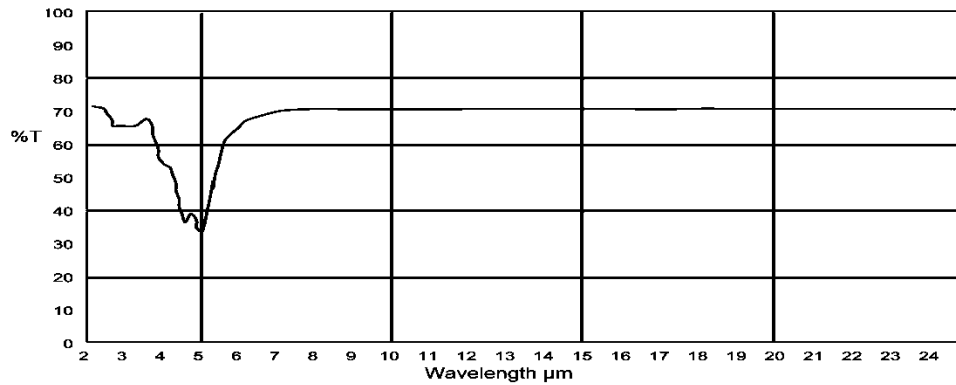


Figure 8: IR transmission spectrum of CVD diamond [20].

The optics used in the project were type IIa monocrystalline diamond prisms. Their dimensional specifications are shown in Figure 9, where the diameter of the prism is Ø2.4 mm.

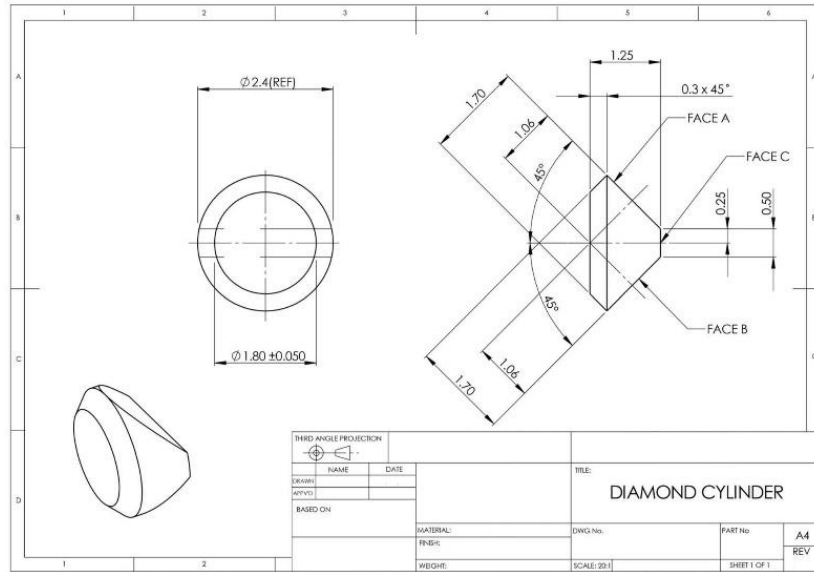


Figure 9: Drawing of the diamond prism used in the project.

The BBAR coating had to be applied to the entrance facet, Face A, and exit facet, Face B, so that the signal to noise ratio is increased through increase of energy throughput of the ATR accessory.

Since diamond and ZnSe have a similar refractive indexes, 2.3-2.4, a similar BBAR could be used on diamond once the binding layers of the coating were appropriately selected [27,28].

2.4 PVD Sputtering Techniques

There are number of methods available for optical coating deposition in the industry. The most common one is the deposition under vacuum which is known as Physical Vapour Deposition, PVD, within which there are different techniques including Thermal Evaporation, Sputtering and other energetic processes [2]. In the sputtering technique, the target material, electrode, is bombarded with energetic ions from a reactive gas, such as oxygen or nitrogen, or a transporter gas, typically argon. The ejected atoms and molecules from the target then travel toward the substrate, condense and form a film [2,3,29].

2.4.1 RF Magnetron PVD Sputtering

Research into the area of electrode and gas-phase phenomena in variety of glow discharges (especially RF discharges) has resulted in the development of many

useful processes for thin films deposition. One of the processes is called magnetron sputtering [29]. The magnetic field is generated by using a magnetron which creates a static magnetic field at the cathode location, parallel to the cathode surface. This results in more production of secondary electrons emitted from the cathode due to ion bombardment to be constrained and move in a direction perpendicular to both the electric field and the magnetic field, known as $E \times B$ drift, Figure 10 [30]. That in turn can result in an extremely dense plasma that can reach the substrate more easily and rapidly which results in a dramatic increase in the deposition rate [31].

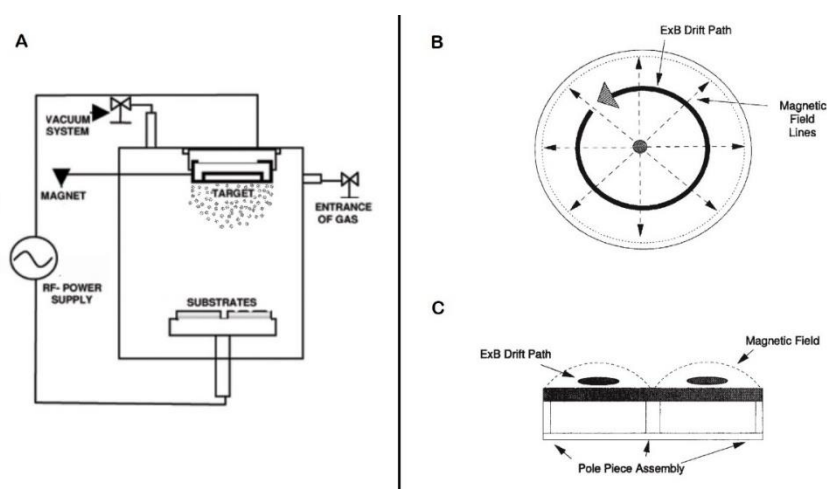


Figure 10: A, Basic illustration of RF Magnetron Sputtering. B, Top view of the cathode illustrating the magnetic field and ExB drift path caused by the magnetron. C, Side view of the cathode [30,32].

When dealing with inorganic compounds, which are electrically non-conducting materials, DC voltage cannot be applied. Therefore, RF power is applied between the two electrodes, cathode and anode. With alternating electric field resulted from the RF supply, the positive ions and electrons flow in sequence to the target and neutralise the surface charge accumulation, Figure 11 [31,33]. RF power supply is essential for the deposition of dielectric materials such as Y_2O_3 and Yb_2O_3 . Working with coating machines requires extreme care and attention when deciding on the coating parameters, such as base pressure, sputtering pressure, sputtering power, dc bias voltage and temperature which are discussed in the experimental and discussion sections.

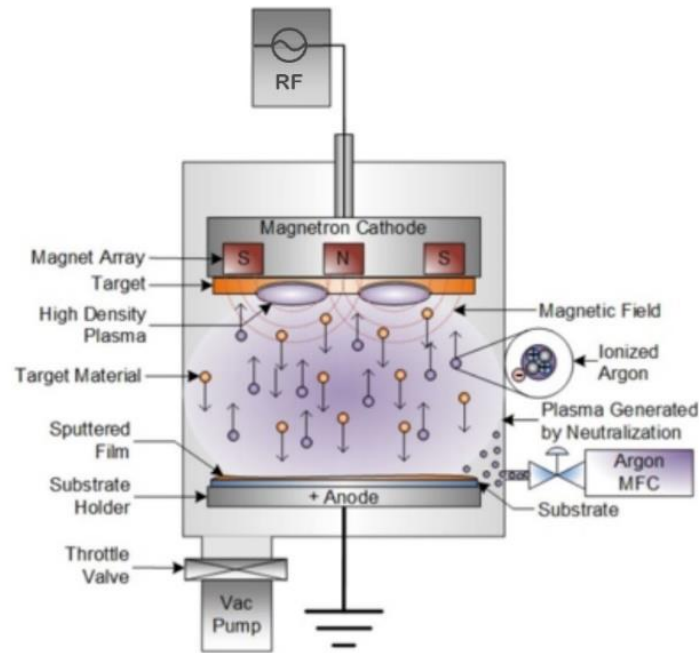


Figure 11: Detailed illustration of the RF magnetron sputtering [34].

2.4.2 Effect of RF Power Mode and DC Self-bias on Sputtering

When an RF electric field is applied to the electrode, the electrons continuously move forward and backward and hit the powered electrode at every alternating half of the RF cycle. A blocking capacitor acts as an isolator for a self-induced DC field. The impinging of electrons on the powered electrode allows the build-up of a negative DC field in addition to the AC field. This negative potential is called the DC self-bias [35].

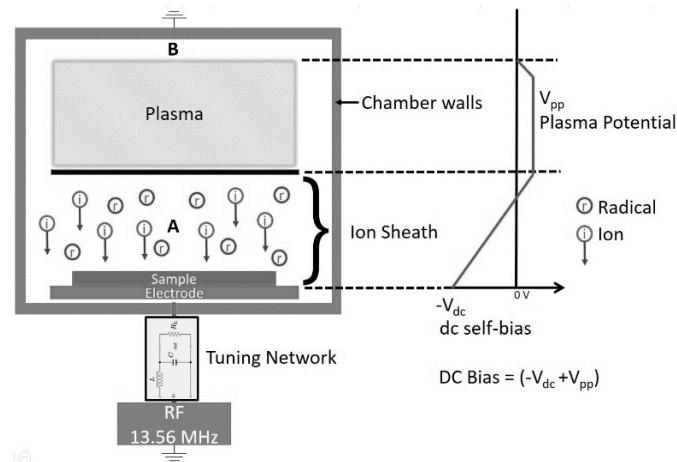


Figure 12: A simple illustration of the plasma distribution across the chamber [35].

Regions A and B, in Figure 12, are the ion sheaths which are typically a few millimetres layers that are between the plasma bulk and the electrodes, both anode and cathode [35,36].

$$DC\ BIAS = -V_{dc} + V_{pp} \quad (2-4)$$

Where *DC Bias* is the average energy of ions accelerating towards the cathode, powered electrode, V_{dc} is the self-bias voltage and V_{pp} is the plasma potential [35].

The RF power generator which is set as forward power control contributes to a proportional increase of the dc self-bias. Even though it might look as if it is a linear relationship, but in reality, this proportionality is affected by the chamber pressure, too [37,38].

The dc self-bias voltage can be controlled by the chamber pressure. The dc self-bias can increase by reducing the chamber pressure. The relationship between the dc self-bias and the pressure is linked to the mean-free-path of electrons, Figure 13. The larger mean-free-path of electrons, the higher dc self-bias voltage which its inverse proportionality to pressure is defined by the kinetic theory of gas [35,39].

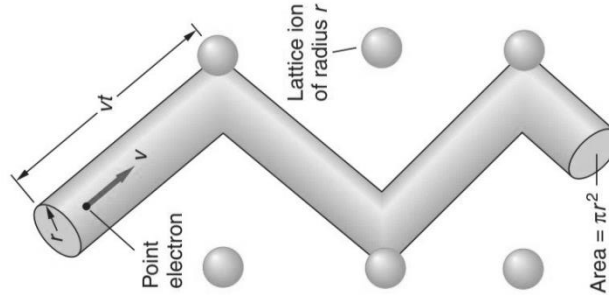


Figure 13: illustration of the mean free path [39].

The formula of the mean free path is as follows:

$$\lambda = \frac{vt}{n_a \pi r^2 vt} = \frac{1}{n_a \pi r^2} \quad (2-5)$$

where, vt is the distance the electron moves in time t and collides with every ion in the cylindrical tube of volume $\pi r^2 vt$ surrounding the path of the electron [39].

2.5 Coating Characterisation

The characterisation of a thin film depends on the process used in creating it as well as the potential application for it. Sometimes it is more sensible to use the characterisation tools to determine the properties of the thin film itself rather than the used substrate [40].

Table 3: Useful characterisation methods based on the information needed [40].

Information	Method	Comments or range of applicability
Composition		
Surface composition	XPS	Outer 10 nm
	AES	Outer 10 nm
	SIMS	Outer 1 nm
	LEIS	Outer < 1 nm
Depth distribution	Ion sputter profiles with XPS, AES, or SIMS	Less than a few μm
	RBS/NRA	Up to 2 μm
Film thickness	XRR	10 nm < thickness < 1 μm
	XPS	1 nm resolution, 10 nm depth
	TEM	Need cross-section
	RBS	Up to 2 μm
Structure	Ellipsometry	
	XRD	Phases and orientations
	RHEED	Structure during growth
	LEED	Surface structure
	TEM electron diffraction	Structure with spatial resolution
Film surface roughness	AFM	
	Profilometry	
Molecular structure	Raman/IR	Non-destructive
	TOF-SIMS	Destructive

Table 3, which was copied from Baer and Thevuthasan, 2010, organise the characterisation methods by types of information that can be extracted from a specific sample.

2.5.1 Profilometry

Profilometry can be used to measure the physical thickness of the thin film using a contact probe by dragging the stylus along a step created in the order between the coated and uncoated part of the substrate. It can also measure the substrate and thin film surface roughness [41]. There are number of vary accurate profilometers such as DektakXT which can measure step heights, trench depths and roughness on thin films, Figure 14. It provides a step height repeatability of 0.6 nm [42]. In using profilometer it is always a good practice to take multiple measurements and use the average value, so it gives better representation of the surface measured.

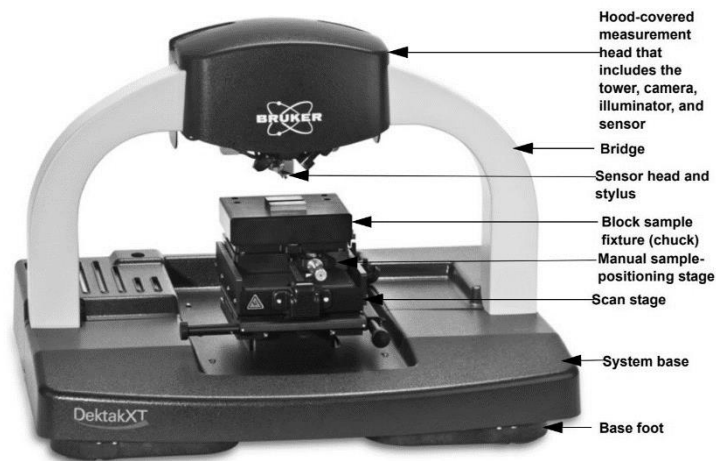


Figure 14: DektakXT profilometer [42].

2.5.2 Ellipsometry

Ellipsometry is an optical instrument used for the analysis of many thin films, Figure 15. The technique is based on the analysis of the change in the polarised light which is reflected from the sample which in turn probes the complex refractive index (or dielectric function. It can extract information such as film thickness, crystal quality, chemical composition, or electrical conductivity [40,41].



Figure 15: Rudolph Ellipsometer AutoEL used in the experiments.

Ellipsometry measures the differences in reflectivity using two parameters by recording the differences in the amplitude and phase of the reflected waves by:

$$\rho = \frac{R_P}{R_S} = \tan \Psi \exp(i\Delta) \quad (2-6)$$

Where ρ is the amplitude ratio between reflected R_P and R_S polarisation which are the amplitude reflectivity parallel and perpendicular to the incidence of light. Δ is “the difference between the phase angle of the parallel and perpendicular components of the incoming wave and outgoing wave”, and ψ is “the angle whose tangent is the ratio of the magnitudes of the total reflection coefficients” [40].

2.5.3 IR Spectroscopy

IR spectroscopy is one of the characterisation tools used for molecular structure analysis by measuring absorption of IR radiation passing through a sample. The IR radiation, over a range of different frequencies, results in molecular vibrations within molecules and different bond vibration can give different information about the compound [43,44].

Conventional IR spectrometers, Figure 16, have two beams of radiation, one passes through the sample and the other passes through a reference cell. When the radiation across a defined frequency range is passed through the sample, frequencies are absorbed by the sample which result in less radiation transmitted and collected by the detector. The detector compares the intensity passing through the sample with the intensity passing through the reference, which can also be air, and record the spectrum as transmittance against the IR wavelengths [45].

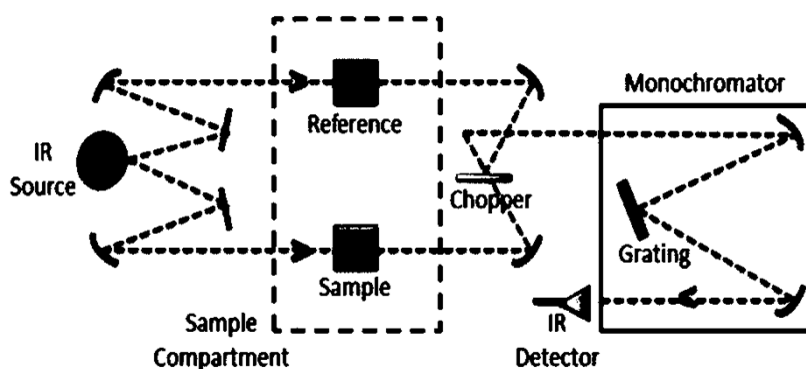


Figure 16: Schematic diagram of dispersive IR spectroscope [46].

The basic interrelated formulas in spectroscopy are:

$$c = \nu\lambda \quad (2-7)$$

where c is velocity of light 3.0×10^8 (m s⁻¹), ν is the frequency in (Hz) and λ is the wavelength in (m),

$$E = h\nu L \quad (2-8)$$

where E is the energy for a mole of photons (kJ mol⁻¹), h is Planck's constant 6.63×10^{-34} (Js) and L is Avogadro constant 6.02×10^{23} (mol⁻¹).

For calculating the frequency (cm⁻¹) of absorption of a bond, the following formula can be used:

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k(M_1 + M_2)}{M_1 M_2}} \quad (2-9)$$

where k is the force constant of a bond between atoms of masses M_1 and M_2 .

3 EXPERIMENTAL PROCEDURES, RESULTS AND DISCUSSION

3.1 Machine Description

The desktop RF dual magnetron sputtering machine, a compact research machine manufactured by IONVAC-Process, was made by an Italian based company specialised in design and manufacture of thin film deposition systems Figure 17.

The machine is a dual magnetron as it has two magnetrons where each holds a 2" inch diameter target. The targets are mounted and attached to the magnetrons on the lid of the chamber and the substrates are fixed on the rotary table which has a diameter of 180 mm, Figure 18. The deposition occurs downwards as the target material sputters the substrate which is mounted on the table. The size of the chamber is considerably small where the chamber's diameter is 200 mm and the height is 220 mm. The maximum output power is 300 W which is generated by a BDS-HF300 RF generator for low pressure plasma applications. It is controlled by a touch panel and software for automation. Only one magnetron can be connected to the power generator at a time. The cooling pipes are attached to the turbo pump and the two magnetrons to keep them cooled during operations. The water flow is controlled by a manual knob and the flow can vary depending on the number of turns that the nub is turned.

There are three ports in the chamber where the first one is located on the front of the chamber and is used as viewing window and securely sealed. The second port is located on the left side of the chamber and is connected to the turbomolecular vacuum pump. And the third and smallest port is connected to the pressure gauge. Both, vacuum pump and pressure gauge have their own control panels which can also be controlled manually.

There is a gas inlet valve that controls the flow of the sputtering gas, argon in this case, into the chamber. Before entering the chamber, the argon gas passes through a furnace at a temperature of 700 °C to make sure no oxygen enters to the chamber. A gate valve allows the gas into the chamber.

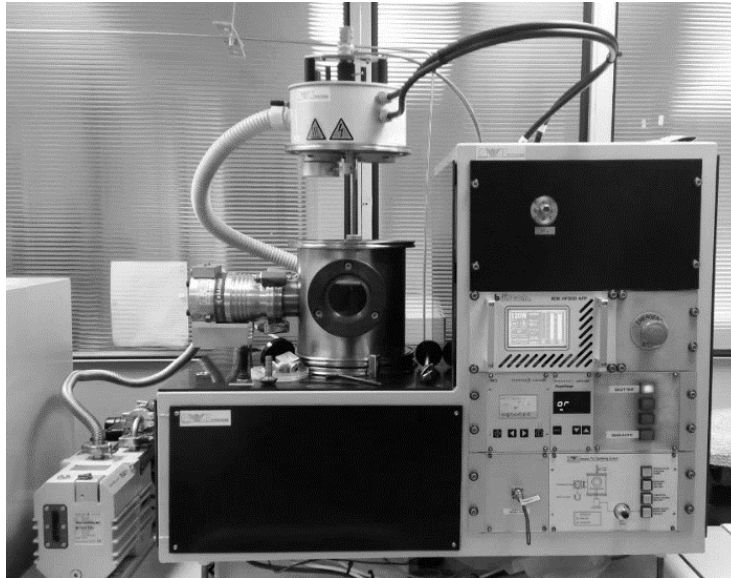


Figure 17: IONVAC-Process RF dual magnetron sputtering machine

The substrate holding table is attached to a rotary mechanism that can be rotated at a specific speed. For the purpose of the experiments, the speed has been fixed at 40 rpm. The height of the table is adjustable in accordance with the size and shape of the substrate. Even though the maximum distance between the target and rotary table is 10.5 cm, the movement is limited to a maximum of 6.6 cm due to the shutter holder obstructing any further movement. A single shutter is attached to the top lid and covers one of the magnetron at a time. The shutter can alternate depending on which magnetron is in use by operating a switching mechanism on the control panel.

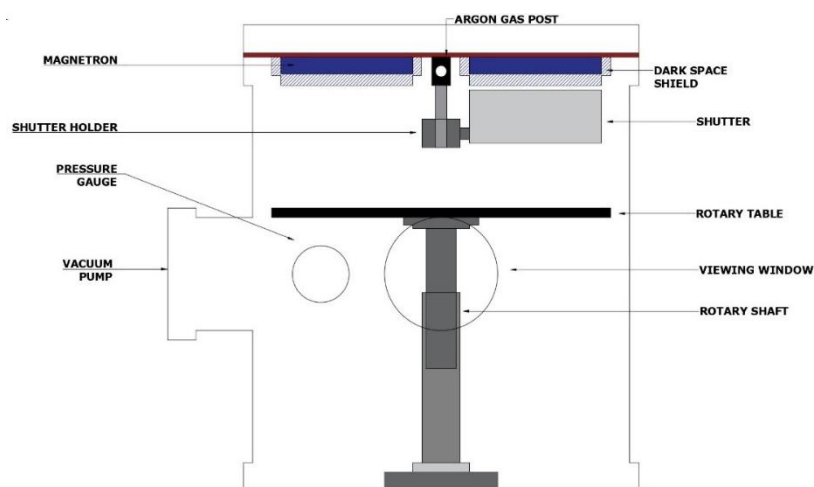


Figure 18: Schematic of the chamber from inside.

The machine is grounded at the rotary table, the base plate of the chamber and the sealants of the bottom lid of the chamber. There is a plug-in option for applying DC Bias to the rotary table, if required.

As mentioned in the introduction, the machine had no previous usage history and its capabilities and features were unknown to the company. Therefore, a basic standard operating procedure was developed to run the machine manually which is shown in the following section.

3.2 Experimental Procedure

By describing the machine and its capabilities, it was evident that the machine could not be used for coating development and production before undergoing a major restoration process. The restoration process of the machine which became a major part of this project was conducted through use of the PDCA (Plan-Do-Check-Act) cycle. PDCA is a systematic iterative 4-steps methodology used mainly in continuous improvement process. It is a tool used for systematically improving processes or machines in a direct feedback loop.

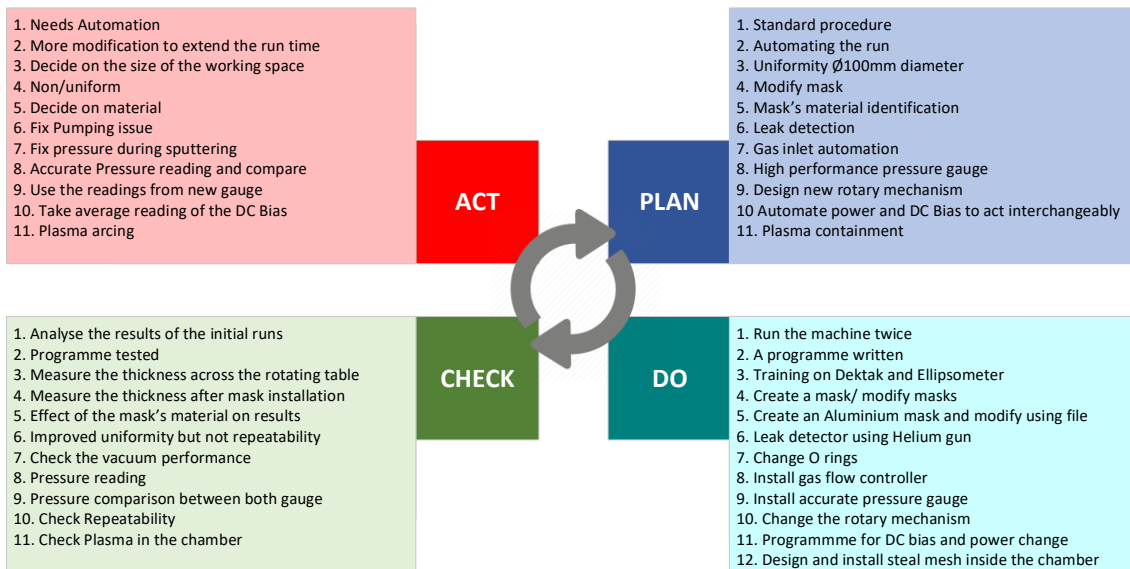


Figure 19: PCDA for restoring the sputtering machine

It starts with defining specific problems, objectives, in the PLAN section. And then it is followed by the DO section which is the implementation stage with focus on data collection. In the CHECK section, the collected data are then analysed, and

the results are compared against the expected results. On the ACT section, based on the results obtained, conclusions are made on whether a specific change should be made or not. And the cycle repeats itself until all objectives are met. For more details on the PDCA process, refer to references [47][48][49]. Figure 19 shows the whole PDCA cycle used in restoring the machine.

Even though the PDCA cycle was the basis for the whole machine restoration, it was only structurally discussed in developing the standard procedure and machine automation to demonstrate its importance and its impact in the overall restoration process.

Following the PDCA cycle, to have consistency in the results, a standard procedure for running the machine was written and followed in the plan section. The procedure started with substrate preparation where a silicon strip was cut from a silicon wafer. Then, it focused on the machine set up including step-by-step instructions on machine pumping down to base pressure, gas line bleeding, warming up period, sputtering power set up, sputtering pressure control, venting the machine and finally sample measurement. A detailed flow chart describing the standard procedure is shown in Figure 20.

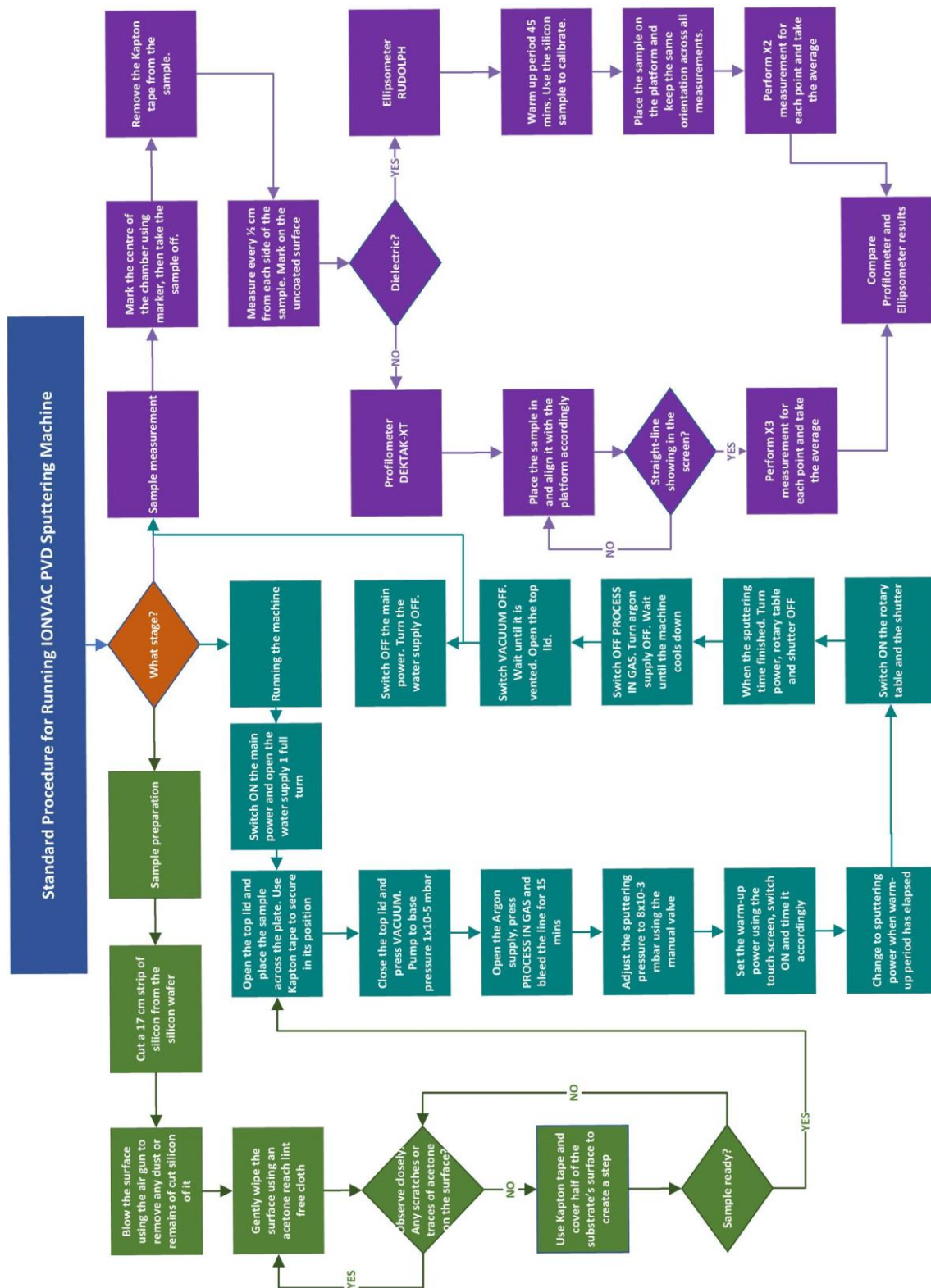


Figure 20: Standard procedure for running the IONVAC sputtering machine, including sample preparation and measurement.

In the second step of the PDCA cycle, the machine was run twice, using similar parameters as shown in Table 4 in order to check its repeatability. The parameters included the warm-up period which is the time were the machine is sputtering while the shutter is closed. The pressure, which is the recorded pressure before and while sputtering. And the set power during warm up period and actual sputtering. While following the procedure, it was seen that there were some variations in the recorded parameters including the sputtering pressure and dc bias.

Running the machine only two times was one of the weaknesses in the analysis at this stage, because repeatability cannot be determined by having results from two trials only. More runs were required to analyse the repeatability of the machine. However, due to time constraint, it was decided to carry out with the experiments and use at least three trials to determine the repeatability of the machine.

Table 4: Recorded parameters for Trial 1 and Trial 2.

Parameters						Parameters				
Trial 1	Warm-up time (mins)	Pressure (mbar)	DC (v)	Power (w)		Trial 2	Warm-up time (mins)	Pressure (mbar)	DC (v)	Power (w)
	5	8.92E-03	n/a	50			5	8.83E-03	n/a	50
	Sputtering time (mins)	Pressure (mbar)	DC (v)	Power (w)			Sputtering time (mins)	Pressure (mbar)	DC (v)	Power (w)
	15	8.23E-03	338	50			15	8.48E-03	330	50

On the third step of the PDCA cycle, the coating thickness was measured on the long silicon strip substrate, which was placed across the centre covering the whole diameter of the rotary table, Figure 21, using the profilometer, DektakXT.



Figure 21: Silicon strip taped down across the rotary table using Kapton tape.

For every 0.5 cm away from the centre of the substrate, three measurements were performed. The average of the three measurements was used for identifying the coating thickness. Thickness variations in the results were obvious by looking at the profile of the coating in Figure 22. The maximum thickness in Trial 1 was 161 nm while the maximum thickness in Trial 2 was 174 nm.

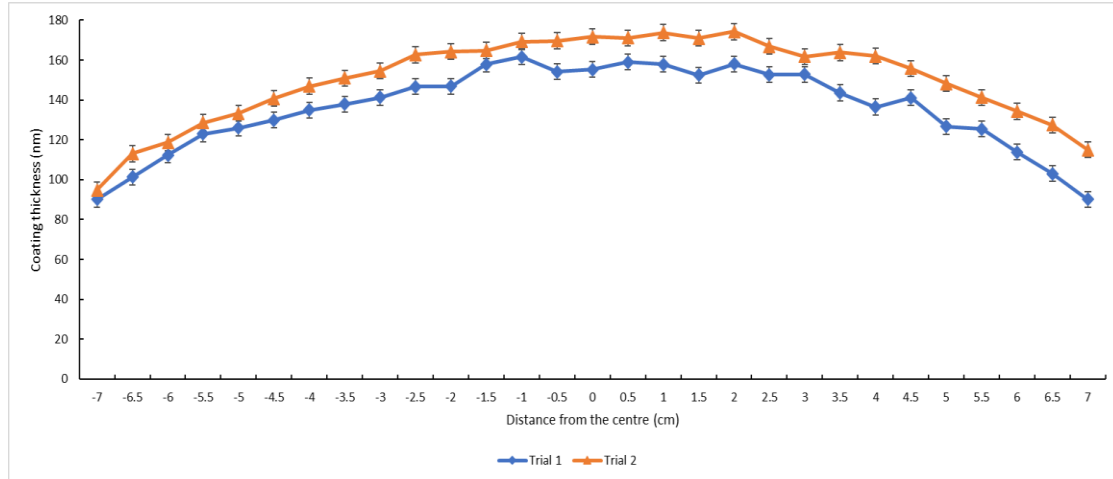


Figure 22: Coating thickness measurement in trial 1 and trial 2 before automation.

It was very difficult to control the process parameters to the same values and at the same times at each run, e.g., the warm-up time, ramp-up power and open and close the shutter promptly. Even though the machine was run manually, it had the hardware and software capability to be automated.

On the fourth step of the PDCA cycle, based on the results obtained from the step three, it was decided that process automation was vital for controlling basic parameters and steps while the machine was in operation.

Therefore, a programme was developed to automate the machine that allowed the user to control the input RF power, the substrate table rotation, the shutter open and close commands and the timing for each step during the sputtering. The programme was able to include functions necessary in the warming up and cooling down periods.

The automated programme resulted in more consistency on the basic operations of the machine which in turn allowed to focus on other enhancement to improve machine's performance and repeatability.

3.3 Experimental Results and Discussion

3.3.1 Coating Materials

Before going into the details of the machine restoration process, the coating materials had to be selected. Materials used in the development of ARC for ZnSe and diamond optics include ZrO_2 , ZnS , Y_2O_3 , Yb_2O_3 , YbF_3 , YF_3 , SiO_2 , MgF_2 , HfO_2 , ZnSe and PbF_2 which were discussed previously in the literature review.

From the materials been discussed, only few could be potentially used for the project to develop ARC. To identify the most suitable materials, a qualitative approach known as multiple decision criteria was used. Four criteria were identified to be key in the process of selecting most suitable materials for ARC. The first three criteria were based on the material showing excellent transmission in the short, mid, and long wavelength of the IR region. The Short Wave IR Range is called (SWIR) which covers the 1-3 μm wavelengths. The Mid Wave IR Range, (MWIR) covers the 3-5 μm wavelengths. And the Long Wave IR Range (LWIR) covers 8-12 μm wavelengths. The fourth defined criteria was that the material should have good adhesion to the diamond surface. This was established by collating different research papers and scoring the materials used against the predefined criteria. The scoring for the first three criteria was based on score from 0-3, zero being poor transmission and three being excellent transmission. And the scoring for the fourth criteria was either:

- -1, for poor adhesion,
- 0, for no information, and
- 1, for good adhesion

Based on the scoring results, the most promising materials to be used for ARC development in the project were Y_2O_3 and Yb_2O_3 .

Table 5: Multiple decision criteria for material selection for ARC development

Material Selection using Multiple Decision Criteria							
Material	Chemical Formula	Criteria				Score	Literature references
		SWIR 1-3 m	MWIR 3-5 m	LWIR 7-14 m	Adhesion (+/-1)		
Silicon	Si	3	3	0	1	7	[6][9][11][18]
Silica	SiO ₂	3	3	0	1	7	[8][18]
Magnesium Fluoride	MgF ₂	3	3	1	0	7	[6][18]
Zinc Sulfide	ZnS	3	3	2	0	8	[6][14][15][16][17]
Zinc Selenide	ZnSe	1	3	3	1	8	[6][14][18]
Ytterbium Fluoride	YbF ₃	1	3	3	1	8	[17]
Yttrium Fluoride	YF ₃	3	3	2	0	8	[15] [16]
Lead (II) Fluoride	PbF ₂	0	0	3	-1	2	[4][14]
Hafnium Dioxide	HfO ₂	3	3	3	-1	8	[4] [10][11]
Zirconium Oxide	ZrO ₂	3	3	0	1	7	[4][11]
Yttria	Y₂O₃	3	3	3	1	10	[4][10][11][12][13]
Ytterbia	Yb₂O₃	3	3	3	1	10	[11]

Yttria (Y₂O₃)

Is a white rare-earth dielectric ceramic that is air-stable. It is normally in the form of powder but using Hot Isostatic Pressing, HIP, can be formed into different size target for sputtering purposes. It is a promising material for optical applications due to its excellent properties. It has high refractive index, high band gap energy, great thermal conductivity and broad transparency range [50–52].

Table 6: General specifications of Yttria target [2,53].

Material	Symbol	Melting Point (°C)	Density of g/cm ³ @20°C	Refractive Index @589 nm	Target Diameter (mm)	Target thickness (mm)
Yttria	Y ₂ O ₃	2410	5.01	1.79	Ø50.8	3.18

Ytterbia (Yb₂O₃)

Is one of the more commonly encountered oxides of ytterbium. It is also a white dielectric ceramic that is stable in air. Yb₂O₃ targets are also manufactured by forming the powder into solid plates through HIP process. It is a highly insoluble thermally stable suitable for glass, optic and ceramic applications. High purity

Yb₂O₃ targets with the highest density and smallest possible grain sizes are used in CVD and PVD of optical components [54].

Table 7: General specifications of Ytterbia target [2,53].

Material	Symbol	Meting Point (°C)	Density of g/cm ³ @20°C	Refractive Index @550 nm	Target Diameter (mm)	Target thickness (mm)
Ytterbia	Yb ₂ O ₃	2346	9.17	1.9	Ø50.8	3.18

After choosing Y₂O₃ and Yb₂O₃ as target materials, it was time to progress into machine restoration.

3.3.2 Coating Thickness Uniformity

Making sure the coating thickness is uniform across the substrate is crucial in developing optical thin films. Non-uniform thickness directly resulted in varying refractive index which resulted in having poor performance AR films. To check the coating uniformity of the machine, in trial 3, the machine was run for 30 minutes using the new automation setup. The recorded process parameters were detailed in Table 8.

Table 8: Process parameters for trial 3.

Parameters					
Trial 3	Warm-up time (mins)	Pressure (mbar)	DC	(v)	Power (w)
	2	1.60E-02		n/a	50
	4	1.60E-02		n/a	70
	5	1.60E-02		n/a	80
	Sputtering time (mins)	Pressure (mbar)	DC	(v)	Power (w)
	0	1.60E-02		328	90
	15	1.60E-02		358	90
	30	1.60E-02		356	90

Figure 23 clearly showed that the deposition was not uniform and there was major thickness variation across the whole chamber. The highest deposition thickness was measured in the centre of the chamber and the lowest was measured on the sides, near the walls of the chamber. The refractive index of the deposited thin film was also measured using the Ellipsometer at every 5 mm across the substrate. The refractive index turns to change in a similar pattern as the thickness but taking an inverse shape.

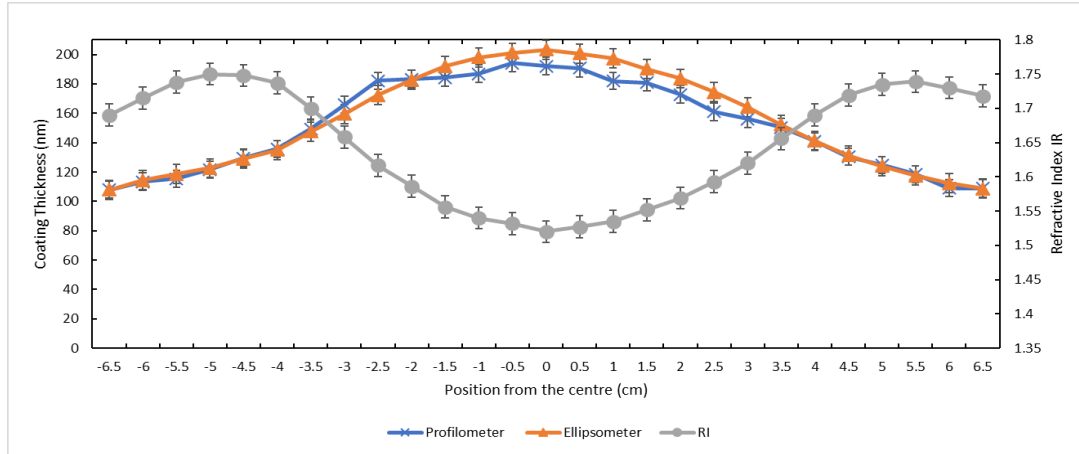


Figure 23: Trial 3, coating thickness uniformity measurement.

To be able to produce high performance AR thin films, it was determined that the thickness uniformity was key. Lack of uniformity causes a shift of characteristic wavelength and thickness errors could cause serious reduction in thin films performance [2].

Therefore, it was decided to create a mask to improve the coating uniformity in the chamber. Before doing so, a decision was to be made on the size of the uniform area within the working space. The size of the effective working space was decided by the space required to fit in 150 diamond optics with dimensions of Ø2.4mm diameter. The specifications of the diamond prisms were detailed in Figure 9.

A drawing of whole working space was created, and a jig was designed to be able to hold the 150 diamond prisms and the ZnSe witness sample. Based on the produced drawing, Figure 24, it was decided that the effective working space where the coating thickness should be uniform is Ø10 cm along the centre of the chamber.

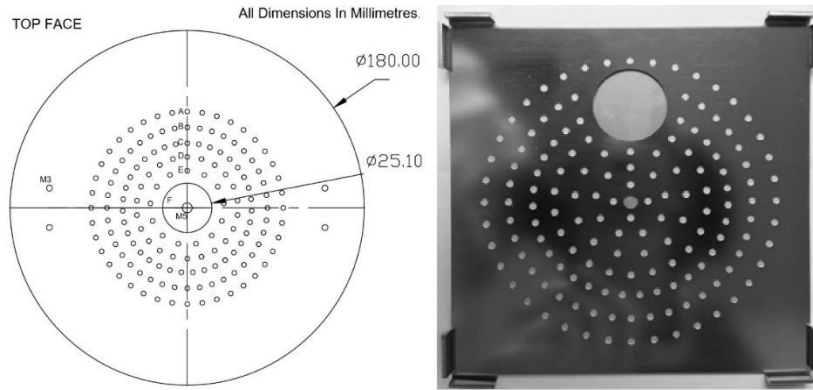


Figure 24: Left: Proposed drawing for the jig. Right, Fabricated jig to hold 150 diamond optics and a witness sample.

As mentioned earlier, the position of the rotary table could only be adjusted in the range of 6.6 cm, limited by the length of the rotary shaft from the bottom and by the shutter fixture from the top. And the closest distance between the target and the substrate was 3.2 cm. The next step was to set the rotary table at the right height which basically dictates the substrate-target distance. Zhang, et al, 2012, in their research of thin film thickness uniformity concluded that in general the thickness uniformity will increase with the decrease of target-substrate distance [55]. Learning from it, it was decided to measure the thickness uniformity at different heights by gradually raising the rotary table towards the target.

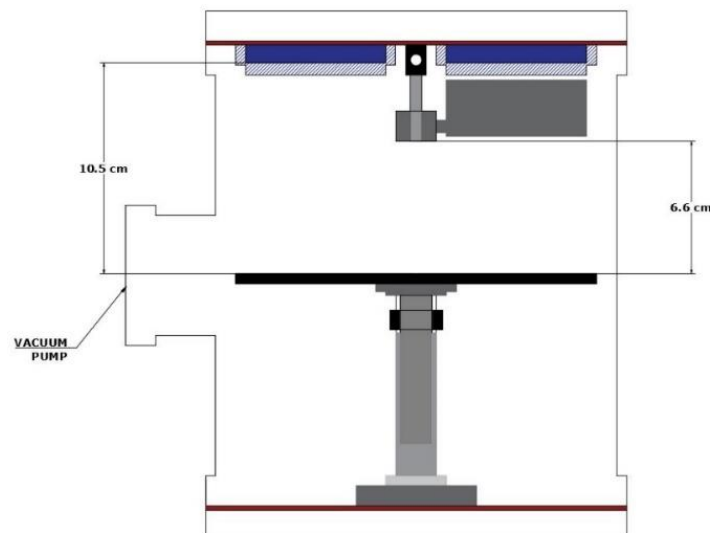


Figure 25: The position of the rotary table at the furthest point from the target.

In trial 4, the target material was SiO₂ and the machine was run for 30 mins. The recorded process parameters are shown in Table 9.

Table 9: Process parameters for trial 4.

Parameters				
Trial 4	Warm-up time (mins)	Pressure (mbar)	DC (v)	Power (w)
	4.5	1.56E-02	n/a	50
	5	1.56E-02	n/a	50
	Sputtering time (mins)	Pressure (mbar)	DC (v)	Power (w)
	0	1.56E-02	398	120
	15	1.57E-02	378	120
	30	1.57E-02	370	120

Looking at the thickness profile, at the lowest height which is shown in Figure 25, the maximum thickness was around 80 nm and the shape of the coating profile was a normal bell shape with a coating uniformity of 5 cm in the centre of the chamber Figure 26.

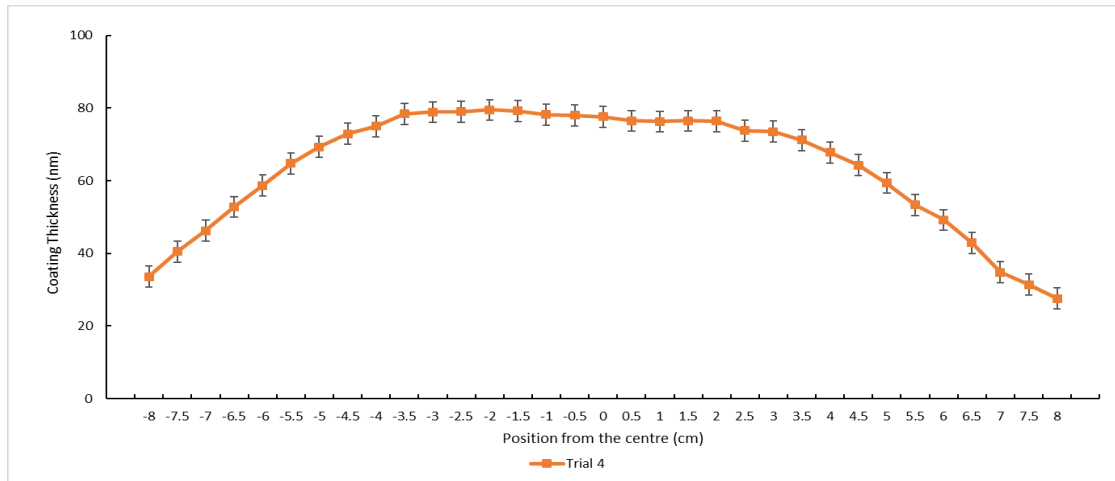


Figure 26: Coating thickness and uniformity at the furthest point from the target.

In trial 5, when the table was raised only above the vacuum port, the thickness has improved while the shape of the coating profile remained same, as shown in Figure 27. The recorded process parameters are in Table 10.

Table 10: Process parameters for trial 5.

Parameters				
Trial 5	Warm-up time (mins)	Pressure (mbar)	DC (v)	Power (w)
	4.5	1.52E-02	n/a	50
	5	1.52E-02	n/a	50
	Sputtering time (mins)	Pressure (mbar)	DC (v)	Power (w)
	0	1.54E-02	450	120
	15	1.53E-02	432	120
	30	1.52E-02	434	120

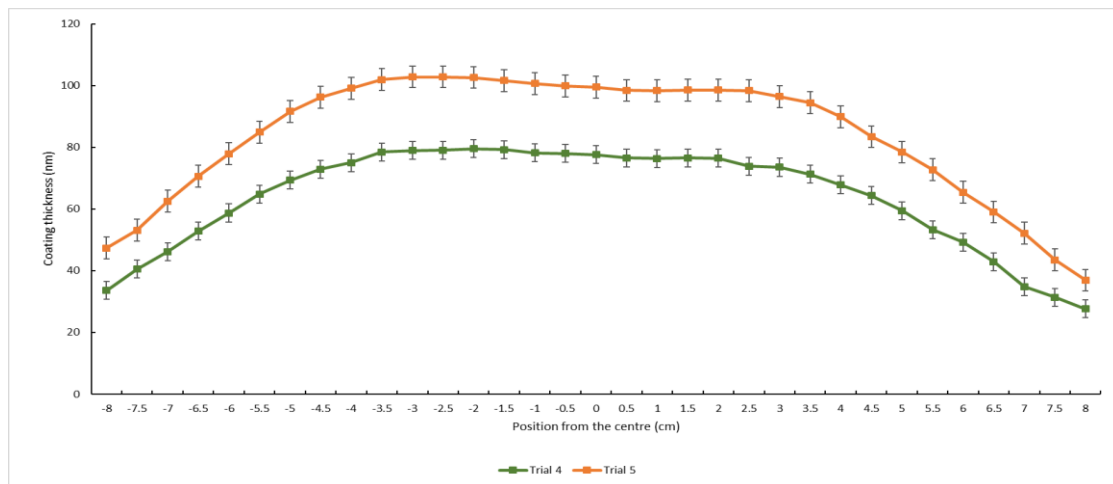


Figure 27: Coating thickness and uniformity at height above the vacuum port.

Next, the table was raised as close as possible to the target. This time, the overall thickness dropped from maximum 101 nm in trial 5 to 89 nm in trial 6. Also, the shape of the coating profile was influenced by the magnetron's magnetic field and resulted in an uneven thickness profile in the centre of the chamber as shown in Figure 28. The recorded process parameters are in Table 11.

Table 11: Process parameters for trial 6.

Parameters				
Trial 6	Warm-up time (mins)	Pressure (mbar)	DC (v)	Power (w)
	5	1.52E-02	n/a	50
	Sputtering time (mins)	Pressure (mbar)	DC (v)	Power (w)
	0	1.55E-02	398	120
	15	1.56E-02	352	120
	30	1.57E-02	370	120

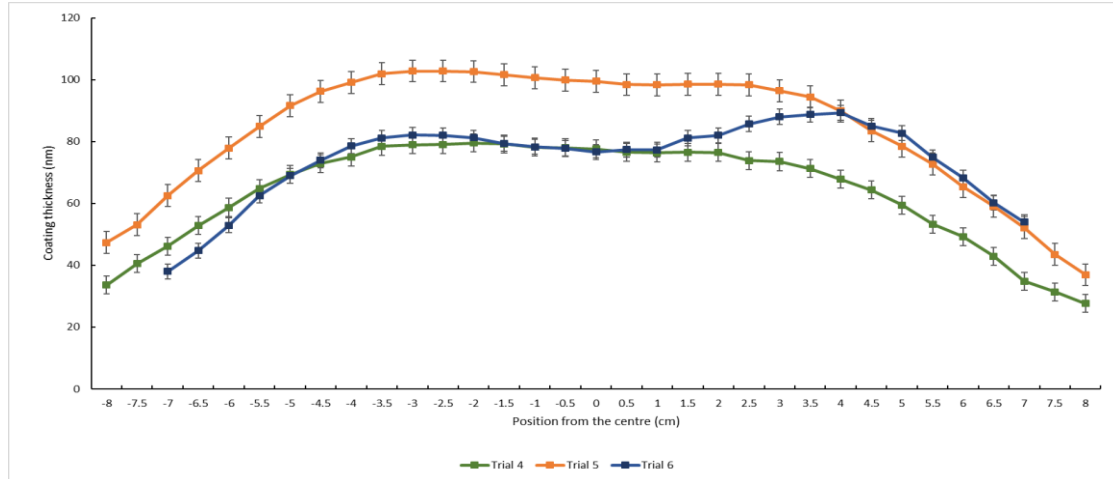


Figure 28: Coating thickness and uniformity at three different heights.

After identifying the best position for the rotary table which was 7.1 cm away from the target surface, the next step was to create a mask, Figure 29. The mask acts as an interceptor of the sputtered material between the target and substrate and can improve uniformity [56].

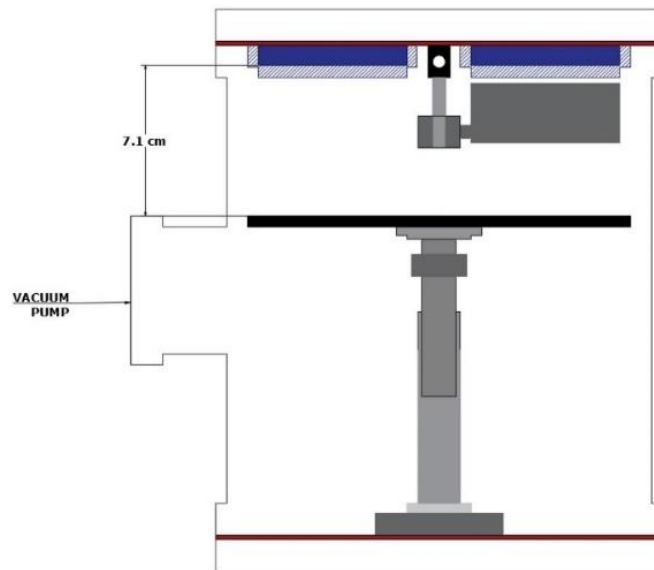


Figure 29: The identified ideal position for the rotary table.

The mask had to be designed in such way that could assist in achieving thickness uniformity of a Ø10 cm area in the centre of the working table. Also, it had to fit within the space between the target and the rotary table considering the presence of the magnetron's shutter and any other obstructing objects, Figure 30.

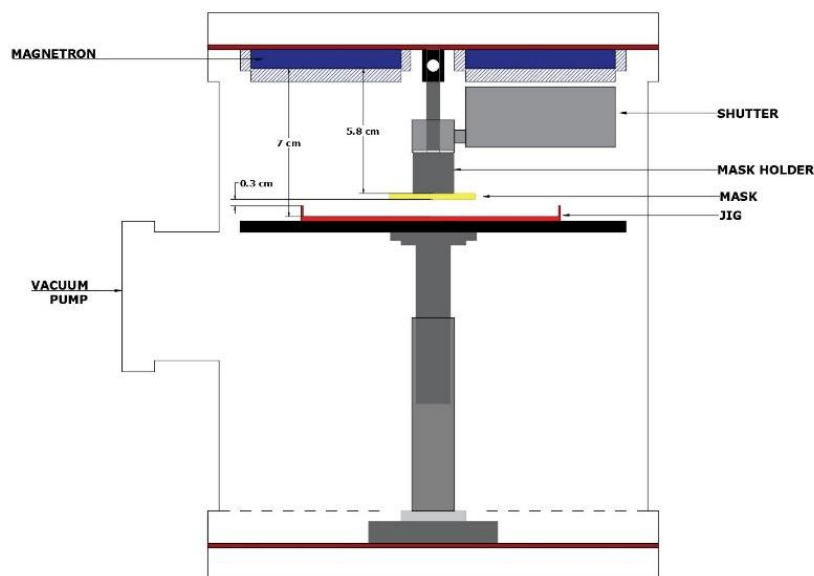


Figure 30: Mask's position in the chamber.

Taking the thickness of the jig into account, the mask could only be placed below the shutter. Before developing the mask, a mask holding fixture was designed and fabricated. It was designed to fit it on top of the argon gas inlet post with clearance holes on its sides to avoid blocking the gas flow entering the chamber. The material used in the fixture was stainless steel and it was made of two-part assembly unit. The first part was a collar with a long post which was designed to fit on the gas inlet post. The second part was a movable collar used to hold the mask and adjust its position, Figure 31.

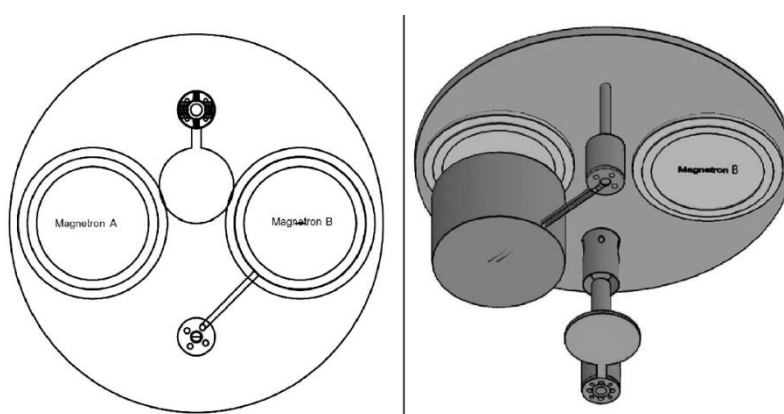


Figure 31: Left, Drawing of the magnetrons and the location of the temporary mask holder and mask. Right, 3D view of the mask and mask holder.

Initially, a circular shape mask with diameter of Ø4.00 cm was created to cover the centre of the working space. By doing so, it was hoped it can bring the coating thickness of the centre down and change it more like the sides of rotary table. An extension arm, with a length of 1 cm and width of 0.3 cm was used to connect the mask to the movable collar as illustrated in Figure 31. The mask was made of 1 mm thick aluminium sheet, Figure 32.



Figure 32: Mask #1 made of 1 mm thick aluminium.

Two trials, 7 & 8, were performed with sputtering time of 30 mins. The process parameters for both trials are shown in Table 12. The power was ramped up during the 5 mins warm up period from 50 to 70 W, before sputtering at 120 W.

Table 12: Process parameters for trials 7 & 8.

Parameters				
Trial 7	Warm-up time (mins)	Pressure (mbar)	DC (v)	Power (w)
	4	1.50E-02	n/a	50
	5	1.50E-02	n/a	70
	Sputtering time (mins)	Pressure (mbar)	DC (v)	Power (w)
	0	1.52E-02	424	120
	15	1.54E-02	426	120
	30	1.54E-02	426	120

Parameters				
Trail 8	Warm-up time (mins)	Pressure (mbar)	DC (v)	Power (w)
	1	1.50E-02	n/a	50
	3	1.50E-02	n/a	70
	5	1.50E-02	n/a	80
	Sputtering time (mins)	Pressure (mbar)	DC (v)	Power (w)
	0	1.58E-02	430	120
	15	1.60E-02	426	120
	30	1.60E-02	426	120

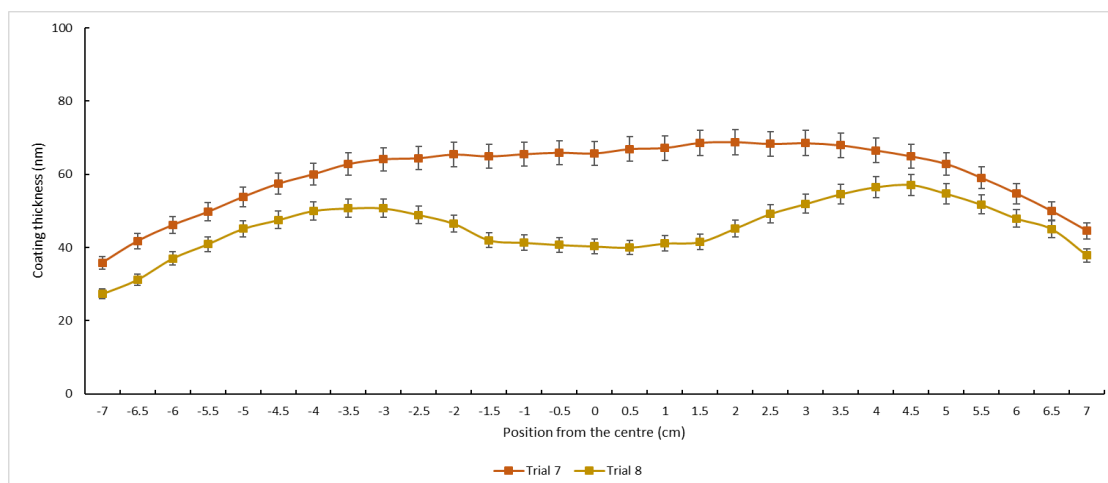


Figure 33: Trial 4 and 5 using the Mask #1.

As it is obvious from Figure 33, the coating profile has changed, and the coating profile was no longer flat in the centre due to the insertion of the mask between the target and the substrate. Table 13 shows the average measurements of the coating from the centre to the sides of the substrate in both trials. It was also noticed that the mask has affected the overall coating thickness rather than only the centre part. The coating thickness from 3.5 – 5 cm has dropped in average by 9.9 nm. The variation in uniformity from the centre to 5 cm was calculated as 25%.

Table 13: Average measurements from the centre to the sides of the substrate for trials 7 & 8.

Average measurement from the centre to the side (Ellipsometer)					
Left side	Right side	Left measurements (nm)	Right measurements (nm)	Average Trial 8 (nm)	Average Trial 7 (nm)
-7.5	7.5	0	26	26	34.6
-7	7	27.3	37.8	32.55	40.15
-6.5	6.5	31.2	45	38.1	45.8
-6	6	37	47.9	42.45	50.4
-5.5	5.5	40.9	51.7	46.3	54.35
-5	5	45.1	54.7	49.9	58.3
-4.5	4.5	47.5	57.1	52.3	61.15
-4	4	50	56.5	53.25	63.25
-3.5	3.5	50.7	54.6	52.65	65.35
-3	3	50.7	51.9	51.3	66.3
-2.5	2.5	48.9	49.2	49.05	66.35
-2	2	46.5	45.2	45.85	67.1
-1.5	1.5	42	41.5	41.75	66.75
-1	1	41.3	41.1	41.2	66.35
-0.5	0.5	40.7	40	40.35	66.4
0	0	40.3		40.3	65.7
Uniformity centre to 5 cm =				12.95	8.8

The next step was to modify the mask and get the thickness uniformity across 0-5 cm as flat as possible. The target material was changed to Y_2O_3 as it was one of the selected material for the experiments. The target was mounted on

magnetron B. The mask was modified from 1-7 cm by sticking cardboard on the original mask, Figure 34.

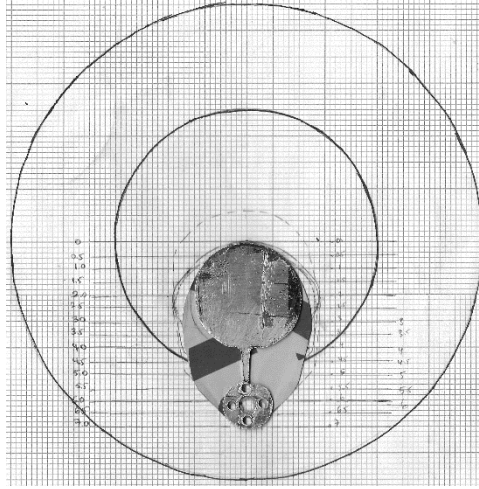


Figure 34: Demonstration of Mask #2, aluminium mask thickened from 1-7 cm by cardboard.

The base pressure was recorded as 4.4×10^{-5} mbar and sputtering pressure at 1.6×10^{-2} mbar. The warm up period was set for 5 mins and the sputtering time was set to 45 mins. The power for sputtering Y_2O_3 was set to 90 W and the power was ramped up during the warm up period from 50 to 70 W.

The recorded process parameters are in Table 14.

Table 14: Process Parameters for trial 9.

Parameters					
Trial 9	Warm-up time (mins)	Pressure (mbar)	DC	(v)	Power (w)
	2	1.60E-02		n/a	50
	4	1.60E-02		n/a	70
	5	1.60E-02		n/a	80
	Sputtering time (mins)	Pressure (mbar)	DC	(v)	Power (w)
	0	1.60E-02		320	90
	15	1.60E-02		324	90
	30	1.60E-02		304	90
	45	1.60E-02		296	90

Based on the results obtained, it was obvious that the modified mask had to be altered more by thinning the mask from 3-5 cm away from the centre, Figure 35. The variation in thickness from the centre to 5 cm was 13.9%, Table 15.

Table 15: Coating thickness measurements for trial 9.

Position from the centre	Average (nm)
7	112.9
6.5	113.8
6	116.75
5.5	119.05
5	120.95
4.5	124.15
4	127.95
3.5	132.9
3	138
2.5	140.6
2	140.05
1.5	137.5
1	135.95
0.5	135.45
0	136.9
Uniformity Centre to 5 cm=	19.65

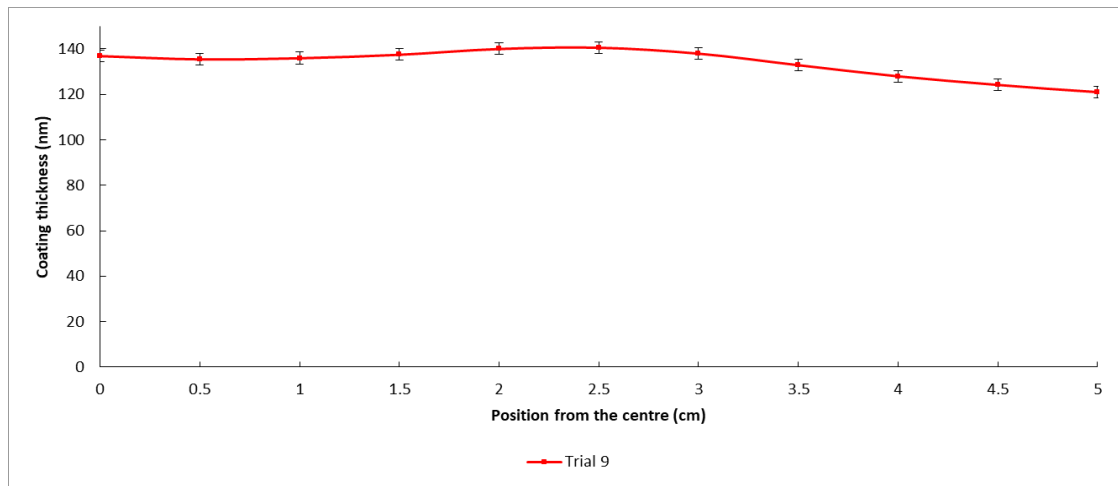


Figure 35: Trial 9 using Y_2O_3 target and mask #2.

The mask was modified 7 times after that, by thinning and thickening it from different places each time. During each run all parameters were kept constant. The sputtering pressure, which is controlled by a manual gas inlet valve, was also kept constant by constantly adjusting the pressure to 1.6×10^{-2} mbar. The only parameter changing from one run to another was the dc bias voltage. It was ranging from 298 to 304 V.

The average coating thickness for all 7 runs was calculated in order to evaluate the thickness uniformity, Table 16.

Table 16: Coating thickness for trial 10-16 and average of all 7 trials.

Position from the centre	Trial 10	Trial 11	Trial 12	Trial 13	Trial 14	Trial 15	Trial 16	Average
7	69.1	85.2	79.9	86	83.3	86.6	86.6	82.39
6.5	67.9	88.7	83.2	88.2	87.6	90.35	90.35	85.19
6	70.05	92.8	86.9	91.15	90.65	93.7	93.7	88.42
5.5	71.85	95.15	88.95	94.25	93.5	97.05	97.05	91.11
5	73.4	97.35	91.9	95.7	95.65	98.9	98.9	93.11
4.5	75.25	98.7	93.9	97.35	96.65	101	101	94.84
4	77.7	99.65	95.95	98.85	99.015	102.9	102.9	96.71
3.5	79.95	101	97.9	100.3	101.49	103.65	103.65	98.28
3	82.1	102.85	99.25	102.15	102.95	104.75	104.75	99.83
2.5	83.6	104.15	100	103.75	105.1	105.1	105.1	100.97
2	84.3	104.55	100.6	104.55	106.9	105	105	101.56
1.5	84.7	103.25	100.5	104.55	107.15	104.3	104.3	101.25
1	84.8	102.75	100.75	104.45	107.6	102.1	102.1	100.65
0.5	85.05	104.2	100.75	104.5	108.05	100.75	100.75	100.58
0	85	104.7	100.4	104.7	108.1	99.8	99.8	100.36
Uniformity Centre to 5 cm=	11.65	7.35	8.8	9	12.45	5.85	9.25	8.44

The average reading, of the 7 trials, showed very promising results as the uniformity from center to 5 cm has improved to 8.44 nm. However, the variation in thickness should be within 5 nm in a 100 nm thick film which translate to $\pm 5\%$ of the overall film thickness.

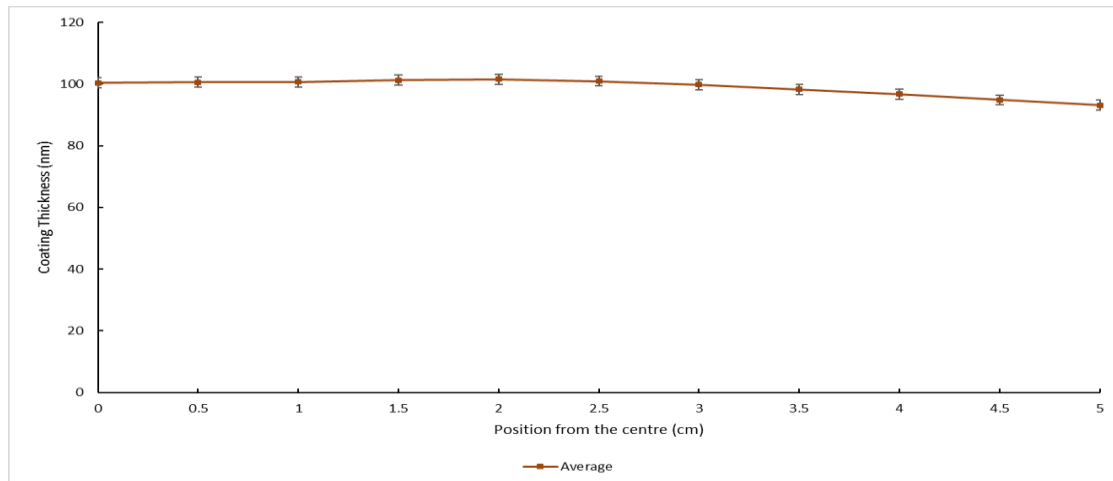


Figure 36: Average coating profile of trial 10-16.

By looking at the average coating profile in Figure 36, it was decided to modify the mask, by thinning it from 3-5 cm, in order to increase the coating thickness on that area, Figure 37.

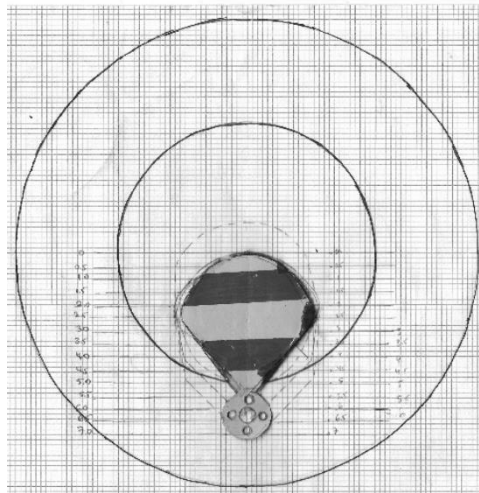


Figure 37: Demonstration of Mask #3 modified by thinning it from 3-5 cm.

Trial 17 was run by the same parameters shown in Table 17. The only changing parameter was the dc bias which was giving different reading at each run.

Table 17: Process Parameters for trial 17.

Parameters				
Base Pressure (mbar):		4.40E-05		Time to Pump down (mins): 20:00
Trial 17	Warm-up time (mins)	Pressure (mbar)	DC (v)	Power (w)
	2	1.60E-02	n/a	50
	4	1.60E-02	n/a	70
	5	1.60E-02	n/a	80
	Sputtering time (mins)	Pressure (mbar)	DC (v)	Power (w)
	0	1.60E-02	284	90
	15	1.60E-02	290	90
	30	1.60E-02	294	90
	45	1.60E-02	264	90

The results were impressive as the thickness uniformity improved dramatically and variation in the thickness reduced to 4.6%, Table 18.

Table 18: Coating thickness measurements for trial 17.

Position from the centre	Thickness (nm)
7	66
6.5	72.85
6	75.85
5.5	77.65
5	79.2
4.5	80.25
4	80.85
3.5	81.35
3	82.2
2.5	82.5
2	82.7
1.5	82.65
1	83.05
0.5	82.9
0	82.9
Uniformity centre to 5 cm =	3.85

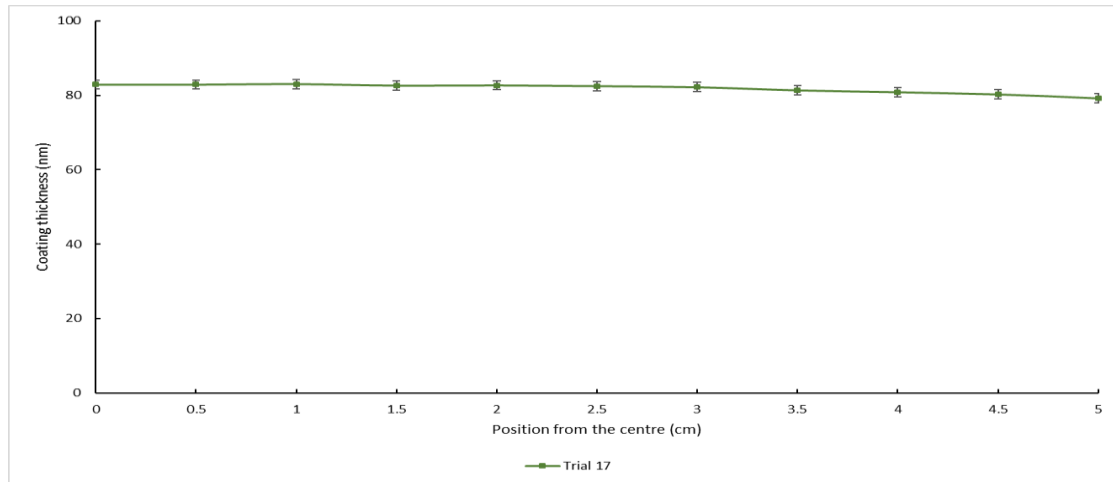


Figure 38: Trial 17 thickness profile using mask #3.

As it is obvious from the graph, the thickness profile was flat and within the defined limits.

Before proceeding any further, a major modification was needed to make sure the mask is permanently fixed and does not move. Earlier, it was mentioned that the mask's fixture was attached to the gas inlet post, but it was not fixed robustly meaning if it was knocked by mistake, it could move and effect the thickness uniformity. Therefore, a hole was drilled behind the gas inlet, on the top lid, to fix the mask fixture permanently to prevent the mask from moving at all, Figure 39.

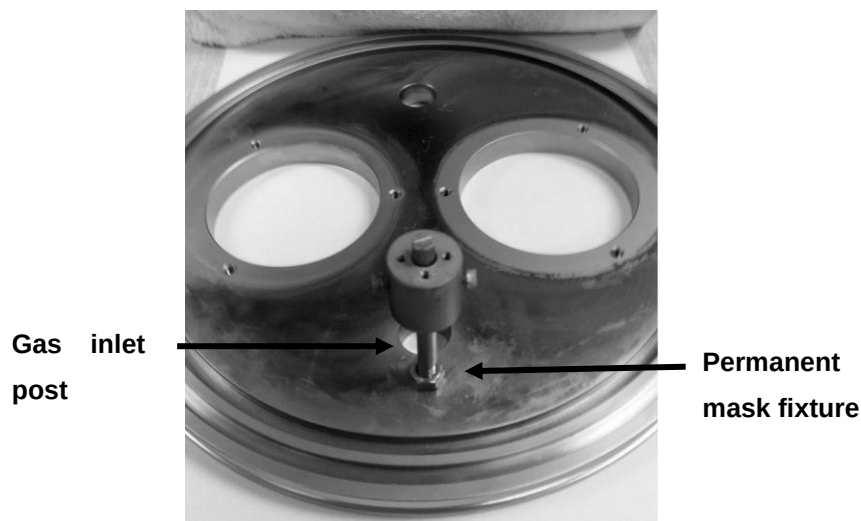


Figure 39: Mask permanent fixture on the top lid of the machine.

As a result of the change, a new mask had to be made to fit on the same post and have the same effect as mask #3. The new mask was made of a 3 mm thick aluminium to ensure flatness and avoid any bending. The center part of the mask was copied from the previous version and then was lengthen from the end to reach the permanent fixture and the mask holder, Figure 40.

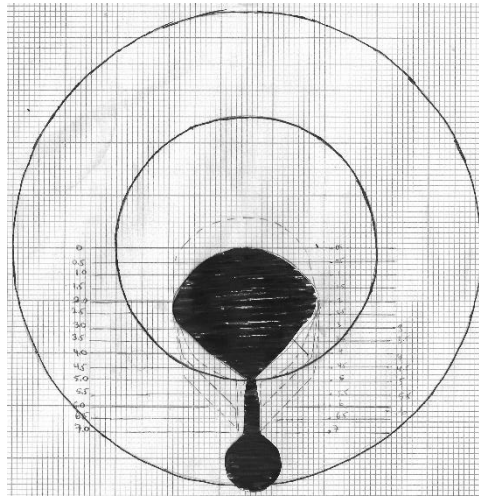


Figure 40: Demonstration of Mask #4 created after permanent fixture placement.

Repeating the run using the new mask was done in trial 18. The same parameters as previous runs were used in this trial; however, the base pressure was reduced to 3×10^{-5} mbar from 4.4×10^{-5} mbar.

Table 19: Process Parameters for trial 18.

Parameters					
Bleeding time (mins):	15:00	Cooling down time (mins):	28:06		
Base Pressure (mbar):	3.05×10^{-5}	Time to Pump down (mins):	13:07		
Trial 18	Warm-up time (mins)	Pressure (mbar)	DC	(v)	Power (w)
	2	1.60×10^{-2}		198	50
	4	1.60×10^{-2}		240	70
	5	1.60×10^{-2}		260	80
	Sputtering time (mins)	Pressure (mbar)	DC	(v)	Power (w)
	0	1.60×10^{-2}		296	90
	15	1.60×10^{-2}		320	90
	30	1.60×10^{-2}		322	90
	45	1.60×10^{-2}		320	90

The results shown in Table 20 and Figure 41 clearly proved that the thickness uniformity was within the specified limit, where the variations in coating thickness

from the center to 5 cm was 4.1%. Therefore, the uniformity within the area of Ø10 cm diameter was achieved.

Table 20: Coating thickness measurements for trial 18.

Position from the centre	Thickness (nm)
7	102.59
6.5	106.64
6	108.02
5.5	110.06
5	111.18
4.5	111.20
4	112.19
3.5	113.31
3	114.74
2.5	115.81
2	116.01
1.5	116.05
1	115.55
0.5	114.83
0	115.33
Uniformity centre to 5 cm =	4.87

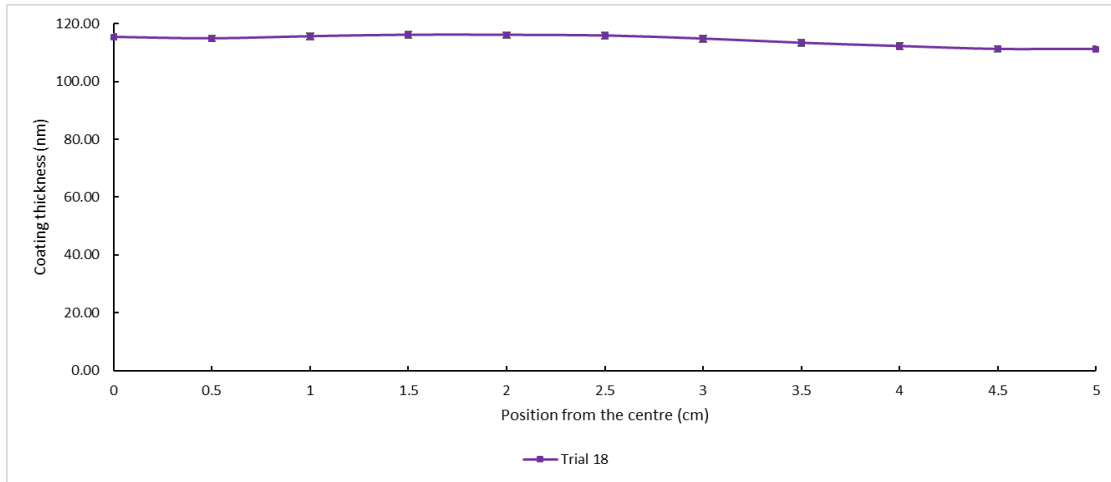


Figure 41: Trial 18 thickness profile using mask #4.

The next step was to check if the thickness uniformity was same for the second magnetron, magnetron A. Therefore, the trial was performed on magnetron A using mask #4. The Yb₂O₃ target was used for the run as it was the other candidate material intended for use in the experiments. The process parameters for sputtering Yb₂O₃ were quite different from Y₂O₃.

The base pressure was reduced to 1.5x10⁻⁵ mbar and the sputtering power was set on 100 W. The warm up period was increased from 5 mins to 17 mins. A cooling period was also added to allow the chamber to cool down for 7 mins. The sputtering period was reduced to 30 mins while power was increased to 100 W.

Table 21: Process parameters for the trial 19 using Yb2O3 target.

Parameters						
Bleeding time (mins):	15.00	Cooling down time (mins):	00:00			
Base Pressure (mbar):	1.50E-05	Time to Pump down (mins):	91.00			
Trial 19	Warm-up time (mins)	Pressure (mbar)	DC (v)	Power (w)	Pressure MFC (mbar)	
	7	1.59E-02	102	30-90	2.61E-02	37.57
	17	1.61E-02	260	100	2.63E-02	37.13
	Avg	1.60E-02	181		2.62E-02	
	Sputtering time (mins)	Pressure (mbar)	DC (v)	Power (w)	Pressure MFC (mbar)	Flow
	0 (90s)	1.60E-02	310	98	2.61E-02	37.00
	15	1.60E-02	308	97	2.61E-02	36.93
	30	1.60E-02	308	95	2.61E-02	36.91
	Avg	1.60E-02	309	97	2.61E-02	
	Cooling down time (mins)	Pressure (mbar)	DC (v)	Power (w)	Pressure MFC (mbar)	Flow
	7	1.59E-02	250	90-30	2.61E-02	36.90
	Avg	1.59E-02	250		2.61E-02	

As it was evident from the results, the thickness profile for magnetron A was not similar to the thickness profile for magnetron B. Thickness variation on magnetron A was 13.3% while the thickness variation on magnetron B was 4.1%.

Table 22: Coating thickness measurements for trial 19.

Position from the centre	Thickness (nm)
7	105.34
6.5	115.04
6	128.96
5.5	135.58
5	139.93
4.5	142.75
4	136.64
3.5	131.21
3	127.85
2.5	126.36
2	125.77
1.5	123.75
1	123.61
0.5	124.49
0	123.99
Uniformity centre to 5 cm =	19.15

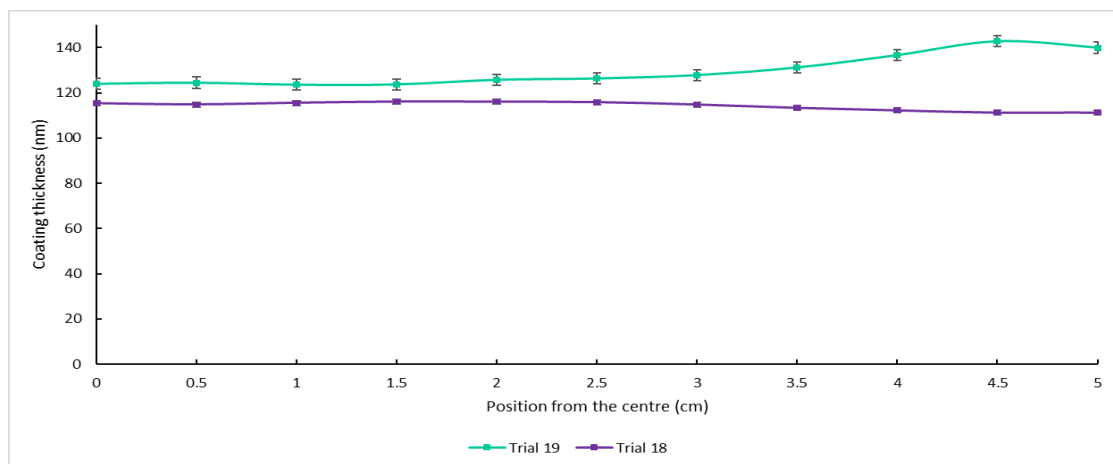


Figure 42: Comparing thickness profiles between magnetron A (Trial 19) and Magnetron B (Trial 18) using mask #4.

Therefore, a new mask was developed to enhance the coating uniformity for magnetron A. After 11 test runs, the mask was finally ready for use, Figure 43.

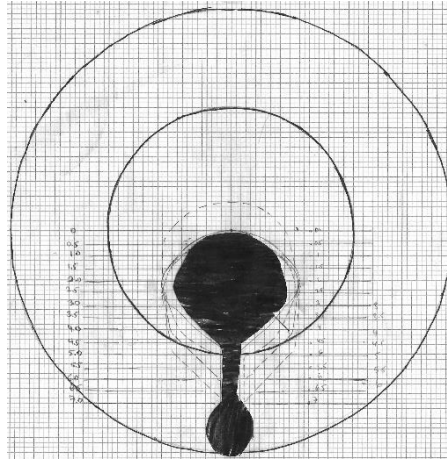


Figure 43: Demonstration of Mask #5 thinned by 6.5 mm from 0-2.5 cm.

The process parameters for trial 20 were same as trial 19 as shown in Table 23, but the sputtering time was increased by 15 mins.

Table 23: Process parameters for the trial 20 using mask #5.

Parameters							
Bleeding time (mins):		15.00	Cooling down time (mins):				
Base Pressure (mbar):		1.50E-05	Time to Pump down (mins):		64.00		
Trial 20	Warm-up time (mins)	Pressure (mbar)	DC (v)	Power (w)	Pressure (mbar)	Flow	
	1-7.5	1.65E-02	126	30-90	2.62E-02	38.50	
	7.5-18	1.66E-02	256	100	2.62E-02	38.18	
	Avg	1.66E-02	191				
	Sputtering time (mins)	Pressure (mbar)	DC (v)	Power (w)	Pressure (mbar)	Flow	
	0 (90s)	1.71E-02	288	98	2.62E-02	39.22	
	15	1.71E-02	288	100	2.62E-02	39.05	
	30	1.71E-02	288	98	2.62E-02	39.02	
	45	1.70E-02	288	98	2.62E-02	38.92	
	Avg	1.71E-02	288	99	2.62E-02		
	Cooling down time (mins)	Pressure (mbar)	DC (v)	Power (w)	Pressure (mbar)	Flow	
	6	1.65E-02	256	90-30	2.62E-02	38.23	
	Avg	1.65E-02	193		2.62E-02		

Table 24: Coating thickness measurements for trial 20.

Position from the centre	Thickness (nm)
7	233.30
6.5	246.73
6	256.42
5.5	272.98
5	284.23
4.5	285.59
4	286.79
3.5	287.91
3	287.98
2.5	283.77
2	284.16
1.5	282.26
1	282.65
0.5	283.36
0	283.26
Uniformity centre to 5 cm =	5.7

The coating thickness uniformity improved greatly, and the variation in overall thickness from centre to 5 cm was 1.9%, shown in Table 24 and Figure 44.

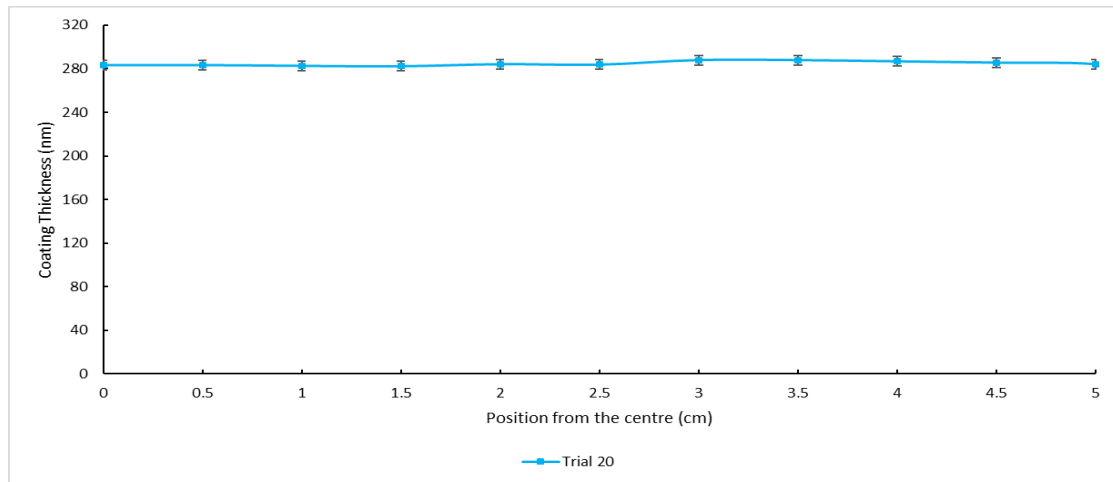


Figure 44: thickness profile of magnetron A using mask #5, Trial 20.

Even though sorting out the coating thickness uniformity was a great step towards restoring the machine, there was a major problem with the findings. Despite using the same parameters on every trial, the overall thickness was never the same in any two consecutive runs. That raised a question: could the machine produce repeatable results given all the parameters are fixed?

To be able to answer this question, a closer look at the problems encountered during the machine's runs was vital.

3.3.3 Pressure Regulation

Looking at the results in previous section, it was suspected that change in the base pressure is affecting the coating thickness in the runs. Therefore, the machine was run 3 times at 3 different base pressures and the results were reported in the Table 25.

Table 25: Trial 21, 22 & 23 run with different base pressures.

Run	Material	Sputtering Time (mins)	Ramping up (mins)	Mask #	Mask Type	Power (w)	Base Pressure (mbar)	Warm up Pressure (mbar)	Sputtering Pressure (mbar)	Max DC volt bias (v)	Max Thickness (nm)	Min Thickness (nm)	Thickness Uniformity
Trial 21	Yttria	45	5	4	Al+paper	90	2.10E-05	1.60E-02	1.60E-02	302	146	109	23.6
Trial 22	Yttria	45	5	4	Al+paper	90	3.00E-05	1.60E-02	1.60E-02	300	105	83	4.75
Trial 23	Yttria	45	5	4	Al+paper	90	4.40E-05	1.60E-02	1.60E-02	294	84	66	3.85

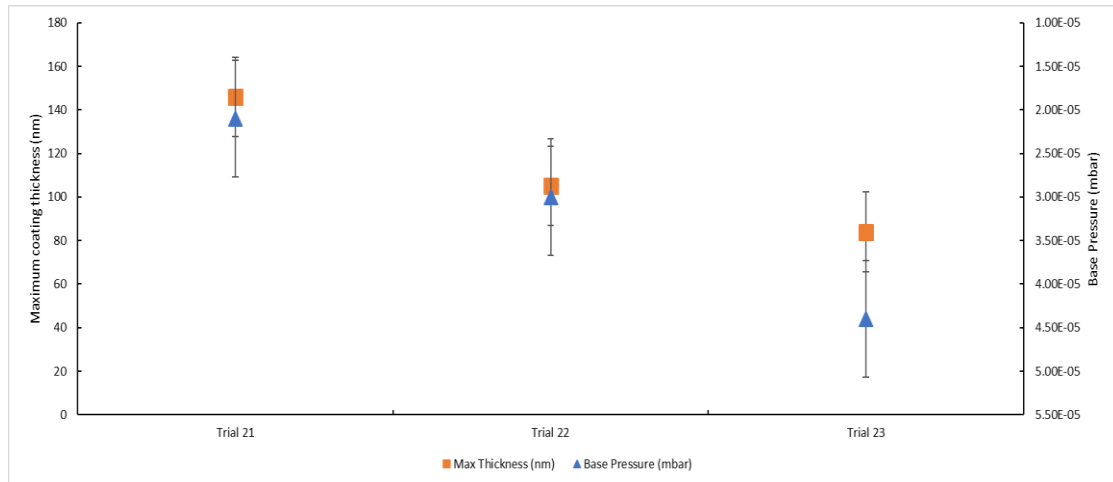


Figure 45: Relationship between the base pressure and coating thickness.

It was clearly obvious from the graph, Figure 45, that generally the lower the base pressure, the higher the coating thickness is. Gaboriaud, 2012, also suggests that the lower the base pressure, vacuum, the higher the energy of the sputtered atoms which arrive on to the substrate surface, which in fact increases the deposition rate [57].

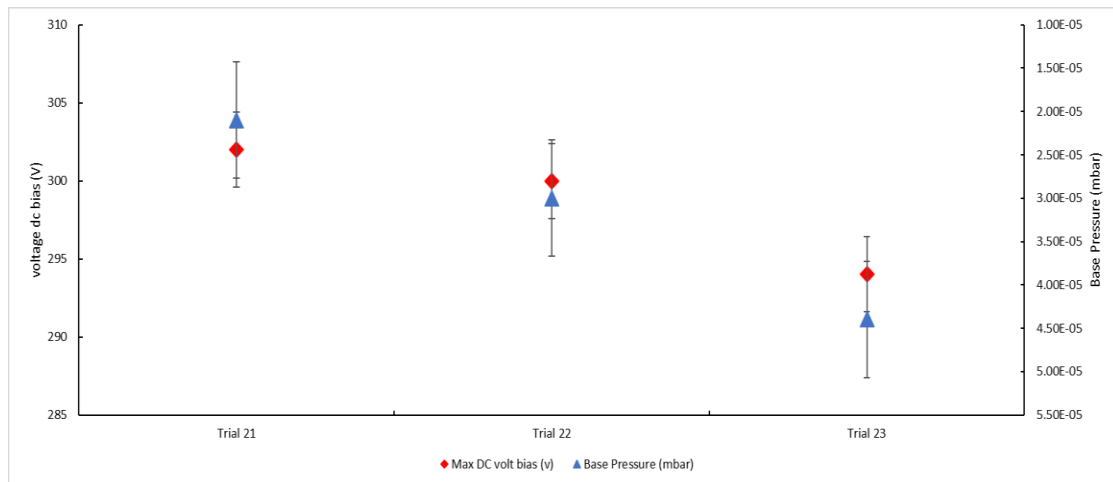


Figure 46: Relationship between the base pressure and dc bias.

By looking at the obtained data from the 3 trials, another interesting relationship could be suggested. The change in the base pressure was also effecting the dc bias voltage during sputtering which in turn could be reason for the increase in deposition rate and coating thickness [58]. This was clearly apparent in Figure 46 and Figure 47.

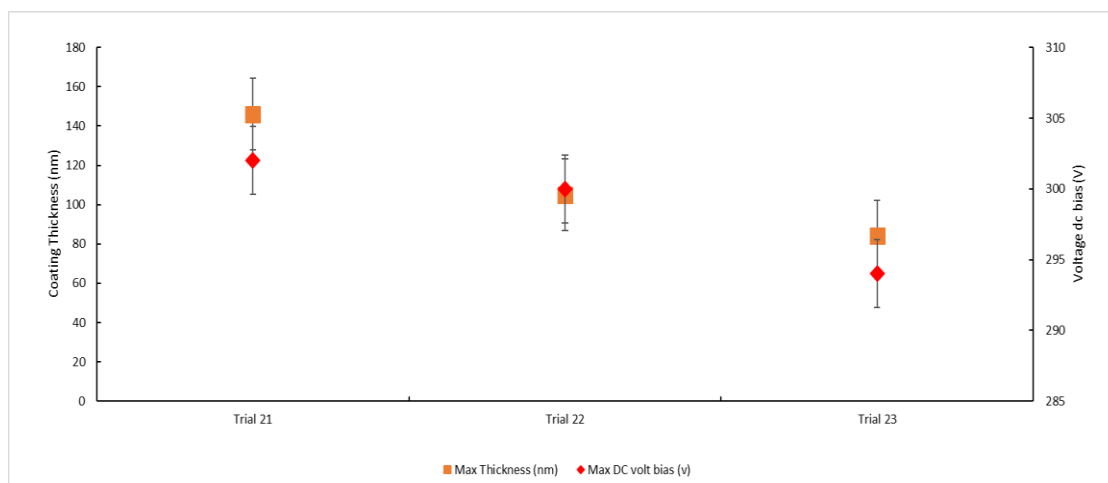


Figure 47: Relationship between the voltage dc bias and coating thickness.

Based on the above findings, it was decided to try and fix the base pressure to 3×10^{-5} mbar. The machine was run 9 times using the exact same parameters, Table 26.

Table 26: Trials 24-32 with exact same parameters including fixed base pressure, sputtering pressure, and power.

Trial #	Sputtering Time (mins)	Ramping up (mins)	Mask	Power (W)	Mask Type	Base Pressure (mbar)	Sputtering Pressure (mbar)	Max DC volt bias (v)	Max Thickness (nm)	Min Thickness (nm)	Thickness Uniformity
Trial 24	45	5	6	90	AL	3.00E-05	1.60E-02	322	191	142	16.14
Trial 25	45	5	7	90	AL	3.00E-05	1.60E-02	320	180	134	29.35
Trial 26	45	5	7	90	AL	3.00E-05	1.60E-02	318	193	139	21.35
Trial 27	45	5	8	90	AL	3.00E-05	1.60E-02	322	103	86	4.58
Trial 28	45	5	9	90	AL	3.00E-05	1.60E-02	324	145	125	12.34
Trial 29	45	5	10	90	AL	3.00E-05	1.60E-02	324	150	123	7.97
Trial 30	45	5	11	90	AL	3.00E-05	1.60E-02	324	182	140	12.45
Trial 31	45	5	12	90	AL	3.00E-05	1.60E-02	324	170	152	18
Trial 32	45	5	13	90	AL	3.00E-05	1.60E-02	306	73	60	4.49

Despite using the same parameters, the results were not close or even comparable to each other at all. It was evident that fixing the base pressure was not resulting in reproducing the same voltage dc bias at each run. And having different voltage dc bias has in turn resulted in variation in the coating thickness on all runs, Figure 48.

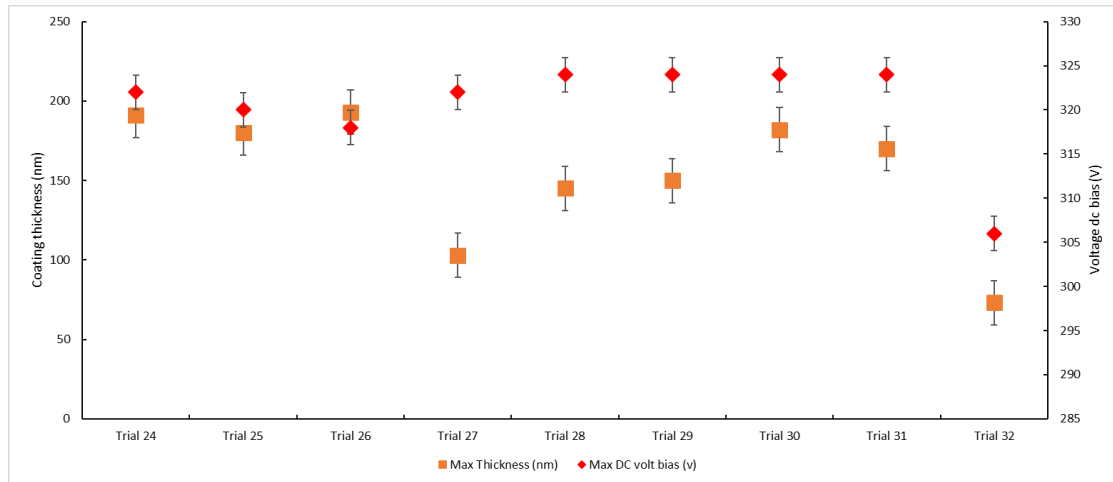


Figure 48: Relationship between the voltage dc bias and coating thickness operating at 3×10^{-5} mbar base pressure.

By investigating the issue further, it was found that the accuracy of the pressure gauge, Compact Full Range Gauge from Pfeiffer, was within $\pm 30\%$ and its results reproducibility was $\pm 5\%$ in the range of 1×10^{-8} – 100 mbar. Also, it was found that the measuring signal is calibrated for N_2 , O_2 , dry air and CO, which meant it should have been corrected for other gases such as argon [59].

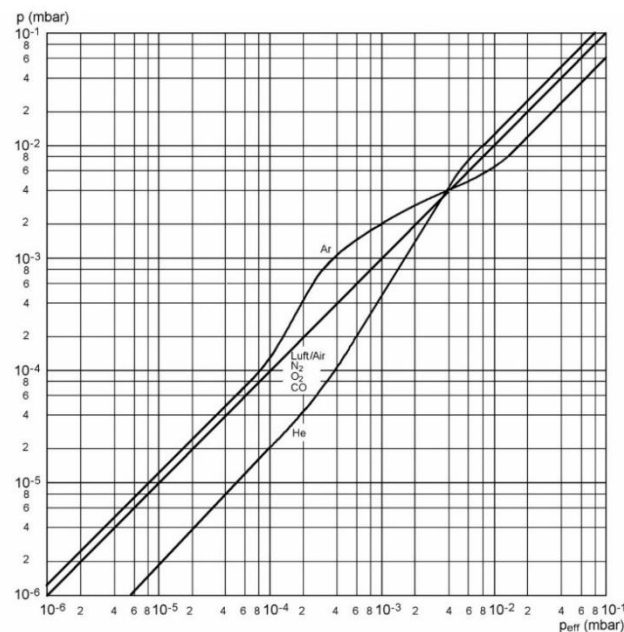


Figure 49: Calibration graph for converting Pfeiffer gauge readings to air pressure for different gases [59].

Therefore, an accurate pressure gauge, Baratron capacitance manometer, was installed on the machine to monitor the pressure alongside the original pressure gauge. The unit of the Baratron was Torr and its accuracy was $\pm 0.12\%$ [60]. The Baratron could operate independent of the gas composition used in the chamber, eliminating the need for calibration for different gasses.

An automated mass flow controller, MFC, was also installed to automatically regulate the flow of the gas to the chamber. The MFC had an accuracy of 1% of the set point. Its installation removed the necessity of manually adjusting the gas flow throughout the run which also helped in making sure the sputtering pressure stayed same at every run.

The machine was run for 3 times to check if the changes had any effect on fixing the dc bias or producing repeatable thickness results.

Table 27: Trials 33-35 with new pressure gauge and automated MFC.

Trial #	Sputtering Time (mins)	Ramping up (mins)	Mask	Power (w)	Base Pressure (mbar)	Warm up Pressure (mbar)	Warm up Pressure MFC (mbar)	Sputtering Pressure (mbar)	Sputtering Pressure MFC (mbar)	Max DC volt bias (v)	Max Thickness (nm)	Min Thickness (nm)	Thickness Uniformity
Trial 33	45	5	30	90	3.00E-05	1.67E-02	1.97E-02	1.64E-02	1.96E-02	300	55	46	2.54
Trial 34	45	5	30	90	3.00E-05	1.65E-02	1.97E-02	1.60E-02	1.93E-02	310	74	63	3
Trial 35	45	5	30	90	3.00E-05	1.65E-02	1.97E-02	1.60E-02	1.93E-02	314	118	95	13.18

Even though the installed MFC made it easier to run the machine, it had no positive impact on the dc bias whatsoever, Figure 50. In fact, it had a negative effect on the coating thickness as it dropped from an average of 154 nm in the trials 24-32 to average of 82 nm in the trials 33-35.

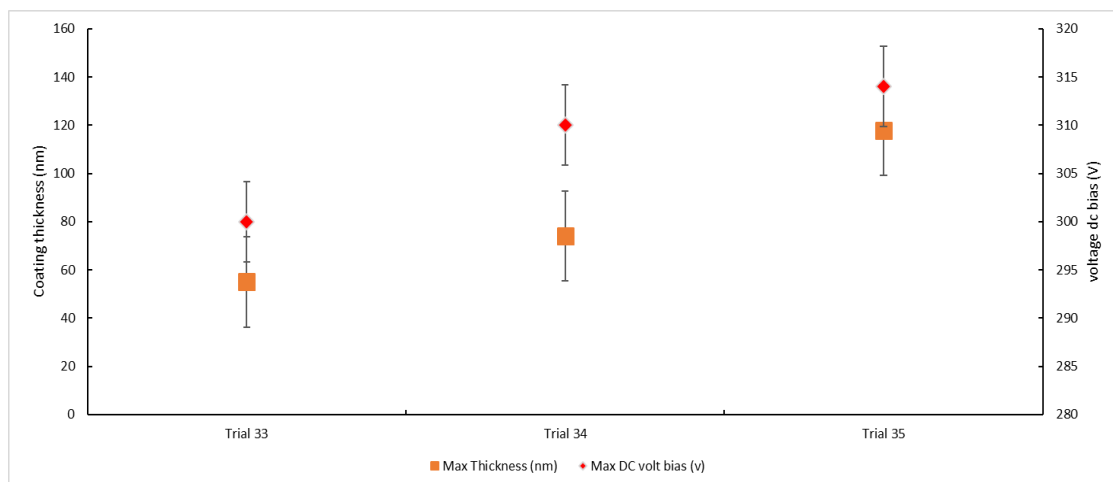


Figure 50: dc bias and coating thickness on trials 33-35.

While keeping the new setup in place, it was decided to find a new approach to fix the voltage dc bias in order to get the same coating thickness and improve the repeatability of the machine.

3.3.4 DC Bias vs rf Power

When the RF power is applied, ultimately it creates a dc self-bias voltage. The developed DC bias level may fluctuate due to thermal changes in sheath resistance because of changes to the substrate's surface or changes in the overall process conditions [35,37].

To control the dc bias, a new programme was developed to keep it constant during deposition by adjusting the forwarding power. An upper limit of 150 W was put in place in the programme in order to avoid excessive power going through the target and possibly damaging it.

The machine was run 6 times, 3 consecutive runs a day, to check the effectiveness of the programme and to determine if it produced repeatable results. A new Yb₂O₃ target was mounted on magnetron A. The programme duration was set to 45 mins. Based on the recommendations on how to sputter ceramic targets, longer warming up and cooling down periods were set in order to avoid any damage to the target as a result of thermal shock. The warming up period was set at 10 mins so the power is ramped up from 30-110 W. The sputtering power was put on 120 W. The cooling down period was set for 11 mins for the power to ramp down from 110-20 W. The only difference between the runs in the first day and the second day was the base pressure, as can be seen in Table 28.

Table 28: Trials 36-41 with the new programme (Fixed dc bias).

Uniformity and Repeatability Tracking Table									
Trial #	Day	Sputtering Time (mins)	Power (w)	Base Pressure (mbar)	Sputtering Pressure MFC (mbar)	Max DC volt bias (v)	Max Thickness (nm)	Min Thickness (nm)	Thickness Uniformity
Trial 36	1	45	120	2.00E-05	2.61E-02	402	241	212	23.98
Trial 37	1	45	120	2.00E-05	2.61E-02	410	315	264	9.83
Trial 38	1	45	120	2.00E-05	2.61E-02	402	315	258	19.71
Trial 39	2	45	100	1.50E-05	2.61E-02	340	251	207	14.74
Trial 40	2	45	100	1.50E-05	2.61E-02	346	291	246	26.79
Trial 41	2	45	100	1.50E-05	2.61E-02	340	288	246	22.35

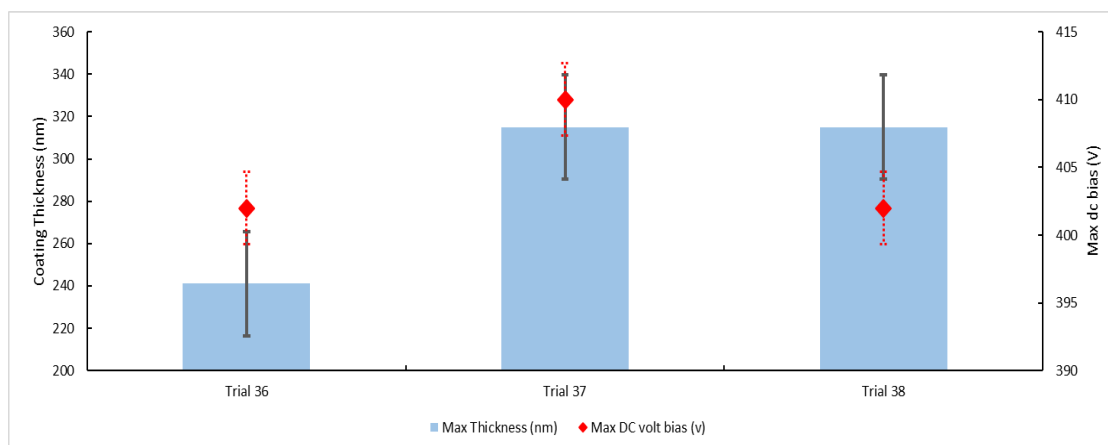


Figure 51: Results of the Trial 36-38 with fixed dc bias (day 1).

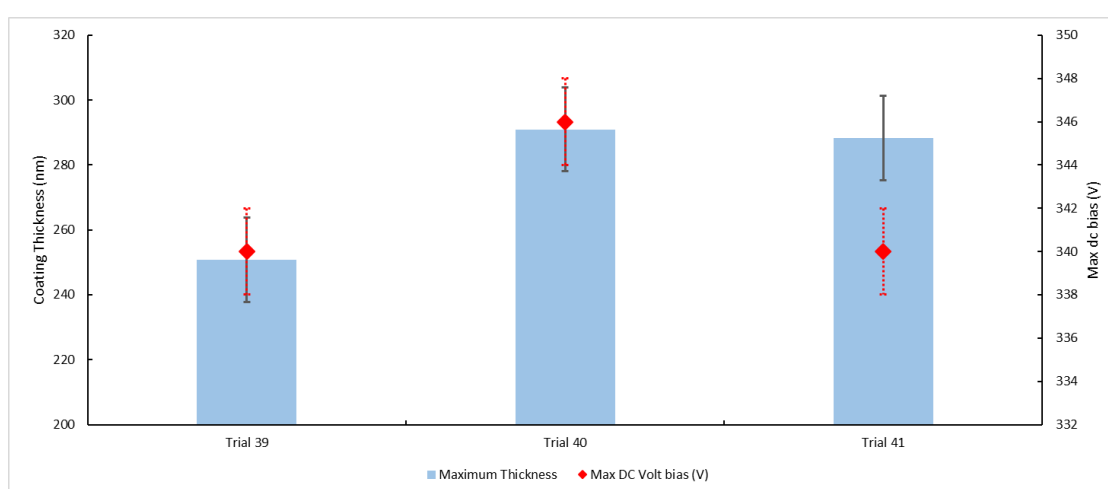


Figure 52: Results of the Trial 39-41 with fixed dc bias (day 2).

By looking at the results from both days, it was evident that the thickness on the 2nd and 3rd runs of each day were very similar, which indicates that the new control software is working properly. That means fixing the dc bias was the right step in solving the repeatability issue of the machine; however, an important question had to be answered, the reason behind different thickness at the first run of each day? It can also be seen that the readings on trial 36 were highly scattered compare to the rest of the measurements. Errors in the measurements could be potentially the reason for that scattering.

3.3.5 Vacuum Performance and Outgassing

Few potential reasons could create varying results in the first run of both days. The most important reason might be outgassing, which is the “flux of a solid or

liquid, and is quantity of gas leaving the surface per unit time at a specified time after the start of evacuation” [61].

Inside a vacuum chamber, all parts including the walls, the rotary table and the shutter “release the gases they absorbed because the same forces that helped trap gasses in them have diminished” [62].

The most serious and common source of outgassing comes from hydrogen due to water vapour resulting from the exposure of the system to air, [63]. The machine used in the experiments, was always left overnight at atmospheric pressure, and sometimes even for few days. That increases the chance of building up moisture inside the chamber as all compartments absorb a considerable amount of water vapour. That increased the rate of outgassing and could potentially have influenced the results in the first run.

The machine did not have a heating system to reduce the outgassing through a baking process which was suggested by Lofgran, 2013. Therefore, it was suggested to increase the warming up period by another 10 mins and sputter at high power, 120 W, while the shutter is closed in order to heat up the chamber and reduce the effect of outgassing as much as possible. The other reason for sputtering for another 10 mins was to reduce the chance of outgassing of the target material as it was exposed to the air, too.

The attempt was unsuccessful due to cooling pipes installation around the chamber to control the temperature during sputtering, Figure 53. The cooling pipes prevented the chamber from getting hot and stopped the effect of the so-called backing process. Hence, the repeatability of the results did not improve at all.



Figure 53: Water cooling pipes for temperature control.

Dirtiness of the chamber is the second major cause for outgassing in vacuum chambers. The coating layers developed on the walls of the chamber, the substrate holders, the rotary table, the shutter and the dark space shields are all major sources of contamination and outgassing in the chamber. Grinham and Chew., 2017, stated for aspects related to reducing outgassing in vacuum chambers which were: choice of material, cleaning and handling, surface treatment and baking [64].

By looking at the condition of the chamber, it was decided to strip the machine down and perform a thorough cleaning of the walls and all parts of the chamber by removing all the coatings which were stuck on them. The main stainless steel was carefully removed and cleaned using ScotchBrite. The top lid and the target holders were also cleaned with ScotchBrite carefully. The rotary plate, mask, shutter and dark space shield were sand blasted, as suggested by [65]. All parts were wiped using Isopropyl Alcohol, IPA, and put back together. A liner was fabricated and put inside the chamber so to prevent the coating deposition on the wall of the chamber. By doing so, the liner could be removed for cleaning purposes and put back without the need to take the machine apart, Figure 54.

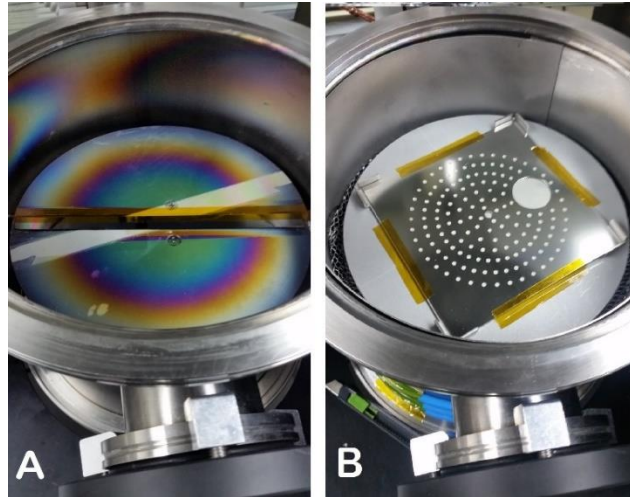


Figure 54: the chamber before cleaning, B, Chamber after cleaning.

The Baratron was also replaced, as it was reported that its response rate was very slow. Therefore, a new Baratron with 0.1 mbar resolution was installed which had a 20 msec response time. The old Baratron had only 2 hours warm up period; however, the new one had a 4 hour warm up period.

The machine was run 4 times, 2 consecutive runs a day, to check if the machine was going to produce repeatable results. All other parameters including the fixed dc bias were fixed untouched.

Table 29: Trials 42-45 after cleaning the chamber and installing of a new Baratron.

Uniformity and Repeatability Tracking Table												
Trial #	Material	Sputtering Time (mins)	Power (w)	Base Pressure (mbar)	Warm up Pressure (mbar)	Warm up Pressure MFC (mbar)	Sputtering Pressure (mbar)	Sputtering Pressure MFC (mbar)	Max DC volt bias (v)	Max Thickness (nm)	Min Thickness (nm)	Thickness Uniformity
Trial 42	Ytterbia	45	100	1.50E-05	1.62E-02	2.62E-02	1.62E-02	2.62E-02	324	311	267	19
Trial 43	Ytterbia	45	100	1.50E-05	1.60E-02	2.62E-02	1.61E-02	2.62E-02	320	316	275	13
Trial 44	Ytterbia	45	100	1.50E-05	1.64E-02	2.62E-02	1.64E-02	2.62E-02	314	296	253	30
Trial 45	Ytterbia	45	100	1.50E-05	1.61E-02	2.62E-02	1.60E-02	2.62E-02	312	307	264	29

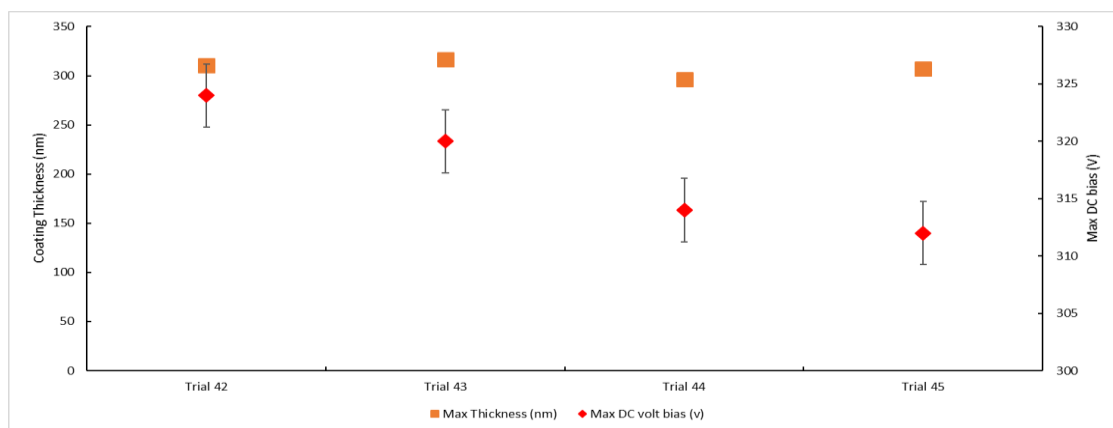


Figure 55: Trial 42-45 after cleaning the chamber and installing a new Baratron.

The results of the runs were much improved, Figure 55. Despite having different dc biases the runs produced almost same coating thickness. The average coating thickness was 307 nm and the standard deviation was 4.22 nm.

The fact that the trials were conducted on two different days, using the exact same parameters, gives the confidence that the machine was now capable of producing repeatable results which was the main aim of the restoration process. Whether cleaning the chamber was the major factor in getting repeatable results or the new Baratron is something that should be investigated later.

3.3.6 Plasma Ignition and Arcing

During sputtering, occasionally, arcing could be noticed. Even though the arcs were not constantly occurring, they caused a real concern. As when they occur, they can cause damage by locally melting the surface of the target or even the substrate. The result of this could be contamination to the source and degradation of the structure [66].

Generally arcing occurs as a result of electric field anomalies due to growth of the ionisation of the gas and the subsequent breakdown of the insulating qualities of it which results in a short circuit between the electrodes [66]. However, there are two other classes of arc sources which are the mechanical and disruption of surface equilibrium in the chamber. For details on all classes and sources of arcs in sputtering machines and the physics of arcs, please refer to reference [66] [67].

In trial 37, by looking at the target surface while sputtering, it could be noticed that there was arcing near the target surface and all over the chamber too. Few minutes into the run, a long crack appeared on the surface of the target and a sudden drop on pressure and power was observed, Figure 56.

The cause of the crack could be due to several factors, including local arcing. Other reasons for it, might be due to poor bond between the target and the copper plate which were glued using conductive silver epoxy or temperature variations caused by higher temperature on the surface of the target compare with the bulk material, [66].

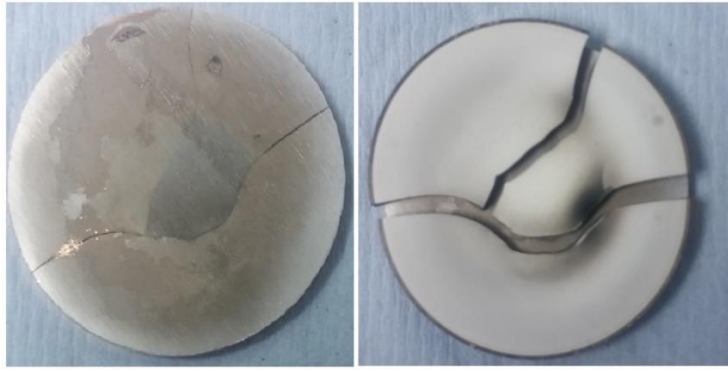


Figure 56: Cracked Yb_2O_3 target.

Another reason could be the sudden pressure drop due to outgassing of the temperature sticker which was placed on the rotary table to monitor the temperature before and after the cooling pipes installation. As it appears, the arcing only happened when the stickers were placed in the chamber.

In another note, after the installation of the cooling pipes, the plasma was not igniting at low power. Therefore, it was decided to start the warm up period at high power for 5 seconds, while opening and closing the shutter, to get the plasma ignited. This technique was not working consistently at each run. While investigating the issue, it was noticed that a plasma was appearing under the rotary table, too. Therefore, a cylindrical metal mesh was fabricated and to cover the area under the rotary table, Figure 57. By doing so, the plasma was contained within the area above the rotary table. The mesh has resulted in plasma ignition consistently at every run.



Figure 57: Mesh installation in the chamber.

The idea of the mesh was to basically ground the whole area under the rotary table and to avoid the plasma traveling any further by trapping the electrons near the mesh. This technique was used by Roy, et al., 2014, to increase the intensity of ion beams by preventing uncontrolled ion beam neutralization by stray electrons. The unwanted secondary electrons were suppressed using a radial mesh liner that was positively biased inside a beam drift tube [68].

Unfortunately, a day prior conducting the experiments on ZnSe substrates, both target materials, Yb_2O_3 and, broke while performing test runs to get the thickness to the required level.

The Y_2O_3 was a new target used for the first time, when a crack appeared on its surface after 40 mins of deposition. Some black spots appeared around the target holder and along the crack and the power gradually dropped from 90 to 68 W. By looking at the target closely, the bonding material has disintegrated and oxidised on the surface of the target which meant it could not be used anymore. As ordering new targets takes few weeks to arrive, it was decided to work on the theoretical side of coating designs using Macleod software.

3.3.7 Coating Design and structure

Based on the multiple decision criteria results, the materials that showed promising results for development of BBAR were Y_2O_3 and Yb_2O_3 [10,11]. The studies also showed that both materials have good adhesion to diamond and they would not necessarily require an underlay such as Si or AlN [11]. Therefore, it was decided to use a single layer Y_2O_3 and Yb_2O_3 on both substrates.

For the diamond optics, using Macloed software, a single layer quarter wavelength coating was designed at 9 μm wavelength to achieve maximum transmittance from 3-5 and 8-12 μm [10].

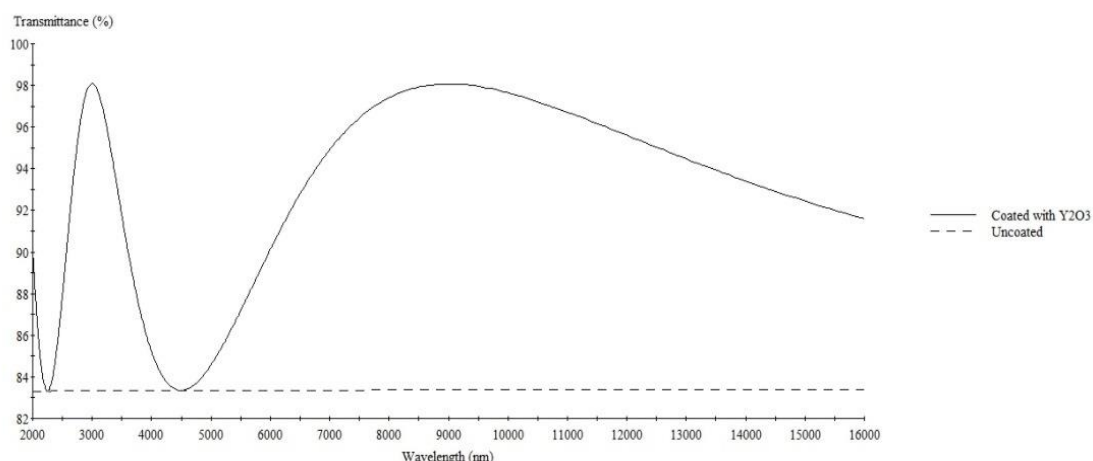


Figure 58: Transmission spectrum for diamond optics coated with quarter wavelength of Y_2O_3 at $9\ \mu m$.

The coating thickness, was given by the software as 1269 nm. The refractive index for Y_2O_3 was 1.773 and for diamond was 2.376. That means the optical thickness of the layer is 2249.93 nm.

The same approach and parameters were used for developing a single layer quarter wavelength coating design for ZnSe sample at $9\ \mu m$. The coating thickness was 1269 nm and the refractive index of ZnSe was given as 2.412.

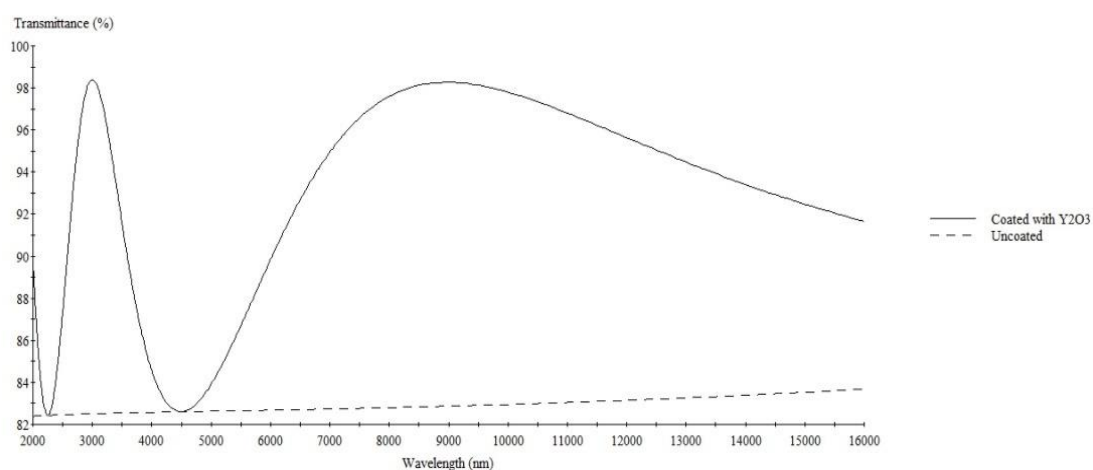


Figure 59: Transmission spectrum for ZnSe optics coated with quarter wavelength of Y_2O_3 at $9\ \mu m$.

The transmission spectrum of the ZnSe was very similar to the coated diamond optics spectrum with a difference that the transmission was slightly higher in ZnSe

in the range of 3-5 and 8-12 μm . The maximum transmission for coated ZnSe increased from 82.61% to 98.39 at 3 μm and while the maximum transmission for the coated diamond optics increased from 83.33% was 98.07%, Figure 60.

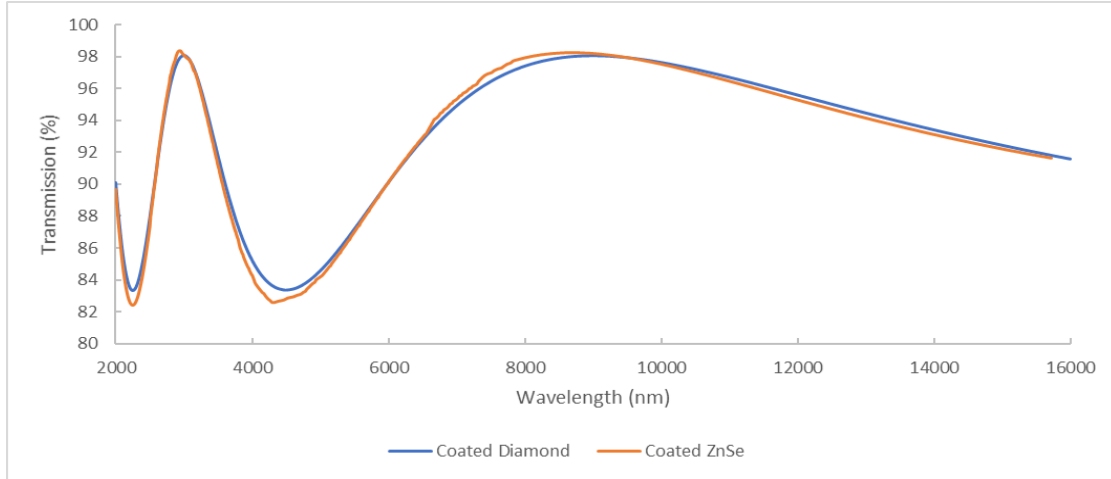


Figure 60: Transmission comparison between coated diamond and ZnSe optics with quarter wavelength Y_2O_3 at 9 μm .

As shown, in the graph there is a great variation in the transmission from 2-7 μm due to the transmission pattern in the diamond structure. In order to reduce this variation in transmission, it was suggested to design the coating using a quarter wavelength at 5 μm .

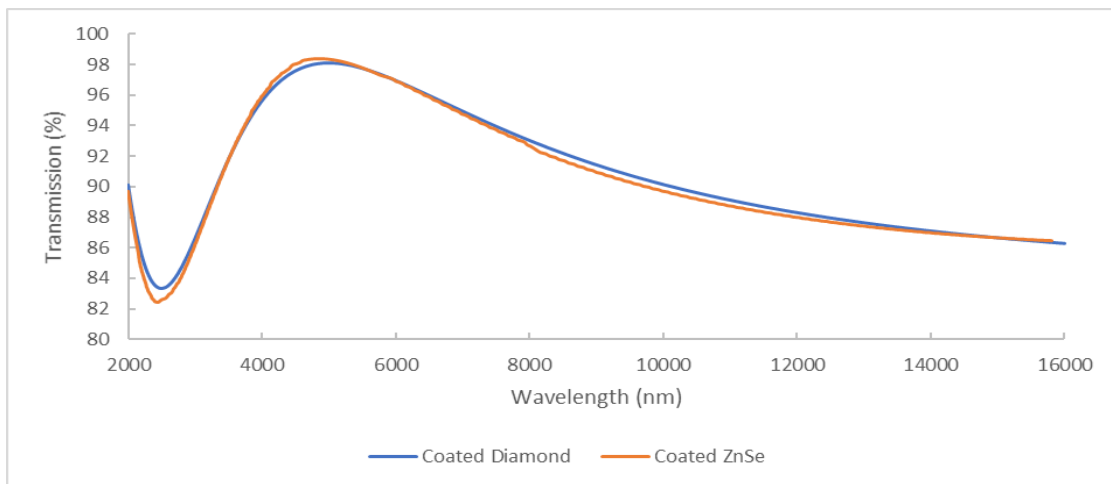


Figure 61: Transmission comparison between coated diamond and ZnSe optics with quarter wavelength Y_2O_3 at 5 μm .

By looking at the statistics of the two wavelengths, Table 30, the maximum and minimum transmission in both cases is almost same with the difference that the local minimum and maximum are at different wavelengths. However, as the aim is to develop a BBAR 2-16 μm , then the best option is to use the quarter wavelength that gives a better transmission across the whole of the specified spectrum. To identify which one is one of the two wavelengths is better, the standard deviations of both spectra were calculated, Table 30. Based on the results, the standard deviation of quarter wavelength of Y_2O_3 at 5 μm was better. Therefore, it was decided to use the quarter wavelength of Y_2O_3 at 5 μm for developing the coating.

Table 30: Statistical comparison between the Y_2O_3 coating at two different quarter wavelengths.

Statistical comparison of the transmission spectrum				
	at 5000 nm		at 9000 nm	
	Coated Diamond	Coated ZnSe	Coated Diamond	Coated ZnSe
Max Transmission	98.08	98.36	98.08	98.39
Min Transmission	83.33	82.47	83.32	82.43
Std dev	4.14	4.40	4.48	4.82

By choosing the quarter wavelength of Y_2O_3 at 5 μm , the time required for deposition is also reduced by 44.4% as the coating thickness was dropped from 1269 nm to 705 nm.

In order to calculate the time required for deposition, the deposition rate should be calculated. By looking at the results from trial 18, where the uniformity of the coating was almost flat for Y_2O_3 , the maximum coating thickness was measured as 114.74 nm. To calculate the deposition rate, the maximum coating thickness was divided by the length of the deposition which was 45 mins. That resulted in having the deposition rate as 2.55 nm/min^{-1} . It meant, it would take 277 mins, equivalent of 4.6 hours, to create a single layer Y_2O_3 coating with thickness of 705 nm on either diamond or ZnSe optics.

The same procedure was followed for Yb_2O_3 material, too. For the diamond optics, using Macloed software, a single layer quarter wavelength coating was

designed at 9 μm wavelength to achieve maximum transmittance from 3-5 and 8-12 μm .

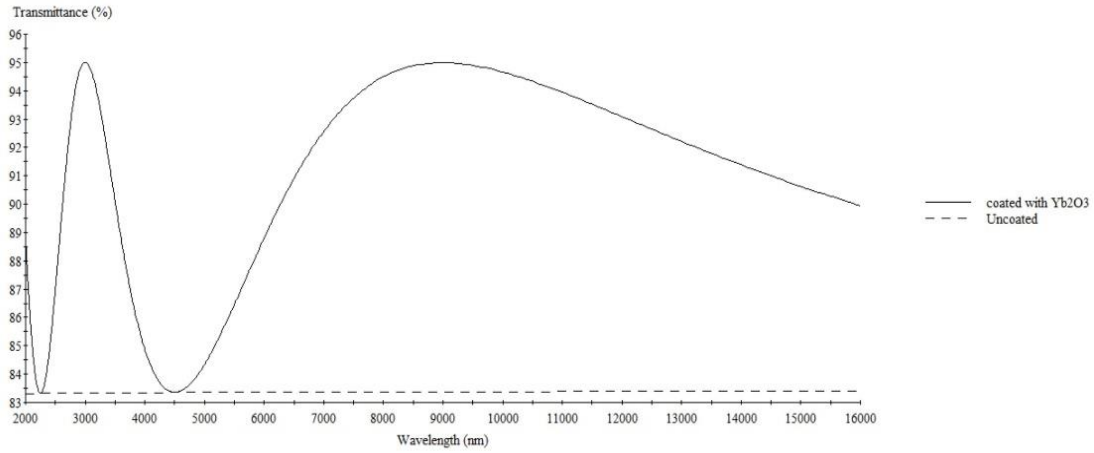


Figure 62: Transmission spectrum for diamond optics coated with quarter wavelength of Yb_2O_3 at 9 μm .

The coating thickness, was given by the software as 1162 nm. The refractive index for Yb_2O_3 was 1.935 and for diamond was 2.376. That means the optical thickness of the layer is 2248.87 nm.

For developing a single layer quarter wavelength coating design for ZnSe sample at 9 μm , the coating thickness was 1269 nm and the refractive index of ZnSe was given as 2.412.

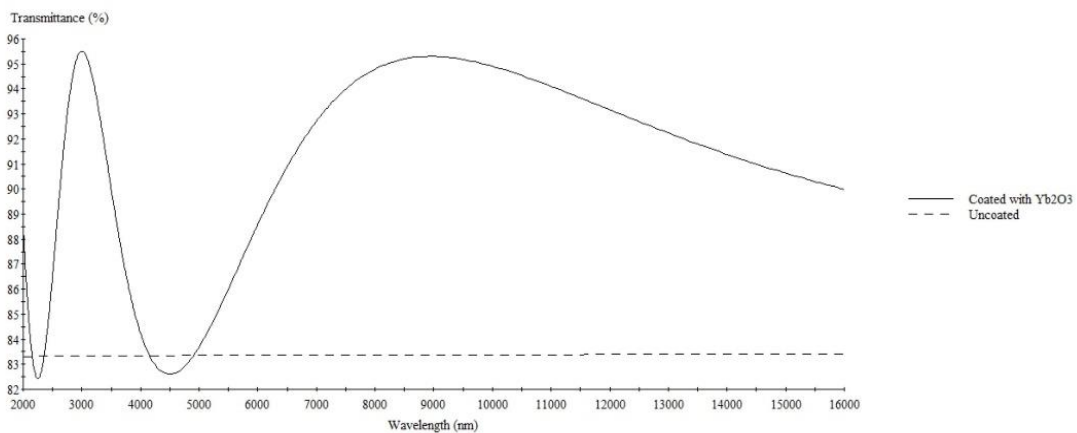


Figure 63: Transmission spectrum for ZnSe optics coated with quarter wavelength of Yb_2O_3 at 9 μm .

The transmission spectrum of the ZnSe was different from the diamond transmission spectrum. The transmission of the coated ZnSe drops below the uncoated ZnSe at the range of 2-2.5 μm and 4-5 μm which indicates that the proposed coating design is not fit for purpose.

Therefore, it was decided to re-evaluate coating design. By looking at different wavelengths, it was found that a quarter wavelength coating of Yb_2O_3 at 3370 nm was a giving good transmission results.

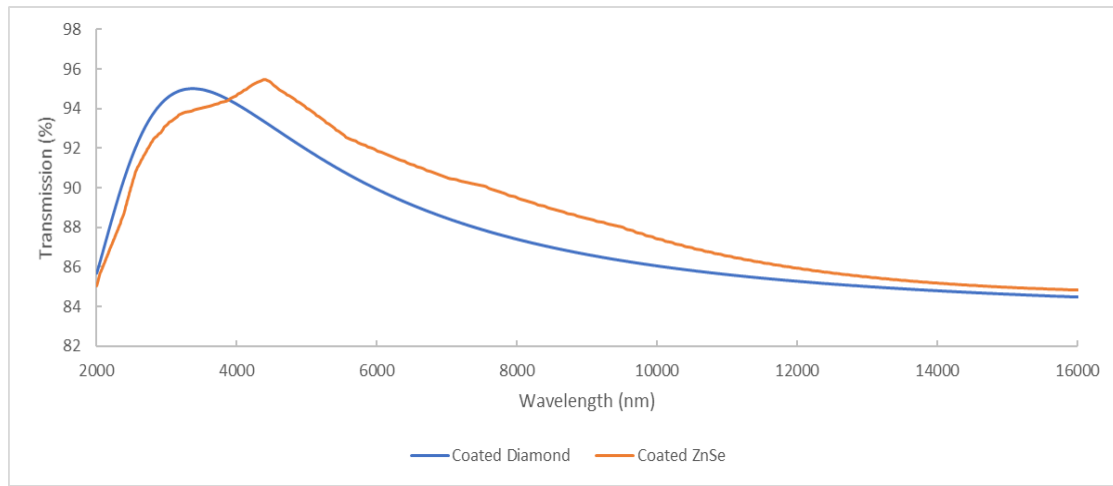


Figure 64: Transmission comparison between coated diamond and ZnSe optics with quarter wavelength Yb_2O_3 at 3370 nm.

By choosing the quarter wavelength of Yb_2O_3 at 3370 nm, the transmission increased from 83% to 95% in both diamond and ZnSe coated optics, Figure 64.

Table 31: Statistics for Yb_2O_3 coatings at 3370 nm wavelength for both diamond and ZnSe.

Statistical information of the transmission spectrum		
	at 3370 nm	
	Coated Diamond	Coated ZnSe
Max Transmission	95.01	95.50
Min Transmission	84.50	84.73
Std dev	3.32	3.48

The coating thickness was 435 nm. By looking at the results from trial 20, where the uniformity of the coating was almost flat for Yb_2O_3 , the maximum coating

thickness was measured as 287.98 nm. To calculate the deposition rate, the maximum coating thickness was divided by the length of the deposition which was 45 mins. That resulted in having the deposition rate as 6.4 nm/min^{-1} . It meant, it would take 68 mins to create a single layer Yb_2O_3 coating with thickness of 435 nm on either diamond or ZnSe optics.

The designs discussed in this section, were single layer coatings. The reason for that is a limitation in the machine's capability which was discovered in the coating uniformity section. Based on the findings, for each magnetron a specific mask was developed so as to produce uniform coating thickness. That meant, for multilayer coating deposition, the machine would have to stop for every layer of coating, so that a suitable mask is used based on the magnetron in use. That would be a major problem for the company as it will make the process costly and very time consuming. There is a way to solve this problem, by designing a compromising mask that would work well for both magnetrons, but not produce the best thickness uniformity for either of them. That might be able to solve the problem but could potentially result in low quality thin films.

However, for single layer coatings, the next step is to use the sputtering machine to coat the ZnSe and diamond optics and use the ATR accessory for IR spectroscopy in order to measure the transmission for both coated and uncoated diamonds and ZnSe optics and compare their performance in terms of transmission and reflection and the signal to noise ratio.

4 CONCLUSIONS

In this project the overall aim was to produce BBAR coatings on ZnSe and diamond substrates operating in 2-16 μm . The coatings had to be produced using a desktop based research- RF magnetron sputtering machine, which had never been used for AR coatings, nor had its intended use been specified by the manufacturer. Therefore, it had to be restored, adapted and calibrated in order to be used for developing ARCs. The machine has gone through successful cycles of restoration and adaption: Firstly, the coating thickness uniformity for each magnetron, A and B, was improved to less than 5% in overall thickness of 114 and 288 nm, accordingly.

Secondly, the machine's vacuum performance was improved as result of a series of changes, aimed at taking accurate readings of the pressure in the chamber, and regulate the gas flow within the chamber. This was achieved by installing an accurate Baratron pressure gauge which had a fast response time and installing a mass flow controller to regulate the flow of gas inside the chamber. Which when linked with software control allowed accurate setting of the chamber pressure.

In order to improve the repeatability of the machine, the 3rd improvement was a programme developed to fix the dc bias throughout the sputtering time by changing the RF input power. This has resulted in a massive improvement to the repeatability of the machine.

But further change was required to complete a successful restoration cycle. That was the analysis of outgassing in the chamber and how to minimise its effect on coating's performance. That was done, firstly, by increasing the warm up period by 10 mins so that the machine is heated up and the water vapour is extracted from major parts of the chamber including the walls, rotary plate and the shutter. The second method used to reduce the effect of outgassing was to take the machine apart and clean every single part that was covered with the coatings. This in fact has resulted in getting repeatable results and improved the machine's performance.

Finally, single layer ARCs were developed to coat on ZnSe and diamond optics. The material used, Y_2O_3 and Yb_2O_3 , were selected for the development of ARCs through the search in literature. Both materials have shown promising results in terms of increasing the transmission in diamond and ZnSe and in terms of their adhesion to diamond surface.

Therefore, single layer coatings for ZnSe and diamond optics were designed using Macleod software. The proposed designs for Y_2O_3 , suggested a single layer quarter wavelength at 5 μm , where maximum transmission could reach 98%. The coating thickness of the layer was calculated to be 1269 nm which would take 4.6 hours with a deposition rate of 2.55 nm/min⁻¹. For Yb_2O_3 , a single layer quarter wavelength at 3370 nm wavelength could potentially boost the transmission to 95%. The coating thickness layer was calculated to be 435 nm which could take 68 mins to achieve that level with a deposition rate of 6.4 nm/min⁻¹.

Unfortunately, the theoretical and experimental results could not be compared at this stage due to targets being broken. Once the materials arrive, the coating can be deposited on ZnSe and diamond optics. Finally, the coated optics could be examined using IR spectroscopy technique to compare their performance against the uncoated optics.

If successful, the restoration of the sputtering machine and the ability to coat such small optics in a mass production will help in the development of a new capability which creates a great business opportunity for TMF to give them a competitive edge over other local and regional companies.

5 FURTHER WORK

There is wide range of further work for future students interested in optical coatings. Being able to use the machine to consistently produce repeatable results would give future researchers work on improving the machine even further and improve the ARC quality. The immediate works that can be carried out are as follows:

- Establish if the new programme that records the dc bias of the first run and uses it for consecutive runs, works properly.
- Use the sputtering machine to deposit the designed coatings on ZnSe and diamond optics.
- Use the transmission measurements obtained by IR spectroscopy on the manufactured coated and uncoated diamond optics which were measured while installed in the ATR accessory. Investigate if the Y_2O_3 and Yb_2O_3 coated diamonds, using the restored machine, have equal or better transmission and reflection performance.

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