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INVESTIGATION OF SPUTTERING TECHNIQUES FOR CYCLOTRON TARGET
MANUFACTURING: EMPHASIZING MATERIAL EFFICIENCY

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I DEDICATE THIS WORK TO MY SON, LUKAS. I HAD MY FIRST PhD INTERVIEW WHEN YOU WERE JUST TWO WEEKS OLD, AND I BECAME A PhD STUDENT WHEN YOU WERE ONLY FOUR MONTHS OLD. BOTH OF THESE JOURNEYS, AS A FIRST-TIME MOTHER AND AS A PhD STUDENT, WERE CHALLENGING, BUT I HOPE YOU WILL BE GENUINELY PROUD OF ME WHEN YOU GROW UP. YOU ARE ALWAYS MY GREATEST JOY AND MY BIGGEST LOVE, A REMINDER OF THE FUTURE WE ALL ASPIRE TO BUILD.

Abstract

The development of innovative radiopharmaceuticals has garnered significant global interest. Non-conventional radioisotopes offer extensive possibilities for advanced diagnostics and disease treatments. Nowadays, medical or high-power cyclotrons using solid targets can generate many of these isotopes. Achieving high production yields requires increased currents, making the study of manufacturing methods for solid targets capable of withstanding higher energy loads a crucial area of focus.

Solid target requirements can vary based on their application, whether for production or nuclear cross-section studies, as well as the specific intended radioisotope. Consequently, various manufacturing methods can be adopted. Establishing a universal method for all materials proves unfeasible; thus, proposing, studying, and optimising new methods and approaches is essential.

The Surface Technologies and Superconductivity Service (STSS) at LNL, renowned for its expertise in film deposition, actively contributed to the LABoratory of RADionuclides for MEDicine (LARAMED) program. This program investigates various innovative techniques to enhance solid target production through different projects.

This dissertation focuses on the magnetron sputtering technique for solid target manufacturing. It introduces two novel approaches for thick film deposition that address material efficiency limitations. Magnetron sputtering deposition can produce high-density films that adhere firmly to the substrate. Additionally, it has fewer limitations regarding substrate shapes and materials, enabling the deposition of thick films on complex surfaces.

This study details the successful manufacturing of yttrium solid targets, achieving thicknesses of up to 200 μm . The process development involved overcoming challenges related to yttrium coating oxidation, film stress, and purity concerns. While further refinements are needed in developing and optimising the process for monoisotopic materials, the primary objective lies in devising a deposition approach adaptable to expensive isotopically enriched materials.

One of the proposed approaches in this work involves using a recovery shield, enabling the collection and retrieval of a substantial amount of material during the deposition process. Additionally, it was demonstrated that magnetron sputtering outperforms diode sputtering for solid target manufacturing. However, a material loss ranging from 5 to 10% must be considered. This approach created a 70 μm thick chromium coating on an Nb substrate.

A second proposed approach is the inverted magnetron configuration. Theoretically, with proper optimisation, such a magnetron source could significantly enhance the material efficiency of the deposition process. The unconventional sputtering process employed in this study demonstrated a notable increase in deposition rates for ceramic materials such as ^{nat}ZnO in the reactive deposition process.

The findings of this PhD study indicate that the magnetron sputtering technique has the potential to become a powerful tool in solid target manufacturing, provided that challenges related to material efficiency are overcome. As demonstrated in this research, the inverted magnetron approach could play a pivotal role in facilitating the utilisation of isotopically enriched materials.

Sommario

Lo sviluppo di radiofarmaci innovativi ha suscitato un notevole interesse a livello globale. Gli isotopi radioattivi non convenzionali offrono ampie possibilità per diagnostica avanzata e trattamenti delle malattie. Al giorno d'oggi, ciclotroni medici o ad alta potenza che utilizzano bersagli solidi possono generare molti di questi isotopi. La resa di produzione e la corrente del fascio sono direttamente correlate, un nodo cruciale della ricerca riguarda la produzione di bersagli solidi in grado di sostenere gli elevati carichi energetici richiesti.

I requisiti dei bersagli solidi variano in base alla loro applicazione: che sia per la produzione o per studi di sezione d'urto nucleare. Di conseguenza, possono essere adottati vari metodi di produzione. Stabilire un metodo universale per tutti i materiali risulta impraticabile; pertanto, è cruciale proporre, studiare e ottimizzare nuovi metodi e approcci.

Il Servizio Tecnologie delle Superfici e Superconduttività (STSS) presso LNL, rinomato per la sua competenza nella deposizione di film, ha contribuito attivamente al programma Laboratorio di RADionuclidi per la MEDicina (LARAMED). Attraverso i diversi progetti, questo programma esplora una serie di tecniche innovative per migliorare la produzione di bersagli solidi.

Questa tesi si concentra sulla tecnica di magnetron sputtering per la produzione di bersagli solidi. Introduce due nuovi approcci per la deposizione di film spessi che affrontano le limitazioni dell'efficienza del materiale. La deposizione tramite magnetron sputtering può produrre film ad alta densità con ottima adesione al substrato. Inoltre, presenta minori limitazioni in termini di forma e materiale del substrato, consentendo la deposizione di film spessi su superfici complesse.

Questo studio descrive la riuscita produzione di bersagli solidi di ittrio, raggiungendo spessori fino a 200 μm . Lo sviluppo del processo ha comportato la soluzione al problema legati all'ossidazione del rivestimento di ittrio, allo stress del film e alle purezza. Sebbene siano necessarie ulteriori ottimizzazioni del processo per materiali monoisotopici, l'obiettivo principale è ideare un approccio di deposizione adattabile a materiali isotopicamente arricchiti e costosi.

Uno dei metodi utilizzati prevede l'uso di uno schermo di recupero, consentendo la raccolta di una quantità sostanziale di materiale durante la deposizione. Inoltre, è stato dimostrato che il magnetron sputtering è più efficace dello sputtering a diodo nella produzione di bersagli solidi. Tuttavia, è necessario considerare una perdita di materiale che varia dal 5 al 10%. Questo approccio è stato utilizzato per creare un rivestimento di cromo spesso 70 μm su un substrato di Nb.

Una seconda tecnica proposta è la configurazione del magnetron invertito. Teoricamente, con una corretta ottimizzazione, una tale sorgente potrebbe migliorare significativamente l'efficienza di deposizione. Tale metodo non convenzionale impiegato in questo studio ha dimostrato un notevole aumento delle velocità di deposizione per materiali ceramici come ZnO nel processo di deposizione reattiva.

I risultati di questo studio di dottorato indicano che la tecnica di magnetron sputtering ha il potenziale per diventare uno strumento potente nella produzione di bersagli solidi, purché siano superate le sfide legate all'efficienza del materiale. Come dimostrato in questa ricerca, l'approccio del magnetron invertito potrebbe svolgere un ruolo fondamentale nel facilitare l'utilizzo di materiali isotopicamente arricchiti.

Introduction

Radiopharmaceutical production is a rapidly expanding sector in nuclear medicine, garnering considerable attention and investment. Research groups worldwide are actively pursuing the manufacture of novel non-conventional isotopes, envisaging their potential as potent diagnostic tools and promising disease treatment agents. A modern approach known as "theranostics" has gained a lot of interest lately. The theranostic approach targets specific areas accurately by combining therapeutic and diagnostic isotopes. This allows for diagnosis, treatment, and evaluation of treatment all at once. The ideal theranostic agents comprise chemically identical (or similar) radioisotope pairs, have similar half-lives, and have complementary emissions.

One promising method for novel isotope production involves cyclotron-driven processes, mainly using solid targets. The increasing demand for production necessitates stricter requirements for these solid targets. Elevated beam currents must generate higher activity levels of a specific isotope, intensifying the target's thermal load. As a result, more advanced strategies must be developed to create a target system capable of withstanding the required demand. The design of the solid targets can be different depending on the desirable characteristic and its specific application. Targets can be self-supported or attached to a backing of different materials. Target production is a highly complex task that involves the collaboration of various scientific specialists, including materials engineers, chemists, physicists, and many others [1].

Legnaro National Laboratories (LNL), a part of the National Institute for Nuclear Physics (INFN), actively participates in the investigation of non-conventional emerging radioisotopes. The Laboratory of RADioisotopes for MEDicine (LARAMED) program, initiated in 2012, has been actively involved in cyclotron-based radiopharmaceutical production, encompassing production rough, cross-section studies, and different solid target production techniques [2].

The Surface Technologies and Superconductivity Service of LNL [3], with over 20 years of experience in thin film development using PVD techniques, plays a significant role in solid target research and development. Magnetron sputtering deposition is one of the actively investigated techniques for solid target manufacturing, which is the focal point of this thesis. Based on the STSS laboratory experience, the process of ^{nat}Mo solid targets was developed, and the method of solid target preparation was patented.

While the magnetron sputtering technique is a well-established method for thin film deposition across various industries, its application in the medical field, particularly for coating metal implants and surgical instruments, has gained attention [4]. Some works also report its potential use in nuclear medicine as a corrosion-resistant coating for liquid cyclotron targets [5, 6]. This technique provides precise control over film thickness and ensures strong adhesion between the film and substrate.

However, a significant challenge associated with the sputtering technique is the high material loss during the deposition process, limiting its widespread adoption. While this loss might be a concern in specific applications, industries often prioritise the economic and practical benefits of magnetron sputtering, quickly recovering capital losses from material waste. The technique's advantages outweigh the material loss within the vacuum chamber in industrial settings, where materials are less expensive and purity requirements are lower.

Unfortunately, achieving elevated radionuclide purity and activity in producing conventional or emerging medical radionuclides requires manufacturing solid targets from isotopically enriched material (metal or compound). The cost of such material is extremely high, and the recovery process of the material must be included in each production chain [7].

Reporting a classification of the various methods that can be used for solid target manufacturing is not easy. In the work of [8], the authors suggested dividing them into three large groups: mechanical reshaping with power processing and physical and chemical methods. Each method has its benefits and limitations. For example, standard powder pressing is a relatively simple and quick method, especially whether the material of interest is available in powder form. The losses are minimal, and the target can be produced with a very small amount of material. The limitations, in the case of radioisotope production, are the mechanical properties of the achieved targets. When the target may endure a high beam power and for an extended duration, advanced sintering methods such as spark plasma sintering may be recommended [9, 10].

Since there is no ideal cyclotron solid target production technique, it is essential to investigate and upgrade new methods. This PhD dissertation shows the recent development of the magnetron sputtering technique for solid target manufacturing, emphasising attention to the high material loss problem, a limited sputtering technique from border utilisation in the nuclear medicine field. The work focuses on better understanding the magnetron sputtering techniques concerning nuclear medicine and proposing an alternative solution to exciting challenges.

The dissertation is organised into several essential chapters, each contributing distinct elements to the overall framework of the study.

Chapter 1: Nuclear Medicine. This chapter provides an overview and scientific context of the nuclear medicine field, where the fundamental element is a radionuclide. It shows the complete chain of radionuclide production, describing its main challenges. In the end, a short overview of the isotopes considered (^{89}Zr , ^{64}Cu , $^{51/52}\text{Mn}$) in this work is provided.

Chapter 2: Fundamentals of sputtering deposition. This chapter demonstrates the fundamentals of the sputtering process as a plasma-based deposition method. Moreover, it provides an overview of different sputtering techniques and their main configurations, emphasising the scientific context of magnetron sputtering as a technique for solid target manufacturing. A short overview of the materials Y, ZnO, and Cr sputtering process is provided.

Chapter 3: Experimental set-up & Characterisation. This chapter presents a detailed overview of the methodologies and instrumental setups employed throughout this research. This chapter describes utilised sputtering systems, characterisation instrumentation and analysis methods.

Chapter 4: Optimisation of yttrium solid target manufacturing: ultra-thick depositions. This chapter presents a successful case study of yttrium solid target preparation, reaching the ultra-high thickness (up to 200 μm) and promising results of ^{89}Zr production.

Chapter 5: New deposition approach: recovering shield. This chapter compares diode and magnetron sputtering processes, considering material losses and dissipation inside the vacuum chamber. This study used a novel recovery shield configuration to prepare the first Cr target prototype.

Chapter 6: New deposition approach: inverted magnetron. This chapter presents the design and production of an inverted magnetron, along with preliminary results using a Cu cathode. As a proof of concept, it demonstrates the successful deposition of thick ZnO coatings through the reactive deposition process.

Chapter 7: Discussion and future works. In this chapter, the magnetron sputtering is compared with other target manufacturing methods, discussing its advantages, limitations, and future possibilities.

Contents

DEDICATION	iii
ABSTRACT	v
SOMMARIO	vii
INTRODUCTION	ix
LIST OF FIGURES	xvi
LIST OF TABLES	xxi
I NUCLEAR MEDICINE	1
1.1 Radionuclides	2
1.1.1 Radiation decay	2
1.1.2 Radionuclide properties and characteristic	4
1.1.3 Diagnostic utilization	5
1.1.4 Therapy and Theranostic approach	8
1.2 Radionuclide production	11
1.2.1 Cyclotron production	12
1.3 Solid targets	16
1.3.1 Solid targets requirements	17
1.3.2 Solid targets manufacturing methods	19
1.4 Solid targets laboratory	21
1.4.1 Radionuclides of interest	24
2 FUNDAMENTALS OF SPUTTERING DEPOSITION	29
2.1 Glow discharge	30
2.1.1 Types of discharge	32
2.1.2 Sputtering process	33
2.2 Sputtering Configurations	33
2.2.1 Diode Sputtering	34
2.2.2 Magnetron Sputtering	35
2.2.3 Cylindrical magnetron's configurations	36
2.3 Reactive Magnetron Deposition	38
2.4 Films growth	40
2.4.1 Thin films	40
2.4.2 Thick coatings	43
2.5 Magnetron sputtering for target manufacturing	46
2.5.1 Material Efficiency Issue	47
3 EXPERIMENTAL SET-UP AND CHARACTERISATION	49
3.1 Vacuum systems	50

3.1.1	Multi-chamber deposition system	50
3.1.2	Baking process and ultra-high vacuum	52
3.1.3	ZnO deposition dedicated system	53
3.2	Non-commercial planar magnetron source	55
3.3	Cathode and substrates materials	57
3.3.1	Cleaning protocol	58
3.4	Characterisation techniques	59
3.4.1	Scanning Electron Microscopy and Energy Dispersive spectroscopy microanalysis	59
3.4.2	Profilometry	60
3.4.3	X-Ray diffractometry	61
3.4.4	Material-efficiency and density measurements	63
3.5	Thermo-mechanical evaluation via irradiation test	64
4	YTTRIUM SOLID TARGET MANUFACTURING: THICK FILM DEPOSITIONS	67
4.1	Yttrium deposition: state of the art at LNL	68
4.2	Process optimisation	68
4.2.1	Vacuum optimisation	69
4.2.2	Sample holder	70
4.2.3	Coating protocol upgrade	71
4.3	Yttrium depositions: Y2, Y3 and Y4	72
4.3.1	Thickness evaluation	74
4.3.2	Density evaluation	76
4.4	Process upgrade for thicker film sputtering	77
4.4.1	Parameter optimisation	78
4.4.2	Uniformity study	81
4.5	Thick yttrium deposition: Y5.0	83
4.6	Irradiation results	85
4.7	Conclusion and suggestions for future works	87
5	RECOVERING SHIELD DEPOSITION APPROACH	89
5.1	Recovering shield as a solution	90
5.1.1	Design of the system components	90
5.2	Sputtering depositions	93
5.2.1	Magnetron Sputtering	93
5.2.2	Diode Sputtering	94
5.3	Comparison study results	95
5.3.1	Material efficiency	95
5.3.2	Cathode utilisation	96
5.3.3	Growing behaviour comparison	97
5.4	Cr deposition test	100
5.4.1	Cr target manufacturing	102
5.5	Conclusion and suggestions for future works	106
6	INVERTED MAGNETRON DEPOSITION APPROACH	109
6.1	Inverted magnetron prototype design	110
6.1.1	Simplified design	111
6.1.2	Dedicated sample holder	111
6.1.3	Power connection issue	112

6.1.4	System adjustment	113
6.2	Preliminary test with copper cathode	115
6.3	Zinc oxide reactive sputtering deposition	120
6.3.1	Morphology and growing behaviour	122
6.3.2	Compound evaluation	125
6.3.3	Thermo-mechanical irradiation test	127
6.4	Cr deposition with IM configuration	128
6.5	Conclusions	132
7	DISCUSSION AND FUTURE WORKS	135
	GENERAL CONCLUSION	141
	REFERENCES	143
	ACKNOWLEDGMENTS	153

Listing of figures

1.1	Schematic representation of radiation types and their main applications.	2
1.2	Standard four-component, radiopharmaceutical design.	5
1.3	Simplified SPECT and PET scanners schemes and principals of radiation detection.	7
1.4	Linear Energy Transfer (LET) for different particle types (β^- , α and Auger electron).	10
1.5	A comparison of the number of cyclotrons globally and the number of reactors reported by the IAEA.	12
1.6	Scheme and principals of cyclotron work: S indicates ion source.	13
1.7	Radiometal cyclotron production cycle (A) and involved competence and inter-related tasks and contribution (B).	15
1.8	Different targets design produced by different groups: (A) capsule design, using powder pellets; (B) Pressed CaO target (6 mm $\times$ 0.5 mm) in Al capsule for ^{44}Sc ; (C) ^{nat}Tl Target assembly for ^{203}Pb production ; (D) Electrodeposited ^{70}Zn targets form fresh and recycled electrolyte; (E) Different Cr targets on the Cu backing for ^{52}Mn production; (F) Fused Zn target for ^{68}Ga production.	16
1.9	Scheme of solid targets requirements and characteristics.	17
1.10	Different proposal of solid target design for efficient heat exchange.	19
1.11	Layout of the RILAB solid targets laboratories on the second floor of the SPES building.	22
1.12	Solid targets for radionuclide production investigated at LNL.	23
2.1	Electrical breakdown in a gap between the electrodes with a distance d	30
2.2	The Paschen curves for different gases.	31
2.3	Current-voltage characteristic curve of DC electrical discharge in vacuum.	32
2.4	Different sputtering cathode configuration and magnetron's setups.	34
2.5	Cylindrical sputtering sources classification.	36
2.6	Hollow magnetron: (A) structure and (B)-Typical Current-Voltage (I-V) characteristic curve.	37
2.7	Reactive sputtering process:(A) Classical hysteresis effect of the reactive process and (B) calculated pressure vs the flow of reactive gas according to Berg model.	39
2.8	The Structural Zone Diagram (SZD) evolution from Movchan (1969) until Andres (2010).	41
2.9	Residual stress formation in the film: tensile and compressive stresses and their effects.	43
2.10	Stress measurement in the chromium thin films: (A) stress versus film thickness and (B) the relation of a coefficient α to the working pressure.	44
2.11	Conceptual images of the evolved SZM as a function of (A) effective particle energy per depositing atom (E_{Effect}), (B) T_{sub}/T_m , and (C) the combination of (A) and (B).	45
3.1	Four-chamber vacuum system (A) with dedicated controlling setup (B).	50
3.2	Diagram of multi-chamber vacuum system: blue line - gates control, yellow - compressed air line, red - gas line, green - venting line for system and turbo molecular pump.	51

3.3	The baking controlling system adopted for yttrium deposition: (A) dedicated vacuum chamber with resistance heating hoods and (B) dedicated ultra-high vacuum (UHV) baking controller.	52
3.4	Two-chamber vacuum system dedicated to ZnO deposition with its controlling setup.	54
3.5	Diagram of ZnO dedicated vacuum system: blue line - gates control, yellow - compressed air line, red - gas line, green - venting line for system and turbo molecular pump.	54
3.6	Two-inch planar magnetron configuration designed by STSS laboratory.	56
3.7	Non-commercial magnetron sputtering assembly: (A) copper base plate, (B) sputtering cathode, (C) centring ring, used to press and centre the sputtering cathode, (D) standard ground shield, used to ensure erosion only of the cathode.	57
3.8	Scanning Electron Microscope available at LNL (A) and the scheme of the principal components (B).	59
3.9	Linear contact profilometer Veeco Dektak 8. Add a standard profile of the measurements	61
3.10	X-Ray diffractometry (A) machine installed in STSS laboratory and (B) principal of its work.	62
3.11	Scientific balances: (A) EL303 with accuracy 0.001 g and (B) 0.01 mg	63
3.12	(A) Photo of ACSI TR19 cyclotron at SCDCH. (B) The solid target station of TR19/300 cyclotron. The blue arrow indicates the target coin's position inside the target station. Both photos courtesy of Sara Cisternino	64
4.1	Yttrium cathode analysis: (A) picture of the magnetron and cut yttrium target of Y1.0 deposition. Results of its energy dispersive spectroscopy (EDS) analysis: (B) mapping with different elements and (C) mapping of Ag element.	69
4.2	Sample holder for yttrium deposition: (A) base plate of the sample holder, (B) assembled with seven Nb disks, and (C) mounted with a dedicated mask.	70
4.3	The upgraded protocol of yttrium solid targets manufacturing with standard magnetron sputtering method.	71
4.4	The sample holder and yttrium eroded the cathode after the Y2.0 deposition. . .	73
4.5	Results of Y3.0 deposition: (A) sample holder, (B) yttrium eroded cathode, (C) copper base plate after the deposition, (D) completely eroded yttrium cathode with visible holes	74
4.6	Deposited mass and thickness of deposited targets (1-7) at three deposition batches (Y2.0, Y3.0 and Y4.0).	75
4.7	The coating thickness profile of yttrium targets, measured by contact profilometer: top - deposited at the central position of different batches; bottom - deposited at the side position, measured by the contact profilometer.	76
4.8	Graphical representation of the density calculation of each target in the three deposition batches: Y 2.0 - Y 4.0.	77
4.9	Cross-section SEM thickness evaluation compared with the results obtained by contact profilometer.	79
4.10	Thickness uniformity evaluation, by contact profilometer, over the 76 mm distance: top - samples picture; bottom - graphical representation of results, positioned in respect to the sample holder shown in the top of the figure.	82
4.11	Current (A) and new (B) sample holder design for yttrium solid targets depositions. 83	

4.12	Graphical representation of measured weight and thickness, together with the density calculation of each target in the Y 5.0 deposition	84
4.13	Y5.0 deposition results: (A) sample-holder with yttrium deposition, (B) single targets with and without defects, (C) seven targets packed in vacuum bags to prevent oxidation.	84
4.14	Visual inspection of irradiated yttrium targets Y4.7 and Y5.3	86
5.1	Designs:(A) Recovering shield (96 mm in diameter, 45 mm total height) and (B) sample holder inside the recovering shield with the variable working distance range 2–5 cm.	91
5.2	Produced recovering shield mounted in standard planar magnetron configuration (A) and design of its possible modification (B).	92
5.3	Sample holder designed (external diameter 44 mm) for the material efficiency study.	92
5.4	Recovering shield after the deposition at 4 (A) and 2.5 cm (B) working distance.	93
5.5	Diode sputtering deposition, test 2.1: (A) eroded centring ring (diameter 85 mm) and (B) thin copper coating on the sample holder.	95
5.6	Erosion of copper cathode in diode sputtering (A) and magnetron sputtering process (B).	96
5.7	Plasma light intensity in diode (A) and magnetron (B) sputtering process with distance 4 cm.	98
5.8	SEM analysis of thick copper coatings obtained by magnetron sputtering in test 1.1 (working distance 4 cm).	98
5.9	Picture of one-millimetre thick copper coating (A) and its SEM cross-section analysis. Coating sputtered within 6.5 hours by magnetron deposition technique with a working distance of 2.5 cm.	99
5.10	SEM cross-section analysis of copper coatings obtained by diode sputtering in test 2.2 (working distance 2.5 cm).	100
5.11	Sample holder before (A) and after (B) chromium deposition using the magnetron technique at a distance of 2.5 cm. Recovering shield with Cr deposition on its wall (C).	101
5.12	Morphology (left) and cross-section (right) SEM analysis of chromium film sputtered with Recovering shield for 6.5 hours, distance 2.5 cm.	102
5.13	SEM morphology analysis of chromium onto Nb (test Cr-7).	103
5.14	Deposition results of Cr-8 test: picture of sample holder after the deposition (A) and manufactured target (B).	103
5.15	Photos of sample holder before (A) and after (B) deposition Cr-9	104
5.16	SEM morphology analysis of Cr target (test Cr-9)	104
5.17	Diffractiongrams of Cr films sputtered onto Nb and quartz substrates.	105
6.1	Initial design of inverted cylindrical magnetron concept (A) and details on sealing and water cooling system.	110
6.2	Inverted magnetron prototype: (A) simplified design of inverted cylindrical magnetron source for solid target manufacturing with sample holder in axial position,(B) as produced and (C) with Cu cathode.	111
6.3	Sample holder for solid target manufacturing in IM, designed for horizontal and axial configuration.	112
6.4	Inverted magnetron and sample holder scheme.	113
6.5	Coil systems characteristic, measured in the central position.	114

6.6	Visual plasma evaluation. (A) sample holder inside the IM, (B) plasma light, (C) plasma evaluation under protective glass - no arcs detection, (D) plasma evaluation with arcs.	114
6.7	Manually prepared sample holder used in test Cu-16 (A), Si samples on the cover plate (B), quartz sample on the body of the sample holder (C). A sample holder for solid target manufacturing in the axial position was used in test Cu-17 (D). . .	116
6.8	SEM cross-section analysis of Cu deposition deposited in test Cu-16.	116
6.9	Copper deposition in IM configuration: (A) test Cu26, (B) test Cu-27	117
6.10	SEM cross-section analysis of test Cu-27, performed on Si samples and morphology analysis	117
6.11	Copper deposition in IM configuration: (A) plasma emission, (B) the overheating effect on the sample holder immediately after the power switch-off.	118
6.12	Cu-30 deposition test: (A) sample holder inside the IM before the deposition and (B) sample holder after Cu deposition.	119
6.13	SEM cross-section analysis of test Cu-30, performed on Si samples.	119
6.14	SEM morphological analysis on Cu coating deposited on Nb disks.	120
6.15	Test ZnO-8: (A) Zn cathode after the deposition; (B) sample holder after the deposition, covered by flakes; (C) quartz and Nb sample with ZnO deposition. . . .	121
6.16	SEM analysis of ZnO deposition onto Si substrate (ZnO-8): (a,b)cross-section and (c) morphology.	122
6.17	Cross-section SEM analysis of ZnO deposited (A) in IM configuration (ZnO-8), (B) in recovering shield approach (fixed current 0.3 A, 1-hour deposition, Ar flux - 1.8, O ₂ flux -1.2 sccm.)	123
6.18	Defects on the surface of produced solid targets: a and c - Target 1; b and d - Target 2.	124
6.19	Cross-section SEM analysis of ZnO on Nb coin (test ZnO-9).	125
6.20	Diffraction patterns of ZnO films sputtered onto Nb and quartz substrates compared to the diffraction pattern of ZnO powder, used for target sintering production. . . .	126
6.21	nat-ZnO sputtered solid targets: before (left) and after (right) the irradiations under the 19 MeV proton beam of the TR19 ASCI cyclotron (Negrar, Verona, Italy). 127	
6.22	Preparing of the cylindrical Cr cathode: (A) sputtering process using a planar magnetron source, (B) Cr deposits inside the cylindrical cathode, (C) protective bottom cover deposited with Cr layer.	128
6.23	Chromium deposition setup with IM configuration: (A) Sample holder with Cr protective cover, (B) sample holder inside the IM, in the vacuum chamber, (C) plasma emission during the deposition process.	129
6.24	First Cr solid target prototype, deposited with IM configuration.	130
6.25	SEM morphological analysis on Cu coating deposited on Nb disks.	130
6.26	Results of EDS analysis of Cr-IM-2 deposition surface areas.	131
7.1	The multi-target deposition approach: (A) scheme of the deposition process with inverted magnetron source and (B) a pentagon sample holder concept design, with dedicated masks for 20 targets manufacturing.	136
7.2	Scheme of the double-side deposition approach for inverted magnetron configuration.	137

Listing of tables

1.1	Radionuclides conventionally used for diagnostic using Single photon emission computerised tomography (SPECT) and Positron Emission Tomography (PET).	6
1.2	Main radionuclides used for therapy and theranostic applications.	9
1.3	Cyclotron distribution based on its operating energy.	13
1.4	Different target manufacturing methods.	20
1.5	Radionuclides conventionally used for therapy and theranostic applications. . . .	24
2.1	General parameters which influence future film's properties and characteristics. .	40
3.1	Baking process for ultra-high vacuum (UHV): parameters and results.	53
3.2	Cathode and substrate materials utilised in the work.	58
4.1	Base pressure obtained in all deposition batches after the baking process.	70
4.2	Yttrium deposition process (Y2.0): parameters and result.	72
4.3	Yttrium deposition parameter and deposition rate results at working distance. . .	73
4.4	Stress evaluation in yttrium deposition with reduced working distance 4 cm. . . .	78
4.5	Stress evaluation in yttrium deposition with 2.5 cm working distances and 1.2 A current.	80
4.6	Stress evaluation in yttrium deposition with 4 cm working distances and 1.4 A current.	81
4.7	Yttrium deposition parameters and results of Y 5.0 sputtering run.	83
4.8	Yttrium deposition parameter and deposition rate results of Y5.0 deposition. . . .	85
4.9	Activity measured in the recovery process for the irradiated targets.	86
5.1	Parameters of magnetron sputtering deposition process. Working current - 1A, Ar flux - 15 sccm, deposition time - 390 minutes.	94
5.2	Diode sputtering deposition parameters and deposition rate results: Ar flux 80 sccm, pumping speed 375 Hz.	94
5.3	Material dissipation results (in mg/min) for diode and sputtering process (working distance 2.5 cm).	95
5.4	Material efficiency evaluation (in %) for diode and sputtering process (working distance 2.5 cm).	96
5.5	Magnetron sputtering deposition parameters of Cr cathode.	100
5.6	Material efficiency evaluation for magnetron sputtering process for Cr deposition	101
5.7	Magnetron sputtering parameters of Cr deposition with working distance 4 cm, current of 1 A, and Ar flux 28.5 sccm.	102
6.1	Inverted magnetron sputtering deposition parameters of copper films, performed on different sample holders.	115
6.2	Inverted magnetron sputtering parameters for ZnO deposition.	120
6.3	Magnetron sputtering deposition parameters of ZnO.	122
6.4	Nat-ZnO targets characteristics and thermo-mechanical irradiation results.	127
6.5	Inverted magnetron sputtering parameters of Cr deposition: coil current 7A and working pressure $1.2 \cdot 10^{-2}$ mbar.	130

1

Nuclear medicine

Nuclear medicine is a branch of the medicine service that uses radioactive molecules, known as radiopharmaceuticals, to diagnose and treat various diseases and conditions, for instance, cardiovascular, oncological, and neurodegenerative diseases. It involves using small amounts of radioactive atoms to visualise the pathologies in the body's organs and tissues and to study physiological processes. Nuclear medicine, therefore, plays an essential role in achieving personalised medicine, a modern approach to diagnosis and selecting treatment tailored to the individual patient's condition or predisposition towards disease.

This chapter provides an overview and scientific context of the nuclear medicine field, where the fundamental element is a radionuclide. A radionuclide (or a radiotracer) is part of a complex radiopharmaceutical system whose properties are discussed in this chapter. It also explores the different methods of radioisotope production, with a particular emphasis on cyclotron production and the utilisation of solid targets as the initial material. Lastly, the chapter addresses solid targets' requirements and manufacturing techniques. The characteristics of radionuclides important for the dissertation are summarized at the end of the chapter.

I.1 RADIONUCLIDES

A radionuclide is an unstable isotope of an atom that emits radiation of different types and characteristics. Knowing the nature of the radiation gives us a greater understanding of handling and utilising possible radionuclides. A chemical formula usually describes the isotope:

$${}^A_ZX^N, \quad (1.1)$$

Where X indicates the chemical element, Z - is the atomic number of the element (number of protons), N is - the neutron number in the nucleus, and A - is the mass number of the nucleus (Z+N). Figure 1.1 schematically shows different types of radiation and utilisation potential, described below.

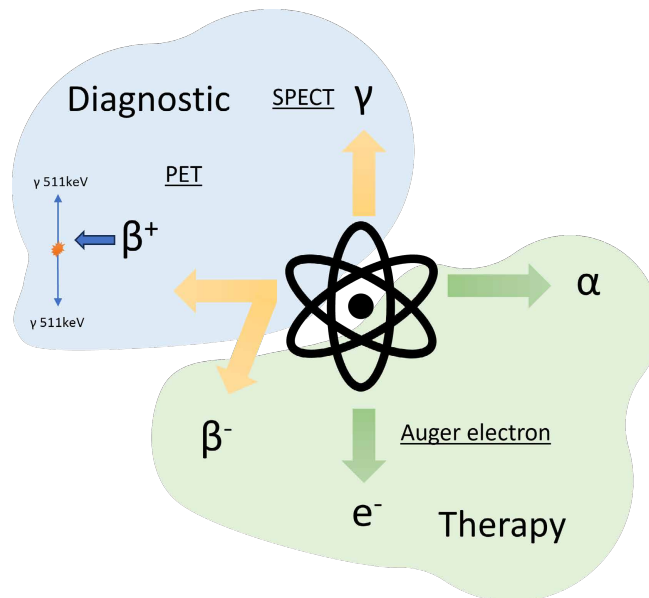


Figure 1.1: Schematic representation of radiation types and their main applications.

I.1.1 RADIATION DECAY

The α radiation. The α particle is a helium ion consisting of two protons and two neutrons. As a result of the decay, the daughter nucleus has four units of mass and two units of charge less than the parent nucleus. The reaction can be represented with the following formula:



The α decay is a characteristic radiation type for heavy ions. The energy associated with an emission ranges between 1 and 7 MeV. It corresponds to the energy gap between the parent nuclide and the daughter nuclide, so this energy can be measured to identify the emitting radionuclide.

The β^- decay. During the β^- decay, neutron essentially decays into a proton and a β^- particle (electron e^-). After the β^- decay, the atomic number of the daughter radionuclide is higher by one than that of the parent radionuclide, as can be represented by the reaction:



The β^- particle is emitted with an energy variable from 0 up to the decay energy (which is the difference in energy between the parent nuclide and the daughter one). If the daughter radionuclide is excited, the β^- decay can be followed by γ ray emission.

The positron β^+ decay. In contrast to the previous one, β^+ decay consists of transforming a proton into a neutron. The transformation occurs with the emission of a positive charge, the β^+ (positron e^+), and a neutrino. The element produced by positive beta decay has the same mass number; the atomic number decreased by one unit, the number of neutrons increased by one unit, and the number of protons or electrons decreased by one unit compared to the parent isotope, as shown in the following reaction:

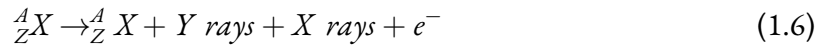


The positron has a short life and is quickly annihilated in a reaction with an electron, producing γ photons that are emitted in two opposite directions of characteristic energy (0.51 MeV), as shown in Figure 1.1.

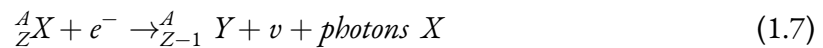
The γ radiation: electron capture, isomeric transition, internal conversion. When the emitted particles do not carry away all the energy associated with the decay process, the daughter nuclei do not acquire their ground state. Such nuclei can be in either an excited state or a metastable (isomeric) state. The transition of a nucleus from a metastable state to a stable state is called an **isomeric transition (IT)** [11, 12] and can be shown as the following formula:



In some cases, an alternate process called **internal conversion** can occur, resulting in the emission of an orbital electron (a conversion electron), as shown below:



An alternative to beta-plus decay for proton-rich radionuclides is **electron capture (EC)**. In this process, an inner shell orbital electron is absorbed into the nucleus, leading to the reduction of Z and the increase of N by 1, as represented by the following formula:



Photons (characteristic radiation) are emitted in the process, which may have considerable energy. These photons may knock out orbital electrons from outer orbits before leaving the atom, creating **Auger electrons**. Auger electrons may be helpful for therapeutic application (targeted therapy) due to their short range in the medium. Its therapeutic potential is shown in the following section.

I.1.2 RADIONUCLIDE PROPERTIES AND CHARACTERISTIC

In order to understand the principle of radionuclide utilization, it is important to consider another significant parameter, namely the half-life ($\tau_{1/2}$) of the radionuclide. Radioactive half-life is the time required for half (50%) of the radioactive atoms to undergo disintegration, representing the velocity of radioactive decay. Some radionuclides have half-lives of some seconds, but others have half-lives of millions of years. This parameter is crucial and must be considered from the radiation safety point of view.

For nuclear medicine applications, the half-life time must be enough to ensure the whole pharmaceutical path production (which is briefly discussed below) and provide enough signal for the medical procedure itself. Different studies require different times. For instance, some metabolic processes must be studied within 24 hours or more. For other diagnostic purposes, even 20 minutes is enough. However, these aspects require precise control since one of the tasks of nuclear medicine is to ensure minimum accumulation of unnecessary doses to the patient.

Radionuclides are used in nuclear medicine in the form of radiopharmaceuticals. A radiopharmaceutical is a drug comprising different components connected.

According to Thomas I. Kostelnik and Chris Orvig [13], the standard and more common four-component radiopharmaceutical design (see Figure 1.2) consists of (i) a radionuclide, (ii) a chelator agent that holds the radionuclide to a (iii) linker molecule, which, in turn, is linked to the (iv) targeting agent, a small molecule (or a biological agent) properly designed to uptake the over-expressed cell receptor.

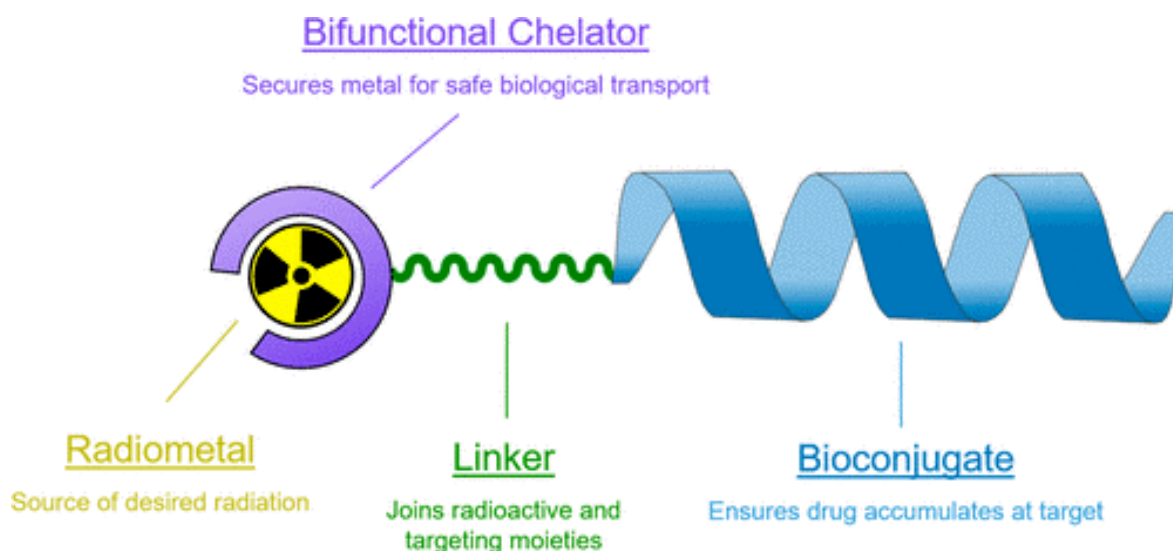


Figure 1.2: Standard four-component radiopharmaceutical design [13].

In this scenario, the decay characteristics of the radioisotope serve as the foundation for diagnostic and therapeutic functions, while the bio-conjugate facilitates the accumulation of drugs within target cells. The chelator and linker unite these two components that would otherwise be incompatible. This approach is widely adopted because it allows adjustments to individual components to fine-tune drug functionality, offering substantial potential [13]. Radiopharmaceuticals are tailored for specific applications to detect pathophysiological, metabolic, cellular, subcellular, or molecular processes.

1.1.3 DIAGNOSTIC UTILIZATION

A diagnostic radiopharmaceutical aims to provide detectable photons with minimal biological effect on the cells or organ, whereas it is desired to produce a cytotoxic effect in a therapeutic procedure. Generally, an ideal radiopharmaceutical for diagnostic procedures should meet the following characteristics: relatively short half-life, which provides a lower radiation dose to healthy organs; suitable radionuclide emission; high target to non-target ratio; target uptake rate; tracer excretion; availability [11].

The two primary components of nuclear medicine diagnostic procedures are radiopharmaceuticals and gamma-ray imaging systems. The latter is a position-sensitive radiation detector that relies on detecting gamma photons emitted from the administered radionuclide. Many single-photon and positron emitters are used in nuclear medicine clinical regimes, and some are shown in Table 1.1.

Table 1.1: Radionuclides conventionally used for diagnostic using Single photon emission computerised tomography (SPECT) and Positron Emission Tomography (PET).

Radionuclide	Decay type	Half-life	Application
^{11}C	β^+	20.4 min	PET Imaging
^{13}N	β^+	9.97 min	PET Imaging
^{15}O	β^+	2.03 min	PET Imaging
^{18}F	β^+	110 min	PET Imaging
^{67}Ga	EC	3.26 days	SPECT Imaging
$^{99\text{m}}\text{Tc}$	IT	6.02 hr	SPECT Imaging
^{123}I	EC	13.2 hr	SPECT Imaging

EC, electron capture; IT, isomeric transition. This table shows data represented in [14]

The gamma photons emitted from the localized tracer are then used to functionally map the distribution of the administered compound within different biological compartments. The imaging systems that detect radionuclide-labeled compounds are scintillation cameras or positron emission tomographic scanners. These devices have passed through several developments since their introduction in the 1950s–1960s and have significantly impacted the practice, diagnostic quality, and accuracy of nuclear medicine examinations. Figure 1.3 shows the simplified scheme of the SPECT and PET devices.

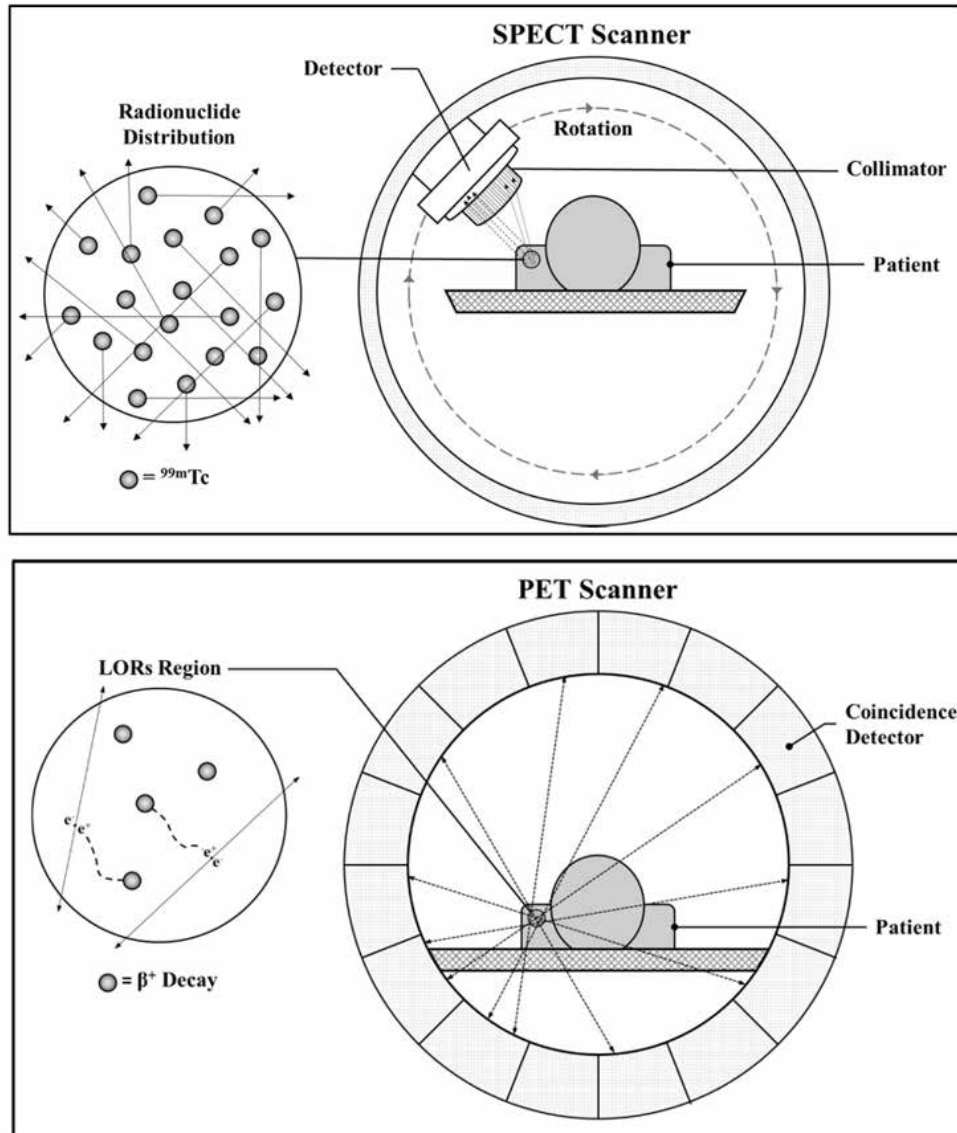


Figure 1.3: Simplified SPECT and PET scanners schemes and principals of radiation detection [15].

Single photon emission computerised tomography - SPECT

One of the earliest techniques used in medical imaging involves detecting single photons through a gamma camera. This camera can view organs from multiple angles and create an image based on the points from which radiation is emitted. The resulting image is then enhanced by a computer and viewed on a monitor for any signs of abnormal conditions. This technology, known as single photon emission computerised tomography (SPECT), is currently the leading scanning technology for diagnosing and monitoring a wide range of medical conditions [16]. Most SPECT scans use ^{99m}Tc -based radiopharmaceuticals.

Positron Emission Tomography - PET

Positron Emission Tomography (PET) was clinically introduced in the early 2000s. The glucose metabolism PET imaging for cancer evaluations and for assessing cerebral function and myocardial viability is a crucial modality in oncology, neurology, and cardiology [17]. The radiopharmaceuticals for PET provide more insights into the metabolic and molecular processes of the disease. This feature, in turn, has made PET a molecular imaging technique that examines biochemical processes at the molecular level.

The physics of PET imaging is based on positron emission, in which nuclei of excess protons exhibit nuclear transition by emitting a positron particle whose half-life is short. The positron travels a short distance based on its kinetic energy and then annihilates by combining with an electron in the surrounding medium to give two opposing 511-keV photons. When PET scanners detect these simultaneous γ -rays, computational methods calculate the radiotracer location by determining the point of annihilation. The distance a β^+ travels before annihilation is proportional to its energy; thus, the emission of low-energy positrons is preferred due to their proximity to the radiotracer at the point of annihilation. By far, the most commonly used PET radiotracer is the glucose analogue, [18F]FDG (18F-fluorodeoxyglucose), which has a natural propensity to be selectively taken up by aggressively growing tumours because of its similarity to glucose. The high radiotracer concentration in tumours and low background activity facilitates the acquisition of high-resolution images [13].

Of the two techniques, PET has superior sensitivity and resolution but is far more expensive than SPECT due to higher instrumentation costs and lower radionuclide availability. PET and SPECT provide high-quality morphological information but lack anatomical perspective. Accordingly, they are often combined with computed tomography (CT) or magnetic resonance (MR) imaging to produce a complete biological representation.

I.I.4 THERAPY AND THERANOSTIC APPROACH

Potentially, it is possible not only to detect tumours but also to treat them with certain types of radiation. In certain medical situations, it can be beneficial to eliminate or reduce malfunctioning cells by radionuclide utilisation. The radioisotope that produces the radiation can be directed to the necessary organ in the same manner as it is used for diagnosis, either by following its typical biological path or by linking it to a suitable biological compound.

In the majority of cases, beta radiation is the cause of the damaged cells' destruction. This is known as radionuclide therapy or radiotherapy. Brachytherapy, a form of short-range radiotherapy, is becoming the primary mode of treatment [16]. Table 1.2 reports the most commonly used radionuclides for radiotherapy.

Table 1.2: Main radionuclides used for therapy and theranostic applications [14, 18].

Radionuclide	Decay type	Half-life	Application
^{131}I	β^-	8.04 days	Therapy/Imaging
^{177}Lu	β^-	6.7 days	Therapy/Imaging
^{188}Re	β^-	17 h	Therapy
^{90}Y	β^-	2.7 days	Therapy
^{149}Tb	α -emitter	4.1 h	TAT
^{211}At	α -emitter	7.2 h	TAT
^{223}Ra	α -emitter	11.4 days	TAT
^{225}Ac	α -emitter	10 days	TAT
^{227}Tb	α -emitter	18.7 days	TAT
^{111}In	Auger e^- -emitter	2.8 days	Therapy
^{125}I	Auger e^- -emitter	60 days	Therapy

TAT - Targeted α Therapy.

Therapy

Radiotherapy makes use of radionuclides with lower penetrating but more energetic, hence, more ionizing emissions (β^- , α or Auger e^- emitters) (see Figure 1.1). As illustrated in Figure 1.4, **beta particles** can irradiate large volumes of multicellular dimensions. Because of their long range in tissue, β^- particles are considered ideal for treating large tumours. However, their long-range penetration also implies that untargeted neighbouring cells may be exposed to irradiation, too (cross-fire effect). **Alpha particles** can irradiate tumours of cell dimensions. Targeted α -therapy (TAT) is generally used to treat small haematological tumours or micrometastases. **Auger electrons** irradiate volumes with subcellular sizes. They are especially appropriate for delivering high radiation levels directly to the nucleus of cancer cells, avoiding off-site damage. The main challenge is, therefore, the careful targeting of the selected area [18].

The ability of an emitted particle to damage DNA is heavily dependent on its linear energy transfer (LET), which measures atom ionization/excitation per unit length and is commonly reported in keV/ μm for biological systems (see Figure 1.4). High LET signifies dense energy deposition and is typical of highly ionizing radiation, causing particles to deposit their energy over shorter distances and be more effective at causing biological or chemical damage.

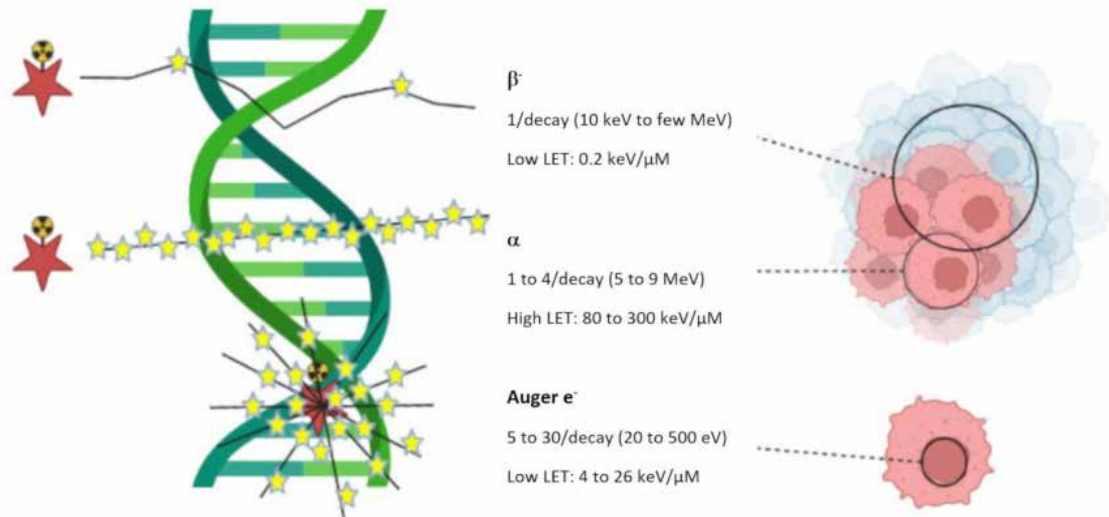


Figure 1.4: Linear Energy Transfer (LET) for different particle types (β^- , α and Auger electron) [18].

For example, the particle with higher LET deposits its energy more rapidly, resulting in a shorter tissue range when two particles have identical energy but different LET. On the other hand, when two particles have identical LET but different energies, the high-energy particle takes longer to deposit its energy, resulting in a greater tissue range. Long tissue range can help treat large tumours but is increasingly undesirable because it is directly linked to off-target toxicity [13, 18].

Theranostic

Correct and precise targeting is one of the most crucial aspects of radiotherapy. The theranostic approach has been proposed to tackle this issue. This approach makes use of combined therapeutic and diagnostic isotopes. This is desirable because it allows for diagnosis, treatment, and evaluation of treatment all at once or following a therapeutic regimen. Some radiometals are inherently theranostic, generally by a therapeutic nuclide having an imageable γ -line (e.g., ^{47}Sc , ^{177}Lu , ^{131}I); however, the ideal theranostic agents are composed of chemically identical radioisotope pairs with similar half-lives and complementary emission, for instance, ^{123}I e ^{131}I , or ^{64}Cu e ^{67}Cu and newer examples are $^{86}\text{Y}/^{90}\text{Y}$ or quadruple of terbium isotopes: ^{152}Tb (beta plus emitter), ^{155}Tb (gamma emitter), ^{149}Tb (alpha emitter), and ^{161}Tb (beta minus particle). In this way, the diagnostic and therapeutic decay modes are optimal (i.e., high branching and appropriate energy), and the radioisotopes exhibit identical (bio)chemical behaviour, notably to the chelator. This behaviour ensures the therapeutic radiotracer behaves identically to the diagnostic radiotracer in vivo, which is crucial for accurate dosimetry [13, 19].

1.2 RADIONUCLIDE PRODUCTION

Nuclear reactors, charged particle accelerators, or radionuclide generators can artificially produce radionuclides used in nuclear medicine. Each production method produces radioisotopes with inherently different characteristics, determining their clinical utility [20].

Nuclear reactors have for many years provided large quantities of radionuclides for nuclear medicine. There are two main ways for radionuclide production through nuclear reactors: directly from the fission process and by neutron flux activation. Fission has been used to produce ^{131}I , ^{133}Xe and the parent radionuclide for ^{99m}Tc production - ^{99}Mo . Such radionuclides tend to decay by β^- emission and may be carrier-free (no stable isotope of the element of interest is produced). The lack of specificity of the fission process is a drawback that results in a relatively low yield of the radionuclide of interest among many other radionuclides. On the other hand, the radionuclides produced by neutron activation have the following general characteristics: the tendency to β^- emission; products are usually not carrier-free and low specific activity [14].

Another production way, as was advised before, is a **radionuclide generator**. This apparatus consists of a parent-daughter radionuclide pair and permits separation and extraction of the daughter nuclide from the parent. The daughter product activity is replenished continuously by the decay of the parent and may be extracted repeatedly. Apart from ^{99}Mo - ^{99m}Tc system, some positron emitters can also be produced this way, for instance, ^{68}Ge - ^{68}Ga , ^{82}Sr - ^{82}Rb systems.

Van de Graaff accelerators, linear accelerators, cyclotrons, and variations of cyclotrons have been used to accelerate charged particles, which can consequently be used for radionuclide production. The cyclotron is the most widely used particle accelerator for producing medically essential isotopes. Many larger institutions have compact biomedical cyclotrons to produce the shorter-lived, positron-emitting radionuclides onsite.

The principles and design of cyclotrons dedicated to producing radionuclides for nuclear medicine are described briefly in the next section. However, it is essential to note that cyclotron-driven radionuclide production is gaining more interest over the years. As seen in Figure 1.5, the number of cyclotrons is growing continuously; meanwhile, the number of nuclear reactors is declining.

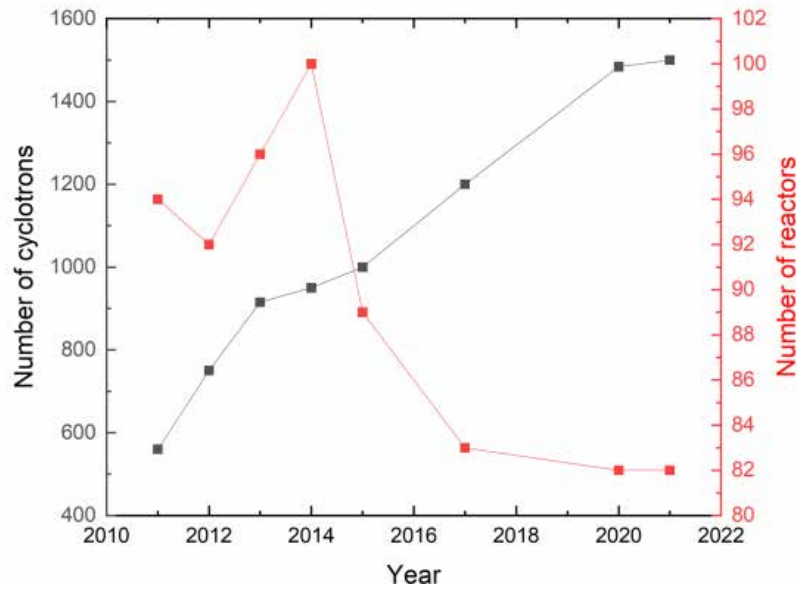


Figure 1.5: A comparison of the number of cyclotrons globally and the number of reactors reported by the IAEA [21].

This trend probably continue since the reactors that produce medical radioisotopes are experiencing ageing issues, requiring major refurbishments or complete replacement with new ones to avoid radioisotope shortages.

1.2.1 CYCLOTRON PRODUCTION

Cyclotrons are used to produce a variety of radionuclides for nuclear medicine. In this case, the projectile particle is typically an alpha, deuteron or proton, which accelerates to high energies (10 – 100 MeV) before bombarding a stable target. The target is our starting material, where the nuclear reaction occurs during the irradiation, producing the desired radionuclide. Compared to nuclear reactions involving neutrons, the charged projectiles must be accelerated to high energies to overcome the Coulomb barrier of target nuclei (the energy barrier that two nuclei need to overcome to get close enough for a nuclear reaction to occur).

A cyclotron consists of a pair of hollow, semicircular metal electrodes (dees) positioned between the poles of a large electromagnet (Figure 1.6). The dees are separated from one another by a narrow gap. Near the centre of the dees is an ion source, S (typically an electrical arc device in a gas), used to generate the charged particles. All these components are contained in a vacuum tank at 10^{-3} Pa.

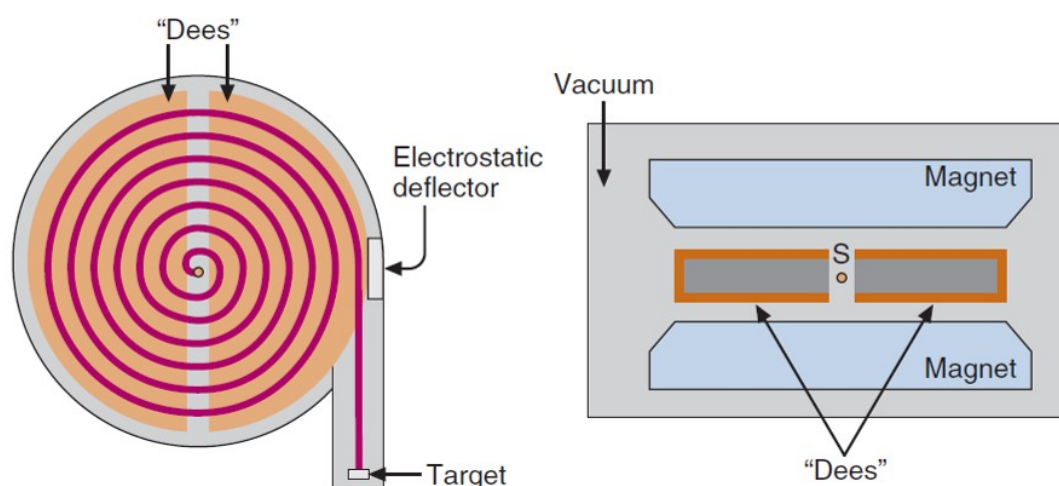


Figure 1.6: Scheme and principals of cyclotron work: *S* indicates ion source [14].

During operation, particles are generated in bursts by the ion source. A high-frequency alternating current (AC) voltage generated by a high-frequency oscillator is applied across the dees. The particles are injected into the gap and immediately are accelerated toward one of the dees by the electrical field generated by the applied AC voltage. There is no electrical field inside the dee, but because the particles are in a magnetic field, they follow a curved, circular path around the opposite side of the dee. The AC voltage frequency is such that the particles arrive at the gap just as the voltage across the dees reaches its maximum value in the opposite direction. Each time the particles cross the gap, they gain energy, so the orbital radius continuously increases, and the particles follow an outwardly spiralling path. The increasing speed of the particles exactly compensates for the increasing distance travelled per half orbit, and they continue to arrive back at the gap precisely in phase with the AC voltage. This condition applies so long as the charge-to-mass ratio of the accelerated particles remains constant.

Among the available cyclotrons, the ones used in medicine can be divided according to the available beam output energy, as shown in Table 1.3.

Table 1.3: Cyclotron distribution based on its operating energy [22].

Cyclotron type	Energy Range	Approximate number
Small medical cyclotron	<20MeV	1050
Intermediate energy	20-35 MeV	100
High energy	>35 MeV	50

The radioisotopes produced in cyclotrons are neutron deficient, as opposed to those produced in a reactor which has a neutron excess, and as such decay via different means, namely electron capture and positron emissions [14, 20].

The products are generally of high specific activity. This is because the target and product usually have a significant difference in atomic number, making the product's chemical and physical separation more successful.

Of special interest are the short-lived positron emitters ^{11}C , ^{13}N , and ^{15}O listed in the Table 1.1. These radionuclides represent elements that are important constituents of all biological substances, and they can be used to label a wide variety of biologically relevant tracers. Because of their very short lifetimes, these positron-emitting radionuclides must be prepared onsite with a dedicated biomedical cyclotron. If desired, this may be used to supply the hospital onsite and surrounding areas. However, production also supplies smaller quantities due to the smaller target areas and low beam intensity relative to a reactor, meaning cyclotron-produced radioisotopes are often more expensive. Nevertheless, because of the importance of several positron emitters—labelled radiopharmaceuticals, there are now many hundreds of cyclotrons worldwide producing short-lived positron-emitting isotopes for nuclear medicine imaging studies.

Usually, targets used to produce medical radionuclides are made of enriched isotopes. They have various dimensions, thicknesses, physical (solid, liquid, gaseous) and chemical (elemental, compound or alloy) forms. They can be self-supporting or attached to a backing; they can be used inside the accelerator (so-called internal targets) or in external setups on the beamlines [8].

Besides the irradiation step, the radiopharmaceutical production through the cyclotron includes different pre and post-irradiation tasks: target production, separation and purification and target recovery. The latest has become increasingly important since highly enriched material utilization is usually the case. In the [1], authors show the interaction of the competence needed for proper radiopharmaceutical development.

For instance, radionuclide production starts with nuclear cross-section studies, where the nuclear reaction is evaluated to employ the correct irradiation parameters, such as projectile types, beam energies and irradiation time. This step provides crucial information for target design development. However, target preparation must also consider subsequent post-irradiation steps - such as target processing, separation and recovery. In the ideal case, the target material must be recovered to the starting form, allowing the application of the same preparation method. Moreover, the cyclotron's target station and transfer system also provide some target requirements. For instance, after the irradiation, the target material is sent to a hot cell, where the radioactive material thus produced can be safely manipulated. Thus, the target design must be adapted to facilitate its use by special manipulators.

As shown in Figure 1.7, the radionuclide production is a constant cycle, where one step influences all others. Thus, radiopharmaceutical production can happen only through productive collaboration between all physics, chemistry, engineering and material science specialists.

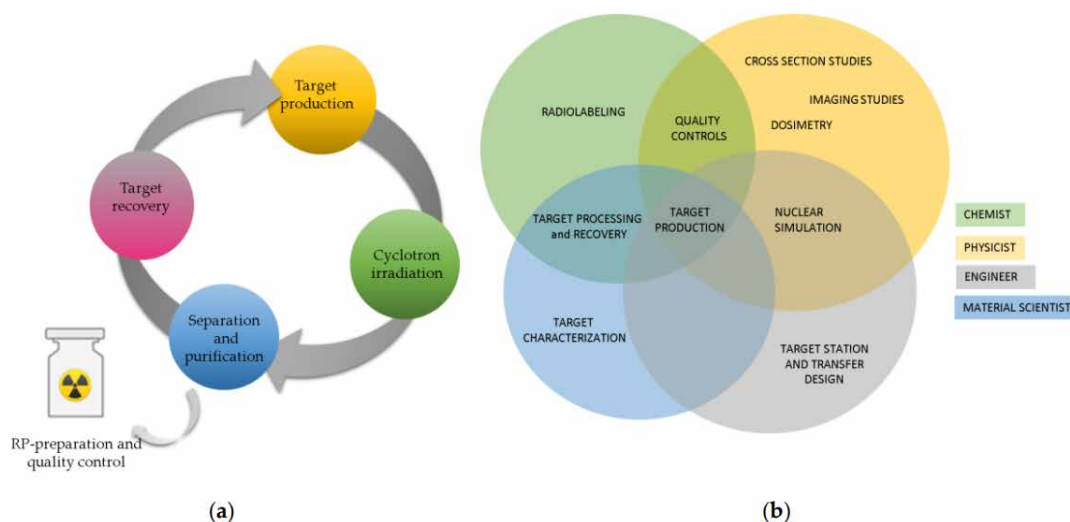


Figure 1.7: Radiometal cyclotron production cycle (A) and involved competence and interrelated tasks and contribution (B) [1].

Many cyclotrons use *liquid targets* for the production of ^{18}F and *gas targets* for the production of ^{11}C . Liquid target systems, while famous for the production of ^{18}F using enriched water, are also used for the production of radiometals such as ^{68}Ga , ^{64}Cu , ^{61}Cu , ^{89}Zr , ^{44}Sc , ^{86}Y , ^{63}Zn and $^{94\text{m}}\text{Tc}$. They can shorten the pre- and post-irradiation target preparation steps (shown in Figure 1.7 (a)) and simplify the target transfer after irradiation. In addition, liquid targets can produce radiometals with existing medical cyclotrons without investment for a solid-target station. Liquid targets should be prepared such that the saturation point is not reached such that precipitation occurs [23]. Solid targets, in the form of metallic foil/coin, metallic powder or oxide form, are mainly used for the cyclotron production of $^{99\text{m}}\text{Tc}$, ^{67}Ga , ^{111}In , ^{64}Cu , ^{61}Cu , ^{68}Ge , ^{103}Pd , and ^{89}Zr [1, 24]. The next section is dedicated to the solid target design and characteristics since they are of interest to this research work.

I.3 SOLID TARGETS

The interest in solid target manufacturing has grown over recent years [7, 1]. Such targets can be used to produce conventional and non-conventional medical radionuclides. Figure 1.8 shows some examples of such targets.



Figure 1.8: Different targets design, produced by different groups: (A) Capsule design, using powder pellets [25]; (B) Pressed CaO target (6 mm × 0.5 mm) in Al capsule for ^{44}Sc [26]; (C) ^{nat}Tl Target assembly for ^{203}Pb production [27]; (D) Electrodeposited ^{70}Zn targets from fresh and recycled electrolyte [28]; (E) Different Cr targets on the Cu backing for ^{52}Mn production [29]; (F) Fused Zn target for ^{68}Ga production [30].

The solid targets' design can differ depending on the desirable characteristic and its specific application. Despite the target's diversity, they all must meet the requirements discussed in the next section.

1.3.1 SOLID TARGETS REQUIREMENTS

The target's requirements are schematically shown in Figure 1.9. These requirements define the target characteristics and can vary depending on the target application. This dissertation concentrates on thick targets used for radiopharmaceutical high-yield production. Another type of target is a target for nuclear cross-section measurements, which are usually much thinner - $1 \mu\text{g}/\text{cm}^2$ up to $10\text{--}20 \text{ mg}/\text{cm}^2$, which corresponds to tens of μm [10, 9].

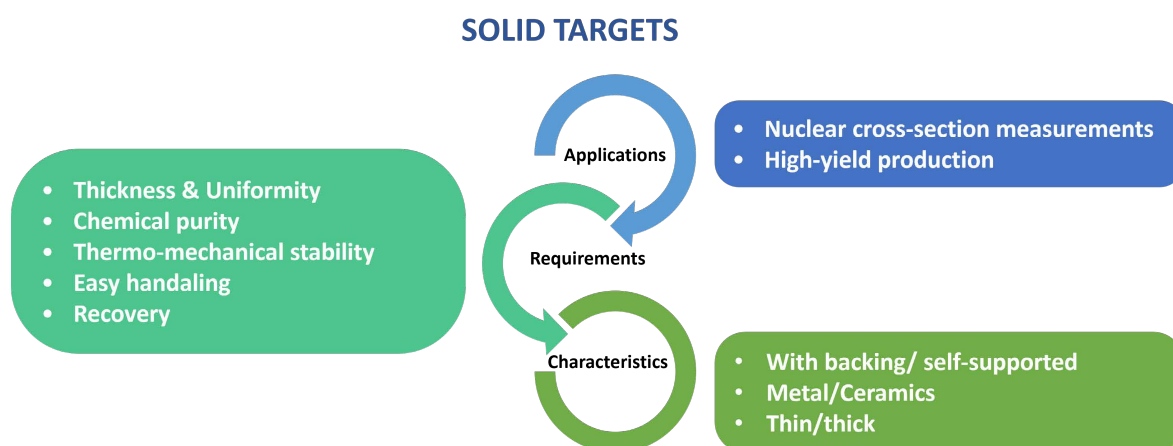


Figure 1.9: Scheme of solid targets requirements and characteristics.

Depending on the desired radionuclide, the first and most important task is to decide the target and the backing materials (if applied). In this case, it is necessary to consider not only a manufacturing method but also irradiation and post-irradiation steps, as represented in Figure 1.7.

There are two critical requirements for the target with backing to be applied for radiopharmaceutical production: the high level of heat dissipation (to use maximum cyclotron current to reach maximum production yield) and the inertness of the base plate in the target dissolution conditions to provide chemical and radio-chemical purity of the product [31]. Thus, evaluating a material's physical and chemical properties is crucial.

Physical properties of target material. Some metals have very low melting temperatures, and the integrity of the solid target for high-yield production is questionable. For such material, it is always possible to search for oxide or another compound with an isotope of interest. Another question is the form of the material available in the market and its possible recovery to this form since, in most cases, the use of isotopically enriched material is preferable, and it is costly and provided by few suppliers in the world.

Heat dissipation and inertness of backing material. Different backing materials can be used for the solid targets. As in the case of backing material, Cu has high thermal conductivity ($400 \text{ W/m} \cdot \text{K}$) and can allow the utilisation of higher currents. However, it can be activated during irradiation and produce contamination during the dissolution and separation processes. It is still utilised but with a thick gold protection layer, ensuring future steps. However, other inert materials like Nb [32] or high thermal conductive ceramics (CVD diamonds, sapphire) [31] can be utilised instead. Nb backing is a good compromise for its acceptable thermal conductivity ($53.7 \text{ W/m} \cdot \text{K}$), high melting temperature ($T_{m_{Nb}} = 2468^\circ\text{C}$), sufficient inertness in HCl (typical solution for dissolution of the target after the irradiation) and its relatively low activation under the beam. Despite the listed properties, in the work [32], it is reported that some amount of Nb is found in the solution after the dissolution step. Thus, depending on the HCl concentration or the temperature used, to ensure chemical purity, the author suggests using a thin gold as a protective layer and using a design dissolution reactor [33].

Thickness. The solid cyclotron target must be manufactured with a well-defined thickness and possible density. Following this requirement is important since it ensures proper radionuclide production and purity in the chosen energy range. Nuclear cross-section measurements are necessary to know this energy range and maximise the production yield [34].

Mechanical strength. Solid targets must possess mechanical strength to ensure their integrity during irradiation, transfer to the hot cells, and all necessary manipulation. Moreover, the target shape and design must provide easy handling of the target at all stages, especially in hot cells where manipulators are used.

Not only the material properties are essential for the target manufacturing. Many groups [35, 36, 37, 38] are working on backing design optimisation. Figure 1.10 shows different target designs to improve heat dissipation and target cooling, resulting in higher current utilisation. Since the highest possible production yield is desirable, such targets increase in future studies.

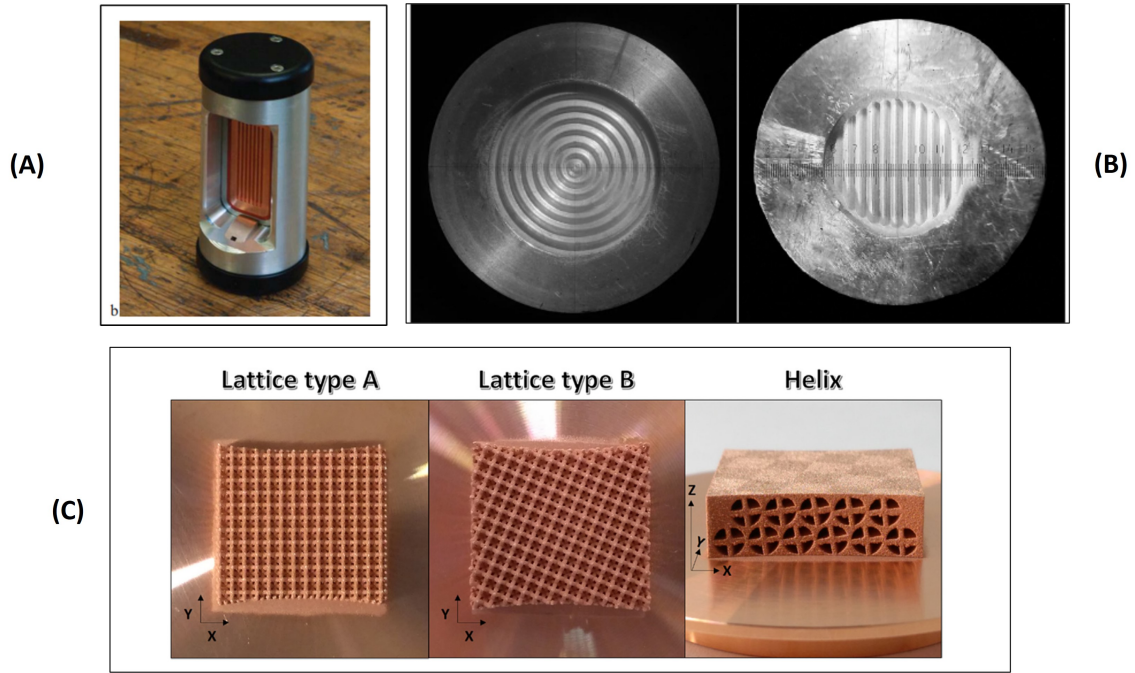


Figure 1.10: Different proposal of solid Target design for efficient heat exchange (A) [35] (B) [36], (C) [37].

The design shown in Figure 1.10 B is developed by the Armenian group and can be used for target manufacturing by different methods, including pressing. On the other hand, Figure 1.10 C shows a design that might have some limitations on pressure-assisted manufacturing methods utilisation but may be potentially used with the manufacturing method described in this work. The heat sink mockup, shown in 1.10C, can be attached to the target backing at the production step (more efficient from a thermal dissipation point of view) or after the complete target manufacturing.

1.3.2 SOLID TARGETS MANUFACTURING METHODS

Reporting a classification of the various methods that can be used for solid target manufacturing is not easy. In the work dedicated to the targets for nuclear medicine measurements (not production) [8], the authors suggested dividing them into three large groups: (i) mechanical reshaping or powder processing, (ii) physical and (iii) chemical methods. This approach can be extended to the targets for the production, considering that elevated thicknesses are required. There is no ideal method for all the materials and radionuclides. Each method has its benefits and limitations; the most used methods in all three categories is described in this section. Moreover, conventional and innovative methods are summarised in Table 1.4. The table consists of data interpretation of the similar tables reported in several works [8, 39, 32].

Table 1.4: Different target manufacturing methods.

Method	Thickness	Limitation	Material utilization Efficiency
Powder pressing	100s μm to mm	Low density and fragile. Require a binder for hard materials	>95%
Sintering	nm to 100mm	Oxygen-sensitive materials require method optimization	>95%
Rolling	10s μm to mm	Can be applied only to metals	80-90%
Melting	100s μm to mm	For high-melting-temperature materials, laser melting should be used	>95%
Electrodeposition	nm to mm	contamination, limited material can be deposited from aqueous solution	80-90%
Sedimentation	100s μm to mm	A binder is needed. Possible impurities	>95%
Sputtering	nm to 100mm	High losses, not applicable for isotopically enriched material	20-30%

Powder processing. Often, the starting material for solid target manufacturing is available only in powder form, which is usually the case for isotopically enriched materials. The pressing method allows working with a minimum amount of material and, as a result, provides a high efficiency of target manufacturing. The powder targets can be produced as a self-supported pellet [25] or compressed into a container [26]. In the [8], it is suggested that pressing should be carried with simultaneous pumping to reduce the amount of gas (air) that may be compressed in the tablet since the excess of the gas may cause its explosion when heated by the beam or when heated in a crucible for evaporation. Targets are usually produced by a simple hydraulic press setup. An advanced sintering method can be suggested to improve the target mechanical strength and ability to sustain high currents for a long time. One of these methods is Spark Plasma Sintering (SPS), which is described in the next section.

Electrodeposition. Another conventional chemical versatile technique is electrodeposition from an aqueous or organic medium. The process of target manufacturing requires a conductive baking substrate. The method guarantees no cross-contamination since each deposition cell is devoted to a particular isotope [8]. The electrodeposition technique assures high efficiency and the ability to produce targets from a small amount of material. It can be applied to many metallic elements, such as Zn, Ni, Cr, and Ta [28, 29, 40, 41]. Moreover, such a method allows for simple material recovery and utilisation. Figure 1.8 D is shown as an example of enriched electroplated ^{70}Zn target produced from fresh and recycled electrolytes.

The electrodeposition technique also allows the preparation of radioactive solid targets. A noticeable drawback of the method is the possibility of introducing impurities from the solvent or the electrodes. For this reason, the electrolyte for depositions must be as simplified as possible.

Physical method. One of the most used methods among the physical - is melting onto the backing. This method can be adapted for different metals (Ge, Zn, Te). To avoid contamination and oxidation, such processes must occur in a vacuum chamber [7, 30, 42]. Another possible physical method is evaporation, which occurs in a high-vacuum environment, thus reducing the contaminants. The source material is evaporated from a heated suitable crucible and collected on a substrate above the vapour source. Volatile impurities present in the source material are removed before evaporation–condensation by heating the material at a temperature close to, but lower than, its melting point. The substrate is protected against those impurities by a movable shutter between the vapour source and the substrate.

The innovative methods for solid target production, under investigation at the Italian Institute of Nuclear Physic-Legnaro National Laboratories (INFN-LNL), is discussed in the next section.

I.4 SOLID TARGETS LABORATORY

As was anticipated in the introduction, this work is a collaboration of STSS service, advancing in PVD techniques, with the LARAMED program of INFN-LNL. The LARAMED program started as a part of the SPES project (Selective Production of Exotic Species) to establish an advanced science and technology hub to study and develop new or more efficient methods for producing radionuclides with high potential medical interest [2]. The core of the SPES project is the model 70p cyclotron by BCSI (BESTTM Theratronics, Canada) installed at LNL in May 2015. It is a dual-beam operational cyclotron, with the proton beam energy tuneable at 70-35 MeV and a high output current (up to 750 μ A). The cyclotron is located in the central bunker on the underground floor of the SPES building.

LARAMED program includes research on different fields, from theoretical and experimental nuclear physics activities to radiochemistry aspects, technical R&D on mechanical engineering and materials science, and up to issues related to nuclear medicine.

In the work [2] described in detail the future SPES facilities. One of the RILAB (RadioIsotope LABoratory) laboratories is dedicated to the R&D of solid target manufacturing by different innovative techniques. Dedicated laboratories are foreseen on the second floor of the SPES building, as shown in the layout in Figure 1.11.

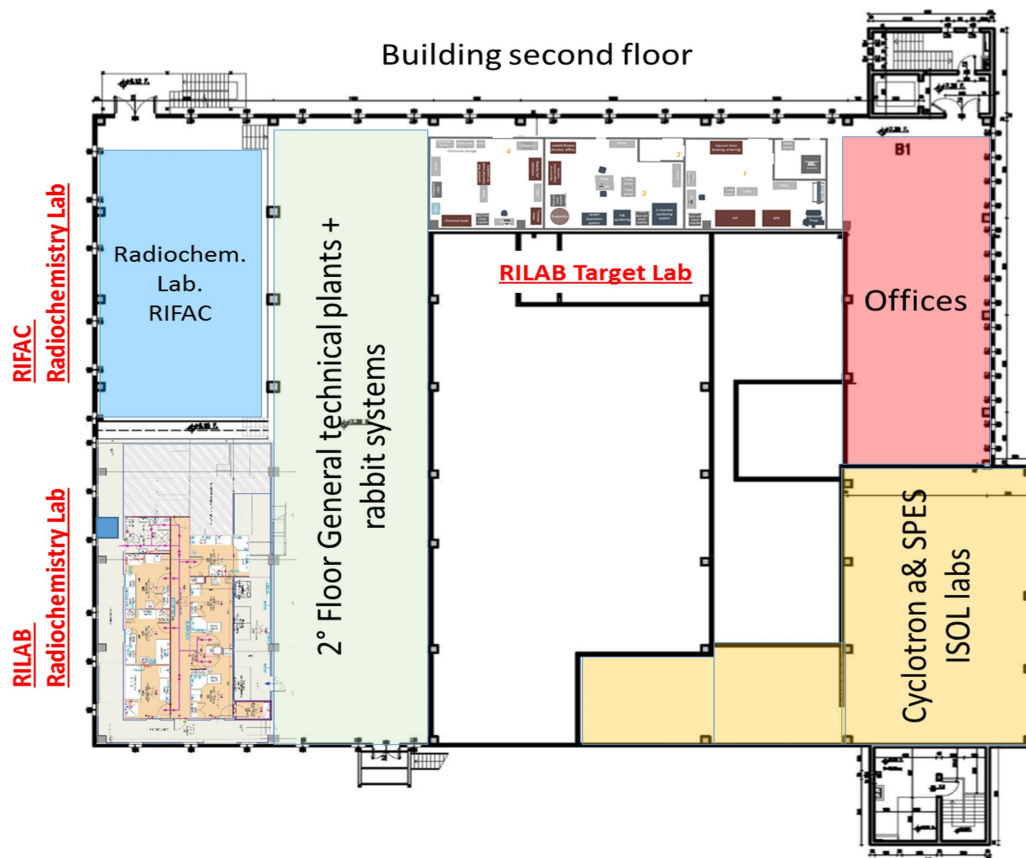


Figure 1.11: Layout of the RILAB solid targets laboratories on the second floor of the SPES building.

The RILAB target laboratory is divided into three main sections: a chemistry laboratory (with electrodeposition setups and recovery systems), a clean room laboratory (for vacuum systems involved in deposition), and an SPS laboratory.

The solid targets produced in the framework of the LARAMED program are shown in Figure 1.12. Currently, three methods are actively investigated: High-energy Vibrational Powder Plating (HIVIPP), Spark Plasma Sintering (SPS) and Magnetron Sputtering (MS).

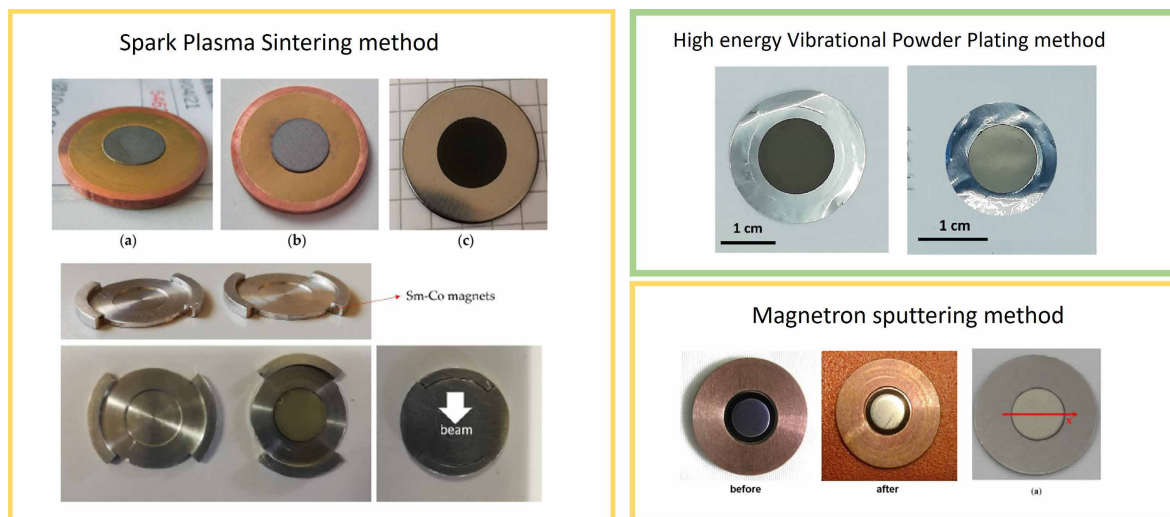


Figure 1.12: Solid targets for radionuclide production investigated at LNL [9, 32, 10].

The HIVIPP method was first proposed in 1997 by a Japanese researcher and has shown promising results. The HIVIPP method allows the preparation of targets with areal densities ranging from $\mu\text{g}/\text{cm}^2$ up to mg/cm^2 with a very high yield and excellent thickness homogeneity, even superior to the one obtained by evaporation. In the framework of LARAMED program, this method was used to produce thin solid targets of expensive Ti isotopes (^{48}Ti , ^{49}Ti , ^{50}Ti) onto Al substrate [43, 44]. The studies show that this method is highly efficient from a material usage point of view. However, the results are highly dependent on the powder shape and distribution. Thus, additional procedures, such as cryo milling [43], must be applied in some cases.

Another method deeply investigated in the LARAMED program is **SPS**. This method is one of the numerous non-conventional sintering methods applied in different research and industrial fields. The SPS technique is very attractive for the manufacturing of cyclotron solid targets. The SPS process allows the sintering of a pellet starting from the exact amount of the target material powder and attaching it onto a backing plate. Good thermo-mechanical contact is guaranteed between the materials, achieving as high a heat power removal as possible during the irradiation. Using the necessary amount of the starting material with minimal losses during the process is crucial because of the high cost of the highly enriched isotope materials, which are usually necessary to produce medical-interest radionuclides. In addition, enriched materials are generally provided in powder form, perfectly fitting the SPS process [32, 9].

In the framework of the LARAMED program, this method was used to produce thick solid targets of ^{nat}Y and ^{52}Cr . Currently, the LARAMED program is focusing on ^{70}ZnO solid target manufacturing by the SPS method for copper isotope production. Sintering of the ceramics required additional investigation. However, some promising preliminary results were already shown in [32].

Over the last decade, the Surface Technologies and Superconductivity Service (STSS) of LNL investigated the magnetron sputtering technique for thick coating deposition. Such a manufacturing method was developed for solid Mo targets to study and establish cyclotron-driven ^{99m}Tc production. Skliarova et al. in the [45, 39, 10] demonstrated deep research of thick ^{nat}Mo solid targets production. As a result of this work, the technological method of solid target manufacturing via magnetron sputtering was patented [46]. Despite the outstanding achievement and realisation of the targets that can sustain high currents, it was impossible to step into the enriched material with high material losses and low method efficiency.

I.4.1 RADIONUCLIDES OF INTEREST

This dissertation is focused on the investigation of sputtering techniques for potential application in solid target manufacturing. This work is taking part in the following projects: METRICS (Multimodal PET/MRI imaging with cyclotron-produced $^{52/51}Mn$ and stable paramagnetic Mn isotopes) and INTEF_TOTEM (Magnetron sputtering cyclotron target manufacturing) and collaboration with the Sacro Cuore Don Calabria Hospital for ^{89}Zr radionuclide production. Table 1.5 shows the radionuclides of interest, their properties and possible utilisation. A short overview of the utilisation and production methods of such radionuclides is discussed.

Table 1.5: Radionuclides conventionally used for therapy and theranostic applications.

Radionuclide	Decay type	Half-life	Application
^{89}Zr	β^+	78.4 hours	PET immuno-imaging
^{67}Cu	β^-	61.83 hours	Theranostic/SPECT
^{64}Cu	β^+	12.7 hours	PET Imaging/Theranostic
^{52}Mn	β^+	5.591 days	PET-MRI

Zirconium-89 is a promising radionuclide under investigation by different research groups. It can be used in so-called immuno-PET, where radionuclide is connected to the monoclonal antibodies and can improve solid tumour diagnostics. It is important that ^{89}Zr has a longer half-life in comparison to the conventional PET radiopharmaceuticals, which also allows studying biodistribution of long-circulating proteins and antibodies [22, 47].

^{89}Zr can be produced by $^{89}\text{Y}(p,n)^{89}\text{Zr}$ reaction. Fortunately, natural yttrium isotopic composition is 100.00% ^{89}Y , which makes the target production relatively cheap. However, contamination problems can still occur due to the other metal contaminants in the target or improper beam range selection [7]. A different method of Y target preparation has been adapted for Zirconium-89 production; for instance, many groups are using Y foils, while others are studying alternative methods such as pressing, sputtering, sedimentation, and even electrodeposition from non-aqueous (ethanol) solutions [48, 47].

Copper-67 is an interesting theranostic radionuclide suitable for SPECT, which gained much attention from the scientific community [49, 50, 28]. Similar to the ^{89}Zr , ^{67}Cu can be used with antibodies and, thanks to its long half-life, be a candidate for slow biodistribution studies. ^{67}Cu is also a pure β^- emitter suitable for the therapeutic application. Moreover, it can be combined with other copper isotopes ^{64}Cu , ^{61}Cu , and ^{60}Cu (all β^+ emitters) to perform pretherapy biodistribution determinations and dosimetry. In this regard, **Copper-64** is the most promising pair candidate since its production techniques are well established. In the case of ^{67}Cu the production of pure high-yield ^{67}Cu is challenging due to the co-production of ^{64}Cu . Despite the large number of nuclear reaction optimisation studies, the pre-clinical and clinical studies are limited by the need for a suitable target to sustain the high proton beam current. The starting materials for the production of copper-67 are the isotopically enriched $^{68/70}\text{Zn}$, for example, through the $^{68}\text{Zn}(p, 2p)^{67}\text{Cu}$ or $^{70}\text{Zn}(p, \alpha)^{67}\text{Cu}$ reactions at middle and/or high proton energies. Since the melting point of metallic Zn is relatively low ($T_m = 419.5^\circ\text{C}$), and the target can be damaged under the high current proton beam, ZnO with higher melting temperature ($T_m = 1975^\circ\text{C}$) has been considered as well. It is important to note that compared to metals, oxides usually have lower thermal conductivity, which limits their utilization. Among the most popular methods for Zn targets manufacturing is electrodeposition onto different backing materials, melting or rolling.

Manganese-52 is a long-lived positron emitter suitable for PET studies. Furthermore, considering that non-radioactive manganese has been employed as a contrast-enhancing agent in Manganese Enhanced MRI (MEMRI), radioactive ^{52}Mn can be combined with non-radioactive manganese to produce a dual-modality signal-enhancing contrast agent for PET/MR imaging. Many research groups extensively studied such an approach, including LNL [51, 29]. Many studies described different possible areas of application of radioactive manganese. The most popular are immuno-PET, as described before, diabetes progression studies, labelling and tracking of cells and liposomes in vivo, bone scintigraphy, and myocardial perfusion imaging.

^{52}Mn has a longer half-life and provides better imaging resolution of PET in comparison to ^{89}Zr and ^{67}Cu due to the lower average β^+ energy. The radiochemistry and chelation of manganese are well-studied. Despite these advantageous characteristics, the complicated dosimetry limits the ^{52}Mn utilisation in pre-clinical studies. On the other hand, this problem is less significant for drug development, where the tracer is used only for drug metabolism study [52]. Manganese-52 can be produced with different reactions using different starting materials - vanadium, chromium or iron. The most studied reaction for ^{52}Mn production through cyclotron irradiation is $^{nat}\text{Cr}(p, n)^{52}\text{Mn}$ reaction, using the natural Cr foils. Nevertheless, as evidenced in existing literature, the co-production of several impurities is possible. To mitigate these impurities' production, an enriched ^{52}Cr target via the $^{52}\text{Cr}(p, n)^{52}\text{Mn}$ reaction at energies below 16 MeV is recommended. The isotopic abundance of ^{52}Cr is 83.789%, and it is relatively costly (approximately 5 USD/mg) [32]. Electrodeposition, powder pressing, and melting are popular Cr target manufacturing methods.

2

Fundamentals of sputtering deposition

Sputtering is one of the physical vapour deposition (PVD) techniques, allowing precise process control to tune the properties of the deposited material. Robert Grove first observed the sputtering phenomenon in 1852 as a side effect of glow discharge, and by the late 1800s, sputter-deposition was routinely used in manufacturing commercial mirrors. The discovery of the magnetron sputtering approach, initially on hollow cathodes in 1921 and later on planar cathodes in 1970, significantly accelerated the industrialisation of the technique. The evolution of magnetron sputtering has continued, resulting in new approaches, such as high-power impulse magnetron sputter deposition (HiPIMS), to meet the industry's high demand.

This chapter describes the fundamentals of the sputtering process as a plasma-based deposition method. Moreover, it provides an overview of different sputtering techniques and their main configurations, emphasising the scientific context of magnetron sputtering as a technique for solid target manufacturing. In this regard, it is essential to address such questions as thick film deposition and the residual stress evolution in the film. Additionally, discussing the low material efficiency problem and ways of overcoming it is essential and takes part in this dissertation.

It should be noted that the term 'target' is commonly used in the radiopharmaceutical field as a starting material for radionuclide production. In contrast, the sputtering field uses it for a material to be deposited, also known as a cathode or sputtering material. To avoid confusion, this dissertation uses 'target' about the radiopharmaceutical field and 'cathode' for the sputtering material.

2.1 GLOW DISCHARGE

The sputtering process is connected to plasma generation and its main characteristics. Plasma is a weakly ionised gas containing electrons, ions and neutral specimens. In this section, is discussed artificially created plasma, whose ion densities range from 10^8 to 10^{14} cm^{-3} . The simplified scheme of glow discharge between two parallel electrodes is shown in Figure 2.1. The electrodes are placed in a low-pressure gas media, and the difference of potential is applied between them.

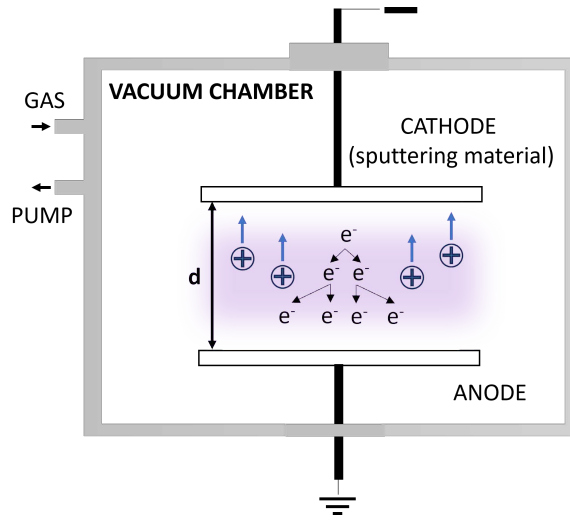


Figure 2.1: Electrical breakdown in a gap between the electrodes with a distance d .

In this case, the plasma is created by electron bombardment. The electron with initial current i_0 is accelerated toward the anode due to the electric field applied between the two electrodes. After the electron with sufficient energy collides with neutral gas specimens creates a gas ion. The following reaction can describe the gas ionisation in the case of Argon gas (Ar):



This process releases one additional electron, which can be accelerated and can create more gas ions. The produced gas ions can be then accelerated to the negatively charged cathode, colliding with it and thus ejecting cathode particles and secondary electrons. This chain of effect continues until a large current accumulates to cause the gas breakdown. One of the critical parameters for maintaining a discharge is the distance, d , between electrodes.

The ionisation process can be described by Townsend equation [53]:

$$i = i_0 \cdot \frac{e^{\alpha \cdot d}}{[1 - \gamma_c(e^{\alpha \cdot d} - 1)]} \quad (2.2)$$

Where i - is a discharge current, γ_e is the secondary-electron Townsend constant, and α is the Townsend ionisation coefficient. Known as the Townsend ionization coefficient, α represents the probability per unit length of ionisation occurring during an electron-gas atom collision.

Another important parameter is a voltage breakdown, which can be described by Paschen's Law:

$$V_B = \frac{APd}{\ln(Pd) + B} \quad (2.3)$$

The plot of V_B vs. Pd , also known as the Paschen curve, shows the breakdown voltage needed to sustain the discharge for different gases. That distance d commonly remains constant while the gas pressure can be adjusted. At low pressure (see Figure 2.2), there are few electron-ion collisions. Thus, the secondary electron yield is also low to sustain the discharge. In this case, the mean free path becomes comparable to or longer than the gap between electrodes. On the other side of the curve, when gas pressure is too high, there are too many collisions, but electrons are not gaining enough energy to produce ions. The self-sustained region usually ranges from a few hundred to a thousand volts.

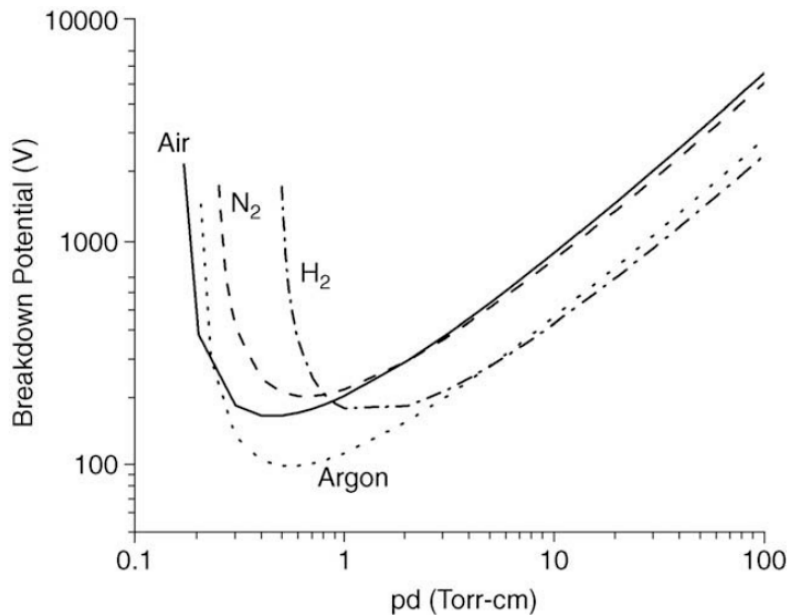


Figure 2.2: The Paschen curves for different gases[54].

The minimum voltage is different for gases since they have different molecule or atom sizes. Noble mono-atomic gases, such as Ar, have smaller diameters and, thus, a higher mean free path length. As a result, a lower V_B is achievable. Additionally, ionization potentials and the speed at which molecules recapture electrons vary, affecting the minimum voltage required.

2.1.1 TYPES OF DISCHARGE

The discharge can also be described by the current-voltage ($I - V$) curve. Figure 2.3 shows different discharge regimes over the voltage increase. As voltage is first applied, the current is shallow and consists of various contributions. Initially, this current stays constant while the voltage is rapidly increasing. This voltage increase can lead to electrons' energy growth, producing more gas ions and, consequently, more secondary electrons. This region is known as the **Townsend regime**. In this regime, the current is growing while the voltage is limited by the output impedance of the power supply. The Townsend discharge is not luminous since the density of excited atoms, which emit visible light, is low.

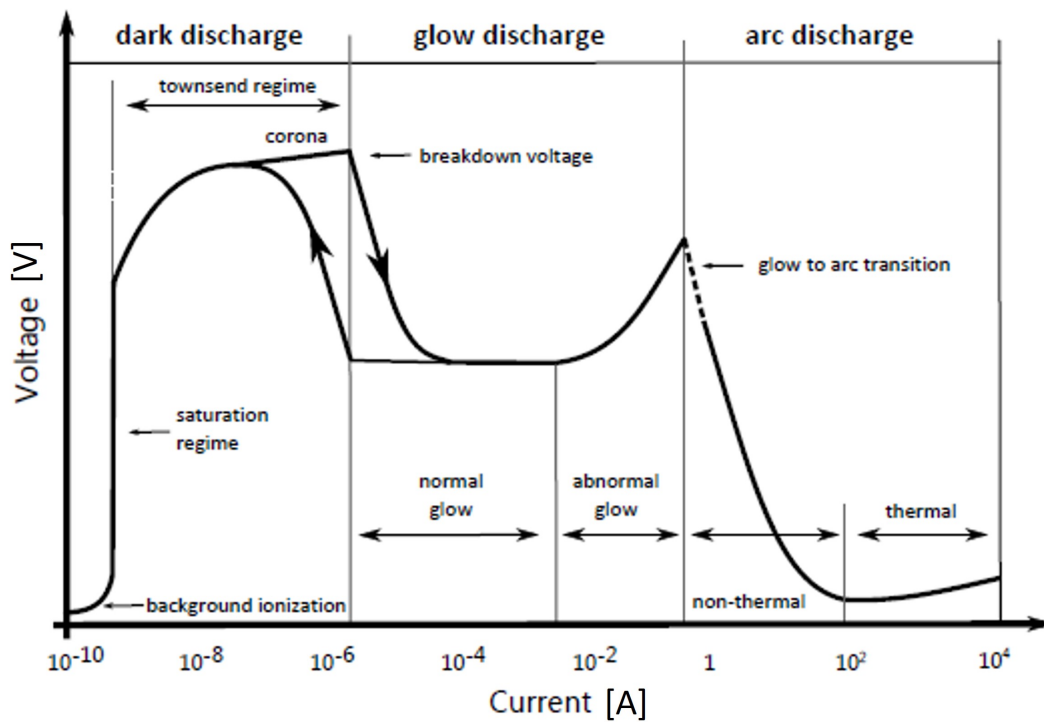


Figure 2.3: Current-voltage characteristic curve of DC electrical discharge in vacuum[55].

The following region, usually known as a **normal discharge**, happens after the critical Break-down voltage point. At this point, the voltage drops together with a sharp increase in the current. At this regime, the glow is already visible and self-sustaining, but it is not yet homogeneous concerning the cathode area [56]. As soon as homogeneity is reached, the current increment leads to the voltage rise, which indicates the transition to **abnormal glow discharge**. This regime is where the sputtering process is occurring. The discharge is more luminous and intense.

With the further increase of the current, the discharge starts to transfer into the arcs. This effect leads to the cathode surface heating, and when the surface is hot enough, the electrons are emitted via thermionic emission. The discharge makes the transition to the **arc regime**. A plasma in this stage is characterised by low voltage (up to 100 V) and high currents (up to 100 A).

2.1.2 SPUTTERING PROCESS

The previous section describes the plasma between two electrodes in the vacuum chamber. As was advised, the sputtering process can occur in the abnormal discharge regime, where homogeneous plasma is created.

An energetic particle can create different effects by transferring its energy to the cathode surface. Most energy appears as heat in the surface region. Some collisions lead to the ejection of sputtered atoms, while others can cause neutral gas ion reflection or even gas implantation.

To describe the efficiency of the sputtered atoms ejection, **the sputtering yield** parameter was introduced. It is a ratio of the number of particles ejected to the number of incident bombarding particles. Sputtering is less energy-efficient than thermal vaporisation. The sputtering yield depends on the energies and dimensions of incident particles together with the nature of the cathode material (atom size, crystal structure).

It is worth saying that the sputtering cathode is commonly cooled down by water circulation. Heat accumulation is undesirable due to particle bombardment and low sputtering yield. On the other hand, reducing the cathode temperature can provide some advantages for the film deposition. The thermally sensitive substrate can be placed near the cathode, enlarging the sputtering deposition application field. Additionally, cooling prevents the diffusion process in the cathode, which can be an issue for alloy sputtering depositions.

2.2 SPUTTERING CONFIGURATIONS

The most straightforward sputtering configuration, as was mentioned in the section 2.1 and shown in Figure 2.1, is two parallel electrodes connected to the DC power supply. Luckily, the development and optimisation of the sputtering technique were of high interest, primarily due to their high industrial potential. Nowadays, there are many commercially available sputtering sources suitable for different applications.

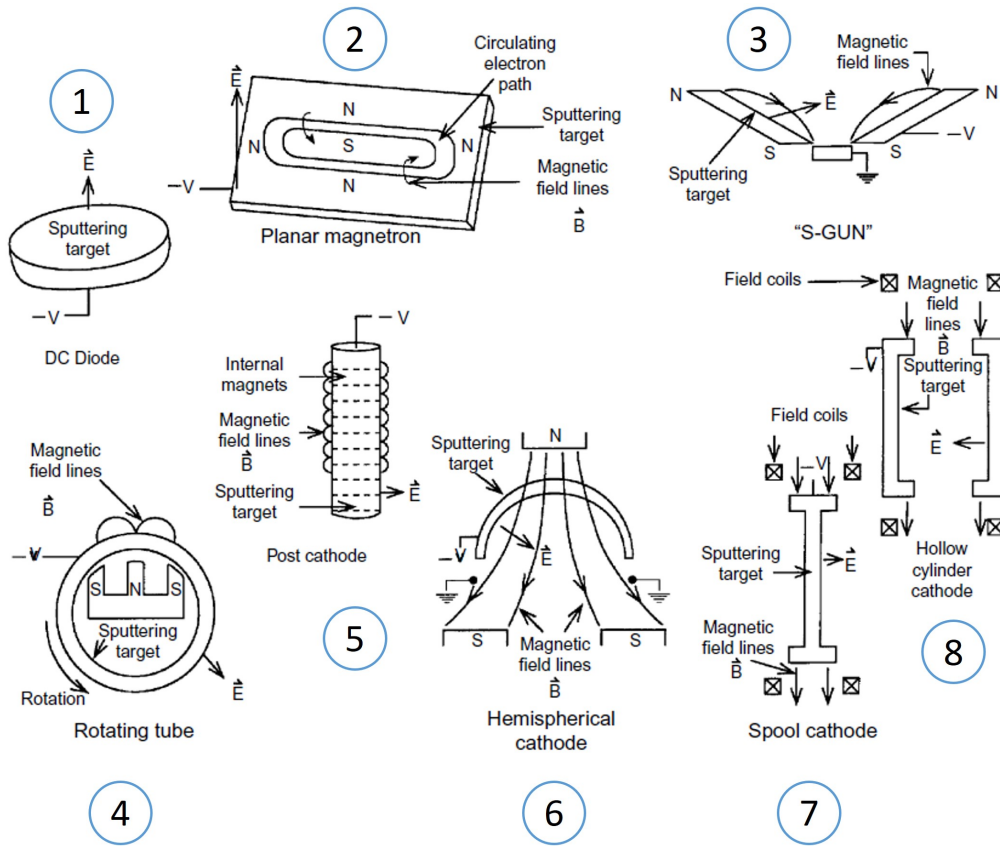


Figure 2.4: Different sputtering cathode configuration and magnetron's setups [57].

2.2.1 DIODE SPUTTERING

Diode sputtering (DS) is the simple sputtering process which can be described with the abnormal discharge regime. The sputtering material is connected negatively, while the substrate takes the place of the anode, as shown in Figure 2.4 1. The gas pressure must be relatively high (more than 1 Pa) to establish the DS process to create enough collisions. Moreover, a high voltage (more than 1kV) must be applied. Diode sputtering can also be performed with different power sources, such as radio frequency (RF). RF diode sputtering can be performed at lower gas pressures, and the usual frequencies used for the sputtering range from 0.5 to 30 MHz (13,56 MHz being the most common commercially used) [57]. RF sputtering can sputter electrically insulating material with a low sputtering rate.

Diode sputtering was considered in this research work as a technique for solid target manufacturing since it can provide uniform cathode erosion and possibly be more efficient from a material point of view.

2.2.2 MAGNETRON SPUTTERING

Magnetron sputtering (MS) is achieved by applying a magnetic field to the standard sputtering process. The magnetic field attracts secondary electrons, keeping them near the cathode surface. Through strategic magnet placement, electrons circulate the cathode in a closed path. This configuration leads to a dense electron concentration, elevating the likelihood of atom-ion collisions and fostering a high-density plasma. The different MS configurations are shown in Figure 2.4 (2,4-8).

Applying magnetic field to the sputtering process brings many advantages, attractive for its fast industrialisation: high deposition rates (1-10 nm/s), low thermal load to the substrates, ease of scalability, and dense, well-adhered coating. With the MS technique, it is possible to sputter almost all metals and their compounds on different substrates[4, 58]. Moreover, MS configuration allows deposition at lower pressures and operating voltages.

MS can be utilised in different configurations of shapes. Figure 2.4 shows different cathode shapes and mechanisms of its operating. Regarding this matter, the focus lies on the planar and hollow cylindrical configurations. **Planar magnetron configuration** can be realised in different forms, for instance, with rectangular or circular cathode shapes. Some interesting approaches, such as dual opposing or triangular magnetron sets, can be adopted.

In function to the difference in intensity between the inner and outer magnets, the magnetron sources can also be divided into **balanced**, **unbalanced**. The plasma is strongly confined to the cathode region in a balanced standard configuration. On the other hand, in an unbalanced MS configuration, one of the magnet sets (outer or inner) is strengthened; in this case, not all field lines between the central and outer poles of the magnetron are closed.

In an unbalanced magnetron, either the central magnet or the outer magnets are stronger than the other, causing magnetic lines to extend into outer space. Electrons in a magnetron follow these magnetic field lines. Specifically, when the central magnet is stronger (unbalanced of the first type), electrons are lost from the plasma radially. Conversely, when the outer magnets are stronger (unbalanced of the second type), electrons may end up close to the substrate. The second type of unbalanced magnetron shifts the plasma toward the substrate, driving more electrons and ions onto the sample's surface. This effect leads to additional substrate heating, thereby assisting the deposition process and facilitating chemical reactions.

Magnetron sputtering can be operated using different power modes: direct current (DC), radio frequency (RF), Pulsed and HiPIMS (High Power Impulse Magnetron Sputtering).

2.2.3 CYLINDRICAL MAGNETRON'S CONFIGURATIONS

One noticeable and high-performant magnetron configuration is cylindrical magnetron sources, already shown in Figure 2.4(4,5,7,8).

It is hard to avoid confusion while discussing the cylindrical magnetrons and their classification. In the early works of Thornton, there are apparent descriptions of **hollow** and **post-magnetrons**. The work [59] mentioned that the hollow magnetron sometimes can be called as **an inverted**. In recent works, the term "hollow" is used for different magnetron configurations, as shown in Figure 2.5. Sometimes, the anode or substrate material is placed outside the hollow cathode [60, 61], with a particular sputtering process called hollow plasma jet sputtering.

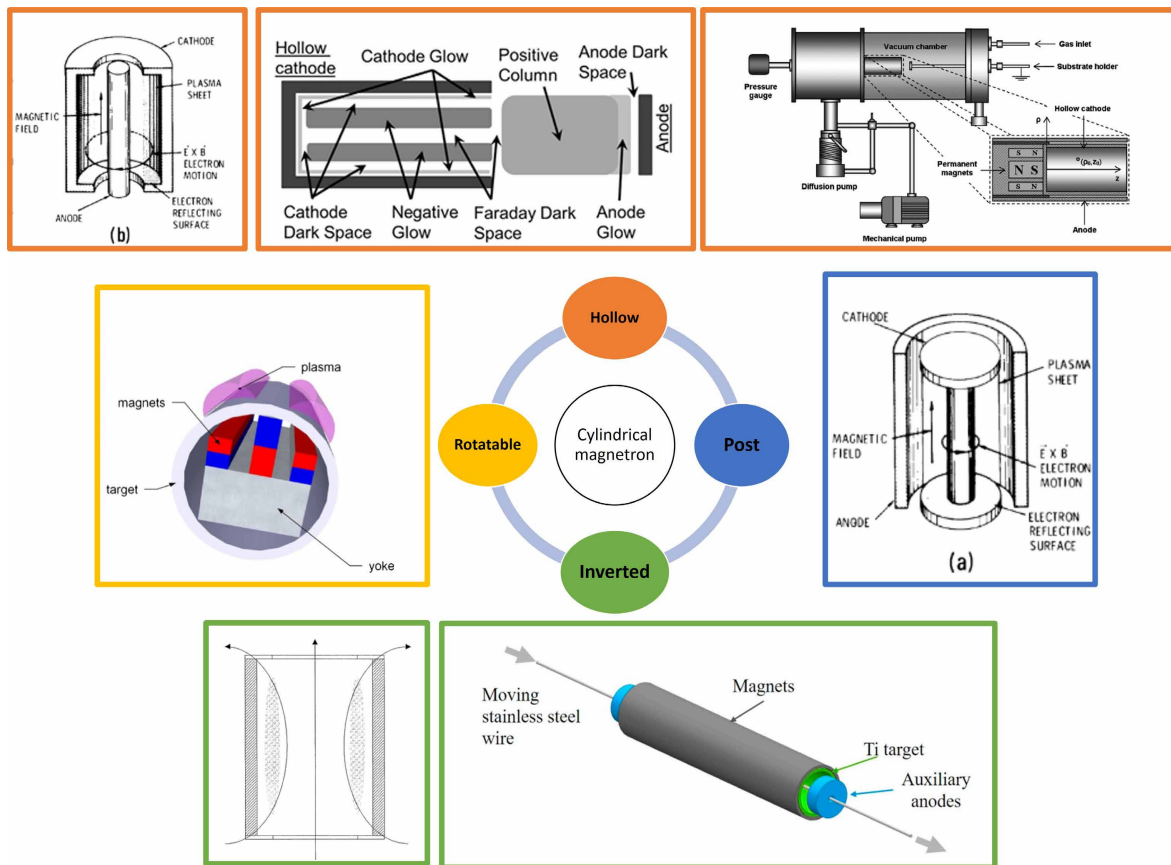


Figure 2.5: Cylindrical sputtering sources classification[60, 61, 62, 63].

The term "inverted" is less utilised but still can be found in some publications, such as [62], where it was used for continuous wire sputtering. Figure 2.5 shows the different variations of cylindrical magnetrons.

Notably, a magnetic field was first applied for the cylindrical post-cathode configurations and patented by Frans Penning in 1936. The term "magnetron" was not yet introduced in the sputtering society [54]. External or internal permanent electromagnets can create a magnetic field.

The classical hollow-cathode scheme is shown in Figure 2.6 A, while the current-voltage dependence is in Figure 2.6 B. In a hollow cathode, there are two main regions: a normal non-resonant discharge in the hollow cathode (D-HC) and a quasi-resonant hollow cathode discharge (DHC). The transition between the two regimes is not always noticeable, but a significant rise in plasma luminosity and density can describe the latter.

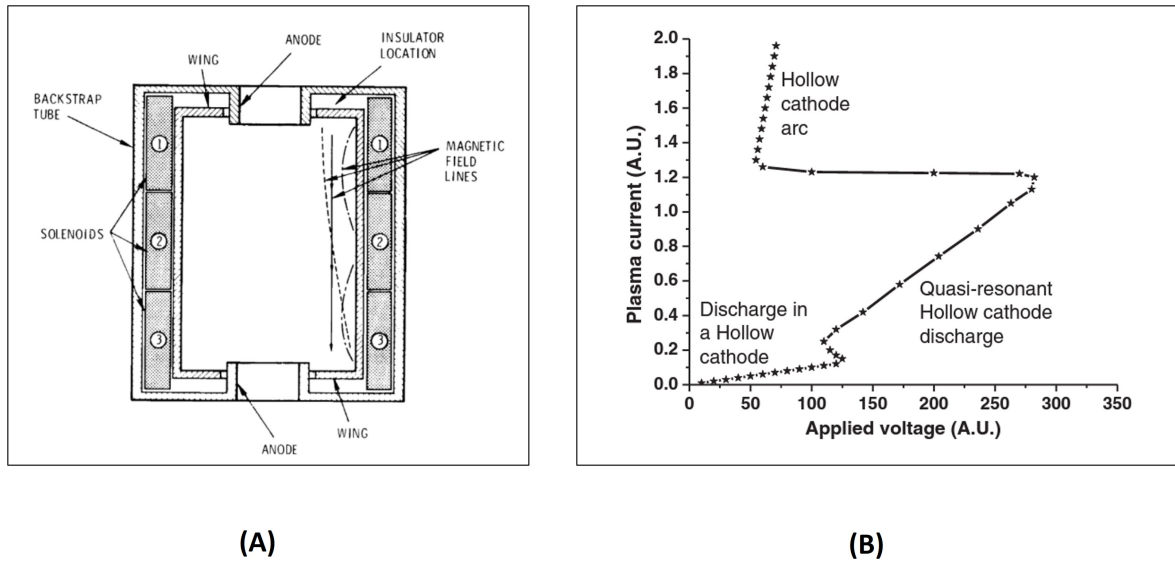


Figure 2.6: Hollow magnetron: (A) structure and (B)-Typical Current-Voltage (I-V) characteristic curve.[60].

As the applied power increases, the glow region becomes wider. This happens because the average electron energy increases due to the increase in the cathode sheath. If the power increases even more, it is possible to reach a hollow cathode arc regime (HCA), similar to arc discharge, which was discussed before. In this case, the cathode accumulates excessive heat, and the thermal field emission of electrons plays a more significant role in sustaining plasma. The transition between DHC and HCA happens rapidly, and the voltage drops below 100 V.

The cylindrical magnetron concept was discovered and described many years ago, but it did not become a commonly utilised technique. Post-magnetron sputtering is utilised when the internal part of the tube, or any cylindrically shaped piece, must be deposited. One great example of such an approach is the sputtering of the Niobium onto the copper accelerating cavity [64]. On the other hand, hollow magnetrons find their utilisation in wire production or when the external surfaces of the tube must be sputtered [62].

2.3 REACTIVE MAGNETRON DEPOSITION

One of the substantial advantages of sputtering deposition is the possibility to sputter not only a pure metal but also create a compound (e.g. nitride or oxide) from the metallic cathode. Often, such a process is more tunable than deposition from compound cathodes.

The reactive sputtering with the metallic cathode occurs in a reactive gas atmosphere. However, such gases as O_2 or N_2 have low atomic masses and do not provide a high sputtering yield. For this reason, inert gas, usually Ar, must be utilised together with the reactive one.

One of the critical aspects of reactive deposition is the "poisoning" effect. It happens when the compound grows faster on the cathode than the sputtering process occurs, which could lead to the cathode being wholly covered with the compound. This may lead to the deposition condition changing, and usually, no stoichiometric compound grows. Figure 2.7 A shows the well-known hysteresis effect of the reactive magnetron process.

Such hysteresis effects are strongly undesirable due to the low process stability and control of the deposition process. Such a phenomenon is widespread for diode sputtering and less in magnetron deposition.

To have better control over the reactive sputtering, it is favourable to have the cathode fully or partially in a metallic state and maintain the minimum reactive gas needed for the reaction. Some approaches have been proposed to overcome the hysteresis issue by varying the pumping speed or the distance from the cathode to the substrate. It is also possible to have a pulsed reactive gas

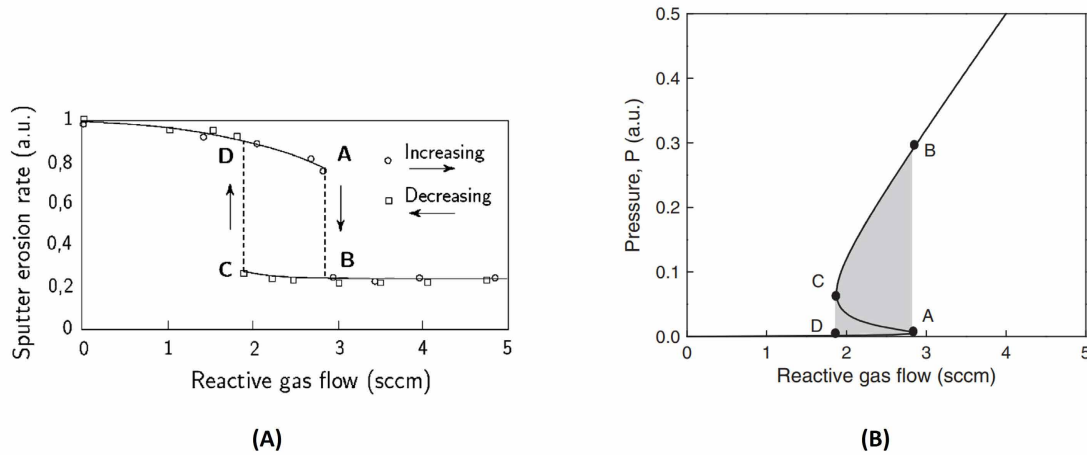


Figure 2.7: Reactive sputtering process: (A) Classical hysteresis effect of the reactive process and (B) calculated pressure vs the flow of reactive gas according to Berg model [65].

flow, where the gas flow has its "on" and "off" times (usually in seconds). Moreover, some system modification was also suggested, introducing a baffle between the cathode and substrate so that the reactive gas inlet is located near the substrate. In contrast, Ar gas has an inlet near the cathode. Such an approach was successfully used to grow transparent oxides, such as ZnO, Cd_2SnO_4 , and ITO [66].

In 2005, Berg et al. [65] proposed a simple model to predict the reactive sputtering process. The original idea was presented even earlier, in 1987. The created curve is shown in Figure 2.7 B. By only varying the total system pressure, operating the process on the A–C part of the curve can not be possible. The width of the S-shape of the curves represents the hysteresis width. It was shown that this model can provide enough accurate information for the system to avoid or reduce the hysteresis effect. The work [65] shows the influence of the following parameters: gas reactivity, sputtering yield, pumping speed, target size, and working distance. The model is based on a simple assumption, but it has proved to be remarkably well aligned with experimental data. Its simplicity and practical accuracy make it commonly recognized.

It is important to note that all the methods to overcome the hysteresis effect lead to low deposition rates. Thus, a fast feedback system is required to operate on the "knee" of the hysteresis curve. The process must be monitored and automatically controlled over the deposition time to stay on the right point. The methods for deposition control can use different process parameters, such as light emitted from the plasma (for plasma emission monitoring method) or voltage. A dual magnetron system can oxidise a thin metal layer on the substrate (sputtered by normal metal mode) using an unbalanced magnetron to produce plasma from an Ar/O_2 mixture. This process is called Successive plasma anodisation or SPA [66].

2.4 FILMS GROWTH

When depositing a film, it is important to have access to not only its composition but also its structural properties and characteristics. Many different parameters influence the future film properties. These parameters are summarised in Table 2.1, adopted from the [57].

Table 2.1: General parameters which influence future film's properties and characteristics.

Group of parameter	Examples
Substrate surface condition	Surface morphology, roughness, inclusions, surface chemistry, outgassing process, homogeneity
Deposition process	Distribution of the angle-of-incident, deposition atoms flux, substrate temperature
System geometry	Concurrent energetic particle bombardment, shadowing effect, gas flux positioning
Details on film growth	Nucleation, interface formation, reaction with deposition ambient, energy input on growing film
Post-deposition process	Thermal and mechanical cycling, corrosion, interfacial degradation, deformation

Some of the parameters were already discussed in the previous section. This section concentrates on events on the substrate, particularly the film growth process. Essentially, the substrate characteristics and conditions strongly influence the film growth. To have the reproducible results, the substrate state must also be reproduced.

2.4.1 THIN FILMS

As was mentioned before, reproducible film growth is a very challenging process. For this reason, the researchers came up with the idea to create a Structural Zone Diagram (SZD) or simply a model that can somehow correlate the process parameter with the results of film structures. Such an approach was first introduced by Movchan for evaporated films in 1969 (see Figure 2.8), considering the material's melting temperature. Thus, different processes (such as shadowing, surface and bulk diffusion, and recrystallisation) can dominate based on T_s/T_m (substrate and melting temperatures, respectively) and determine the film's structure. Such temperature is called homologous temperature - T_b . Thornton described the SZD for sputtered film, considering T_b and sputtering process pressure as two main parameters. Messier adopted the SZD for ion-assisted deposition, while Grovenor considered the influence of substrate morphology [67, 68, 69]. All mentioned SZD is shown in Figure 2.8.

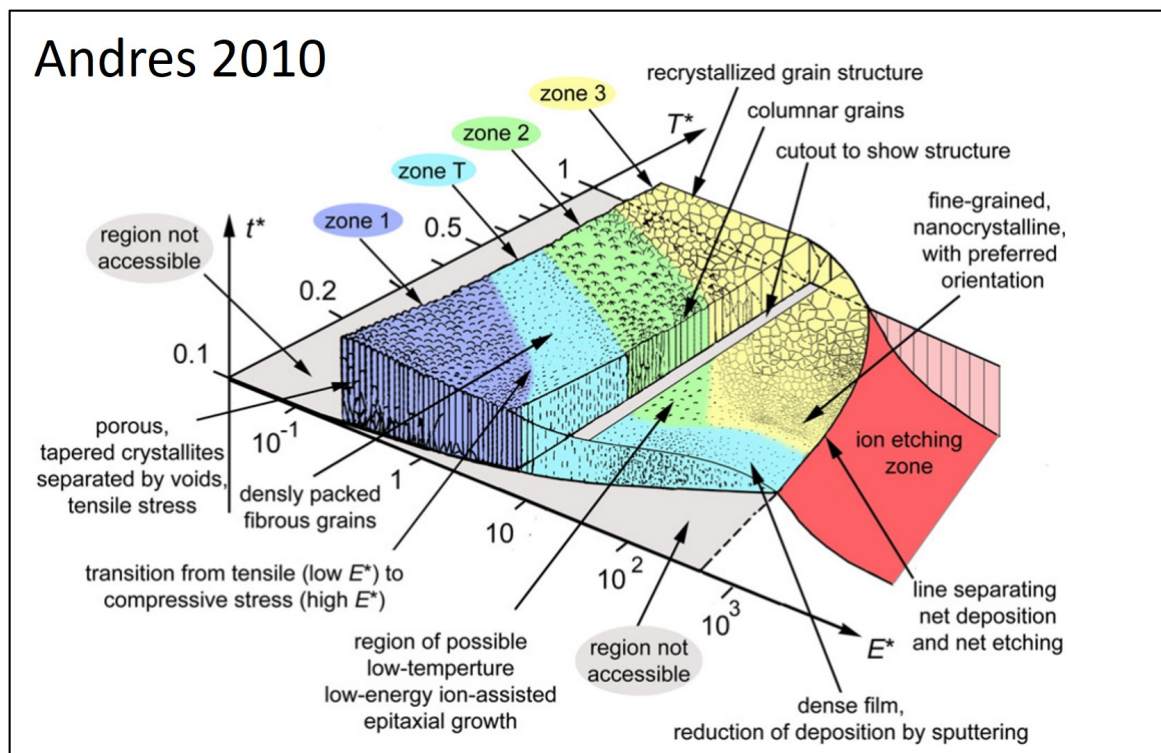
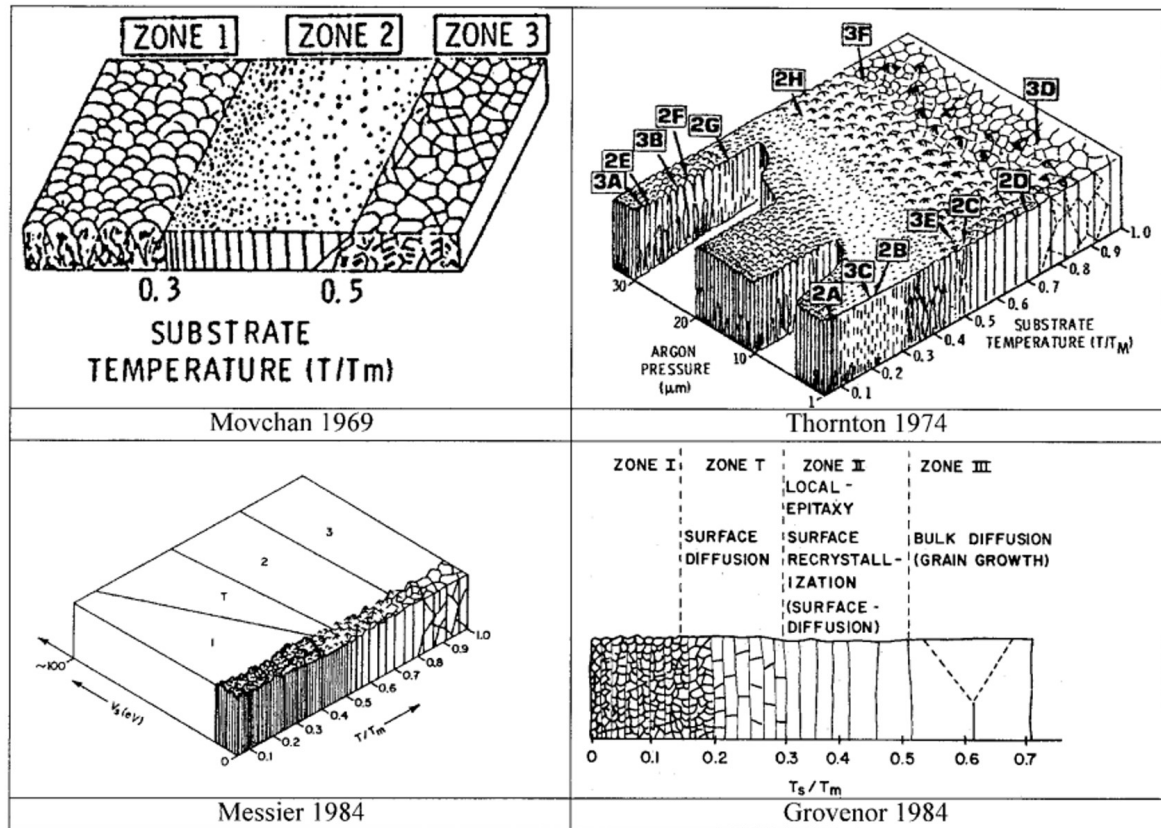


Figure 2.8: The Structural Zone Diagram (SZD) evolution from Movchan (1969) until Andres (2010) [68, 70].

Thornton, in 1974 [71], proposed to divide SZD into four zones, which is described below [69, 57]:

Zone 1: The film texture is open-voided with a fibrous structure. Such morphology resulted from the low angle of the arriving vapour flux and limited adatom (adsorbed atoms) diffusion on the substrate surface. The crystallographic structure is usually amorphous. Zone 1 is wider at high pressure due to the scattering of the sputtered particles. This zone can be observed at $T_b < 0.1$ or 0.2 at pressures < 0.5 Pa and $T_b < 0.4$ at discharge pressure of 4 Pa.

Zone T: The deposit's texture changes into wider columns with flat surfaces due to enhanced surface diffusion. Zone T can be observed at $0.2 < T_b < 0.35$ for pressure < 0.5 Pa. Zone T morphology can be achieved through the ionic bombardment of the film.

Zone 2: In this zone, the thermal surface diffusion significantly increases, which widens the columns and reduces the spaces between them. This zone can be characterised by higher crystallinity and preferred orientation. The pressure influence on the film structure becomes less visible. Zone 2 can be observed at $0.35 < T_b < 0.7$ for discharge pressure < 0.5 Pa.

Zone 3: In this zone, a dense film with large grains is achievable by enhanced bulk and boundary diffusion. This zone is pressure-independent and can be observed at $T_b > 0.7$.

In 2010, Anders proposed modification of a Thornton SZD [70], considering energetic depositions from the plasma phase (such as HIPIMS, filtered cathodic arc deposition, and sustained self-sputtering). For this reason, some changes were adopted to the standard SZD: (i) T_b were changed to T^* , which includes homologous temperature plus temperature shift; (ii) pressure axis was changed to the logarithmic axis of normalised energy E^* ; (iii) z-axis is defined as a net film thickness t^* . Inducing a t^* axis indicates a thickness reduction by densification and sputtering, including a negative thickness, as in the case of ion etching. It is worth mentioning that the SZD can also be adapted to the compound deposition, as it was done at [72] for Cu_2O using a homemade step heater.

Therefore, it is essential to note that SZD is only a qualitative illustration of some dependence between process parameters and the final film structure. It has a limited predictive capability since it is based on different assumptions. Although SZD could assist in predicting film microstructure, empirical studies and proper experiment design are still necessary. For this reason, Banko at [67] proposed to use a machine learning approach to thin film scanning electron microscopy (SEM) surface images and process parameters. Such an approach resulted in the creation of the Generative SZD (gSZD) model, which has advanced prediction capabilities.

2.4.2 THICK COATINGS

One of this research aims is to sputter thick, more than $100\ \mu\text{m}$ films, which is not a trivial task for sputtering techniques. It is crucial to consider stress formation to achieve desired film thicknesses with high mechanical properties. In the literature, there are limited examples of thick films successfully deposited. In [73, 64], reported a method of thick defects-free Nb film deposition ($70\ \mu\text{m}$) onto Cu accelerating cavities, using long pulse DCMS at high temperatures. Skliarova used a similar approach [31] for thick Mo solid target deposition, which is discussed later in this section.

The internal stress in the film may cause deformation, delamination and crack formation of the deposited film. Since then, stress evaluation and methods of its reduction have been in the spotlight of the scientific community [74, 75]. The film stress is an essential factor for the adhesion and stability of thin films and becomes even more crucial for thick coatings. The thin film experiences tensile or compressive stress due to its desire to shrink or expand over the substrates. The two types of stresses and effects that they can cause on the film are shown in Figure 2.9 [57].

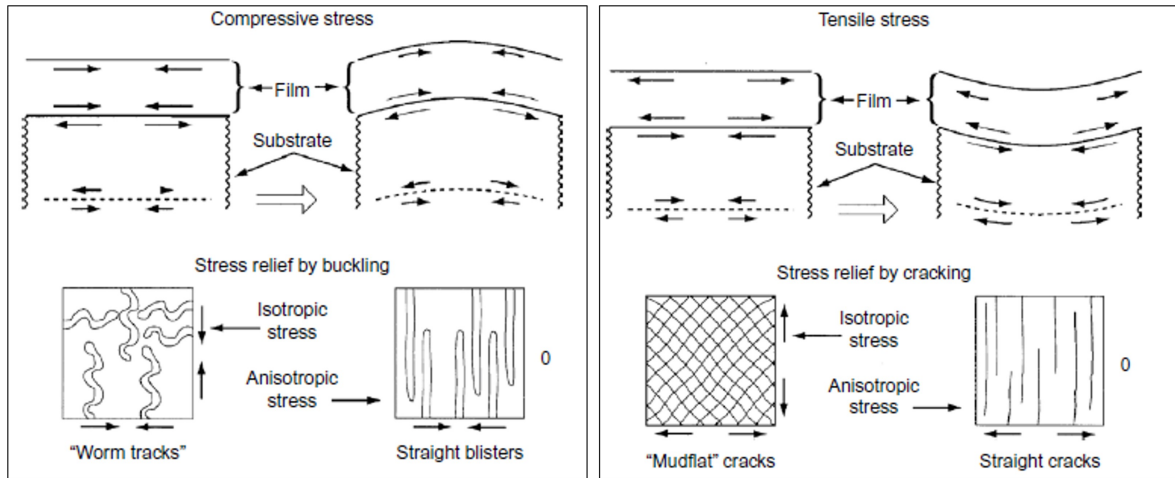


Figure 2.9: Residual stress formation in the film: tensile and compressive stresses and their effects [57].

The stress (σ) in the film is usually described by the internal stress (σ_f). This parameter is a sum of intrinsic σ_i and extrinsic $\sigma(T)$ stresses. **Extrinsic stress** is imposed by unintended external factors, such as temperature gradient. The difference in the thermal expansion coefficient between film and substrate usually causes it. On the other hand, **intrinsic stress** derives from the film growing. Its nature is more complicated and still under discussion. It is, however, clear that process parameters greatly influence stress evolution. The unit of stress is Pascal [Pa]. Thin films typically experience stresses ranging from negative to positive values. Negative values indicate compressive stress, while positive values indicate tensile stress [53].

The total stress in the film is determined as a sum of stresses, which can vary through the film thickness. However, it was shown [75] that the thicker films have lower internal stress, which results in being inversionally proportional to the film thickness.

$$\sigma_{av} \propto t_f^{-\alpha} \quad (2.4)$$

This was shown for different metal and compound films. Figure 2.10 A shows the stress measurement results on the Cr films. The etch-back method and curvature measurement were combined to evaluate average stress. Figure 2.10 B plots the coefficient α dependent on the working pressure in case of Cr deposition. For low pressures with long mean free paths - a low α is obtained, and vice versa.

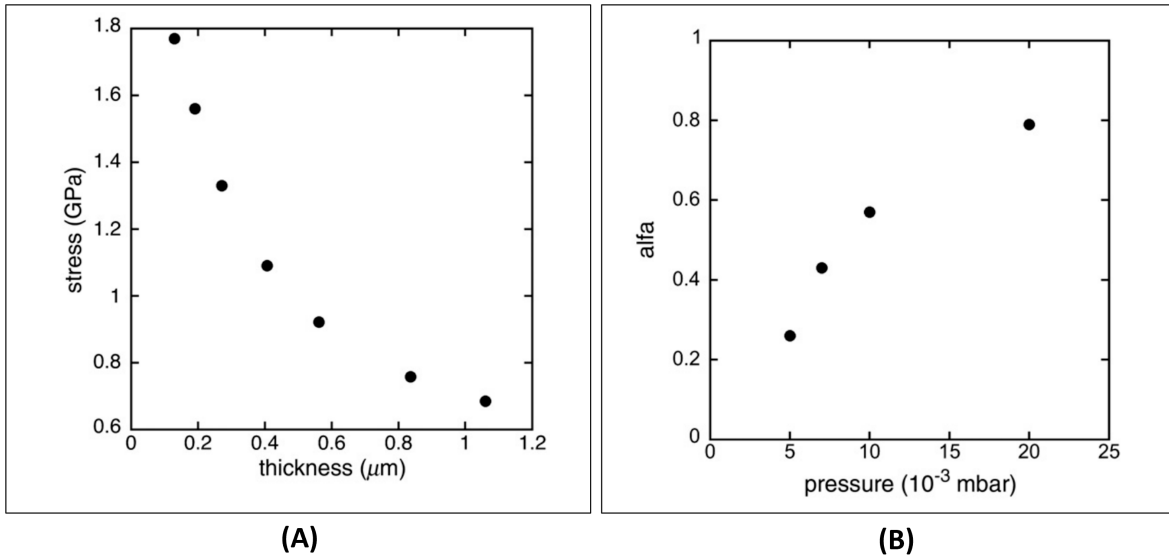


Figure 2.10: Stress measurement in the chromium thin: (A) stress versus film thickness and (B) the relation of a coefficient α to the working pressure [75].

The mentioned correlation is valid for the **Zone T** type of microstructure. In zone T, the number of grain boundaries in the film is a function of the height in the film. The tensile stress is generated at the grain boundaries by shrinking the distance between adjacent grains due to interatomic forces across the grain boundary together with the adherence of the film to the substrate. Thus, the stress in the film is also a function of the height in the film, as was demonstrated by different research groups. In the case of **Zone 2** where $T_b > 0.35$, the microstructure does not reflect the growth history.

Density is another essential characteristic of the film that must be addressed concerning thick films. It can determine a number of material properties, such as electrical resistivity, index of refraction, mechanical deformation, and corrosion resistance. At low temperatures (Zone 1), the density of the film is determined by its morphology, which mainly depends on geometrical effects. On the other hand, under bombarding conditions or high temperatures, the film's microstructure is influenced by different effects such as recoil implantation, forward sputtering, sputtering and redeposition. Thus, the mobilities of adatoms increase, increasing film density.

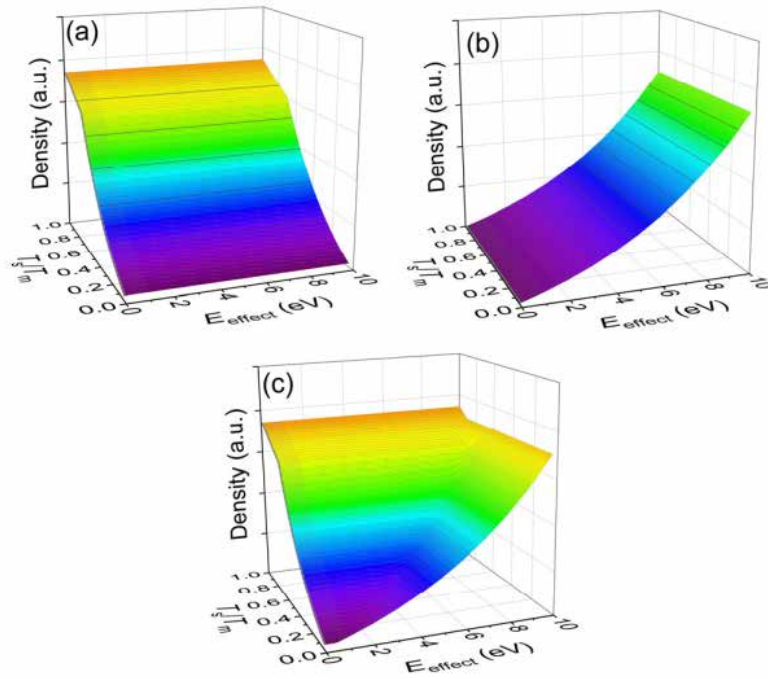


Figure 2.11: Conceptual images of the evolved SZM as a function of (A) effective particle energy per depositing atom (E_{Effect}), (B) T_{sub}/T_m , and (C) the combination of (A) and (B)[69].

As shown in Figure 2.11, the effective particle energy (E_{Effect}) and T_{sub}/T_m have their effect on the resulting density of the achieved film. Figure 2.11 C) does not show the synergetic effect, which is present. In reality, the film densification and crystallisation are accelerated with the synergistic effects of the two components.

It is necessary to mention that with high particle energies, the high-density films may be overstressed and full of defects. High-density film resulting from high homologous temperatures, on the other hand, is more likely stress-free and has a faced surface. This happened due to the induced film structure densification and crystallisation under a thermal-equilibrium condition [69].

2.5 MAGNETRON SPUTTERING FOR TARGET MANUFACTURING

The magnetron sputtering is a relatively new technique for the solid target manufacturing. However, the possibility of process optimisation, thickness control and low-stress depositions makes it attractive to the nuclear medicine field. The solid target requirements and production methods details are described in Chapter 1. This work discusses the possibility of a solid target manufacturing via MS of three materials: yttrium, chromium and zinc oxide.

Several works [47, 48] reported utilisation of the **yttrium sputtered targets** for ^{89}Zr production. However, fewer details are available about the deposition system or parameters. There are no papers published specifically about the Yttrium deposition and eventual deposition properties, despite the work by Skliarova et al. [10]. In the literature, metallic yttrium cathode is utilised to create thin compound layers, mostly oxide, and there are no papers on thin metallic film deposition.

The chromium sputtering films, despite being a popular material in the sputtering field, have not been reported deposited for solid target manufacturing. There are studies about the relatively thin (1-10 μm) Cr sputtering deposition being compared with conventionally electroplated. The works [76, 77] have demonstrated that MS Cr films exhibit higher homogeneous thickness, superior corrosion resistance, and higher hardness. Moreover, the MS process avoids using a high cancerogenic commercial electroplated solution containing Cr(VI).

Zinc oxide has unique properties [78] and can be used in different applications, such as transparent conductive oxide (TCO) [79, 80], piezoelectric devices, chemical sensors [78, 81], biosensors, and many others. Many works report ZnO deposition by using a sputtering technique with a planar sputtering source, emphasising radio frequency (RF) over the direct current (DC) deposition [82, 83, 84, 85, 86]. The particular interest for this material is also rising since it is considered a possible cheaper substitution of commonly used ITO (indium tin oxides) in microelectronic devices [87, 79]. However, in all mentioned studies where ZnO is deposited, the thickness ranges from 50 to 2000 nm. For the solid targets manufacturing, the thickness typically starts from tens of μm for nuclear cross-section analysis. It can reach a few millimetres for maximising radionuclide production [8].

As was already mentioned at LNL, a method of solid target preparation based on a case study of the Mo thick ($100\text{ }\mu\text{m}$) targets [46] was patented. The possibility of manufacturing thick metal layers was investigated by Skliarova and co-workers and results in several publications [31, 39, 10, 45]. It is crucial to highlight the main findings. For the first time, a thick Nb and Mo film deposition method on different substrates (metal and ceramics) was studied and developed. The primary approach to depositing stress-free thick coatings was using a pulsed DCMS technique at high temperatures ($500\text{ }^{\circ}\text{C}$) for 10 to 14 h deposition. It shows the potential of the magnetron sputtering technique to become a valuable tool for the radiopharmaceutical field. However, a crucial problem has arisen: the low material efficiency of the sputtering process, caused mainly by low cathode erosion efficiency and material lost in the vacuum chamber. For Mo targets, the recovery path, including the dissolution and reduction steps, with an overall recovery of 90%, was proposed. Recovery is an inevitable process for almost any radiopharmaceutical production. However, it is also time and cost-consuming. For this reason, the deposition system and MS source must be studied for possible optimisation to reduce and localise possible material losses.

2.5.1 MATERIAL EFFICIENCY ISSUE

One of the strong magnetron sputtering disadvantages is a low efficiency in cathode utilisation. Due to the "racetrack" appearance, in the standard planar configuration, only 30% of the sputtering material can be used to deposit a film. Some attempts were made to optimise the magnetic field over the cathode surface. However, their efficiency was no higher than 60%. A rotatable cylindrical magnetron was the most successful cathode utilisation (see Figure 2.4), where the active sputtering zone constantly changes. Thus, the material efficiency can be raised to 90%. Rotatable cathodes are usually more complex than planar magnetrons and have been used chiefly for large-area coatings [4]. The dissipation over the vacuum chamber is another aspect influencing the low material efficiency. The material ejected from the cathode has a different trajectory and is sputtered all over the vacuum chamber surfaces and deposited on all the components.

This dissertation aims to evaluate and address the material efficiency problem, which can be potentially interesting for the radiopharmaceutical field and any sputtering deposition involving highly costly materials.

3

Experimental set-up and characterisation

This chapter thoroughly explores the methodologies and instrumental setups employed throughout this research. Initially, the focus is on an overview of the utilised sputtering systems, delving into their specifications and configurations. The planar magnetron configuration, developed by STSS, is described. A detailed description of the analytical instrumentation employed for coating characterization is also provided.

Furthermore, an overview of the materials utilised in the study is presented, offering insights into the selection criteria and the significance of each material in the experimental context.

A dedicated section details the irradiation test, the methodology, the parameters, and the significance of this crucial phase in the research.

3.1 VACUUM SYSTEMS

The vacuum system is a crucial component for sputtering deposition. Depending on the application, the vacuum can be at high ($10^{-3} - 10^{-7} \text{ mbar}$) or ultra-high ($< 10^{-8} \text{ mbar}$) level. Typically, the industrial sputtering machine works at a vacuum level of 10^{-6} mbar , while this level can be even higher for the microelectronics field. To reach such low-pressure levels, it is essential to consider the system construction and usage of the adequate pumping system. This work used two separate vacuum systems: one multi-chamber system already dedicated to different conventional depositions and another for non-standard deposition processes or non-conventional approaches. The latest system can be quickly customised with different components for personalised applications while remaining compact.

3.1.1 MULTI-CHAMBER DEPOSITION SYSTEM

The multi-chamber vacuum system was used in this research to study and evaluate the standard planar magnetron configurations. Chamber four (4), shown in Figure 3.1, is dedicated to the yttrium deposition (see Chapter 4). At the same time, chamber three (3) was used for the optimisation of the magnetron sputtering technique from the material point of view (see Chapter 5). Such a multi-chamber system has provided a possibility for better process organisations.

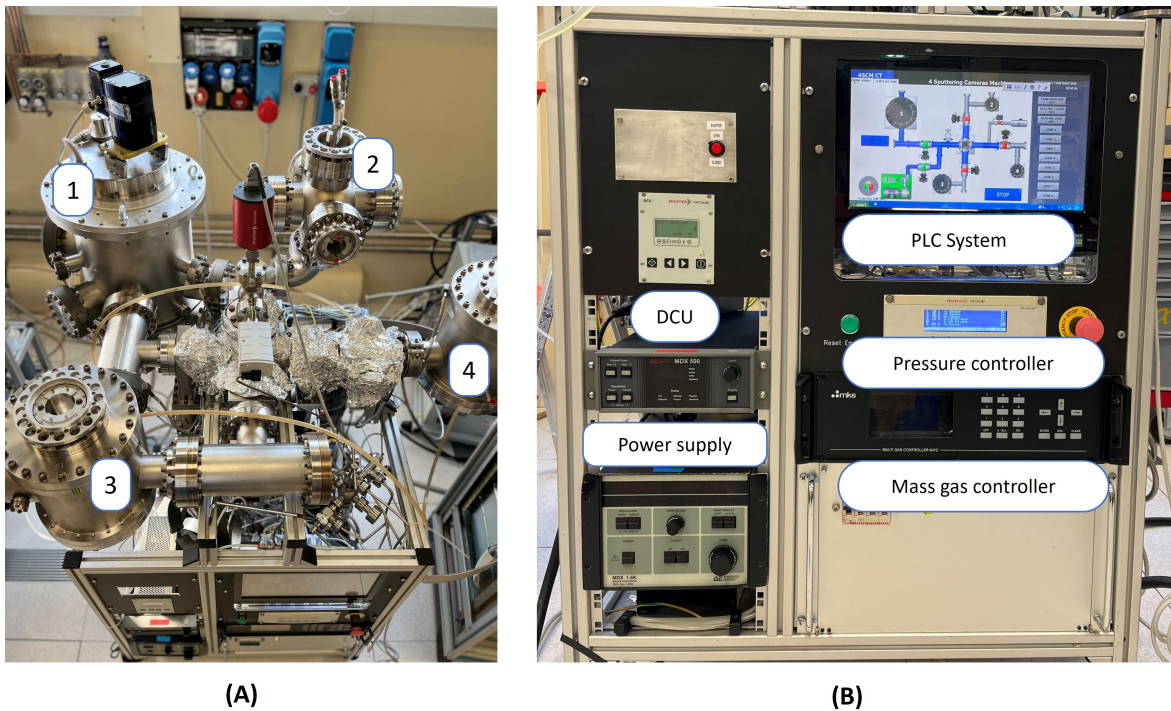


Figure 3.1: Four-chamber vacuum system (A) with dedicated controlling setup (B).

The multi-chamber system prototype has been designed to benefit from the simultaneous vacuuming of all chambers. Once the desired base pressure is achieved, each chamber can be separated and used while the others are maintained at static vacuum pressure. Such a design ensures effective time reduction in the case of multiple PVD processes. The base vacuum level is created by a primary and turbo molecular pump (the Edwards nXDS6i of 100 L/min and Pfeiffer turbo molecular pump of 60 L/s, respectively) with a base pressure consistently lower than $5 \cdot 10^{-6}$ mbar without any additional baking procedure.

The controlling panel, shown in Figure 3.1 B, controls the deposition process and includes a non-commercial programmable logic controller (PLC) system with pumping and gates controls. The mass flow controller allows the reproduction of the process's gas pressure and working conditions. Different power supply and operation modes were used during the work, including operation in constant power or current.

Figure 3.2 schematically shows the simplified multi-chamber system diagrams installed in the STSS laboratory. The leak detection connection possibilities can be noticed. The system is connected to three gas lines: Ar (99.9999% purity) as a sputtering gas, O_2 and N_2 (99.9999% purity) as a working gas. The full-range gauge controls the vacuum and working pressure, while the Pirani gauge is installed to control the proper operation of the primary pump.

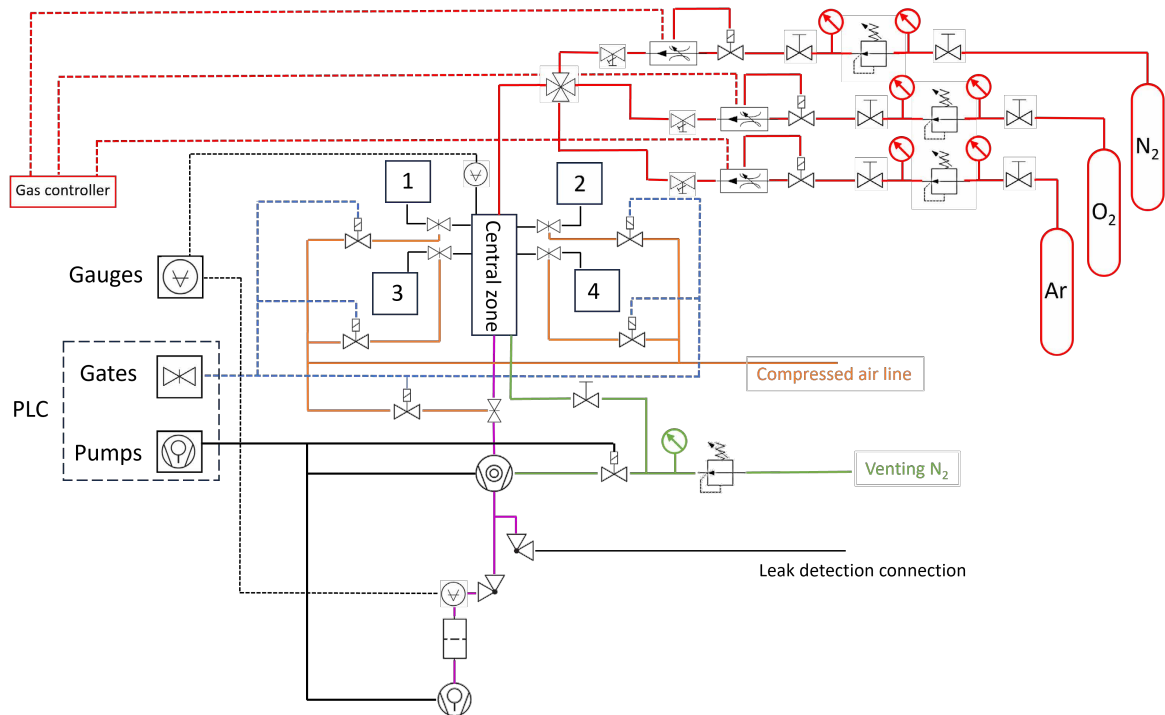


Figure 3.2: Diagram of multi-chamber vacuum system: blue line - gates control, yellow - compressed air line, red - gas line, green - venting line for system and turbo molecular pump.

The vacuum chambers used in this work (3 and 4) are cylinders made of stainless steel AISI 304 (200 mm high and 300 mm wide, volume 12.3 dm^3), water-cooled and sealed with conflat flanges.

3.1.2 BAKING PROCESS AND ULTRA-HIGH VACUUM

The backing system was refurbished and applied for yttrium deposition to reach the ultra-high vacuum level. The vacuum system requires baking to eliminate moisture and reduce residual gases through controlled heating. At pressures around 10^{-6} Pa , desorption of gases and water vapour limit the producible ultimate pressure [88]. The base vacuum level is the pressure at room temperature after the system cools down or pumps for at least 24 hours.

The baking system comprises heating jackets (see Figure 3.3 A) segmented into three autonomous zones (Central, Gates and Chamber) linked to the ultra-high vacuum (UHV) baking control unit (shown in Figure 3.3 B). This external baking system enables precise temperature regulation for distinct sections of the system. The maximum temperature for baking was 120°C for all zones to prevent the Viton o-ring degradation in the gates and possible damage to the view-port and magnetron components. The permanent magnet, used in magnetron sputtering planar configuration, was dismantled for the baking process, and no cooling system was attached.

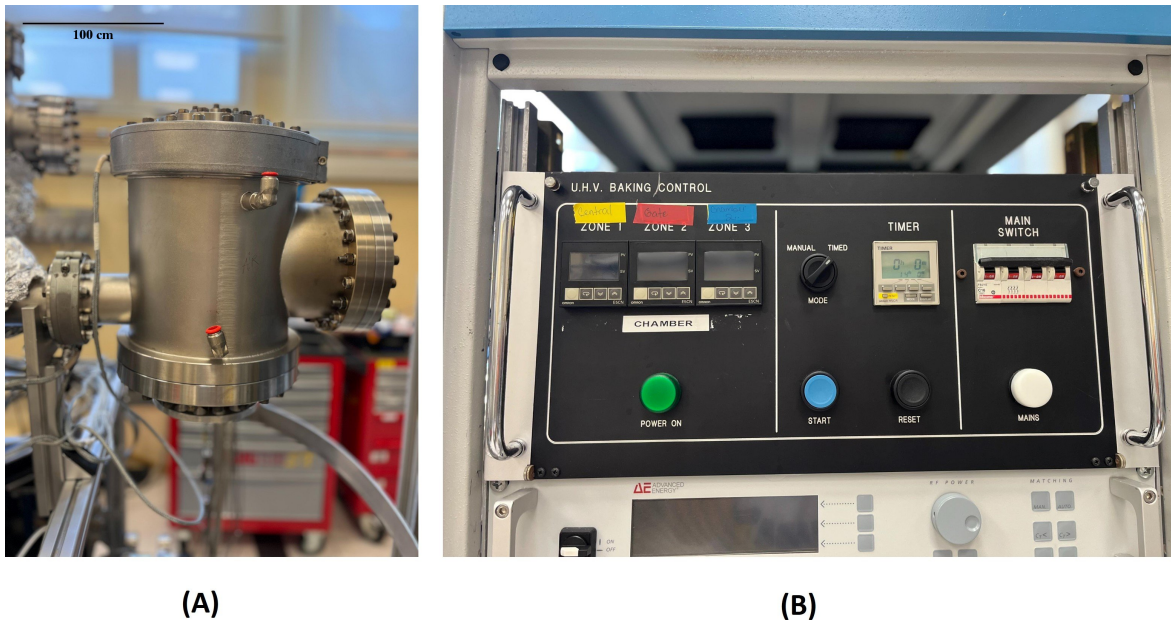


Figure 3.3: The baking controlling system adopted for yttrium deposition: (A) dedicated vacuum chamber with resistance heating hoods and (B) dedicated ultra-high vacuum (UHV) baking controller.

Since the baking process was done continuously for a long time, a security valve was installed in the system as a safety measure. Such a valve breaks if the pressure rises over 1.7 bar.

The first baking attempt for vacuum level improvement of the yttrium deposition system is summarised in Table 3.1. However, future baking processes were performed for a maximum of 90 h, allowing always to reach pressures at level $\cdot 10^{-8}$ mbar.

Table 3.1: Baking process for ultra-high vacuum (UHV): parameters and results.

Baking round	Pressure before [mbar]	Baking parameters	Resulted pressure [mbar]
Round 1	$5.6 \cdot 10^{-7}$	120 h with 120 °C	$3.4 \cdot 10^{-8}$
Round 2	$3.4 \cdot 10^{-8}$	24 h with 300 °C in central zone	$1.27 \cdot 10^{-8}$
Round 3	$1.27 \cdot 10^{-8}$	64 h with 300 °C in central zone	$8.23 \cdot 10^{-9}$

The utilisation of high baking temperatures in the central zone, as can be noticed in Table 3.1, leads to leaks opening due to the copper gasket damage. As a result, for following the baking process, the temperature of a maximum of 120 °C was set.

3.1.3 ZNO DEPOSITION DEDICATED SYSTEM

Zinc (Zn) is a particular material for vacuum technologies, and its utilisation, even in alloys, is limited due to the high vapour pressure and low melting point. This results in Zn evaporation and condensation in the vacuum system. In this case, the system is limited to the vacuum level, and all future deposition can be contaminated.

Nevertheless, to study the possibility of thick oxide coating deposition, a dedicated vacuum chamber in a previously available deposition system was assembled. The sputtering process was held in the stainless steel cylindrical vacuum chamber with a volume of 5.8 dm^3 . The vacuum system with a dedicated vacuum chamber and controlling setup is shown in Figure 3.4. This system consists of a central zone and two vacuum chambers separated from the central zone by gates.

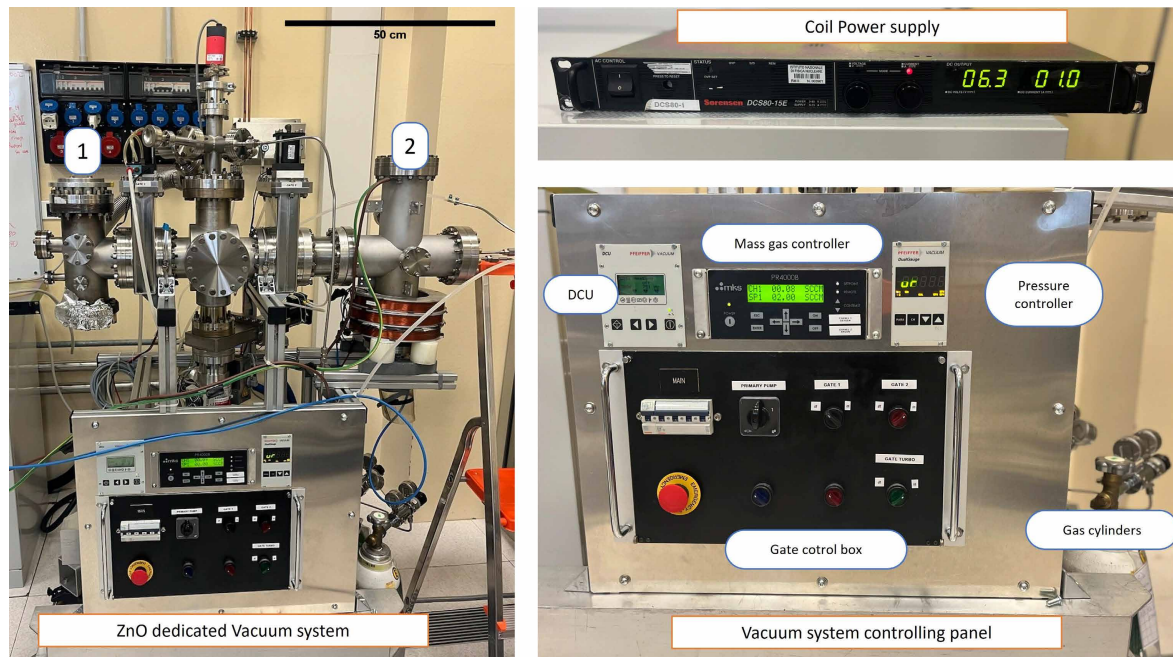


Figure 3.4: Two-chamber vacuum system dedicated to ZnO deposition with its controlling setup.

The system has the same advantage as the multi-chamber system, allowing the reduction of the time consumption for achieving the desired vacuum level. The diagram of the vacuum system is shown in Figure 3.5.

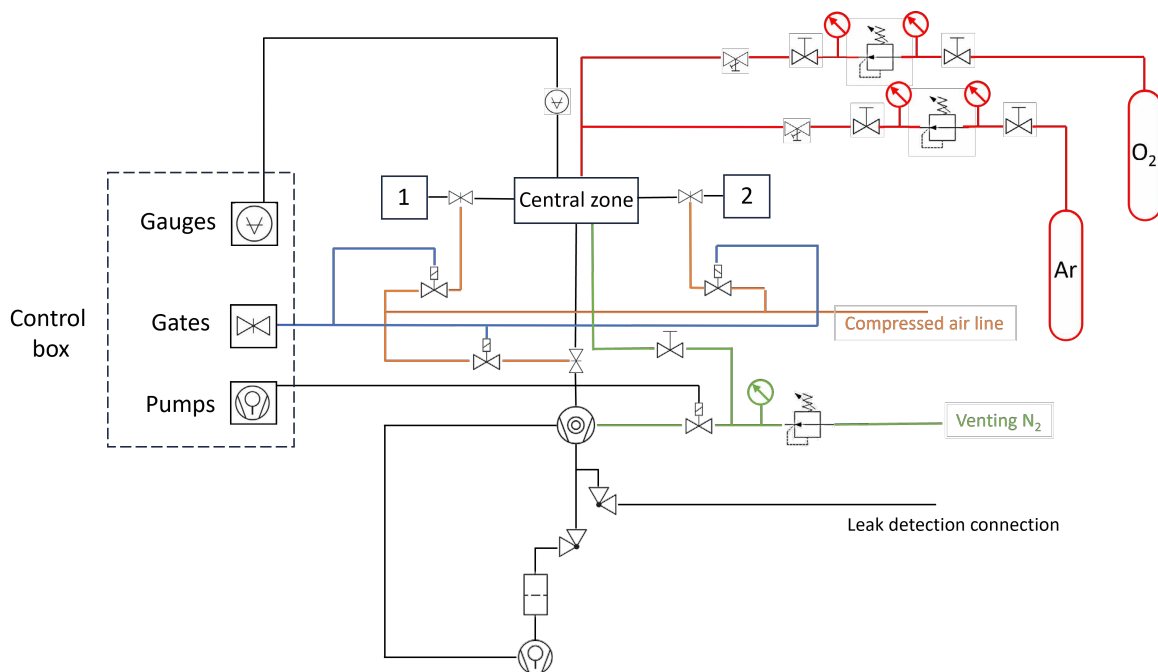


Figure 3.5: Diagram of ZnO dedicated vacuum system: blue line - gates control, yellow - compressed air line, red - gas line, green - venting line for system and turbo molecular pump.

The base vacuum level was created by a primary and turbo molecular pump (the Edwards nXDS6i of 100 L/min and Pfeiffer turbo molecular pump of 60 L/s, respectively) with a base pressure always lower than $6 \cdot 10^{-6}$ mbar without any additional baking procedure. The deposition system is connected to the two working gases: Ar (99.9999% purity), used as a sputtering inert gas, and O_2 (99.9999%), used as the reactive gas for oxide creation. A dedicated power supply (Sorensen DCS80-15E), depicted in Figure 3.4, was used to power the coils. This power supply boasts a maximum voltage of 80 V.

3.2 NON-COMMERCIAL PLANAR MAGNETRON SOURCE

This work used two different magnetron sources: planar and cylindrical magnetrons. Both devices are non-commercial and were designed and produced onsite. However, the planar magnetron was optimised over the years in the STSS laboratory. Meanwhile, the cylindrical source shown in this work is the prototype. The inverted cylindrical magnetron source is described in the dedicated Chapter 6, while here, a detailed description of the planar magnetron is provided.

Figure 3.6 shows the planar magnetron design. The source belongs to the unbalanced Type II magnetrons, where the outer ring of magnets is strengthened concerning the central pole. Some field lines between the central and outer poles are not closed. Instead, they are directed towards the substrate. This means that the plasma is not confined solely to the target region but can also flow out in the direction of the substrate.

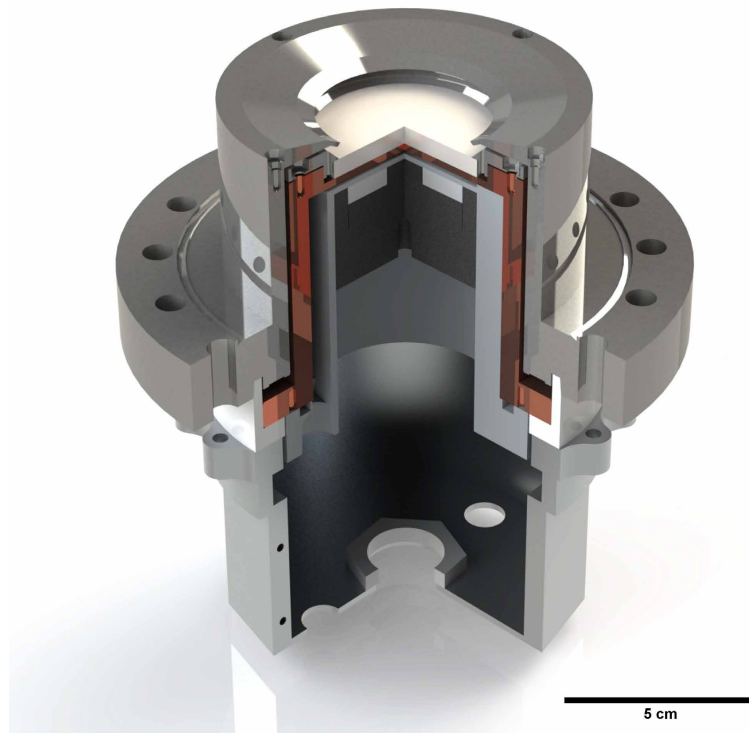


Figure 3.6: Two-inch planar magnetron configuration designed by STSS laboratory.

The source is water-cooled during the plasma discharge to prevent damage to the Viton O-rings and NdFeB magnets (maximum temperature of 80°C). Moreover, efficient water cooling must also prevent the overheating of the cathode. The processing power suitable for the magnetron sputtering source is a maximum of 2 kW in DC configuration.

Figure 3.7 shows the magnetron source and step-by-step cathode assembly. The source can hold the cathode of two inches (50.8 mm) in diameter and 1-5 mm in thickness. A thin layer of silver paste or carbon foil ($0.25\ \mu\text{m}$) guarantees the thermal connection between the cathode and the copper base plate.

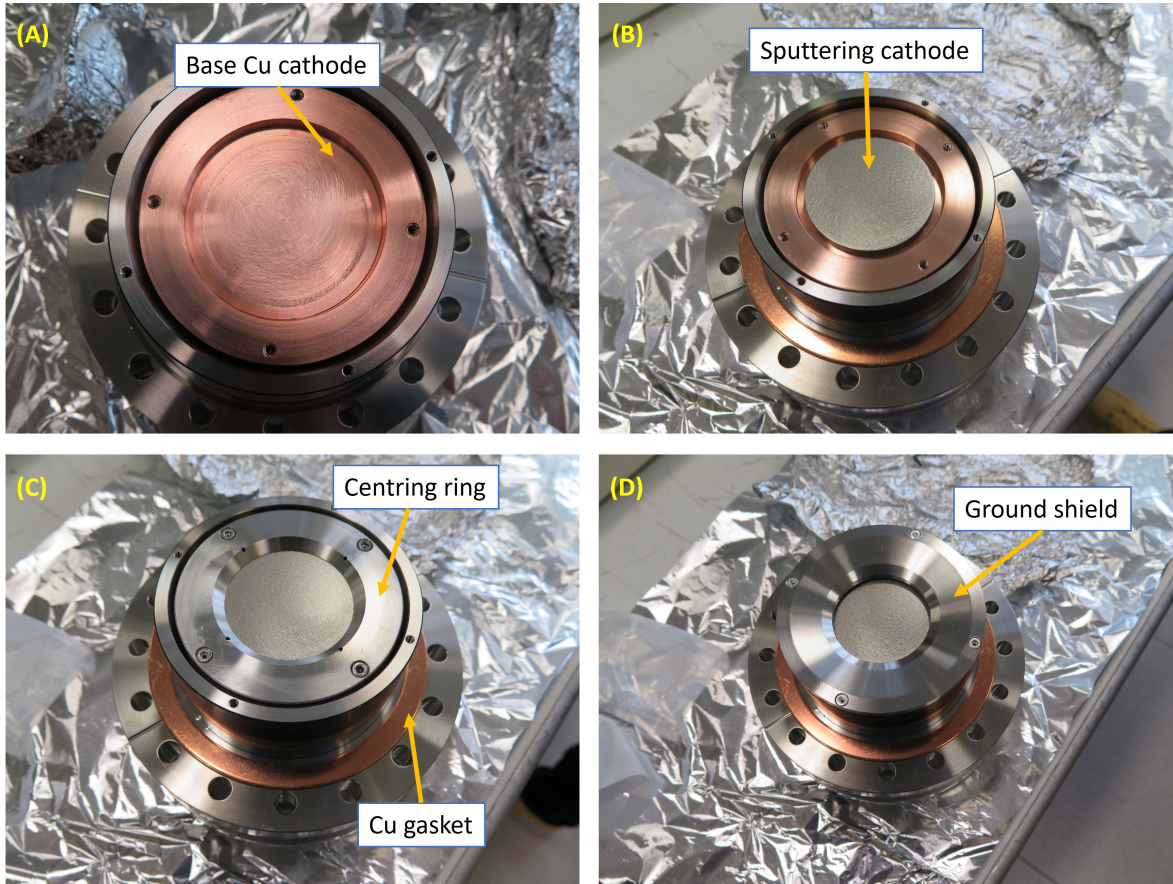


Figure 3.7: Non-commercial magnetron sputtering assembly: (A) copper base plate, (B) sputtering cathode, (C) centring ring, used to press and centre the sputtering cathode, (D) standard ground shield, used to ensure erosion only of the cathode.

The magnets are positioned out of the water-cooling circuit to prevent oxidation and their consequent embrittlement. The magnets can be disassembled from the source without a vacuum break, which allows a safe baking process. Simple magnet disassembling allows a diode sputtering process to be performed - simply substituting the magnet set with an aluminium block with corresponding dimensions. The magnetron has a DN100CF flange to be connected to the vacuum chamber.

3.3 CATHODE AND SUBSTRATES MATERIALS

The sputtering cathodes and substrate materials used in this work are summarised in Table 3.2. The cylindrical cathodes for inverted magnetron configuration were produced using thin (1 mm) Cu and Zn material foils. The cathodes were manufactured at the LNL mechanical workshop. The procedure includes machine bending, welding, and post-polishing with abrasive paper. Buying the foil of Cr was not convenient due to its high price and low availability of sizes. An alternative way was used to manufacture the Cr cathode, described in Chapter 6.

Table 3.2: Cathode and substrate materials utilised in the work.

Materials	Dimensions	Purity	Supplier	Application
Yttrium	Ø 50.8 mm, 5 mm thick	99.9%	Gambetti	Sputtering planar cathode
Copper	Foil 300 × 300 × 1 mm	99.9%	Prodotti Gianni	To manufacture cylindrical cathode
Chromium	Ø50.8 mm, 5 mm thick	99.95%	Spascal	Sputtering planar cathode
Zinc	Ø 50.8 mm, 2 and 5 mm thick	99.99%	Spascal	Sputtering planar cathode
Zinc	Foil 300 × 300 × 1 mm	99.95%	Prodotti Gianni	To manufacture cylindrical cathode
Copper	Foil 300 × 300 × 1 mm	99.9%	Prodotti Gianni	To manufacture cylindrical cathode
Niobium	Foil 100 × 100 × 1 mm	99.9%	Prodotti Gianni	To manufacture Ø24 mm baking plates
Niobium disks	Ø23.5, 1.2 mm	99.9%	Prodotti Gianni	Substrates (backings)
Silicon wafer	2 inches wafer, 0.25 mm	ND	Nanovision	Substrates for SEM cross-section analysis
Quartz	0.9 × 0.9mm, 0.3 mm	ND	Nanovision	Substrates for deposition rate and XRD analysis

ND - no data available, SEM - Scanning Electron Microscopy, XRD - X-ray diffractometry.

For instance, the silicon wafers were used to perform the cross-section analysis. The films were deposited on small pieces of the silicon wafers, which were later broken, and the place of braking was analysed by scanning electron microscopy. The quartz samples were used for thickness evaluation and XRD analysis.

3.3.1 CLEANING PROTOCOL

All stainless steel components were adequately cleaned by applying the following procedures: (i) ultrasound bath with distilled water with the addition of 5 mL of Rodaclean® (NGL Cleaning Technology SA, Nyon, Switzerland) soap for 20 min at 40 ° C) ;(ii) ultrasound bath with distilled water for 20 min; (iii) rinsing with ethanol 96% and drying with the N_2 gas gun (oil-free compression system).

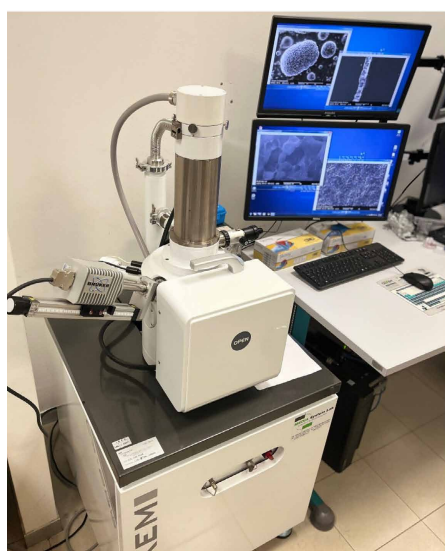
The cleaning procedure followed for the Cu and Zn cathodes was the same as that used for the standard cleaning protocol adopted, but with a different detergent agent, the GP 17.40 SUP soap (NGL Cleaning Technology SA, Nyon, Switzerland).

3.4 CHARACTERISATION TECHNIQUES

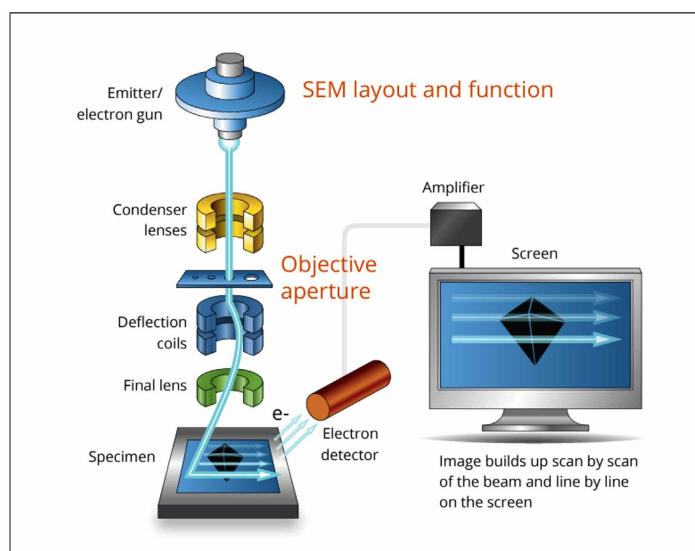
Different characterisation methods were used to analyse the obtained film properties or to evaluate the sputtering process. This section gives an overview of the techniques' principles and the apparatus available for the analysis.

3.4.1 SCANNING ELECTRON MICROSCOPY AND ENERGY DISPERSIVE SPECTROSCOPY MICROANALYSIS

Scanning Electron Microscopy (SEM) uses high-energy electrons generated by the electron gun to scan across the sample and, as a result, receive a raster image of topographical or composition information. The major components of an SEM are shown in Figure 3.8 B: the electron gun, the vacuum system, the column, the specimen chamber, the detectors and the imaging system.



(A)



(B)

Figure 3.8: Scanning Electron Microscope available at LNL (A) and the scheme of the principal components (B) [89].

SEM from COXEM Company, model CX-200plus, shown in Figure 3.8 A, installed in The Surface Technologies and Superconductivity Service of LNL, could work with beam energy in the 1-30 kV range. The different beam energies are used for analysing different materials. When a better understanding of the surface morphology is needed, 10-15 kV is usually used.

The resolution of the SEM is <3 nm at 30 kV. A dedicated sample holder must be used to perform the cross-section analysis. Such analyses are usually performed with coatings deposited on a thin Si substrate. This technique allows us to analyse the growing mode of the coating and its structure.

SEM is also equipped with X-ray detector, XFlash 410-M from Bruker company. Such a system could do a fast elemental analysis with a high energy resolution - 126 eV at Mn K α , 51 eV at C K α and 60 eV at F K α . The error of the experiment in normal conditions does not exceed 5%. This analysis gives fast information about undesired contamination and the chemical composition of the material.

3.4.2 PROFILOMETRY

Profilometry is a technique widely used to measure the surface roughness and the thickness of thin films. The contact profilometers use a diamond tip that moves vertically, and different scans can be set to measure the sample's topography.

Linear contact profilometer Veeco Dektak 8, shown in Figure 3.9, could work in different modes: roughness determination (with various mathematical and statistical functions such as Ra, Rq, Rz and others); step determination (used to calculate the thickness of thin film); mapping (to build a 3-dimensional map of the surface, by proceeding many parallel lines as in roughness determination). The vertical movement of the stylus is 0 - 262 μm , which limits the maximum thickness measurements. Sample dimensions: maximum size is 200 mm, maximum thickness is 25 mm. The maximum sample mass is 2.5 kg. Step height repeatability of 7.5 Å step, one sigma. A high-precision programmable positioning system permits X-Y positioning to any location over a 200 mm diameter (8" x 8") area, with $\pm 5 \mu\text{m}$ repeatability and 3.175 μm resolution.

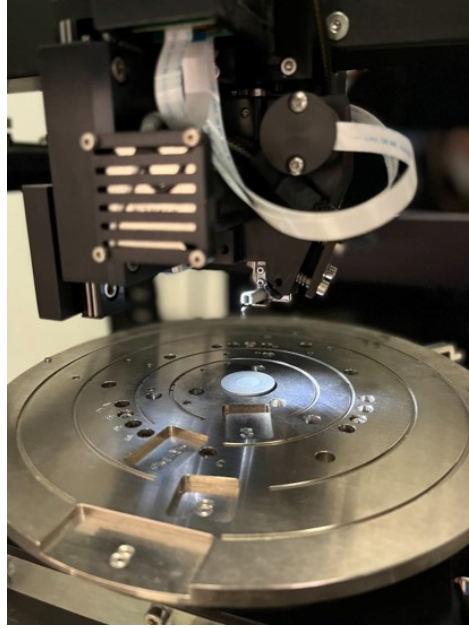


Figure 3.9: Linear contact profilometer Veeco Dektak 8. Add a standard profile of the measurements

3.4.3 X-RAY DIFFRACTOMETRY

The X-ray diffractometry (XRD) method allows the analysis of the crystalline material to study its structure and composition. It can be used to study the crystallographic parameters of known material or to identify the material by its characteristic diffractogram. XRD uses a phenomenon called constructive interference with X-ray, also known as diffraction. At certain angles, the diffraction beam has a higher intensity, which can be characteristic of the material. Bragg Law can describe this effect by the following equation:

$$n\lambda = 2d \sin \theta, \quad (3.1)$$

Where λ is the wavelength of x-rays, d - spacing between the crystal planes, θ - angle of incidence rays. Crystallite sizes can be calculated from the Scherrer formula:

$$D = \frac{K\lambda}{\beta \cos \theta}, \quad (3.2)$$

Where K is the shape factor of the average crystallite, λ is the X-ray wavelength ($\lambda = 0.15406$ nm for Cu target), β is the full width at half-maximum in radians, θ is the Bragg angle, and D is the mean crystallite dimension normal to diffracting planes [90].

The Surface Technologies and Superconductivity Service of LNL is equipped with a diffractometer by X'Pert Powder from Philips Company, a powerful device to determine the crystal's atomic and molecular structure.

Figure 3.10 A shows the inside of the apparatuses with the particular sample holder to determine the correct position of the sample. It is essential for the thin film study, where small quartz samples are used. Additionally, X-ray diffractograms were analysed with dedicated HighScorePlus software (Panaytical) [91]. The analysis program searches for the best matching between our diffractograms and libraries. The diffractogram was acquired using Cu-K α X-ray $\lambda = 1.54 \text{ \AA}$ as the radiation source at 40 kV and 40 mA.

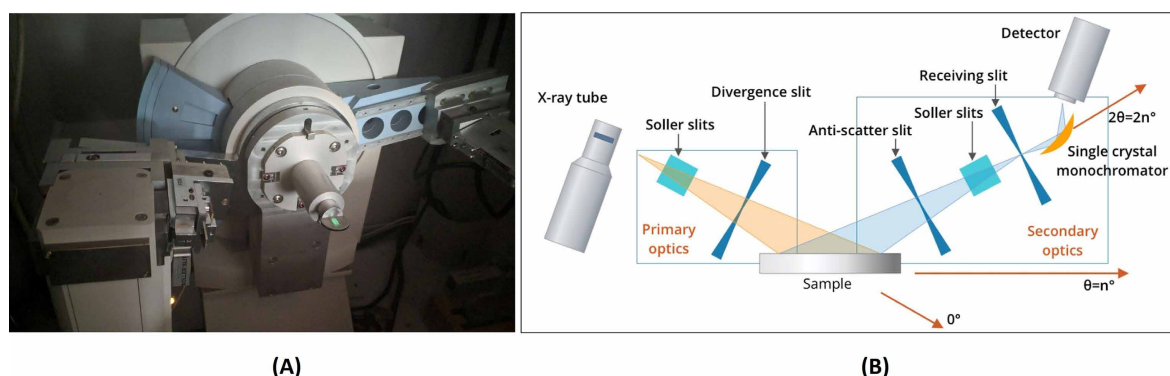


Figure 3.10: X-Ray diffractometry (A) machine installed in STSS laboratory and (B) principal of its work[89].

The spectra can be acquired with a parallel plate collimator in a grazing angle configuration (incident beam fixed at 2θ and moving the detector) or with a programmable receiving slit (PRS) in a gonio configuration (moving the beam and the detector). The right choice of the analysis configuration is related to the intensity of the spectra peaks obtained. Usually operating in gonio configuration, a grazing angle configuration is preferred if the background noise due to the substrate is too high. This setup increases the signal from the thin film concerning the substrate's signal, increasing the analysis's quality.

3.4.4 MATERIAL-EFFICIENCY AND DENSITY MEASUREMENTS

The weight measurements for the material efficiency study (described in Chapter 5) were performed with electronic precision balances (Mettler Toledo group, EL303, accuracy 0.001 g), shown in Figure 3.11 A. The target density calculations were performed, with the weight measured by electronic precision balances (Sartorius MCA225S-2S00-I Cubis® II Semi Micro Balance, 220 g × 0.01 mg), shown in Figure 3.11 B.

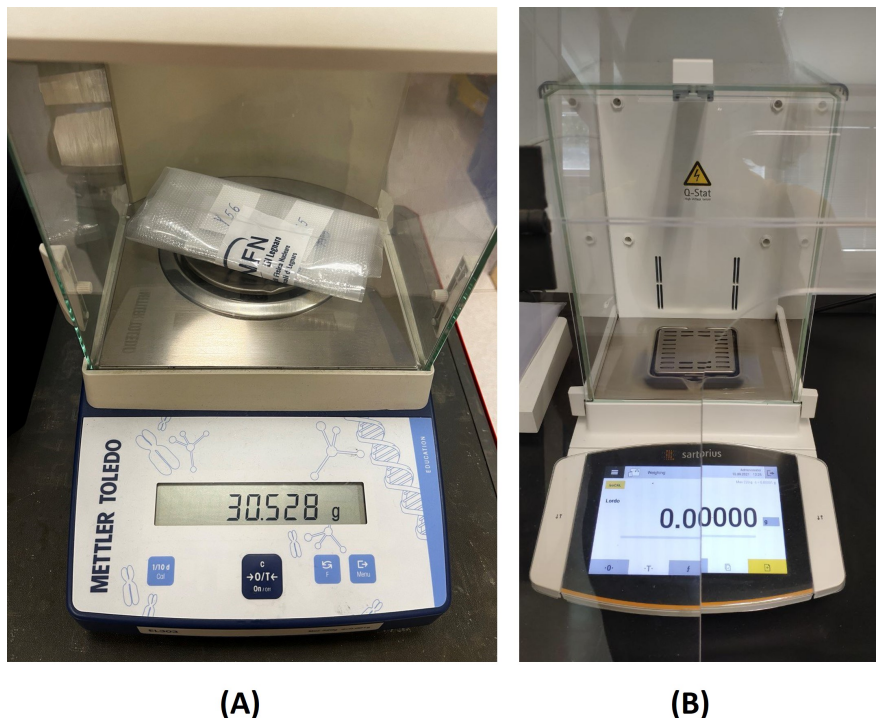


Figure 3.11: Scientific balances: (A) EL303 with accuracy 0.001 g and (B) 0.01 mg

The material efficiency calculations were made by a simple formula, where Δm is a mass deposited on a specified system part (sample holder, recovering shield, etc.) and ΔM is a mass of material deposited from the cathode.

$$Eff = \frac{\Delta m}{|\Delta M|} \cdot 100\%, \quad (3.3)$$

The density was calculated by the following formula, where D is density, Δm is the mass of the deposited material, S is the surface of the deposition, and δ is the film thickness:

$$D = \frac{\Delta m}{S \cdot \delta} \quad (3.4)$$

The achieved value was compared with the noted raw material density and represented in percentages.

3.5 THERMO-MECHANICAL EVALUATION VIA IRRADIATION TEST

The irradiation tests, along with the radiochemistry and radiolabelling of the yttrium solid targets, were conducted at the radiopharmacy and cyclotron facility of Sacro Cuore Don Calabria Hospital (SCDCH) in Negrar (VR, Italy) [92]. This provided the advantage of testing the manufactured targets in a specific environment tailored for such procedures. Additionally, the hospital's cyclotron has two stations suitable for dual-beam bombardment. Routine production includes PET isotopes such as ^{18}F and ^{13}N . The solid target station can produce ^{89}Zr , ^{124}I , and ^{64}Cu .

SCDCH has a radiopharmacy operating under Good Manufacturing Practice standards, research laboratories for radiochemistry synthesis and analysis, and a bunker housing a cyclotron for radionuclide production. The proton irradiation was executed using a variable-energy (13-19 MeV) TR19 cyclotron (ACSI, Richmond, BC, Canada), shown in Figure 3.12 A, equipped with a high-current ion source capable of reaching up to $300\ \mu\text{m}$. The target station (ACSI), shown in Figure 3.12 B, is oriented at 90 degrees and directly connected to the cyclotron target selector.

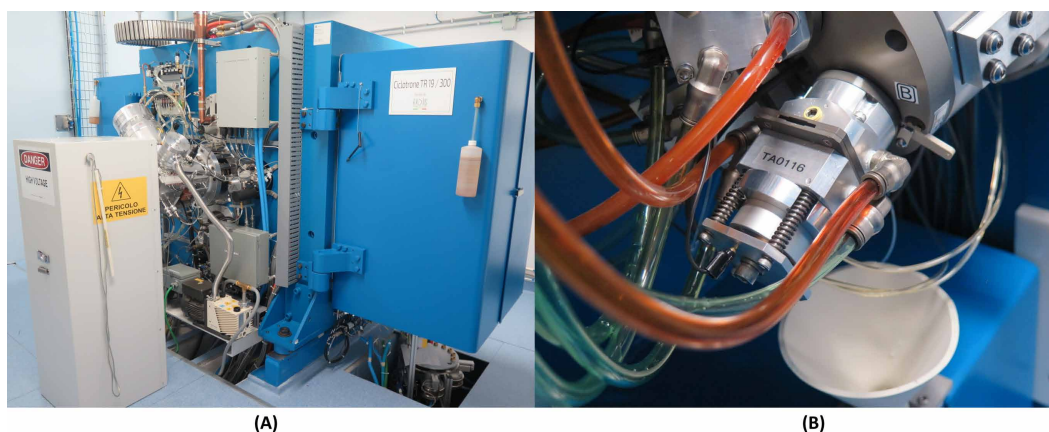


Figure 3.12: (A) Photo of ACSI TR19 cyclotron at SCDCH. (B) The solid target station of TR19/300 cyclotron. The blue arrow indicates the target coin's position inside the target station. Both photos courtesy of Sara Cisternino

Helium gas and water cooling maintain the target coin's temperature during irradiation. The cyclotron target holder accommodates a coin with a maximum thickness of 2 mm and a diameter of 24 mm. A proton beam diameter of approximately 10 mm.

Irradiation tests at increasing current levels were performed in early-stage target manufacturing optimisation. This work evaluated the thermo-mechanical stability of the initial ZnO targets manufactured with the new inverted magnetron setup, following the approach shown in [10].

4

Yttrium solid target manufacturing: thick film depositions

Building upon the successful case study involving ^{nat}Mo solid targets and a patented magnetron sputtering method for target manufacturing [46], a new collaboration with Sacro Cuore Don Calabria Hospital (SCDCH) in Negrar has commenced. The primary goal is to explore various target manufacturing methods, including magnetron sputtering, to optimise ^{89}Zr production, encompassing purification and labelling studies.

This chapter presents a refined deposition process and an improved preparation protocol for contaminant-free yttrium solid targets. Multiple batches of targets were manufactured, analysed, and irradiated using a medical cyclotron in SCDCH. Various strategies were proposed to achieve higher deposition thickness while maintaining low residual stress concurrently. Consequently, substantial improvements have been made, and ultra-high yttrium deposition was obtained. The chapter shows the irradiation test results demonstrating a significant enhancement, particularly from the ^{89}Zr production perspective. The chapter concludes by discussing potential future optimisation routes.

The experiments in this work are denoted as 'YN.0', where N represents the deposition run number from 1 to 5. The targets obtained from these experiments are denoted as 'YN.A', where A represents the target number from 1 to 7 in the Nth experiment.

4.1 YTTRIUM DEPOSITION: STATE OF THE ART AT LNL

Based on STSS facilities, a preliminary study of deposition rate and stress-related problems was conducted. As a result of the work, the first batch of yttrium targets was manufactured using a standard planar magnetron configuration. Summarising findings published in [10], it was studied and defined sputtering parameters to obtain stress-free, thick yttrium coatings. The deposition was successfully carried out at room temperature, with a dedicated mask facilitating the preparation of 7 targets. However, due to unforeseen issues, the deposition ran slightly shorter than planned (6.5 hours instead of 8 hours), resulting in a reduced thickness: 6 samples with $50\ \mu\text{m}$ and one with $70\ \mu\text{m}$. Despite these challenges, all produced targets endured irradiation tests. Preliminary tests, lasting 5 minutes and increasing the current from 30 to $70\ \mu\text{A}$, were followed by a 5-hour irradiation of two targets at $50\ \mu\text{A}$ with a beam energy of 12.7 MeV. However, the desired yttrium deposit thickness was not obtained at this stage.

4.2 PROCESS OPTIMISATION

After the irradiation and dissolution step, over 2.5% of ^{109}Cd impurity was found in the final product [93]. The used and completely eroded cathode was dismantled and visually examined. Figure 4.1 A shows the cathode and Cu base plate contaminated with the silver paint after the Y1.0 deposition. The utilisation of Ag paste is a common practice in sputtering depositions. The appearance of the Ag contaminant in the deposition was not reported for the Mo targets manufacturing and in other processes.

An EDS method was suggested to investigate the origin of the contamination. To perform such an analysis, a cathode piece (see Figure 4.1 A) was cut from the yttrium cathode by sparkerosion machine. It is crucial to acknowledge that the cathode sparkerosion cutting procedure, carried out in water using a brass wire, might introduce uncertainties in the results. Despite this, the EDS mapping images (refer to Figure 4.1 B and C) indicate a higher presence of silver (Ag) on the cathode surface exposed to plasma compared to the surface covered by the central ring (refer to Figure 3.7 C).

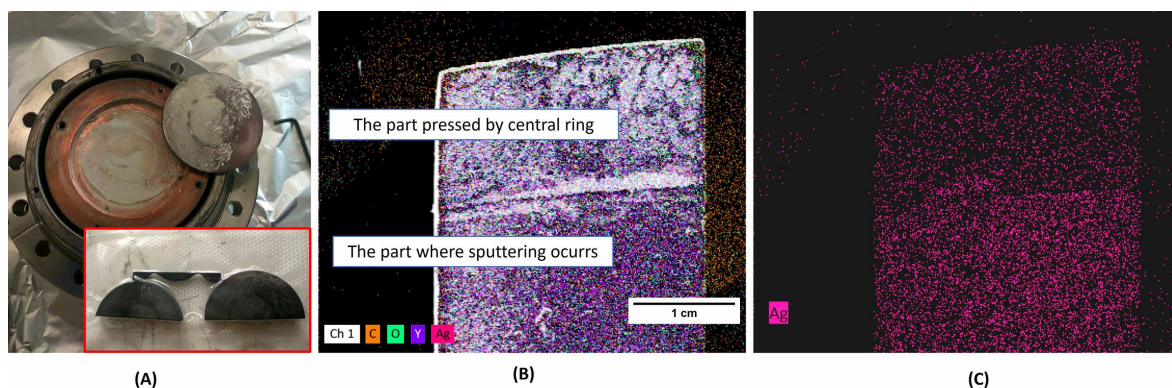


Figure 4.1: Yttrium cathode analysis: (A) picture of the magnetron and cut yttrium target of Y1.0 deposition. Results of its energy dispersive spectroscopy (EDS) analysis: (B) mapping with different elements and (C) mapping of Ag element.

This occurred partly due to an excess application of silver paint, causing some Ag to be on the cathode edges. Subsequently, it migrated to the sputtering area due to temperature gradients or significant overheating. The qualitative EDS analysis does not confirm the presence of Ag, likely because of the relatively low amount (less than 5%) of Ag on the cathode surface.

Upon evaluation, it was concluded that the contamination source was the 'silver paint'. While the exact contamination mechanism remains unclear, the decision was made to discontinue silver paint as a thermal-conductive layer. Alternatively, a thin carbon foil could be used, but it was opted to perform the deposition without any additional material. Further, a new, clean magnetron was assembled for subsequent depositions to ensure contaminant-free processes, especially for such a sensitive application.

4.2.1 VACUUM OPTIMISATION

Another concern about the deposition process was the base vacuum level. In the previous depositions, a base pressure is reported to be $5 \cdot 10^{-6}$ mbar. Such pressure is a bare minimum to avoid oxygen and possibly oxidation of the metallic yttrium. However, at such pressure, the desorption of water vapour still occurs, which can result in cathode oxidation. The baking process and, as a result, lower base pressure can provide a higher level of adhesion between substrate and coating, decreasing impurities. Moreover, a higher density of the coating can be achieved.

To reduce the base pressure, it was decided to perform the baking process described in Chapter 3. Moreover, a leak detection was performed, and problematic zones were identified. After some flanges substitution and baking process, it was possible to reach pressure at 10^{-9} mbar level. Table 4.1 shows the baking time for each deposition run and the base pressure obtained.

Table 4.1: Base pressure obtained in all deposition batches after the baking process.

Deposition batch	Baking time [h]	Obtained pressure [mbar]
Y 2.0	19+26+24	$2.9 \cdot 10^{-8}$
Y 3.0	20+70	$3.87 \cdot 10^{-8}$
Y 4.0	20+70	$4.7 \cdot 10^{-8}$
Y 5.0	48+20	$3.3 \cdot 10^{-8}$

An extreme baking time of more than 120 h is needed to reach such a level with a baking temperature of 120 °C. Higher temperatures are impossible since they can damage sensitive parts of the vacuum system. On the other hand, usually, after 70 h of baking, a level 10^{-8} mbar is achievable.

4.2.2 SAMPLE HOLDER

A dedicated sample holder and mask, shown in Figure 4.2, was designed to perform the yttrium deposition. The new design allows faster and simpler assembling and disassembling of the Nb disks.

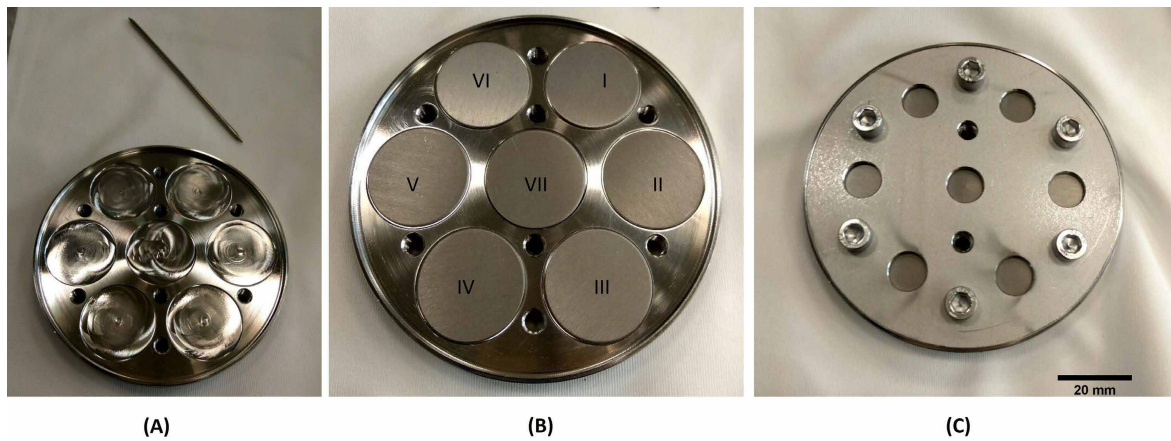


Figure 4.2: Sample holder for yttrium deposition: (A) base plate of the sample holder, (B) assembled with seven Nb disks, and (C) mounted with a dedicated mask.

The sample holder can host seven targets with a diameter of up to 24 mm. To provide the continuous deposition process, two dedicated masks were produced. In this way, the new deposition run can be prepared within a shorter operating time. The mask has seven slots with a diameter of 10 mm, where the yttrium is deposited.

4.2.3 COATING PROTOCOL UPGRADE

The baking procedure was included in the standard protocol for yttrium solid targets manufacturing by MS techniques, shown in Figure 4.3. Thus, the deposition process includes four stages: vacuum system preparation, baking, deposition process, target disassembling and analysis. Hence, the whole manufacturing process can be performed in one week.

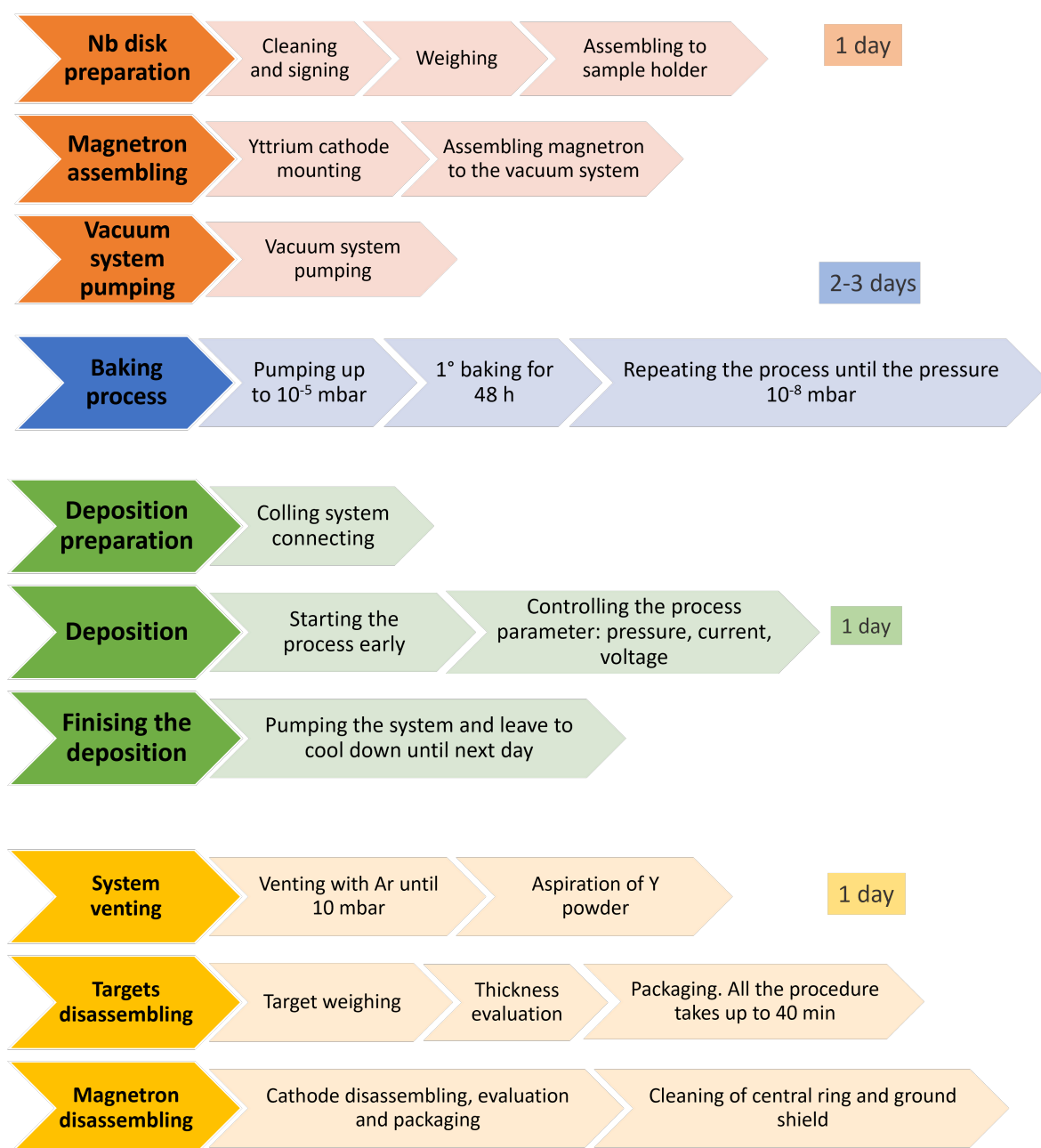


Figure 4.3: The upgraded protocol of yttrium solid targets manufacturing with standard magnetron sputtering method.

During the first step, the Nb coins must be cleaned appropriately and signed with scratching of numbers (from I to VII). All the disks must be weighted and assembled to the sample holder, which must then be assembled in the chamber in the upper position.

The magnetron must be assembled quickly since the yttrium cathode tends to oxidise. The system must be evacuated using dedicated pumps. The first step usually takes one working day. The next step is the baking process, previously described. This step can take two or three days.

The deposition time is around 8 hours, performed without interruption within one working day. The disassembling of the manufacturing targets must be done on the following day. The targets must be exposed to the atmosphere for as little as possible to avoid oxidation. Usually, the analysis, which includes target weighting and thickness measurements, takes about 40 min. Then, the targets are packed in individual vacuum bags marked with related numbers.

4.3 YTTRIUM DEPOSITIONS: Y₂, Y₃ AND Y₄

The first batch with an upgraded procedure was prepared using previously defined process parameters, shown in Table 4.2. The average deposition rate was $10.4 \mu\text{m}/\text{min}$, slightly lower than predicted ($13.3 \mu\text{m}/\text{min}$ [10]). However, such effects are widespread, especially for long-term deposition with complete cathode erosion. The cathode erosion was estimated using a height measuring device (Digimar 816 CL), showing only $580 \pm 3 \mu\text{m}$ remaining thickness in the "racetrack" cave.

Table 4.2: Yttrium deposition process (Y2.0): parameters and result.

Dep. batch	Power [W]	Current [A]	Voltage [V]	Working distance [cm]	Ar flux [sccm]	Time [min]	Dep. rate [$\mu\text{m}/\text{h}$]
Y2.0	400	1.17-1.65	350-254	7	19	480	10.4

The lengthy deposition was successfully performed for 8 hours without pauses and interruptions. As a result, seven yttrium solid targets were manufactured. However, the non-uniform deposition colour on the sample holder, shown in Figure 4.4 A, was a concerning detail. Moreover, a re-crystallisation region on the yttrium cathode can be noticed, as shown in Figure 4.4 B. Both these phenomena suggest a non-uniform magnetic field distribution. The magnetic field evaluation of a magnet set, assessed using a LakeShore 421 Gaussmeter, confirms the observation. It was decided to change the magnet set for a new one and repeat the deposition.

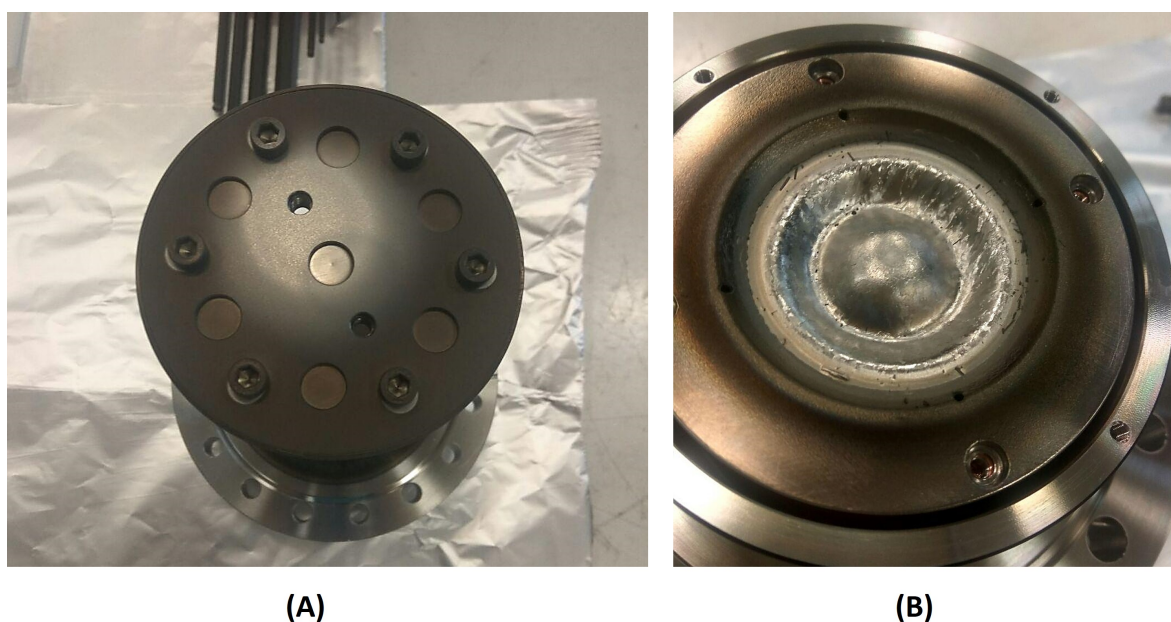


Figure 4.4: The sample holder and yttrium eroded the cathode after the Y2.0 deposition.

The Y3.0 deposition was performed using the same process parameter shown in Table 4.3. A significant voltage drop and much higher current values were observed during the process.

Table 4.3: Yttrium deposition parameter and deposition rate results at working distance.

Dep. batch	Power [W]	Current [A]	Voltage [V]	Working distance [cm]	Ar flux [sccm]	Time [min]	Dep. rate [$\mu\text{m/h}$]
Y3.0	400 ¹	1.18-1.94	344-218	7	19	480	8.4
Y4.0	400 ¹	1.16-1.32	355			75	-
Y4.0*	400-347	1.4 ¹	303-252			405	8.7

¹ operation at this constant

The yttrium deposition over the sample holder was uniform and of good metallic colour, as shown in Figure 4.5 A. During the magnetron disassembling, it was found that the yttrium cathode was eroded entirely, and the holes were visible (see Figure 4.5 D). This fact compromised the use of manufactured targets for the irradiation since they are probably contaminated with Cu from the magnetron base plate, shown in Figure 4.5 C. The explanation for such an effect can be that the magnetic field of the new magnet pack had higher intensity, and the erosion of the cathode was more concentrated at the "racetrack".

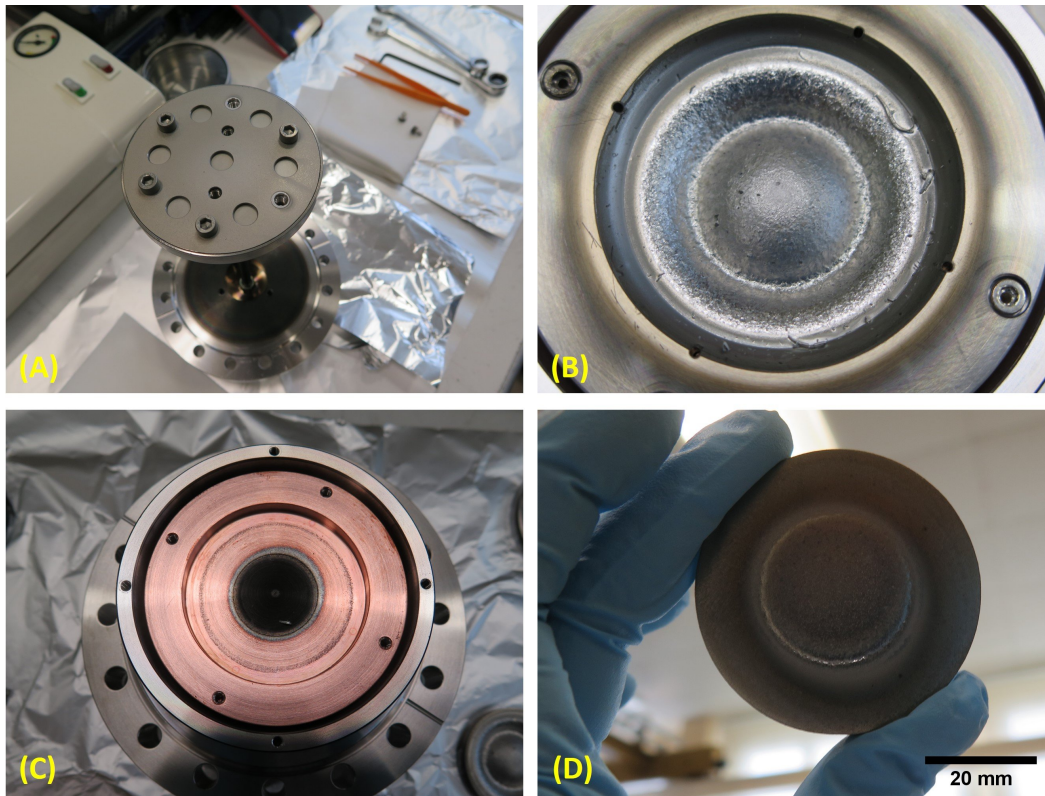


Figure 4.5: Results of Y3.0 deposition: (A) sample holder, (B) yttrium eroded cathode, (C) copper base plate after the deposition, (D) completely eroded yttrium cathode with visible holes

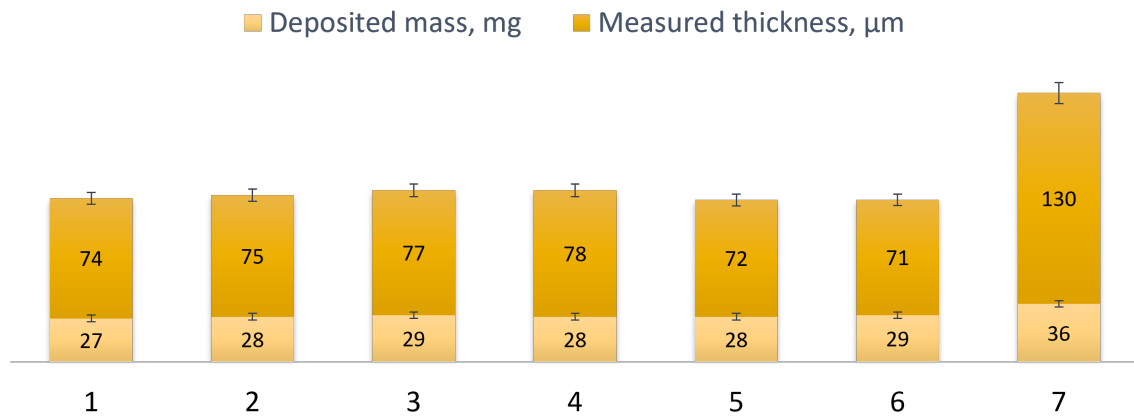
It was decided to return to the old magnet set. The deposition Y4.0 was performed starting with the same parameters as usual, operating at a constant power of 400 W. However, the process was not stable, and after 75 minutes, it was decided to switch to constant current operating mode with 1.2 A. In total, 8 hours of deposition were performed, and a new batch of 7 yttrium targets was produced. The parameters and results of the deposition rate are shown in Table 4.3.

This time, the deposition was uniform in colour. However, the one-side cathode recrystallisation was visible. The eroded cathode was analysed with a height-measuring device. The thickness of the "racetrack" was not equal along the line: from one side, it was $535 \pm 3 \mu\text{m}$ and $653 \pm 3 \mu\text{m}$ from the other.

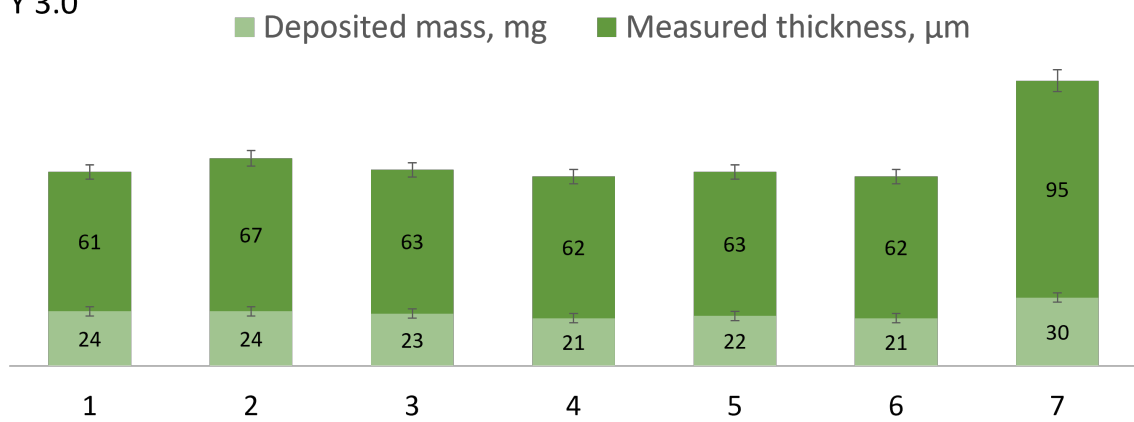
4.3.1 THICKNESS EVALUATION

Figure 4.6 graphically presents the deposited mass and measured thickness. The higher number represents thicknesses in μm ; the lower is a measured mass in mg . All the measurements were performed once to avoid yttrium oxidation. The error bars represent the instrument's errors. As shown in Figure 4.6, the target number 7 was consistently higher in deposition mass and thickness. The target number seven always corresponds to the central target, as shown in Figure 4.2.

Y 2.0



Y 3.0



Y 4.0

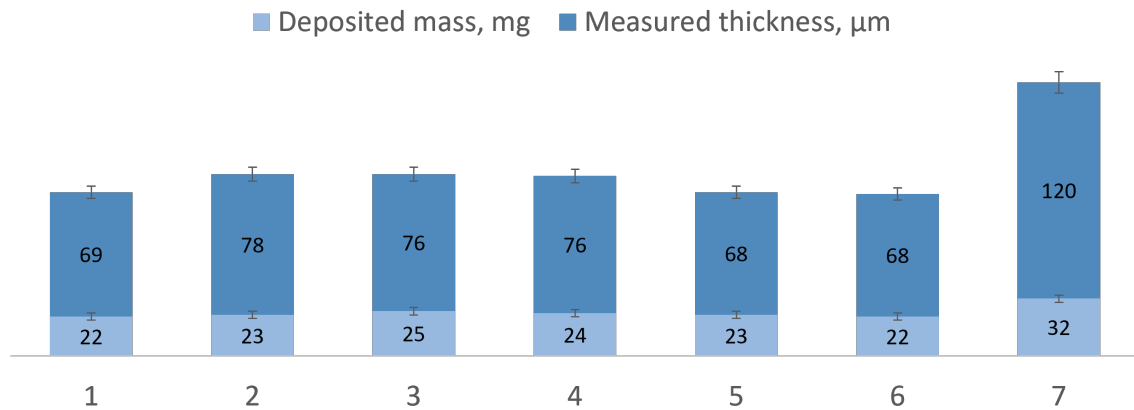


Figure 4.6: Deposited mass and thickness of deposited targets (1-7) at three deposition batches (Y2.0, Y3.0 and Y4.0).

While the higher deposition rate and slightly higher mass deposited are straightforward consequences of the plasma pattern, the extreme thickness rise cannot be explained using the same consideration.

The thickness profile of three targets sputtered in the central position are shown in Figure 4.7 top. It is clear that the deposition is non-uniform over the 10 mm profile and has a maximum value, which is sometimes over the instrument limits. Moreover, such a profile can result from the Nb disk bending due to the sample holder and mask assembling. Figure 4.7 bottom shows the standard thickness profile of the samples deposited on the side position.

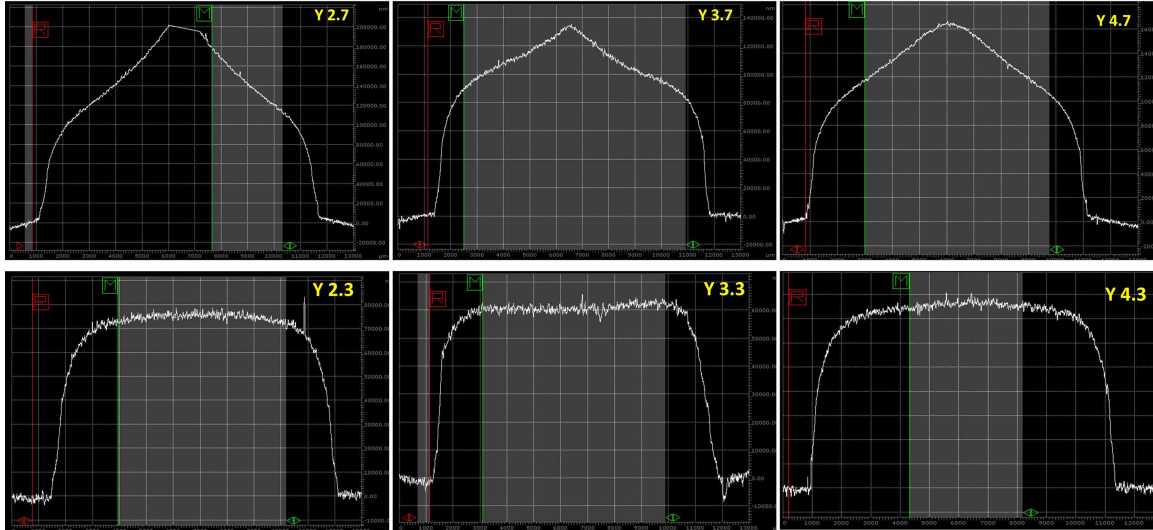


Figure 4.7: The coating thickness profile of yttrium targets, measured by contact profilometer: top - deposited at the central position of different batches; bottom - deposited at the side position, measured by the contact profilometer.

On the other hand, the other six targets are usually uniform, and no significant banding was observed. Despite the described difficulties, two yttrium target batches were manufactured and prepared for future irradiation.

4.3.2 DENSITY EVALUATION

The yttrium deposition density was calculated using the measured weight and thickness, described in 3.4.4. The calculated densities for each target of batch Y 2.0-Y 4.0 are shown in Figure 4.8. All the measurements were performed once to avoid yttrium oxidation. The error bars represent the instrument's and calculation errors.

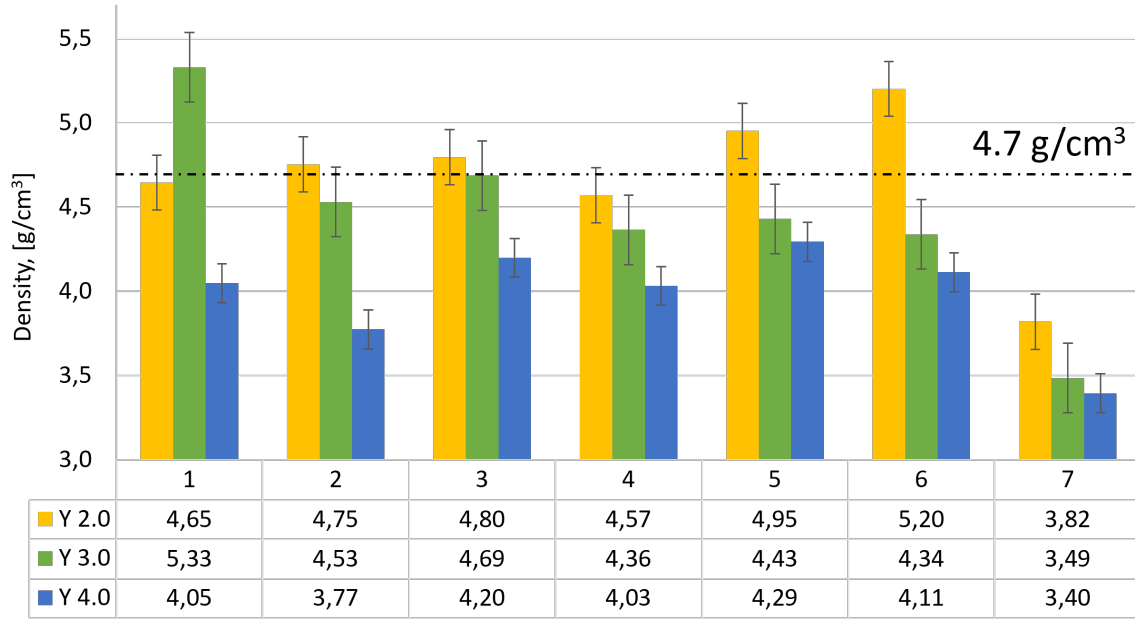


Figure 4.8: Graphical representation of the density calculation of each target in the three deposition batches: Y 2.0 - Y 4.0.

The density of the yttrium bulk material is 4.7 g/cm^3 , while the density of yttrium oxide Y_2O_3 is 5.01 g/cm^3 . In some cases, the density value exceeds the bulk density of yttrium. It is suggested that targets exposed to air for over 40 minutes may undergo oxidation. However, it is more likely that the density calculation cannot be reliable due to difficulties in measuring the thickness, particularly for the central targets.

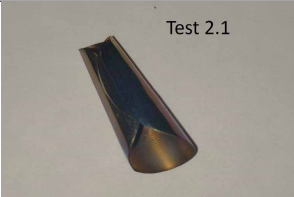
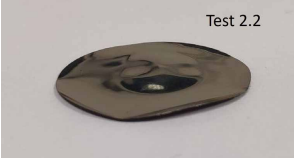
4.4 PROCESS UPGRADE FOR THICKER FILM SPUTTERING

Different deposition strategies can be employed to obtain higher thicknesses. As was suggested in previous works, the multilayer approach is not recommended because of the high tendency of yttrium to oxidation. Any vacuum breakage leads to top-layer oxidation, compromising layer adhesion and stress-related issues. In these circumstances, the deposition must be done within one sputtering cathode. The increase in deposition time is limited by the cathode thickness, and the limit was already reached. The idea was instead of ours, to reduce the working distance between the cathode and the substrate, increasing the deposition rate and allowing us to reach higher thicknesses. The change in working distance leads to a change in the film's stress evolution. For this reason, a new set of experiments is needed to adjust the process parameter to grow thicker, stress-free coatings.

4.4.1 PARAMETER OPTIMISATION

As was previously mentioned, the depositions were performed at a constant current mode to have better control over the deposition rate. The stress evaluation results are in Table 4.4. The depositions were done for 15 minutes on flexible Kapton foils (1 inch (25.4 mm) in diameter). Previous research has suggested that this method can provide quick access to evaluate stress [10], a crucial aspect in thick film growth, as suggested in Section 2.4.2.

Table 4.4: Stress evaluation in yttrium deposition with reduced working distance 4 cm.

Test	Ar flux [sccm]	Current [A]	Working P[mbar]	Qualitative stress evaluation
1	19	1.3	1.01×10^{-2}	
2	23	1.2	1.19×10^{-2}	
4	25	1.2	1.3×10^{-2}	

The first test was performed with a constant current of 1.3 A and the previously used Ar flux of 19 sccm. The result shows a highly compressive stress due to the distance changes. In the following tests, it was decided to increase the Ar flow to 23 sccm and use a lower current, 1.2 A. The results obtained show a combination of the tensile and compressive stress. The intrinsic stress is highly dependent on process parameters, such as working pressure and it leads to the change in the surface energy distribution.

Further increase of the working pressure led to relatively low compressive stress, which did not change after exposure to an air environment. It means that the oxidation of the yttrium does not lead to an increase in stress.

The next step for the process evaluation was measuring a deposition rate during the longer deposition run, together with adhesion evaluation on different substrates. The deposition was performed on Si wafers, quartz and Nb samples for 45 min. The yttrium deposition was well attached to all types of substrates.

The thickness evaluation was done using SEM and profilometer methods. Figure 4.9 shows SEM cross-section analysis of yttrium deposition sputtered on the centre and edge of the sample holder. The edge sample represents the deposition rate of 6 circularly distributed samples. Meanwhile, the centre one corresponds to the central target.

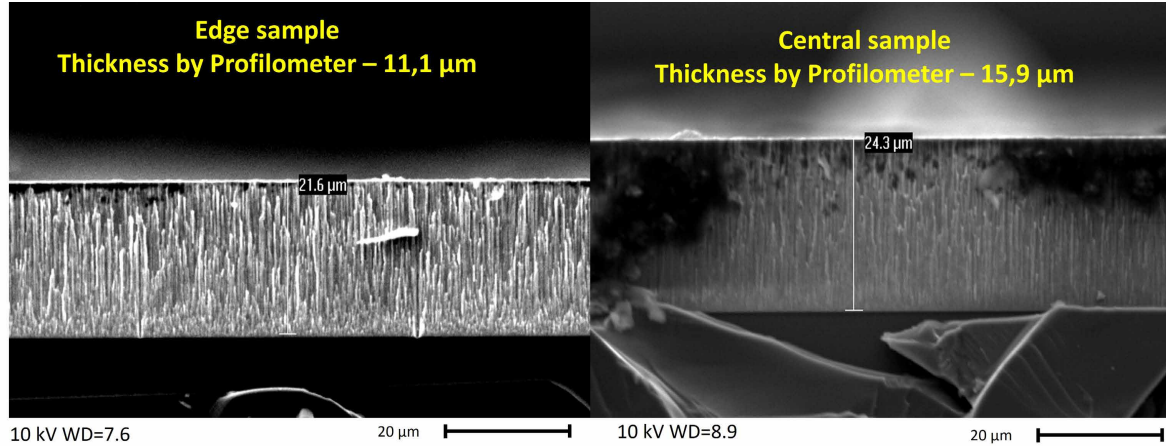


Figure 4.9: Cross-section SEM thickness evaluation compared with the results obtained by contact profilometer.

Thus, the deposition rate calculated by the profilometer for the central sample is $-21.2 \mu\text{m}/h$, meanwhile measured with SEM $-32.4 \mu\text{m}/h$. SEM cross-section analysis can provide more precise measurements on a small distance range.

It is essential to underline that deposition rate evaluations are needed and can be easily performed only on samples with mirror-like surfaces (e.g. silicon or quartz). The roughness of the Nb sample does not allow precise thickness measurements with thin film (less than $10 \mu\text{m}$). However, the thickness evaluation of the final products can and must be performed only on the real targets. Moreover, in Figure 4.9, yttrium film growing behaviour can be observed.

Notably, no film oxidation and defined columnar growth are present, confirming the correct parameter optimisation. The growing type corresponds to Zone T of SZD, mentioned in the previous Section 2.4.

Other tests were also performed to study the possibility of a lower working distance (2.5 cm) or higher working current (1.4 A). Preliminary tests were performed, and their stress-evaluation results are shown in Table 4.5 and 4.6.

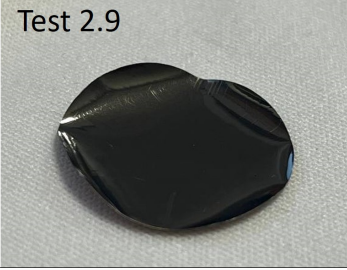
Table 4.5: Stress evaluation in yttrium deposition with 2.5 cm working distances and 1.2 A current.

Test	Ar flux [sccm]	Working P[mbar]	Qualitative stress evaluation
5	25	1.3×10^{-2}	Test 2.5 
6	27	1.42×10^{-2}	Test 2.6 
7	30	1.59×10^{-2}	Test 2.7 

It was possible to continue optimising the process with a working distance of 2.5 cm; however, the deposition of more than one central target can be the problem in this case. More precise thickness and stress evaluations are needed. Since the target manufacturing process takes one week, it was decided to proceed with a multiple-target manufacturing approach.

The results, shown in Table 4.6, suggest that a slight current increase can be used to reach higher thicknesses.

Table 4.6: Stress evaluation in yttrium deposition with 4 cm working distances and 1.4 A current.

Test	Ar flux [sccm]	Working P[mbar]	Qualitative stress evaluation
9	27	1.43×10^{-2}	Test 2.9 
10	28	1.47×10^{-2}	Test 2.10 
11	30	1.6×10^{-2}	Test 2.11 

4.4.2 UNIFORMITY STUDY

It was also considered that distance change leads to different thickness distributions, and uniformity of the yttrium deposition on certain conditions must be verified. To evaluate the deposition uniformity, a one-hour deposition was conducted at the defined parameters: flux of Ar gas - 25 sccm, constant current - 1.2 A.

The thickness uniformity was calculated by Formula 4.1, where δ_{max} and δ_{min} - maximum and minimum thickness on the evaluated lengths (76 mm).

$$WtW = \frac{\delta_{max} - \delta_{min}}{\delta_{max} + \delta_{min}} \times 100\% \quad (4.1)$$

The results of uniformity evaluation are shown in Figure 4.10. The quartz samples, shown in Figure 4.10 top, were used as a mask to evaluate the thickness in different positions.

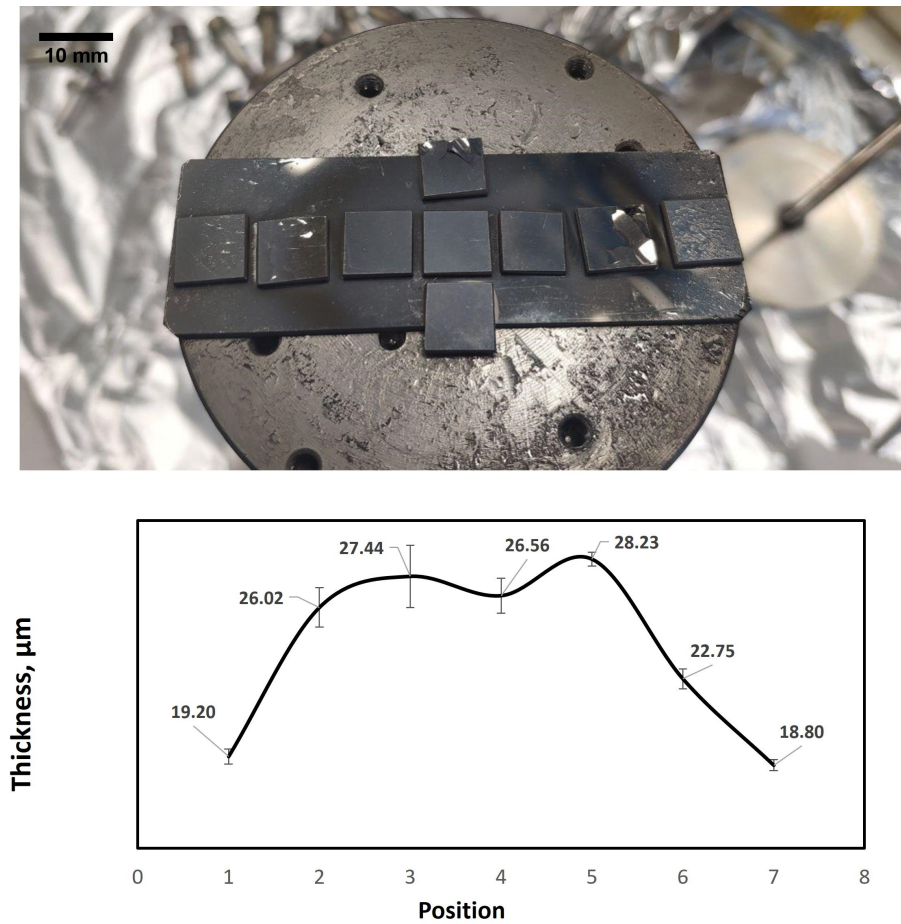


Figure 4.10: Thickness uniformity evaluation, by contact profilometer, over the 76 mm distance: top - samples picture; bottom - graphical representation of results, positioned in respect to the sample holder shown in the top of the figure.

The calculated uniformity appears to be 21.3 %. This means that thickness over the 76 mm length can vary by 20 %. The uniformity test did not show high-performance results with a working distance of 4 cm. However, for the cyclotron solid target manufacturing, the results are good enough and allow us to sputter the solid targets with good uniformity in 10 mm lengths (area of 78.5 mm^2). As advised in the previous section, this non-uniformity is also connected to the non-uniform magnetic field problem.

As a result of such uniformity measurement, the new design of the sample holder shown in Figure 4.11 was proposed. In such a design, the three central targets can reach 170-180 μm thickness in 7 h deposition and the other 100-120 μm . With such a sample holder, it can be sputtered six instead of 7 targets, but a better uniformity level can be reached.

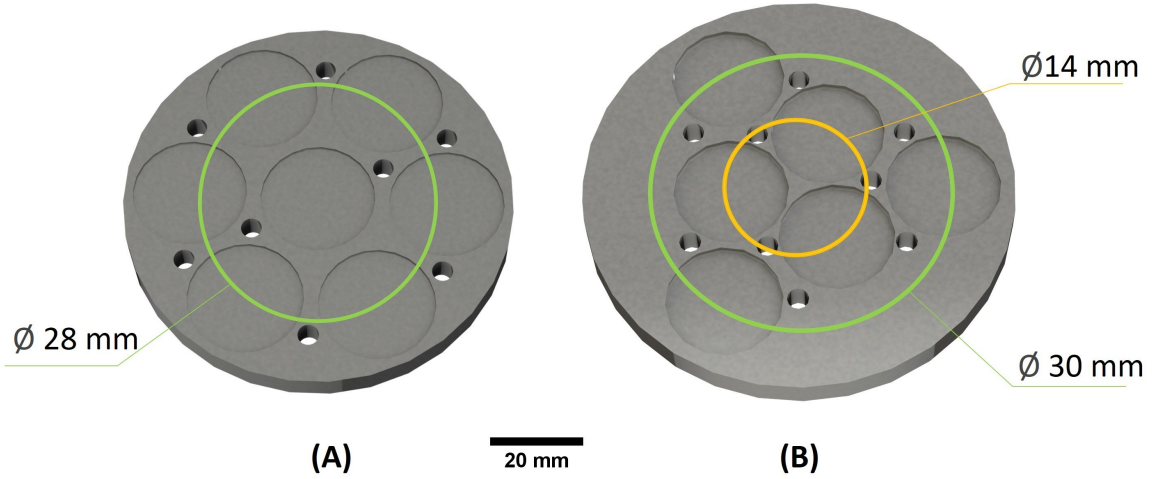


Figure 4.11: Current (A) and new (B) sample holder design for yttrium solid targets depositions.

4.5 THICK YTTRIUM DEPOSITION: Y5.0

Based on the parameter optimisation, the first ultra-thick target batch was manufactured. Table 4.7 reports the final process parameters. The operation at constant current provides a stable process throughout the duration. The deposition was performed for 7 hours to avoid problems with complete target erosion.

Table 4.7: Yttrium deposition parameters and results of Y 5.0 sputtering run.

Dep. batch	Power [P]	Current [A]	Voltage [V]	Working distance [cm]	Ar flux [sccm]	Time [min]	Dep. rate [$\mu\text{m}/\text{min}$]
Y5.0	380	1.2	320-240	4	25	420	16.5

The deposition rate was twice as high compared to the Y 4.0 deposition. Consequently, six out of seven targets have an average thickness of 115 μm , while the central one measures approximately 200 μm . Figure 4.12 graphically represents the mass and thickness measurement in addition to the density calculation. The density calculation still exceeds the bulk yttrium density value. However, it is more uniform with respect to previous batches (see Figure 4.8). It can be suggested that higher thickness and mass deposition improve the quality of performed measurements and calculations.

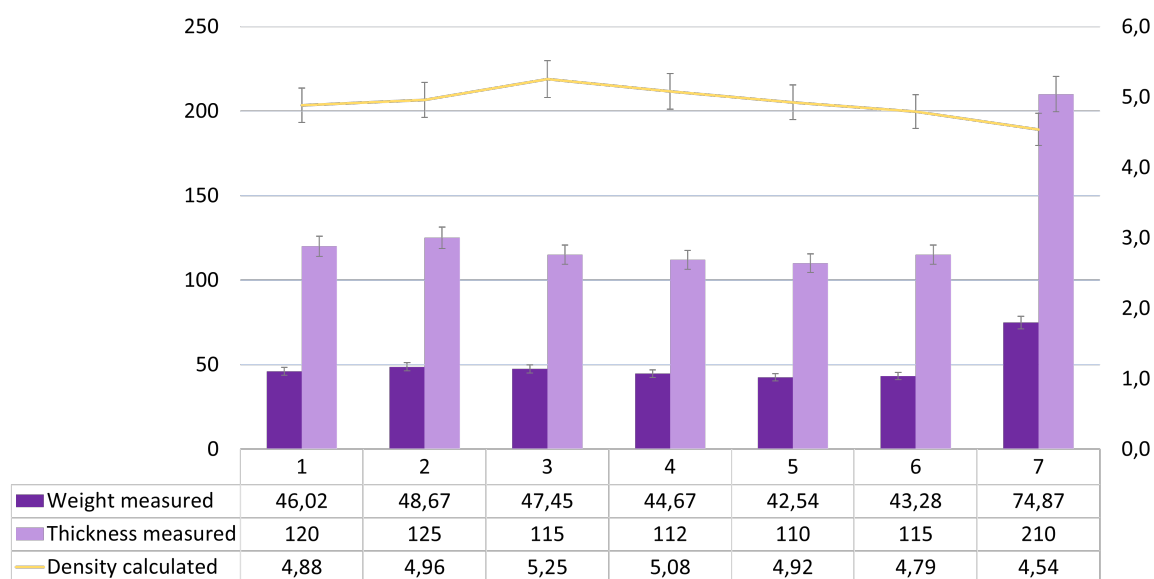


Figure 4.12: Graphical representation of measured weight and thickness, together with the density calculation of each target in the Y 5.0 deposition

Three out of seven obtained targets have pinhole defects. One such target is shown in Figure 4.13 B bottom. Figure 4.13 C illustrates the method of target packaging for delivery to the cyclotron facilities. Each target is enclosed in individually sealed bags, labelled, and then placed into two additional vacuum-sealed bags to prevent oxidation. From the deposition point of view, the targets from 1 to 6 have no particular difference in their properties and deposition rates. While target number 7 is continuously sputtered in a central position, it may show different characteristics.

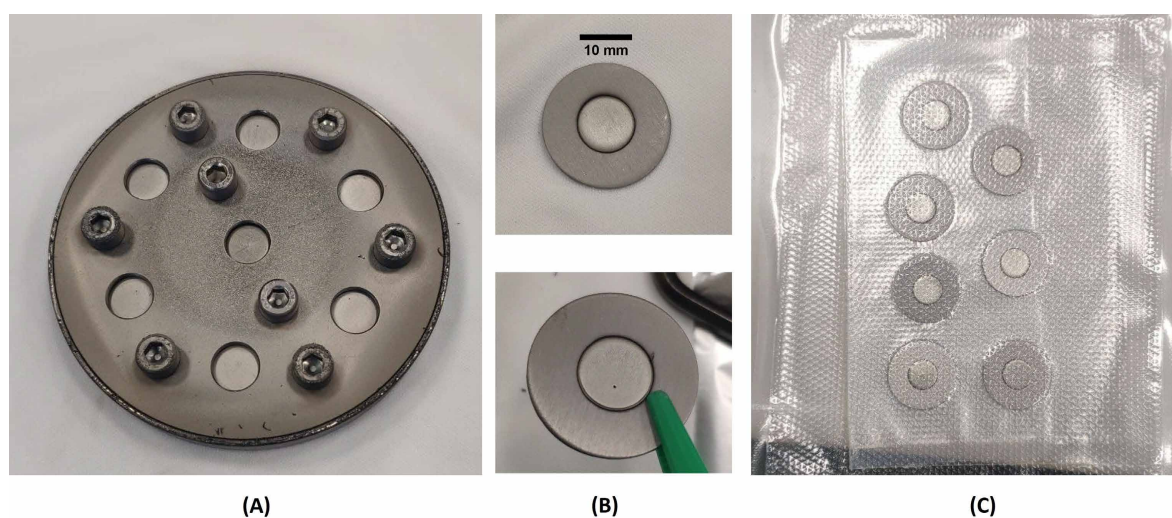


Figure 4.13: Y5.0 deposition results: (A) sample-holder with yttrium deposition, (B) single targets with and without defects, (C) seven targets packed in vacuum bags to prevent oxidation.

4.6 IRRADIATION RESULTS

The cyclotron used for irradiation is described in Chapter 3. The irradiation data in this section was courtesy provided by Dr. Emiliano Cazzola from Sacro Cuore Don Calabria Hospital (SCDCH). Irradiation tests were carried out to compare ^{89}Zr production by sputtering targets with other methods. This comparison is described in the Discussion Chapter 7. This section compares the sputtered targets of different deposition batches.

The irradiation parameters are summarised in Table 4.8. As seen from Table 4.8 in batch Y4.0, only two targets were successfully irradiated. Unfortunately, other targets were damaged due to the cyclotron target station problems.

Table 4.8: Yttrium deposition parameter and deposition rate results of Y5.0 deposition.

Target	Thickness [μm]	Weight [mg]	Irradiation time [min]	Irradiation current [μA]	Beam energy [MeV]	Saturation yield [MBq/ μAh]
5.1	120	46	90	47.6	12	12.165
5.2	125	49	95	50.2	12	12.836
5.3	115	48	92	48.8	12	9.324
5.4	112	45	46	46.5	12	6.654
5.5	110	43	90	49.8	12	6.925
5.6	115	43	90	49.8	12	10.875
5.7	210	75	90	49.5	12	15.801
4.5	68	23	120	49.8	12	2.035
4.7	120	32	120	49.7	12	5.831
2.1	74	27	184	30	12.55	6.341
2.2	77	28	31	27	12.55	5.287
2.3	76	29	245	59.1	12.35	2.449
2.4	75	28	118	59.4	12.35	2.452
2.5	73	28	62	56.7	12.35	4.950
2.6	73	29	61	29.8	12.55	4.663
2.7	130	36	153	34.3	12.55	6.923

Figure 4.14 shows the targets Y4.7 (central one) and target Y5.3 (side one) before and after irradiation. Both targets sustained the irradiation process without damage and delamination. Upon visual observation, Y4.7 has a central irradiated area, whereas Y5.3 is more distributed.

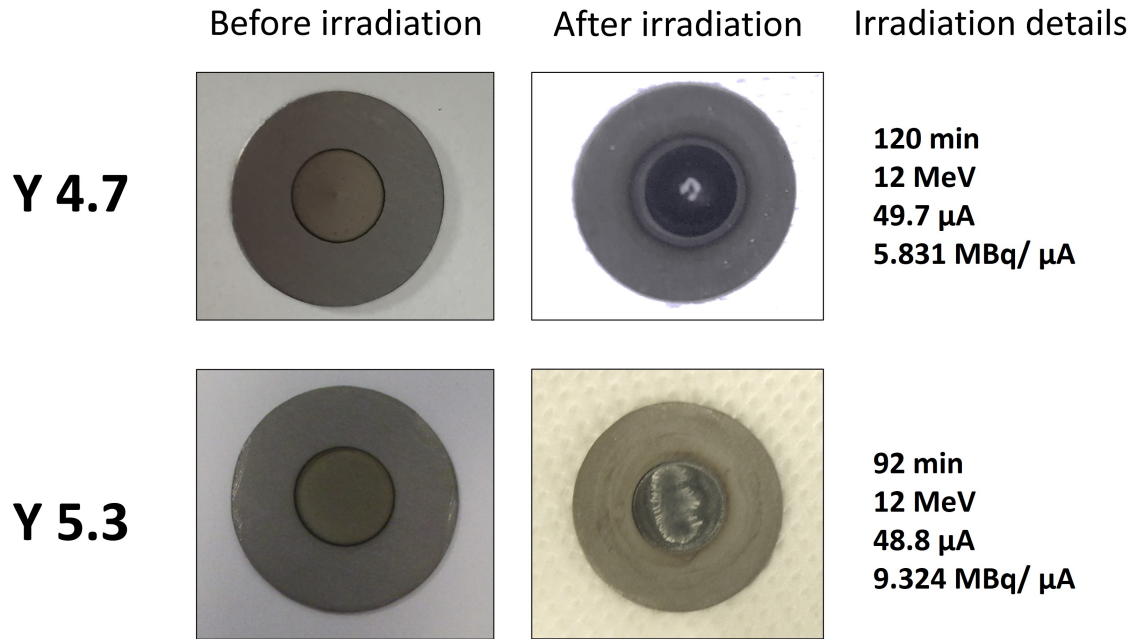


Figure 4.14: Visual inspection of irradiated yttrium targets Y4.7 and Y5.3

Evaluating the results obtained in Table 4.8 is unclear the influence of the deposition process on the saturation yield results. Notably, central targets (Y2.7, Y4.7, Y5.7) perform better than other targets produced in their disposition batches. The best performance was obtained with target Y5.7 with a measured thickness of 200 μ m. However, central targets typically do not have a uniform thickness profile and often have higher thicknesses.

In Table 4.9, the detailed activities of the bulk solution, waste, Zr SPE, and $[^{89}\text{Zr}]\text{Zr-oxalate}$, corrected for the end-of-bombardment (EOB) time for each production, are reported. The recovery procedures were performed for all irradiated targets, and all components were measured to evaluate the process. The average recovery percentage was $94 \pm 3\%$.

Table 4.9: Activity measured in the recovery process for the irradiated targets.

Target	Activity in bulk solution [MBq(mCi)]	Waste activity [MBq(mCi)]	Zr SPE Activity [MBq(mCi)]	$[^{89}\text{Zr}]\text{Ox}$ collected [MBq(mCi)]	^{89}Zr recovery [%]
5.1	936.8 (25.32)	64.8 (1.75)	5.6 (0.15)	866.5 (23.42)	92.51
5.2	1101.9 (29.78)	64.0 (1.73)	20.4 (0.55)	1017.5 (27.5)	92.35
5.3	724.8 (19.59)	4.1 (0.11)	24.8 (0.67)	696.0 (18.81)	96.05
5.4	239.8 (6.48)	2.2 (0.06)	0	237.5 (6.42)	99.03
5.5	566.8 (15.32)	4.8 (0.13)	45.9 (1.24)	516.2 (13.95)	91.07
5.6	875.4 (23.66)	23.7 (0.64)	41.1 (1.11)	810.7 (21.91)	92.61
5.7	1257.6 (33.99)	35.5 (0.96)	51.4 (1.39)	1170.7 (31.64)	93.09

4.7 CONCLUSION AND SUGGESTIONS FOR FUTURE WORKS

In conclusion, this chapter has presented the development of the yttrium solid target manufacturing method by magnetron sputtering technique, implementing an enhanced protocol allowing the deposition of pure yttrium targets. Moreover, the target manufacturing process was upgraded to deposit thicker (more than $100\text{ }\mu\text{m}$) coatings.

As a result, the last deposition batch shows a significant increase in yttrium film thickness, maintaining a low residual stress necessary for successful irradiation under the proton beam. The irradiation of the solid targets with the following ^{89}Zr extraction shows a significant improvement in sputtered targets regarding saturation yield. It becomes comparable to the standard foil or disk target approach described in [48, 9].

This study also provides preliminary results regarding stress evaluation for processes involving extremely low working distances and higher currents. All irradiated targets demonstrated remarkable resilience under high power loads, exhibiting no signs of delamination or damage.

It is essential to note the limitations encountered during this investigation, such as precisely measuring the thickness and density of thin and thick coatings. It can be suggested that density might be a crucial parameter influencing the isotope production, and it might explain the difference in the achieved result among the last batch targets. The higher material density allows better matching of irradiation parameters, given that all calculations were estimated for bulk materials. Despite this, some level of porosity can be beneficial during the dissolution step.

The ^{89}Zr isotope holds significant interest for immuno-PET studies, and its production using monoisotopic yttrium solid targets provides a robust foundation for future magnetron sputtering evaluations. Future work in yttrium solid target manufacturing should include density measurement and optimisation. A biased approach or HiPIMS deposition technique could be suggested as a potential method for enhancing the density of the film. It should be noted that the HiPIMS technique can improve the quality of targets, but it may also significantly reduce the deposition rate.

5

Recovering shield deposition approach

Usually, the production of highly pure radioisotopes needs the use of isotopically enriched materials in target manufacturing. Consequently, the recovery process of the starting material after the radiochemistry step is recommended for most radioisotope production methods. In addition, efficient resource utilisation has become a standard practice in various industrial processes.

This Chapter compares diode and magnetron sputtering processes, considering material losses and dissipation inside the vacuum chamber. In this study, a novel recovery shield configuration was designed and proposed as a replacement for the standard magnetron sputtering deposition setup. The advantages of the magnetron sputtering technique, particularly regarding material conservation, are shown in this chapter. Furthermore, it presents the deposition process of a thick Cr coating, utilising a material recovery method. The results of this study were partially published in the peer-reviewed journal *Applied Physics* [51].

This study has been developed and funded in the framework of the INFN-CSN5 METRICS project, whose goal is the production of pure batches of Mn positron-emitting radioisotopes ^{52}Mn and ^{51}Mn , whose leading properties may allow the implementation of accurate multimodal imaging (MMI) approach by exploiting both Magnetic Resonance Imaging (MRI) and Positron Emission Tomography (PET) diagnostic procedures. Cr is the starting material for the production of Mn through the nuclear reaction $^{52}\text{Cr}(p,n)^{52}\text{Mn}$.

5.1 RECOVERING SHIELD AS A SOLUTION

The magnetron sputtering technique, while advantageous, faces a significant challenge in terms of material efficiency. Skliarova et al. [10] suggest that the material efficiency of the magnetron sputtering technique is approximately 20 %. However, the methodology for this estimation was not provided. As demonstrated in the previous Chapter 4, the sputtering technique exhibits considerable promise with monoisotopic materials like yttrium. Nevertheless, adaptation and optimisation are essential to extend this potential to isotopically enriched materials.

A novel ground shield was conceptualised and proposed to comprehend and quantify material dissipation within the vacuum chamber during deposition. This new shield design encloses the plasma generation and material dispersion within a controlled volume, giving access to material efficiency calculation. This shield was designed for study purposes, and in the course of the work, it was suggested that it could be used for future material recovery. This Chapter refers to this shield as "recovering" because the material collected on the shield walls can be potentially dissolved and recovered in its original form.

5.1.1 DESIGN OF THE SYSTEM COMPONENTS

To achieve the goal of a replacement of the standard ground shield (see Figure 3.7 D), the intended design of the new configuration must meet the requirements of the sputtering process: (i) provide a low outgassing rate, which leads to the proper vacuum level and (ii) give the access for free gas circulation to sustain the working pressure inside the close volume.

The shield construction (shown in Figure 5.1 A) combines a flat plate (repeating the function of a standard ground shield) and a cylinder as a collector for the sputtered material, usually deposited on the vacuum chamber surfaces.

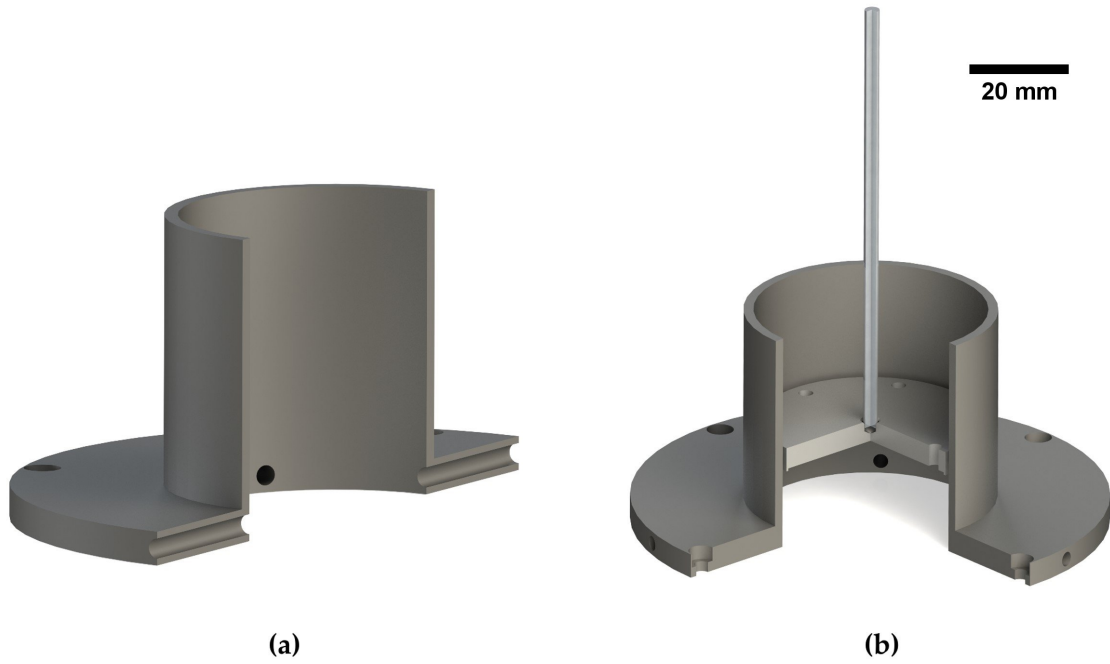


Figure 5.1: Designs: (A) Recovering shield (96 mm in diameter, 45 mm total height) and (B) sample holder inside the recovering shield with the variable working distance range 2–5 cm.

To ensure free gas circulation, it was planned to create an additional six tunnels (4 mm in diameter), indicated in Figure 5.1 A, in the base plate of the recovering shield, perpendicularly to the shield wall. The diameter of the cylinder was chosen according to the cathode size, which was, in our case, 2 inches. The cylinder length was chosen based on the requirement that the deposition occurs as close to the sputtering cathode, as presented in Figure 5.1 B.

Figure 5.2 A shows the produced recovering shield mounted in the sputtering source. The cylinder can be realised in insulating and inert material, such as SiO_2 or Al_2O_3 , for easier material recovery or special applications, as shown by design in Figure 5.2 B. Tests are necessary to verify the effect of insulation material usage on the deposition process, as it may cause differences in material dissipation. However, no tunnelling effect should be noticed due to the presence of the opposite electrode near the cathode.

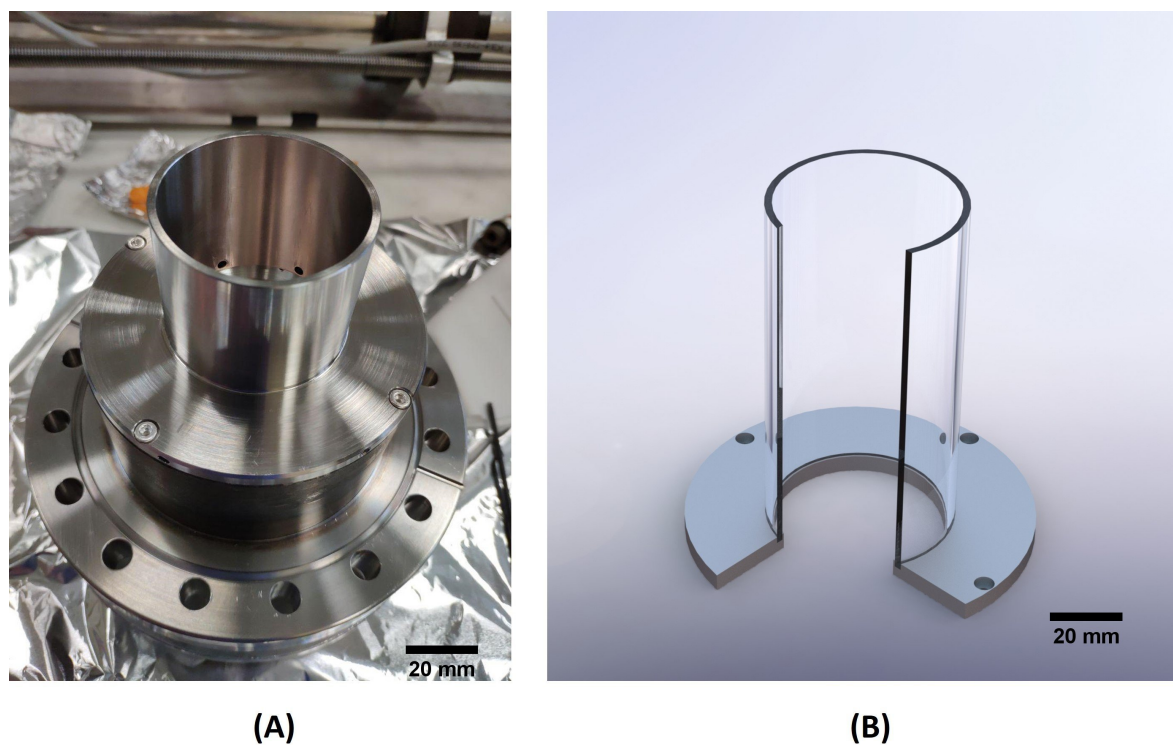


Figure 5.2: Produced recovering shield mounted in standard planar magnetron configuration (A) and design of its possible modification (B).

The new sample holder was designed for this study to host four quartz samples. The sample holder assembly, shown in Figure 5.3 B and C, consists of a stainless steel (AISI 316) base and top discs, four screws, nuts and a rod with a proper length. The sample holder's effective surface area is approximately 5%.

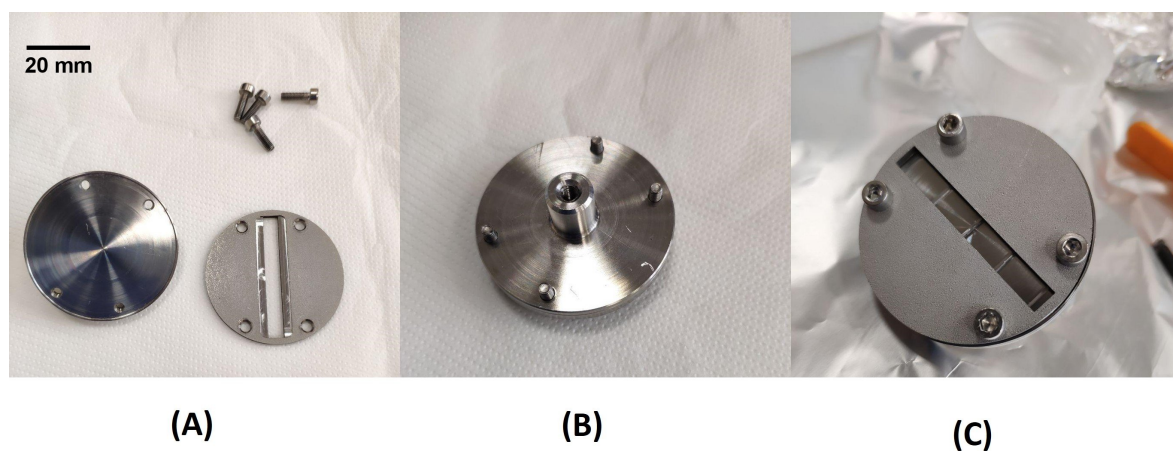


Figure 5.3: Sample holder designed (external diameter 44 mm) for the material efficiency study.

5.2 SPUTTERING DEPOSITIONS

The material efficiency for magnetron and diode sputtering was decided to be evaluated. Diode sputtering is known to be a less energetic process. However, it allows uniform cathode erosion, which can be a substantial advantage for depositing expensive materials. On the other hand, magnetron sputtering can provide higher deposition rates and more dense depositions. However, their performance in the material distribution is not that clear. Copper was chosen as the model material for these experiments due to its low cost and ease of handling.

5.2.1 MAGNETRON SPUTTERING

The magnetron sputtering process was performed for 6.5 hours in several steps. The first deposition was done with a working distance of 4 cm; however, at such a distance, not all the material was limited inside the recovering shield, and no accurate results were obtained. Figure 5.4 A shows the copper film outside the recovering shield in case of the 4 cm working distance and no copper outside the working environment in case of 2.5 cm distance (Figure 5.4 B). The same effect was noticed for diode deposition. During the material efficiency study, no further changes were made to the process parameters in order to improve its quality.

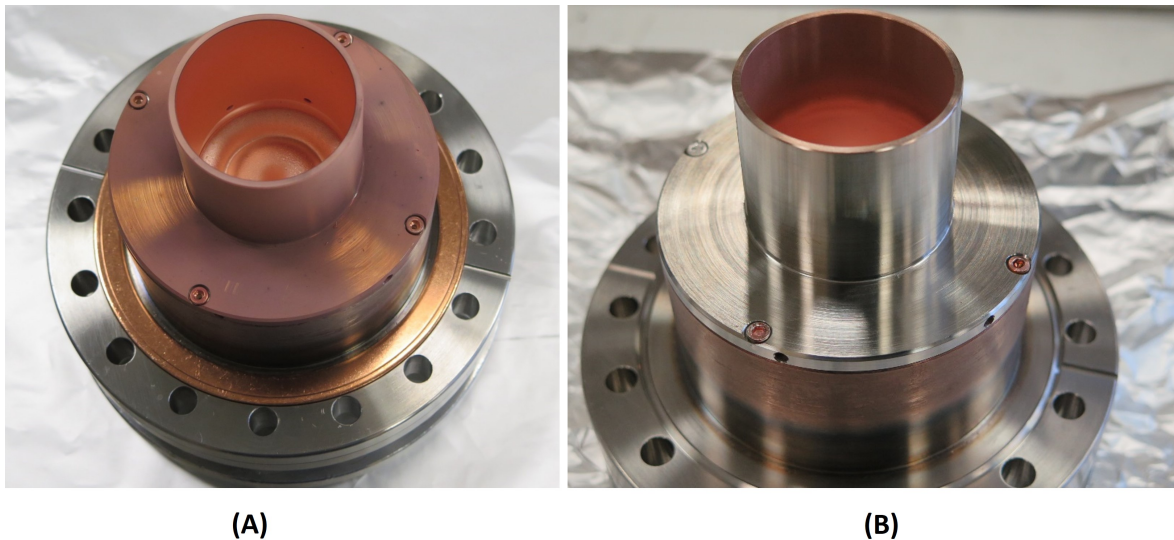


Figure 5.4: Recovering shield after the deposition at 4 (A) and 2.5 cm (B) working distance.

The deposition parameters in both cases are shown in Table 5.1. The deposition rate increases five times, with the distance changing from 4 to 2.5 cm.

Table 5.1: Parameters of magnetron sputtering deposition process. Working current - 1A, Ar flux - 15 sccm, deposition time - 390 minutes.

Test	Working distance [cm]	Voltage [V]	Working pressure [mbar]	Dep. rate [nm/min]
1.1	4	540-430	$8.1 \cdot 10^{-3}$	512
1.2	2.5	584-377	$7.8 \cdot 10^{-3}$	2450

5.2.2 DIODE SPUTTERING

In the case of diode deposition, the magnetic field did not facilitate the sputtering process. Thus, the magnet set was substituted with an aluminium block with corresponding dimensions.

Table 5.2 shows the parameters of the deposition processes. The high working voltage and high working pressures are necessary to perform such deposition. The first test of diode sputtering was performed for 18 hours in several steps. The working distance was set at 4 cm and then reduced to 2.5 cm in the next test.

Table 5.2: Diode sputtering deposition parameters and deposition rate results: Ar flux 80 sccm, pumping speed 375 Hz.

Test	Working distance [cm]	Current [A]	Voltage [V]	Working pressure [mbar]	Time [min]	Dep. rate [nm/min]
2.1	4	0.12	880-1000	$3.4 \cdot 10^{-1}$	1080	2.3
2.2	2.5	0.1	690-840	$3.4 \cdot 10^{-1}$	630	30.1

The turbomolecular pump speed was reduced to 375 Hz (usually 750 Hz) for having high working pressure and adequate gas regulation.

Although the deposition process was lengthy, the results of test 2.1 showed low deposition rates - 2.3 nm/min. The close evaluation of the sputtering source shows that the centring ring was also eroded during the deposition (see Figure 5.5 A). This finding can explain the low deposition rate and poor quality of the obtained copper film, shown in Figure 5.5 B.

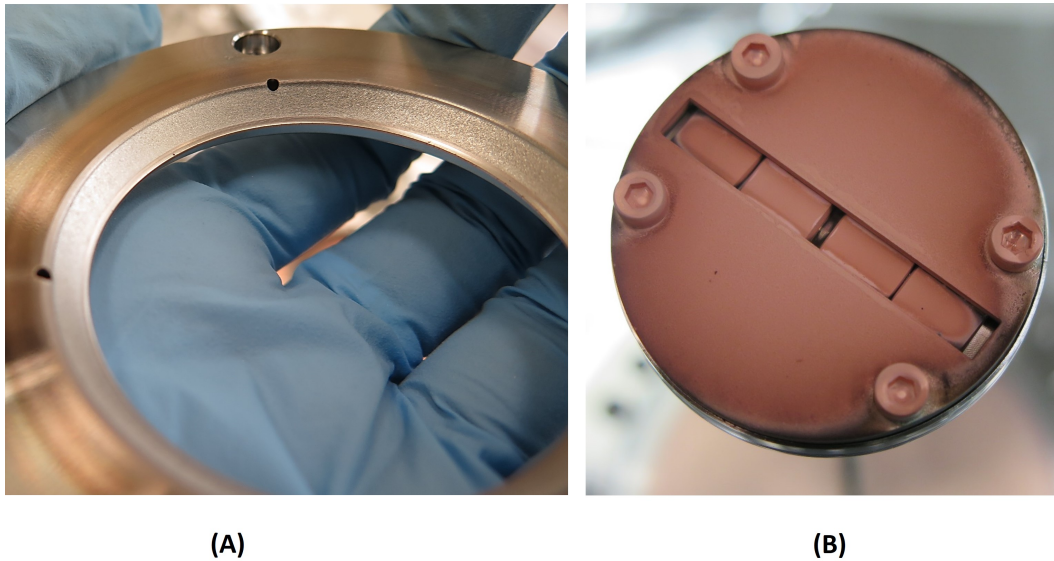


Figure 5.5: Diode sputtering deposition, test 2.1: (A) eroded centring ring (diameter 85 mm) and (B) thin copper coating on the sample holder.

The problem was resolved by adding a sparser between the centring ring and the new recovering shield to prevent plasma formation in that gap. As seen from Table 5.2, the new deposition run with reduced working distance and improved configuration shows a significant rise in the deposition rate.

5.3 COMPARISON STUDY RESULTS

The material efficiency, cathode utilisation, growth behaviour, and deposition rates were analysed to compare diode and magnetron sputtering deposition methods for solid target production.

5.3.1 MATERIAL EFFICIENCY

The material efficiency was evaluated by the weighting method. All components listed in Table 5.3 were weighed before and after the deposition. The difference in mass for each system element is shown in Table 5.3. The value of the cathode mass change is negative to represent the mass loss.

Table 5.3: Material dissipation results (in mg/min) for diode and sputtering process (working distance 2.5 cm).

Source component	Deposition rate [mg/min]	
	Diode sputtering	Magnetron sputtering
Cathode	-0.21	-3.79
Sample holder	0.44	1.47
Recovering shield	1.48	2.13
centring ring	0.07	0.18

Based on the obtained results, the material efficiency was calculated in percentages for the diode and sputtering processes. The mass of each component was divided by cathode mass change.

The material sputtered on the centring ring is considered a loss. The material collected on the recovering shield is considered material that can be recovered or, in the standard situation - lost on the surfaces of the vacuum chamber. Results of material efficiency are shown in Table 5.4.

Table 5.4: Material efficiency evaluation (in %) for diode and sputtering process (working distance 2.5 cm).

Efficiency	Diode sputtering [%]	Magnetron sputtering [%]
Usage of the cathode	68.7*	26.9
On sample holder	21.6 ± 0.04	38.9 ± 0.003
Possible to recover	71.6 ± 0.11	56.3 ± 0.005
Losses	6.8 ± 0.15	4.8 ± 0.008

* theoretically calculated value

According to the calculation, the magnetron sputtering is more efficient than the diode sputtering. Table 5.4 shows that more material is deposited on the sample holder in magnetron deposition compared to the diode process. The utilisation of the recovering shield showed us that in diode sputtering, about 70% is usually deposited all over the vacuum chamber surfaces. In magnetron sputtering, this percentage is lower but still high - 56%. In the recovering shield utilisation case, the losses were less than 5% for magnetron and around 7% for diode sputtering.

5.3.2 CATHODE UTILISATION

Figure 5.6 shows the difference in cathode erosion for the diode and magnetron sputtering process.

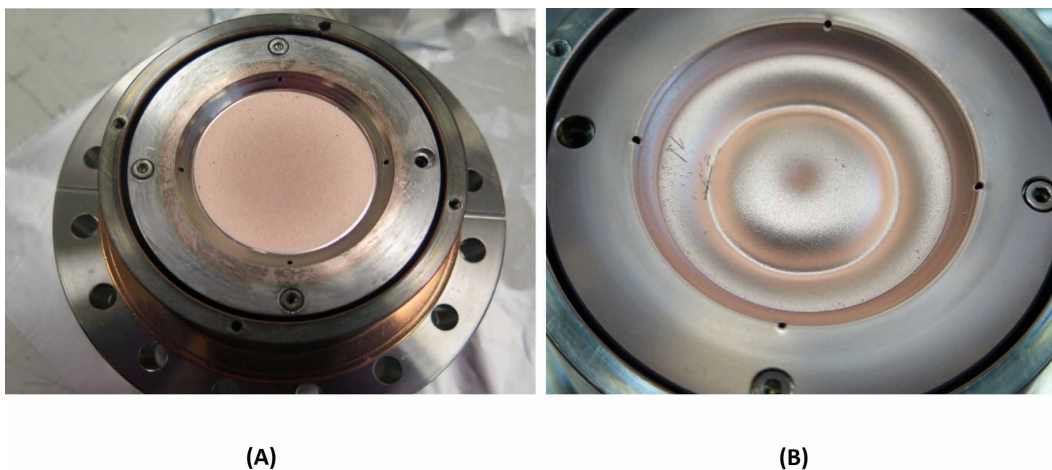


Figure 5.6: Erosion of copper cathode in diode sputtering (A) and magnetron sputtering process (B).

After the magnetron sputtering deposition, a height measuring device (Digimar 816 CL) measured the cathode erosion depth to evaluate the residual thickness. The thinner part of the cathode was reduced from 5 to 0.780 ± 0.003 mm. It is not recommended to perform deposition with a cathode thickness lower than 0.5 mm to avoid contamination.

The weight of the sputtering cathode was evaluated before and after the deposition. The results shown in Table 5.3 point out that, in the case of the magnetron sputtering process, only 23.882 g out of 88.811 g of the cathode mass, which corresponds to 26.9% (shown in Table 5.4, was used during the deposition process.

The cathode erosion depth after the diode sputtering process was not evaluated since it was too low. The thickness change was estimated to be $90 \mu\text{m}$ by calculation. The estimation was done using the following formulas: $m = S \cdot \delta \cdot \rho$, where m - mass, ρ - density and δ - thickness of the copper. In the ideal case, with the continued erosion for more than 20 days, the estimated usage of the cathode of the diode sputtering process would be 68.7%.

The results suggest that diode cathode utilisation efficiency is much higher than in the magnetron process.

5.3.3 GROWING BEHAVIOUR COMPARISON

Another critical aspect of choosing a deposition technique is film growth behaviour. In Physical Vapor Deposition (PVD) methods, the characteristics of film growth significantly influence the material properties, including density, defects, and stress levels. As shown in Figure 5.7, plasma light demonstrates that diode sputtering is less energetic than magnetron sputtering. The presence of argon ions is indicated by violet light, while green light indicates the presence of copper ions. Consequently, differences in deposition growth patterns are to be expected.

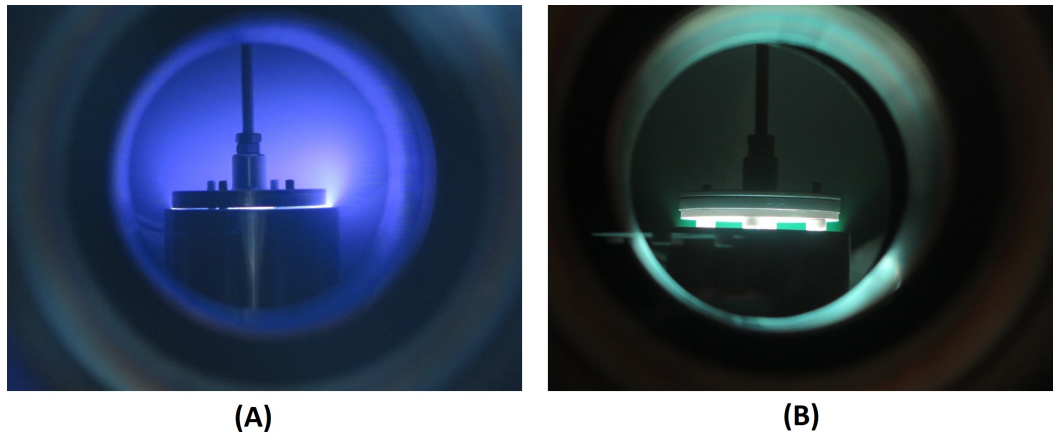


Figure 5.7: Plasma light intensity in diode (A) and magnetron (B) sputtering process with distance 4 cm.

The deposition obtained using the magnetron sputtering technique at a working distance of 4 cm resulted in $200\ \mu\text{m}$ thickness. Even without additional heating and parameter optimisation, the deposited layer was dense and had no visible defects. However, the copper film was easily delaminated. This allowed for a cross-section analysis of sputtered coating, revealing variations in the layer's growth pattern. Figure 5.8 illustrates that the deposition structure transitioned from columnar to nucleation-type growth after reaching $100\text{--}120\ \mu\text{m}$ thickness. The sample was analyzed in its original state without any additional deformation such as cracking or polishing, using its edges. The same approach was used for the next test.

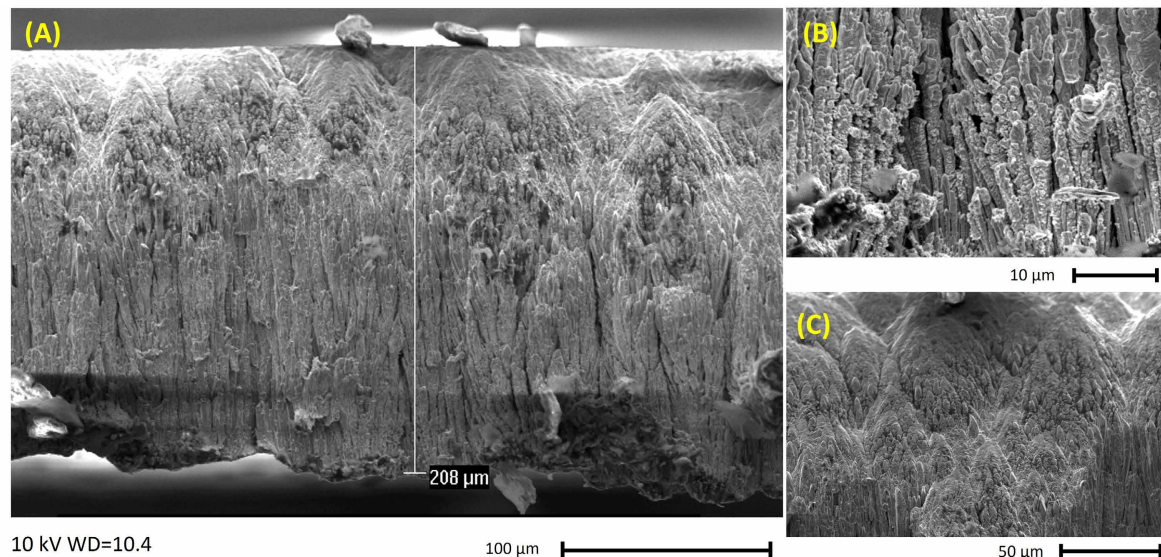


Figure 5.8: SEM analysis of thick copper coatings obtained by magnetron sputtering in test 1.1 (working distance 4 cm).

Studying the growing behaviour presented in Figure 5.8 B, it is possible to see the well-defined columnar dense structure of the Cu crystals, which then changes to the larger and broader structure in Figure 5.8 C. It may suggest that, according to the structural zone diagram (SZD), the deposition grew inside the transition Zone T with $T_b = 0.2\text{--}0.4$ (see Chapter 3) and reached Zone 2 with $T_b > 0.4$. It may be thus assumed that the deposition temperature during the magnetron sputtering process, with the use of the recovering shield and a distance of 2.5 cm, started near 200 °C and increased to 400–600 °C. The direct temperature measurements were not accessible during the deposition process.

Reducing the distance between the source and the sample holder significantly enhanced the deposition rate. In test 1.2, as displayed in Figure 5.9 A, an exceptionally thick copper layer was obtained, measuring approximately 960 μm to 1 mm. However, it was experimentally verified that utilisation of the recovering shield does not influence the deposition rate. The growing behaviour is similar to those previously described, shown in Figure 5.9 B.

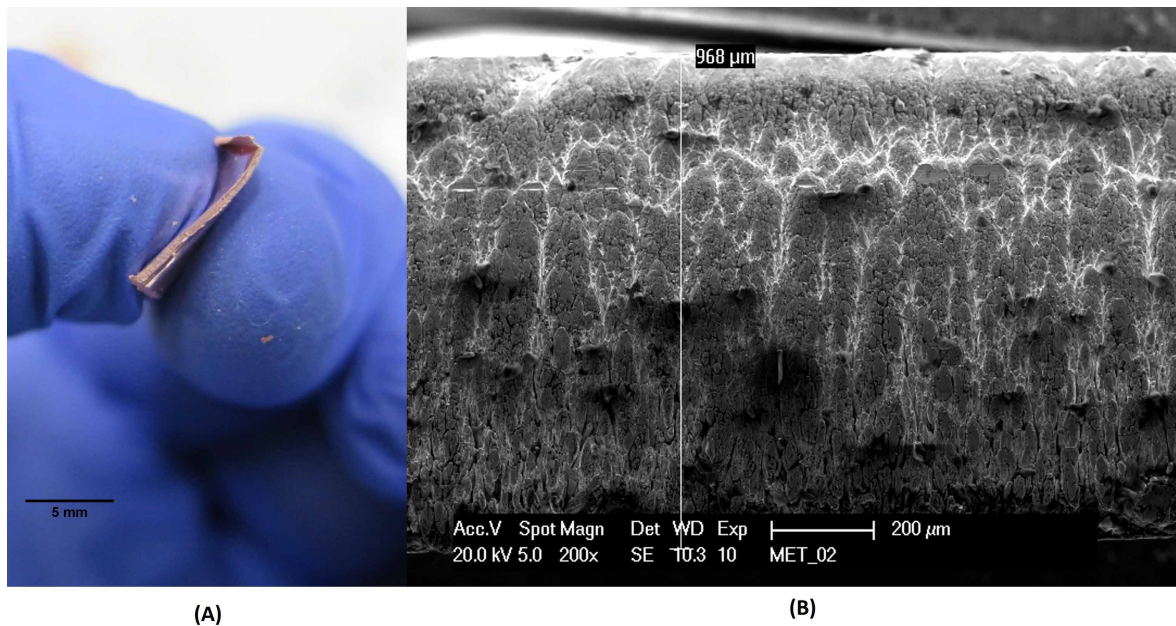


Figure 5.9: Picture of one-millimetre thick copper coating (A) and its SEM cross-section analysis. Coating sputtered within 6.5 hours by magnetron deposition technique with a working distance of 2.5 cm.

The SEM micrographs of diode sputtering deposition, shown in Figure 5.10, present a more uniform structure through the thickness. It is possible to notice that the density of such film can be lower due to the voided structure. The deposition rate in this case was $0.03 \mu\text{m}/\text{min}$. To deposit a comparable thickness of the magnetron sputtering process ($900 \mu\text{m}$ in our case), more than a 20-day-long deposition time would be required. In such a way, the production line and the related cost behind each solid target manufacturing aimed at radioisotope production may thus be unaffordable.

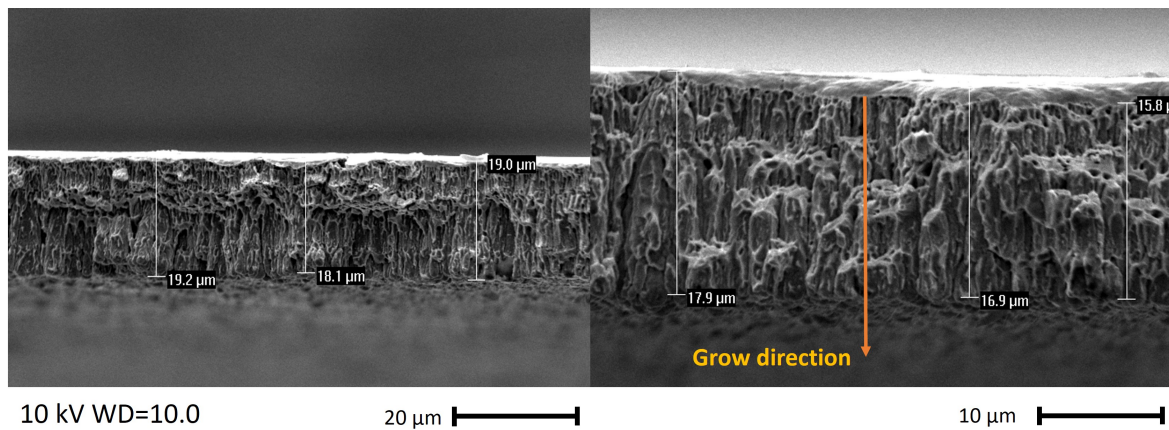


Figure 5.10: SEM cross-section analysis of copper coatings obtained by diode sputtering in test 2.2 (working distance 2.5 cm).

Evaluation of the growing structure of the Cu coating in the case of the diode sputtering deposition (see Figure 5.10) shows a homogeneous behaviour. The columns structure is like that reported in Figure 5.10 and corresponds to the transition Zone 1 with the $T_H < 0.2$ and a temperature range no more than 200°C .

5.4 CR DEPOSITION TEST

Magnetron sputtering appears to be more adapted to solid target manufacturing. For this reason, all experiments with chromium material were done only with the magnetron sputtering technique.

The deposition parameters for the material efficiency test with chromium cathode with a working distance of 2.5 cm are shown in Table 5.5.

Table 5.5: Magnetron sputtering deposition parameters of Cr cathode.

Working distance [cm]	Current [A]	Voltage [V]	Working pressure [mbar]	Ar flux [sccm]	Time [min]
2.5	1	420-333	$1.66 \cdot 10^{-2}$	30	390

The test was conducted similarly to the material dissipation test - lasting 6.5 hours, divided into several steps, using a completely new Cr cathode. The deposition was stressed (see 5.11B); however, all the materials remained attached to the sample holder, enabling a material efficiency calculation. Figure 5.11 displays the sample holder before (A) and after (B) the deposition, along with the Cr deposits on the recovering shield walls (C).

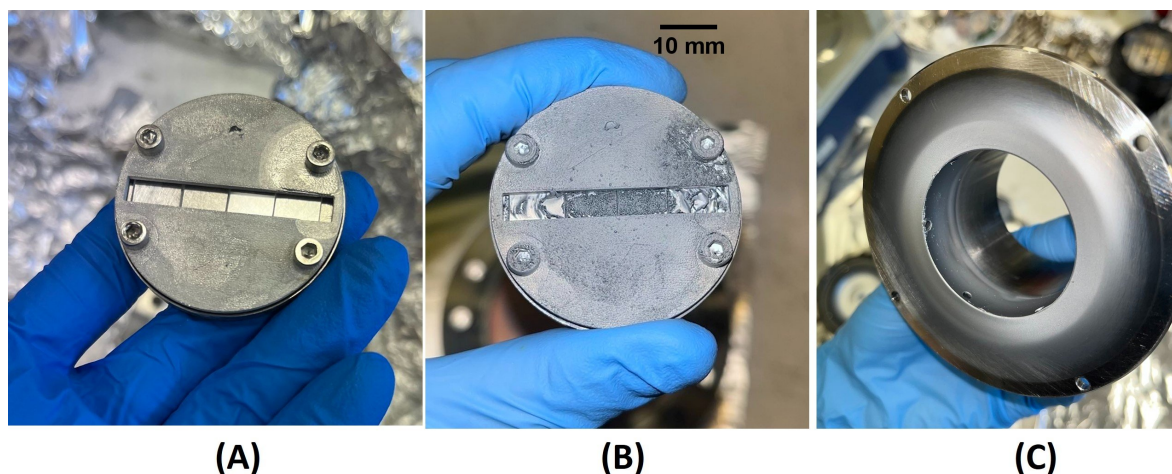


Figure 5.11: Sample holder before (A) and after (B) chromium deposition using the magnetron technique at a distance of 2.5 cm. Recovering shield with Cr deposition on its wall (C).

Table 5.6 displays the results of the efficiency calculation conducted for Cr and Cu. The results for chromium deposition are in good correlation to the result of copper deposition, although the Cr cathode was not wholly eroded, as it happened to Cu deposition. As a result of 6.5 hours of deposition, 10.11 g of Cr was deposited from the cathode. In the case of Cr deposition, the losses are higher, more than 8%.

Table 5.6: Material efficiency evaluation for magnetron sputtering process for Cr deposition

Component	Material efficiency for Cr[%]	Material efficiency for Cu[%]
On Sample holder	38.4 ± 0.008	38.9 ± 0.003
Possible to recover	53.3 ± 0.011	56.3 ± 0.005
Losses	8.3 ± 0.019	4.8 ± 0.008

It was possible to evaluate the morphology and growth behaviour of Cr deposits by performing SEM analysis on detached pieces. Figure 5.12 shows chromium film morphology and cross-section analysis.

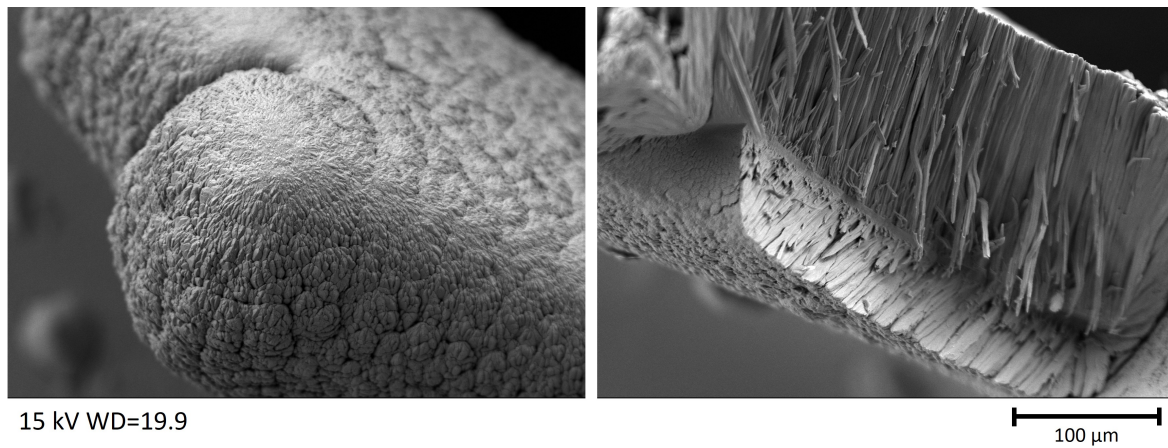


Figure 5.12: Morphology (left) and cross-section (right) SEM analysis of chromium film sputtered with Recovering shield for 6.5 hours, distance 2.5 cm.

In the cross-section analysis, shown in Figure 5.12 B, it is possible to notice that the deposition was growing in two directions. Probably due to stress, the thin layer of Cr material delaminated, and the deposition grew on both sides. Notably, the initial thin layer exhibits a highly dense structure. After the delamination, the growth behaviour changed to a fibrous columnar structure, typical for Zone 1 of SZD. According to Figure 5.12, obtained chromium thickness could reach around $100\text{ }\mu\text{m}$, but a precise thickness control was impossible in this study.

5.4.1 CR TARGET MANUFACTURING

A few unsuccessful attempts were made to find a low-stress parameter for chromium deposition with a working distance of 2.5 cm. Thus, it was decided to switch to a 4 cm working distance. Another change in the deposition process was the use of a copper cylinder as a recovering shield. More details are provided in the next Chapter 6. This Chapter focuses on the obtained Cr deposition on Nb disks.

Table 5.7 shows the deposition parameters of Cr films with changed working distance.

Table 5.7: Magnetron sputtering parameters of Cr deposition with working distance 4 cm, current of 1 A, and Ar flux 28.5 sccm.

Test	Voltage [V]	Working pressure [mbar]	Time [min]	Dep. rate [nm/min]
Cr-7	303	$1.65 \cdot 10^{-2}$	30	215
Cr-8	284		120	290
Cr-9	360-320		240	300

The Cr-7 deposition was performed on quartz and Nb samples. In 30 minutes, a layer of $6.5\ \mu\text{m}$ thick was deposited. The morphology analysis performed on the Nb substrates is shown in Figure 5.13. The left image shows a uniform deposition distribution, which probably repeats the Nb substrate structure. In the right image, it can be closely seen that the atoms on the surface are arranged in clusters with a tridimensional shape.

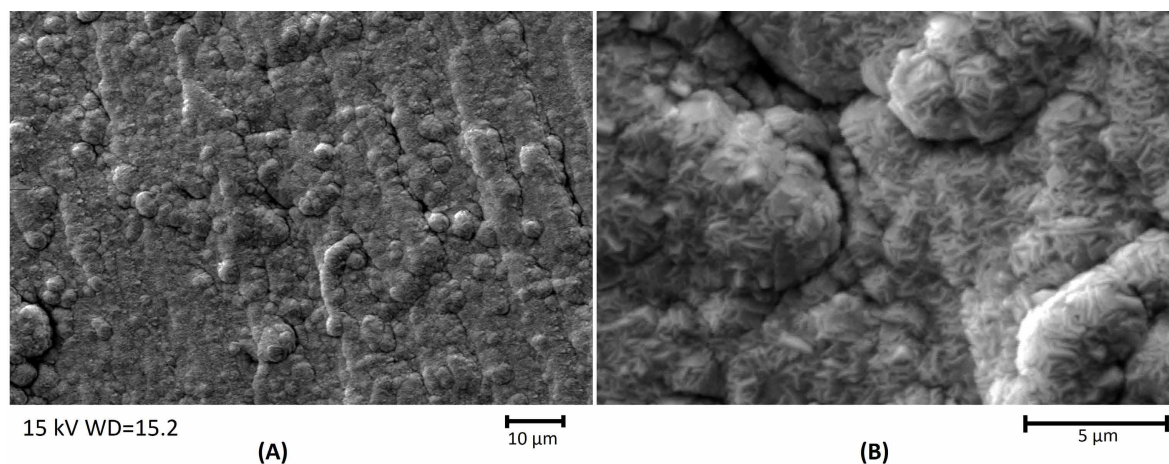


Figure 5.13: SEM morphology analysis of chromium onto Nb (test Cr-7).

It was decided to perform a deposition on a thin Nb coin (thickness $0.5\ \text{mm}$). The parameters of such deposition are shown in Table 5.7 in test Cr-8. The results of the deposition are shown in Figure 5.14. The deposition appears stressed on the sample holder and Si sample, but no delamination was found in the Nb sample. The thickness was measured on Nb samples.



Figure 5.14: Deposition results of Cr-8 test: picture of sample holder after the deposition (A) and manufactured target (B).

A new deposition was performed on a previously weighted Nb sample. The parameters are reported in Table 5.7, and the results are shown in Figure 5.15.

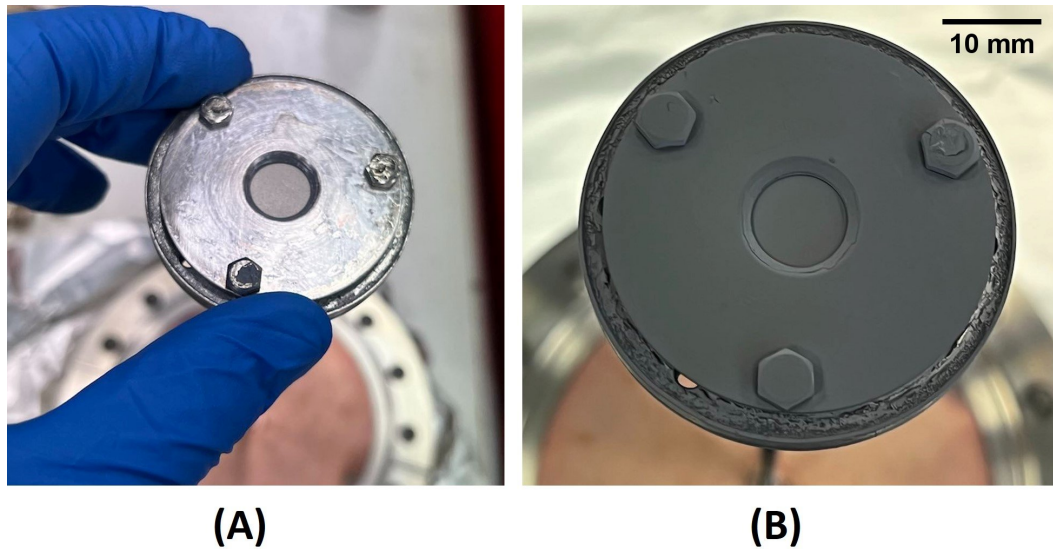


Figure 5.15: Photos of sample holder before (A) and after (B) deposition Cr-9

The thickness of this deposition was measured by a contact profilometer on the Nb sample and resulted in $70\ \mu\text{m}$. It is essential to highlight that such thicknesses are not commonly achievable with PVD techniques. The target has a relative density of 78%. The manufactured target (Cr-9) was packed in a vacuum bag and delivered to SCDCH for future thermo-mechanical irradiation tests.

Figure 5.16 shows Nb samples' detailed deposition morphology. The three-dimensional aspect becomes even more evident with increasing deposition thickness. The thick film shows a meddle-like morphology with a preferential orientation of the needles. In work [94] suggested that such structure shows less mechanical strength and can be characterised by a tensile stress. Moreover, such structure corresponds to Zone 1 ($T_b < 0.2$), which can be described by fibrous structure.

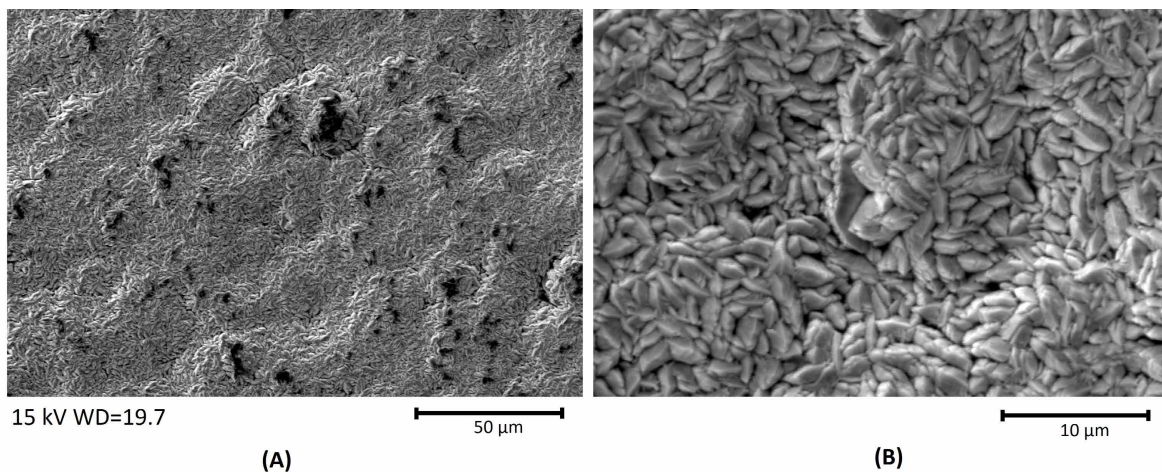


Figure 5.16: SEM morphology analysis of Cr target (test Cr-9)

Cr films deposited by DCMS without substrate heating usually have a crystalline structure with preferential orientation along the (110) direction, as the (110) family of planes has the lowest surface energy in the body-centred cubic Structure [94]. XRD evaluation of chromium coating deposited in tests Cr-7 and Cr-8 shows a preferential growth of (110) orientation, as shown in Figure 5.17. The film deposited on Nb disks shows weak Nb peaks due to the positioning issues.

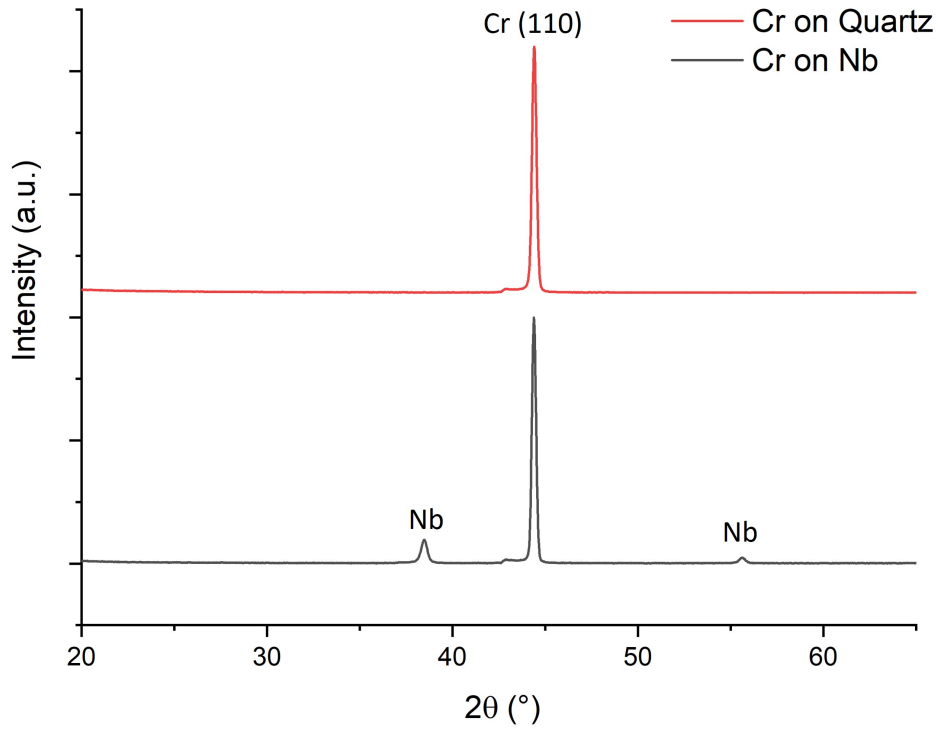


Figure 5.17: Diffractograms of Cr films sputtered onto Nb and quartz substrates.

Based on the calculation, the crystalline size of Cr on the Nb coin appears to be 34 nm, while Cr on quartz is 31 nm.

5.5 CONCLUSION AND SUGGESTIONS FOR FUTURE WORKS

Diode and magnetron sputtering techniques were evaluated and characterised from the material point of view. It was possible to estimate the material efficiency of both sputtering methods by using the recovering shield developed in this dissertation.

The new recovering shield has shown a possible significant recovery of the target material during the sputtering processes, both in the magnetron and diode options. Generally, utilisation of a recovering shield can decrease the losses of the material from 70% down to 10%.

Evaluating the two applied techniques, the magnetron deposition process has shown to be more energetic and efficient from the material dissipation and deposition rate criteria. This contributed to the characteristics of the diode and magnetron discharge process. The DC diode sputtering can be realised only in high gas pressure (more than 1 Pa), which creates many collisions where the electrons lose their energy. In the case of magnetron sputtering, the closed magnetic path near the target creates a high flux of electrons, giving a high-density plasma as a result. A lower operating pressure accelerates ions from plasma to the cathode without energy loss due to collision processes [57].

Despite the magnetron sputtering drawback concerning a special cathode erosion pattern, it was identified as a method of choice for radiopharmaceutical applications among the two evaluated methods. It was shown that a single nat-Cr target with a thickness of 70 μm can be produced, using this approach.

In future developments, the deposition properties can be significantly improved by applying bias or using a HIPMS operational mode. However, the material losses and complicated recovery are still substantial limitations for utilising isotopically enriched materials.

6

Inverted magnetron deposition approach

A novel solution to material efficiency optimisation is proposed: a cylindrical inverted magnetron (IM) configuration. Incorporating a hollow cylindrical cathode enables the placement of a sample holder inside, effectively constraining material loss. For the first time, such a configuration was suggested for solid target manufacturing, although generally, it is not a new concept.

This chapter reveals the design and production of the inverted magnetron, accompanied by preliminary results using a Cu cathode. As a proof of concept, the chapter shows the successful deposition of thick ZnO coatings through the reactive deposition process. Furthermore, the targets' irradiation demonstrates their excellent thermo-mechanical properties. Moreover, the cylindrical Cr cathode preparation method was proposed, with the following chromium deposition in an inverted magnetron.

This research was funded by the Italian Ministry of Economic Development for 2021–2022, in the framework of the INTEFF_TOTEM project ("Innovazione Tecnologica dalla Fisica Fondamentale_magneTron sputtering cyclOtron TargEt Manufacturing") promoted by the National Committee of Technological Transfer of INFN. The results of this study were partially published in peer-reviewed Materials [95].

6.1 INVERTED MAGNETRON PROTOTYPE DESIGN

The concept of an inverted magnetron for manufacturing solid targets was conceived to reduce material losses and enable the use of isotopically enriched materials.

Figure 6.1 A shows the first design of the cylindrical inverted magnetron concept. Such a magnetron is designed to have a copper base plate (cooled by water) and a protective ground shield. The power connection can be through the connection to the water pipes. The sealing of the water-cooling system must be ensured by using proper Viton O-rings. The target is realised in a closed cylindrical shape with wings.

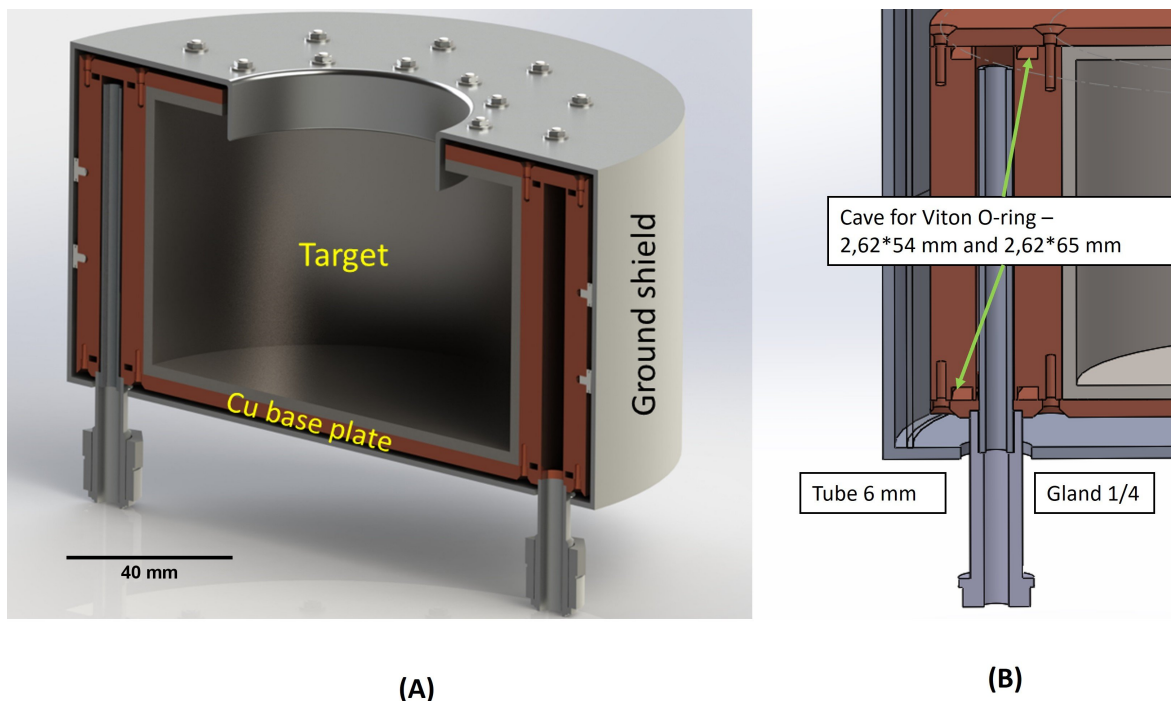


Figure 6.1: Initial design of inverted cylindrical magnetron concept (A) and details on sealing and water cooling system.

The magnetron was modified as a suitable tool for solid target manufacturing, ensuring compatibility with an existing vacuum chamber. The redesigned version now boasts 160 mm in external diameter and 120 mm in height. Special attention was given to meticulously adjusting the cavities for Viton O-rings, making them well-suited for readily available commercially sourced ones, as shown in Figure 6.1 B.

6.1.1 SIMPLIFIED DESIGN

Despite the promising design idea and successful size optimisation, it was decided to test the proposed inverted magnetron utilisation on the more simple prototype. Such a decision was also supported by the high cost of producing the magnetron parts and its complicated assembly.

As a result, a simplified prototype was designed that does not require complicated assembly, and its base cathode plate can be welded to avoid using Viton O-rings. The simplified inverted magnetron, shown in Figure 6.1 B, is made from two stainless steel tubes and welded with two plates. The water cooling was considered as well. In this case, the sputtering material has a cylindrical open-shaped cathode. The produced IM prototype is shown in Figure 6.2 B.

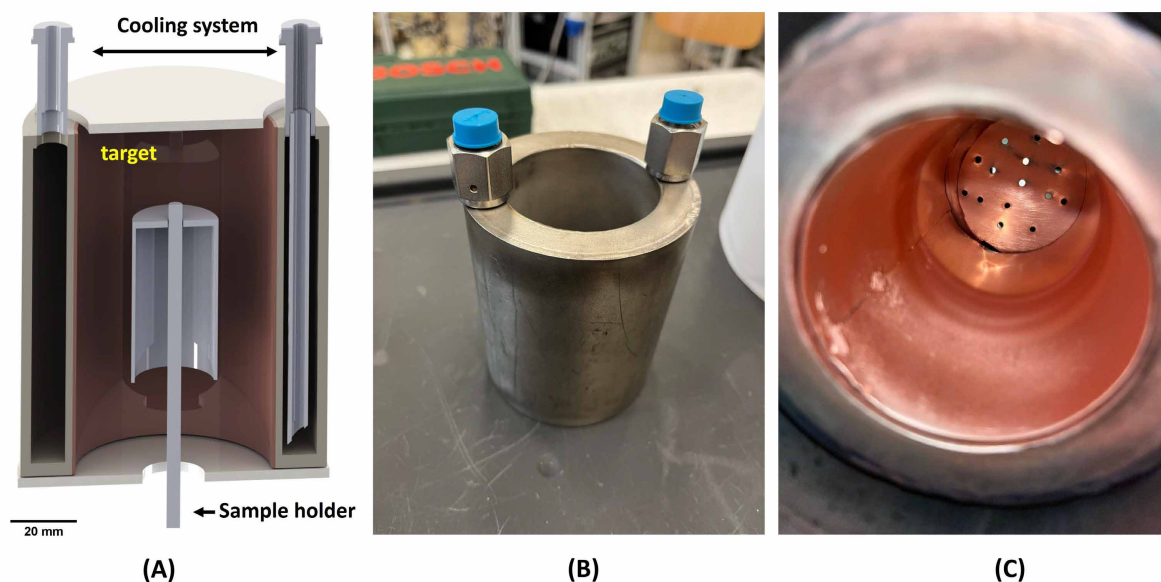


Figure 6.2: Inverted magnetron prototype: (A) simplified design of inverted cylindrical magnetron source for solid target manufacturing with sample holder in axial position, (B) as produced and (C) with Cu cathode.

The prototype has the following dimensions: 106 mm height, 89 mm external, and 59 mm internal diameter. The copper cathode material, shown in Figure 6.1 C, was chosen to test and adjust the IM configuration.

6.1.2 DEDICATED SAMPLE HOLDER

A dedicated sample holder was realised to accommodate substrates of different diameters (24 and 13 mm) and thicknesses (1.2 and 0.3 mm) through the different masks. The mask's apertures are chamfered to promote a uniform deposition above the uncovered part of the substrate, as it is a mandatory requirement for targets in radioisotope production.

During the conceptualisation of the inverted magnetron setup, two sample holder configurations were investigated: horizontal (perpendicular to the cathode walls) and axial (parallel to the cathode walls). A new sample holder, shown in Figure 6.3, has been designed to host Nb coin (or disc) (diameter 24 mm, thickness 1.2 mm).

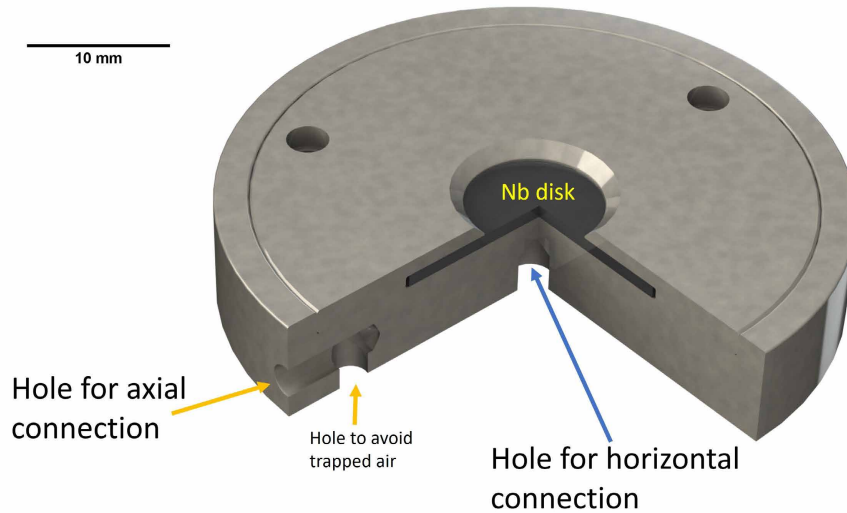


Figure 6.3: Sample holder for solid target manufacturing in IM, designed for horizontal and axial configuration.

6.1.3 POWER CONNECTION ISSUE

After the system construction, it was found that providing proper isolation between the base cathode plate (the main body of the magnetron) and the vacuum chamber was challenging. Conventionally, during the magnetron sputtering process, the difference in potential between the sample and the cathode is generated by giving a negative voltage to the cathode.

It was decided to try an alternative approach: connecting the sample to the positive potential, leaving the base plate and the chamber grounded. The scheme of the power connection and inverted magnetron setup are shown in Figure 6.4.

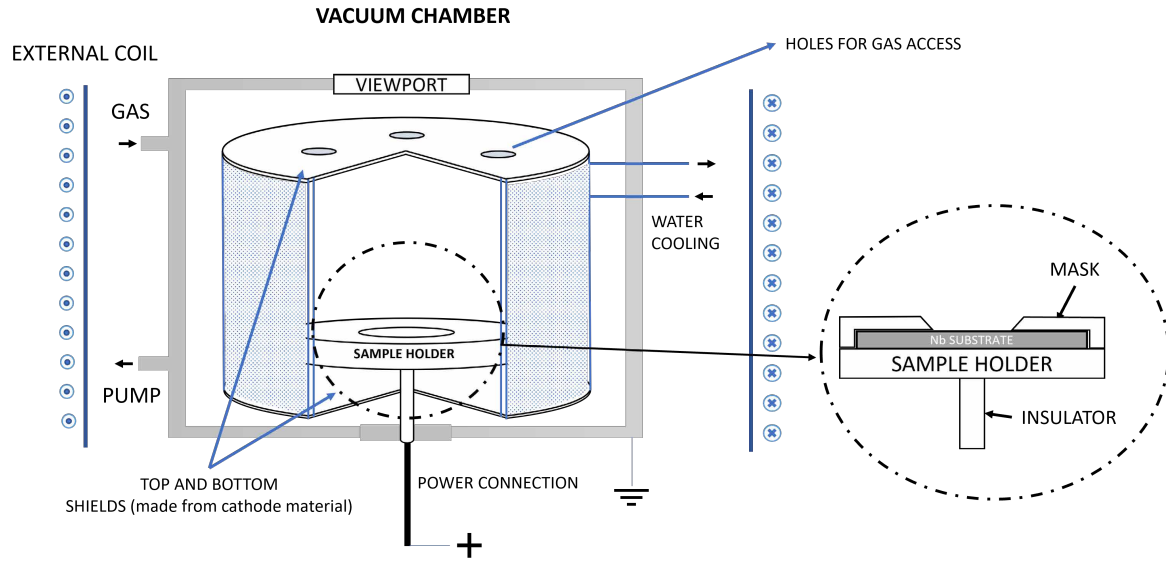


Figure 6.4: Inverted magnetron and sample holder scheme.

Such a connection is less complicated and beneficial to working with low melting point cathode materials such as metallic Zn ($T_m=419.5\text{ }^{\circ}\text{C}$). In the standard configuration, the part of the energy given to the cathode is transferred to Joule heat. For this reason, an efficient cooling system must be applied to the cathode material. Enabling the sample holder to hold power has a similar effect, making it impossible to coat thermo-sensitive materials using this method. However, this did not pose a problem for our deposition.

6.1.4 SYSTEM ADJUSTMENT

Incorporating an external magnetic coil proved necessary for the deposition of ZnO, leading to the evaluation of various coil combinations. Several experiments were performed to optimise the magnetic field generated by the coil with the position of the sample holder and magnetron. As a result, a three-coil system was chosen.

The strength of the magnetic field was assessed using a LakeShore 421 Gaussmeter. The results, illustrated in Figure 6.5, showcase the performance of the three-coil system. Consequently, a stable magnetic field of 250 G at the central position was achieved for ZnO deposition by implementing this external 3-coil system.

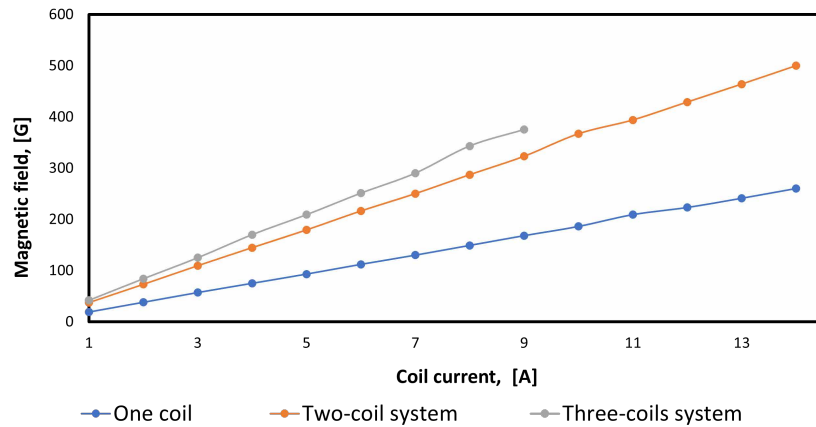


Figure 6.5: Coil systems characteristic, measured in the central position.

By changing the position of the coil system and regulating the coil current, the sputtering process was optimised to prevent arcing and plasma formation outside the working environment. The system setup for this test is shown in Figure 6.6 A. The plasma light, shown in Figure 6.6 B, was filtered through the protective glass to understand the process better. The correct plasma confinement is shown in Figure 6.6C, while the arching mode is visible in Figure 6.6 D.

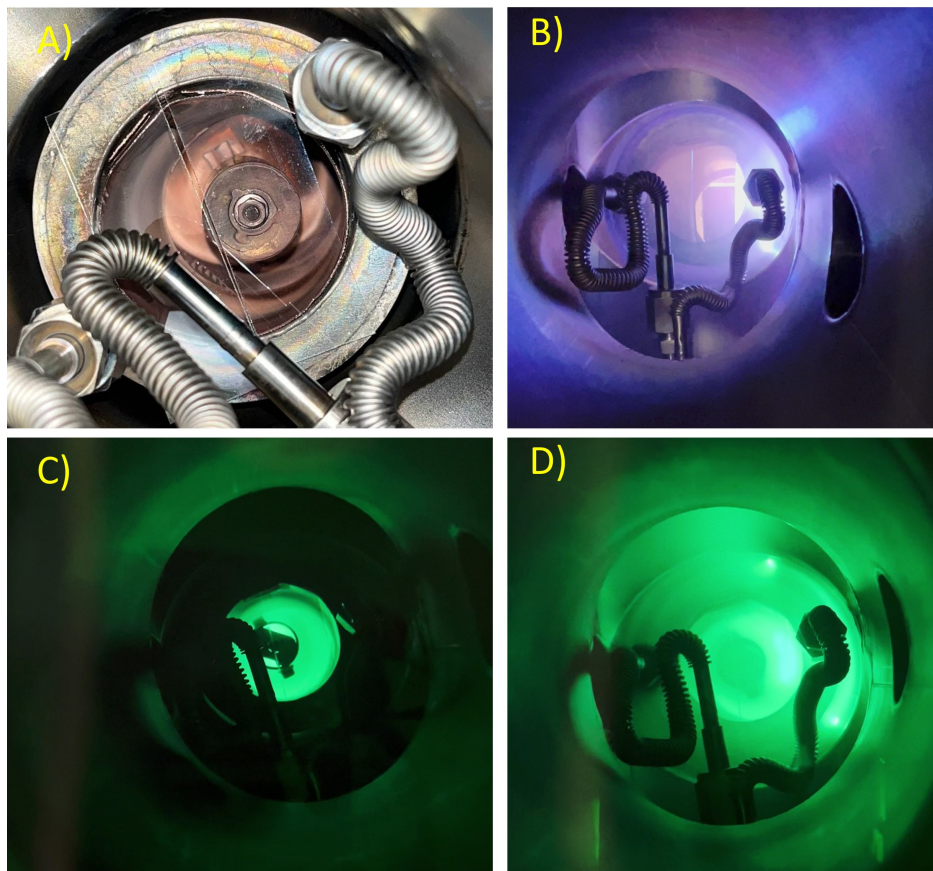


Figure 6.6: Visual plasma evaluation. (A) sample holder inside the IM, (B) plasma light, (C) plasma evaluation under protective glass - no arcs detection, (D) plasma evaluation with arcs.

The correct plasma confinement is essential to prevent plasma formation on undesired system stainless steel components of the vacuum chamber. Additional bottom and top plates (see Figure 6.4), made of cathode material, were applied to fix such an issue. Adding holes in the top shield ensures gas circulation in the closed cathode environment. Both shields can be produced in quartz or glass as an alternative upgrade.

6.2 PRELIMINARY TEST WITH COPPER CATHODE

The copper cathode used in the experiment was made from a 1mm thick copper foil at the LNL mechanical workshop. The procedure includes machine bending, welding and post-polishing with abrasive paper and cleaning.

Table 6.1 shows the parameters of Cu deposition performed with the described system. All tests were performed using a three-coil system; the coil current is indicated in the table. The process parameters were chosen to ensure stability, with a maximum starting tension of 600 V. A relatively high working pressure was selected to facilitate the process, and avoid using higher coil powers.

Table 6.1: Inverted magnetron sputtering deposition parameters of copper films, performed on different sample holders.

Test	Coil current [A]	Current [A]	Voltage [V]	Working pressure [mbar]	Ar flux [sccm]	Time [min]	Dep. rate [nm/min]
Cu-16	5	0.5	430-392	$1.10 \cdot 10^{-2}$	3.5	20×2	50-150
Cu-17	7.5-9	0.5	393-400	$3.8 \cdot 10^{-2}$	8.8	10×2	-
Cu-26	6	0.5	384	$1.2 \cdot 10^{-2}$	3.5	30	150
Cu-27	5.3	1	490			75×2	530
Cu-29	6	0.5	550			20×6	300
Cu-30	5.5	1	458			50×3	400

The primary idea was to perform the deposition with an axial sample holder, potentially allowing the preparation of more than one target at a time. In the test Cu-16, the manually prepared sample holder was used to test the chosen system configuration. The sample holder after the 40-minute deposition is shown in Figure 6.7 A, B, C.

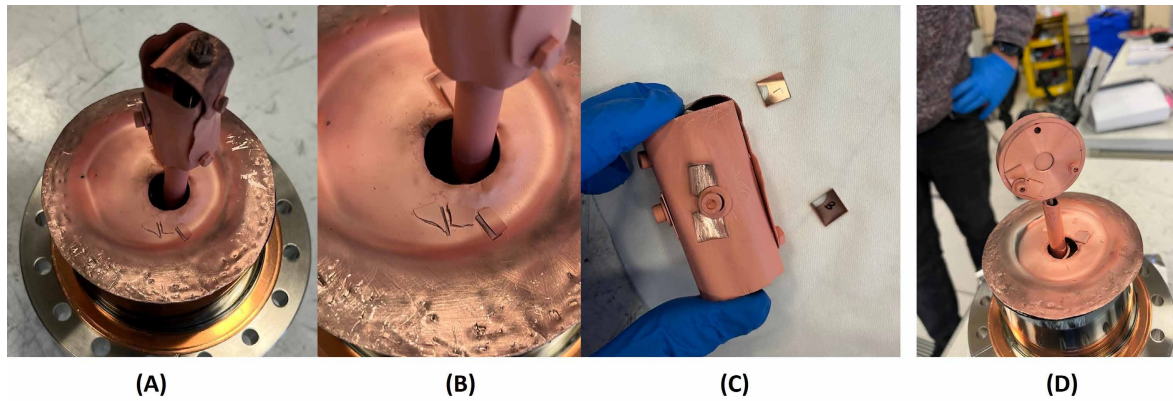


Figure 6.7: Manually prepared sample holder used in test Cu-16 (A), Si samples on the cover plate (B), quartz sample on the body of the sample holder (C). A sample holder for solid target manufacturing in the axial position was used in test Cu-17 (D).

It was found that the deposition rate and even the deposits' morphology differ depending on the sample position. The deposition on the axial part (Figure 6.7 C) appears to be 2-3 times thinner than on the horizontal. At the same time, the deposits on the bottom cover (Figure 6.7 B) are thicker and show columnar growth and crystalline morphology. Figure 6.8 shows the cross-section analysis performed on Si samples. The growing behaviour of films on horizontally placed samples has columnar and voided structure.

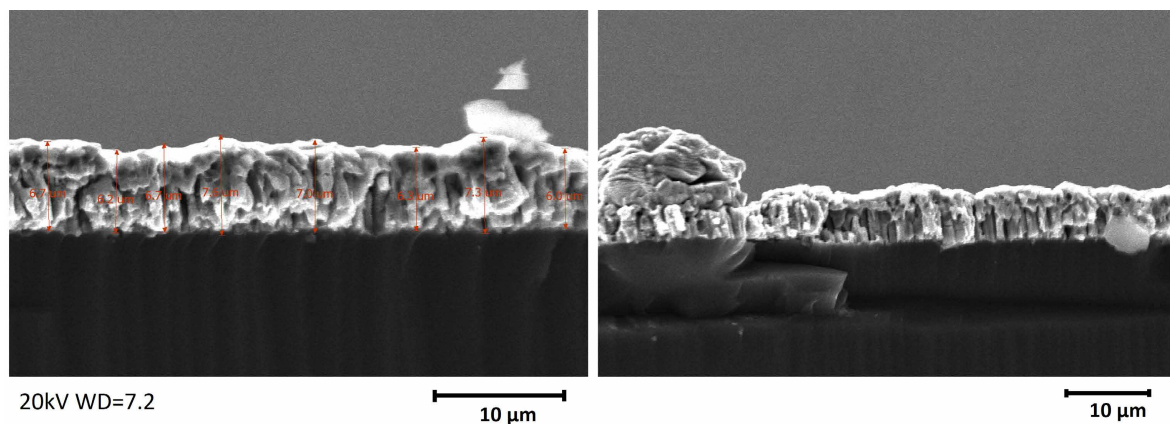


Figure 6.8: SEM cross-section analysis of Cu deposition deposited in test Cu-16.

Figure 6.7 D illustrate the axial position of the sample holder dedicated to solid target manufacturing used in test Cu-17. Unfortunately, the deposition process was hard to sustain due to the high amount of arcs. The high working pressure and coil currents were utilised. Despite the sample holder being metalised, measuring the deposition thickness was impossible, since a very low deposition rate.

In our case, where the powering of the system is made by giving the positive potential to the sample holder, its symmetry plays a crucial role in the system's stability. Due to that fact, it was decided to concentrate our activity on the horizontal sample holder and single target deposition, as illustrated in Figure 6.9.

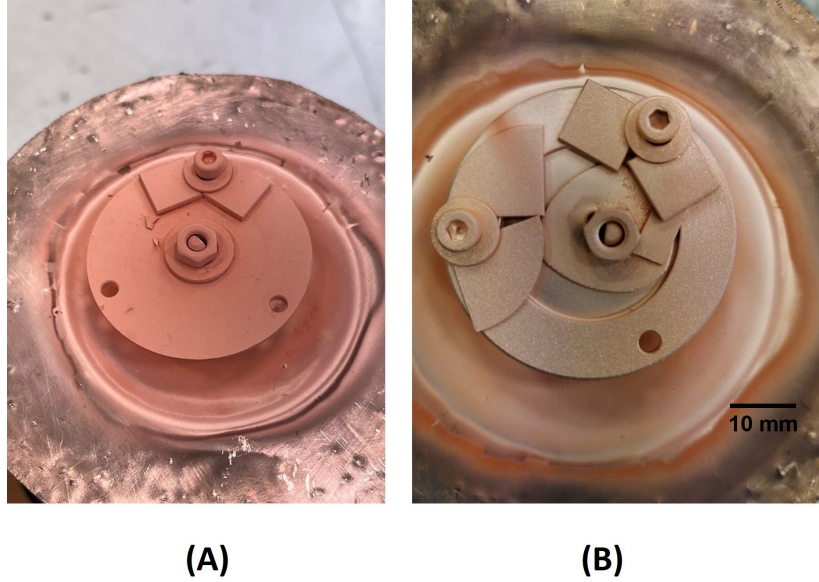


Figure 6.9: Copper deposition in IM configuration: (A) test Cu26, (B) test Cu-27

Increasing the deposition current and extending the deposition step time likely results in a significant increase in deposition rate. The cross-section analysis of copper deposition, shown in Figure 6.10, from test Cu-27, conducted in two steps (75 minutes each), reveals a denser, thicker coating of $80\ \mu\text{m}$.

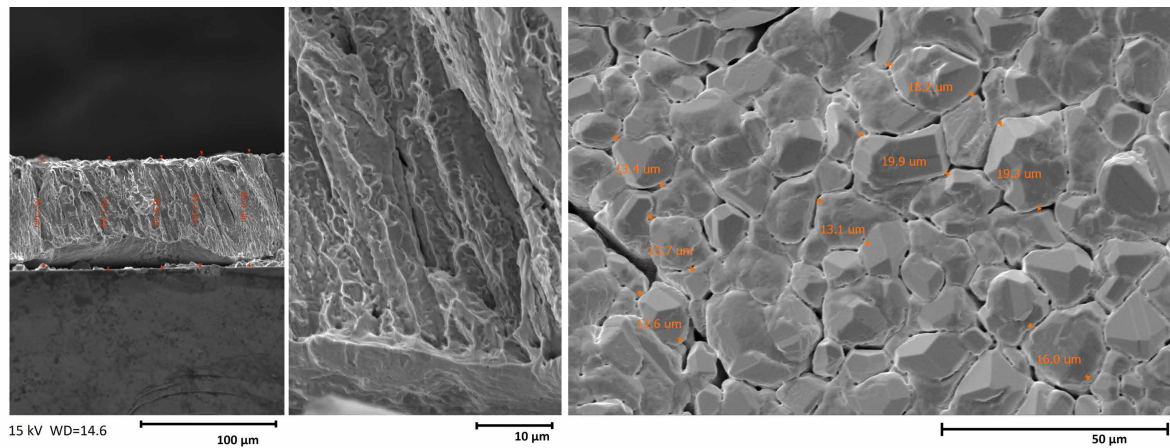


Figure 6.10: SEM cross-section analysis of test Cu-27, performed on Si samples and morphology analysis .

The test with such a configuration was stable. The only drawback remaining was the overheating of the sample holder since it was connected to the power and had no cooling. The sample holder's electrical power was converted to Joule heat, which accumulated without efficient heat exchange. The overheating was visible 1-2 minutes after a long process deposition, as seen in Figure 6.11 B. The overheating of the sample holder was an undesired process and should be avoided if possible.

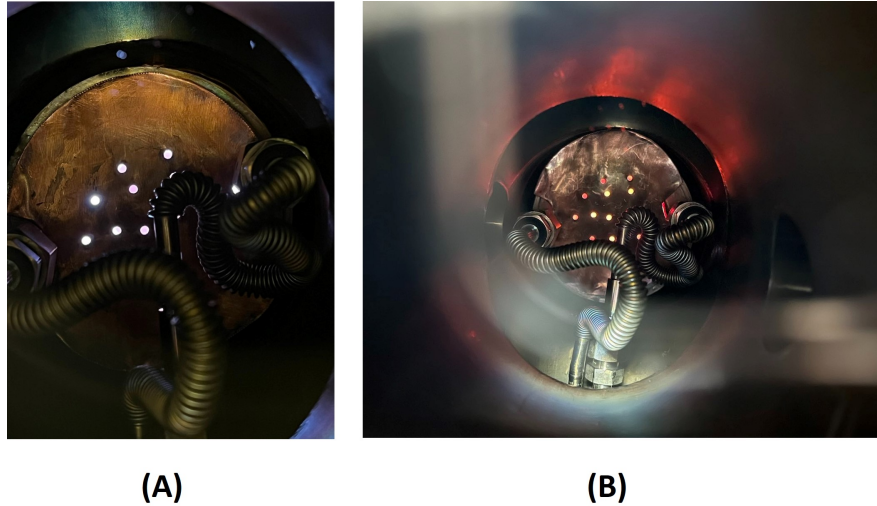


Figure 6.11: Copper deposition in IM configuration: (A) plasma emission, (B) the overheating effect on the sample holder immediately after the power switch-off.

Finally, the deposition tests Cu-30 were performed on the Nb disk (0.5 mm thick) to evaluate the deposition's adhesion and uniformity. The overheating effect does not create difficulties for the sputtering and could help reduce the stress in the deposits.

The test Cu-30, which lasted two hours and was divided into three steps, shows us the difference in the deposition rate between the centre (Nb sample) and the edge of the sample holder (quartz and Si sample), as shown in Figure 6.12. It is necessary to assess the uniformity of the deposition more thoroughly.

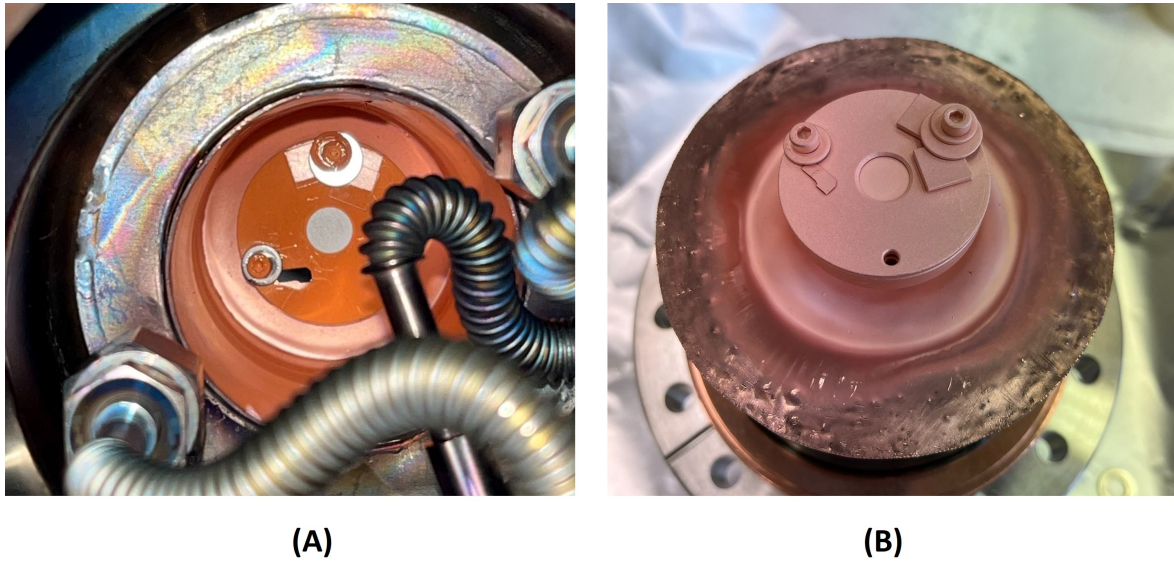


Figure 6.12: Cu-30 deposition test: (A) sample holder inside the IM before the deposition and (B) sample holder after Cu deposition.

As depicted in Figure 6.13, the cross-section analysis was conducted on a silicon (Si) sample, revealing a thickness of up to $60\ \mu\text{m}$. The results also indicate a prominent columnar growth pattern with a large column.

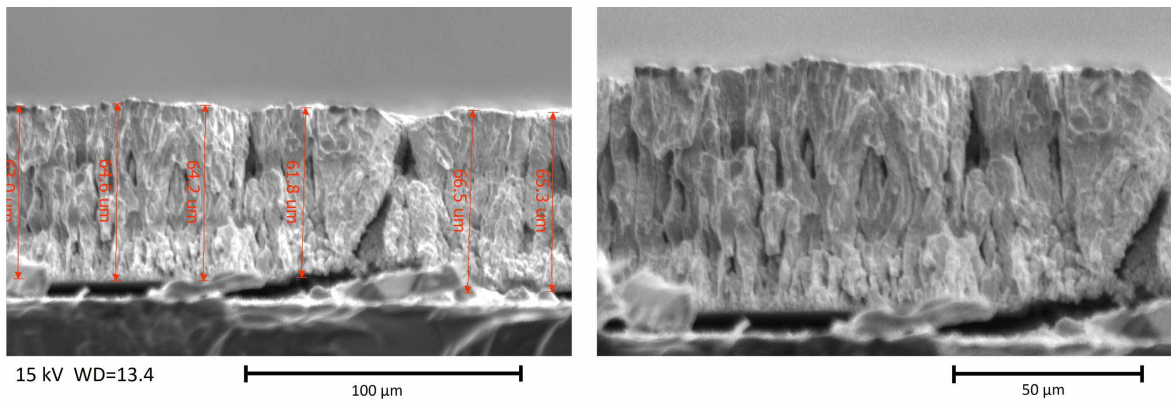


Figure 6.13: SEM cross-section analysis of test Cu-30, performed on Si samples.

The surface morphology analysis, shown in Figure 6.14, was performed on Nb samples and represents a highly crystalline structure due to the influence of the high temperature.

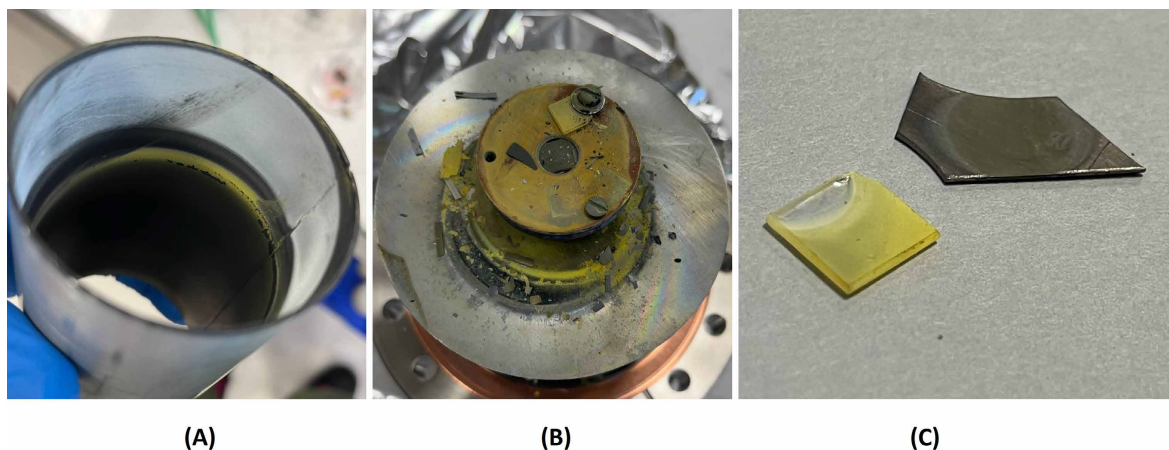


Figure 6.15: Test ZnO-8: (A) Zn cathode after the deposition; (B) sample holder after the deposition, covered by flakes; (C) quartz and Nb sample with ZnO deposition.

From Figure 6.15 A, it is noticeable that not all the cathode surfaces undergo sputtering. In the inactive zone, the deposition of ZnO was occurring. A bigger magnetic coil and proper magnetron size optimisation must be applied to avoid this effect. Clearly, in our condition, the cathode utilisation is not adequate. However, a high performance can be reached by utilising an axial sample holder with multiple target deposition and a bigger coil.

Another concern is the flake formation, shown in Figure 6.15 B. Since the cathode utilisation efficiency is low, the ZnO material was formed not only on the sample but also in the inactive cathode zone. The weak adhesion leads to the coating detachment. Such flakes, material powder, and macro-particle formation influence the process's stability, causing arcs. Moreover, it can significantly change film properties, causing defects in the structure. It can dramatically change the substrate's density and adhesion, leading to poor thermo-mechanical properties.

Placing the sample holder in an upper position may lessen the effect on coating since the flakes should not fall on the sample holder. Such an approach was used in yttrium deposition. Unfortunately, this modification can not eliminate a high material loss since the flakes can be created and remain in the magnetron as a loss. Optimising the cathode size and eliminating inactive areas is the best way to avoid this issue.

Targets 1 and 2 were deposited as the first solid target prototypes. Table 6.3 reports the parameters target depositions.

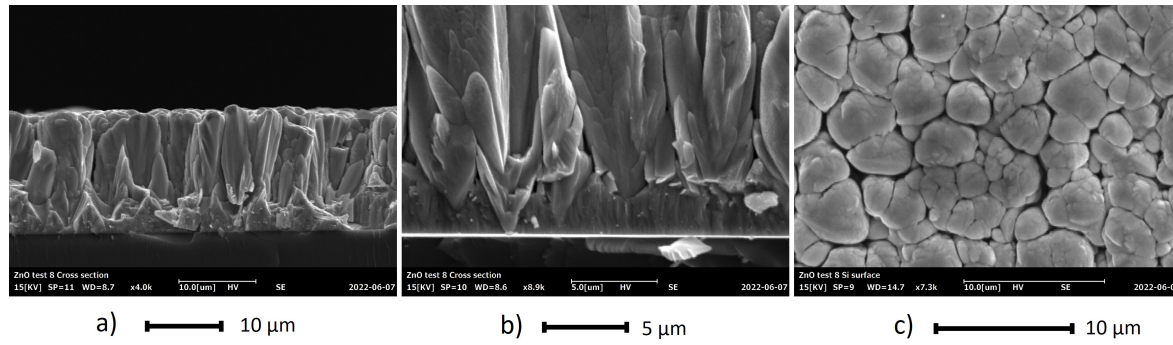
Table 6.3: Magnetron sputtering deposition parameters of ZnO.

Target	Current [A]	Voltage [V]	Working pressure [mbar]	Time [min]	Dep. rate [nm/min]
Target 1	0.7	332-500	$3.0 \cdot 10^{-2}$	130	150
Target 2		290-550		150	200

Both depositions were done with 0.7 A. The working pressure was fixed at $3.0 \cdot 10^{-2}$ mbar with the $Ar : O_2 = 2 : 1$ gas composition. The coil current was set to 6 A. The limitation of the deposition time was mostly due to the formation of flakes (see Figure 6.15B), which resulted in the arcs and instability of the process.

6.3.1 MORPHOLOGY AND GROWING BEHAVIOUR

An SEM cross-section analysis was conducted to investigate the growth behaviours of ZnO coatings on a horizontally placed sample holder. The SEM micrograph is shown in Figure 6.16.


Figure 6.16: SEM analysis of ZnO deposition onto Si substrate (ZnO-8): (a,b)cross-section and (c) morphology.

Two distinct growth patterns are observable. The initial $2\text{--}2.5 \mu\text{m}$ deposition exhibits uniform columnar growth, followed by a transition to forming larger crystals. Temperature measures are not feasible in our case since the sample is powering. In this scenario, the thermocouples are not going to function correctly. However, an accurate structural analysis can explain the reached temperatures. The Structural Zone Diagram (SZD) of Thornton adapted to CuO_2 deposition, presented in the work [72], can be used to analyse ZnO performance. The structure of the surface and cross-section of the film (see Figure 6.16) can be compared to our ZnO to Zone 2, where $T_b = 0.5 - 0.6$.

Additionally, the stainless steel sample holder turned to a red hot colour immediately after the power was switched off, indicating a temperature range of approximately 500 – 800 °C. While these values do not precisely indicate the temperature, they provide an idea of the range that correlates with the SZD. This suggests that our deposition process was facilitated at a high substrate temperature, which may have played a role in adhesion, deposition rate, and residual stress reduction.

As can be noted from Figure 6.16B, the film exhibits growing defects right from the initial stages. These defects, commonly known as nodular defects, are discussed in [96] and typically form on seeds of various origins. It could be a combination of various factors, such as arcs and flakes, associated with the sputtering process, not the substrate nature or preparation. One possible flake source can be a flaking of redeposited nodules from the cathode surface. Reactive MS processes with a planar cathode can lead to this phenomenon, where some parts of the cathode's area, such as the centre and edge, have a low plasma density and do not undergo sputtering. Due to the internal stresses, the redeposited material grows in filaments. The authors [96] indicate that such phenomena can be avoided entirely in an inverted magnetron. In our case, this problem persisted due to the incomplete erosion of the cathode surface.

Additionally, ZnO was deposited with a recovering shield approach to compare the growing behaviour between sputtering techniques. Figure 6.17 clearly shows the difference between the crystal structure. The ZnO growing behaviour, shown in Figure 6.17B, can be described by Zone 1 of SZD. The maximum thickness reached with the planar source was 5 μm , with an 80 nm/min deposition rate at least two times lower than in the case of IM configuration.

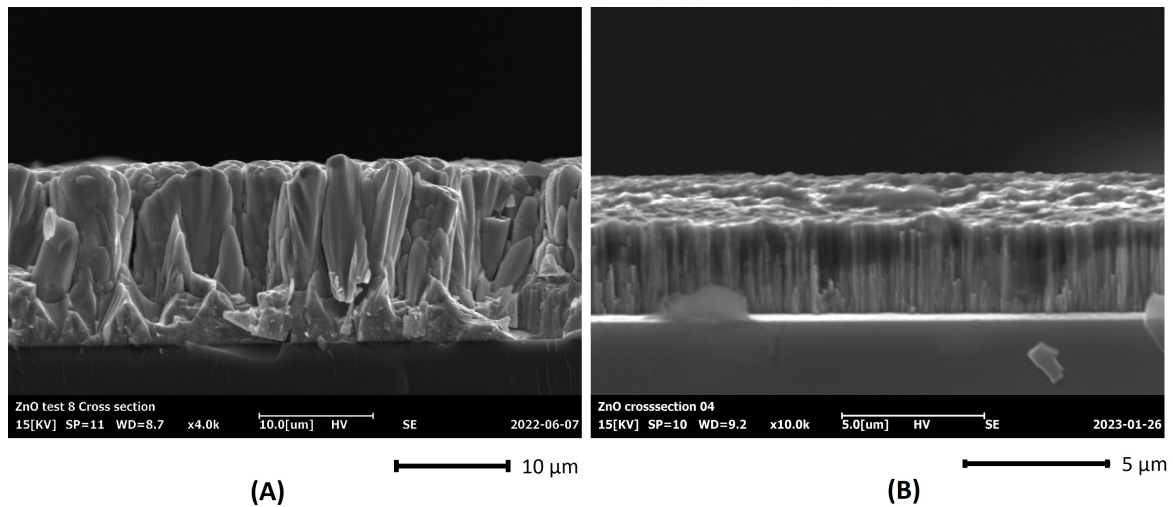


Figure 6.17: Cross-section SEM analysis of ZnO deposited (A) in IM configuration (ZnO-8), (B) in recovering shield approach (fixed current 0.3 A, 1-hour deposition, Ar flux - 1.8, O_2 flux - 1.2 sccm.)

The SEM images in Figure 6.18 show the morphology of Target 1 and 2 deposits. The presence of massive macro-particles and flakes is apparent (sizes around $100\ \mu\text{m}$), which, sometimes, remained embedded into the film (see Figure 6.18 A) or was removed, thus leaving craters-like defect. As seen in Figure 6.18 C, the detachment happened during the ongoing deposition; hence, the crater was redeposited. These phenomena can make evaluating the thickness with the standard contact profilometer challenging, introducing an unpredictable error to the measurements.

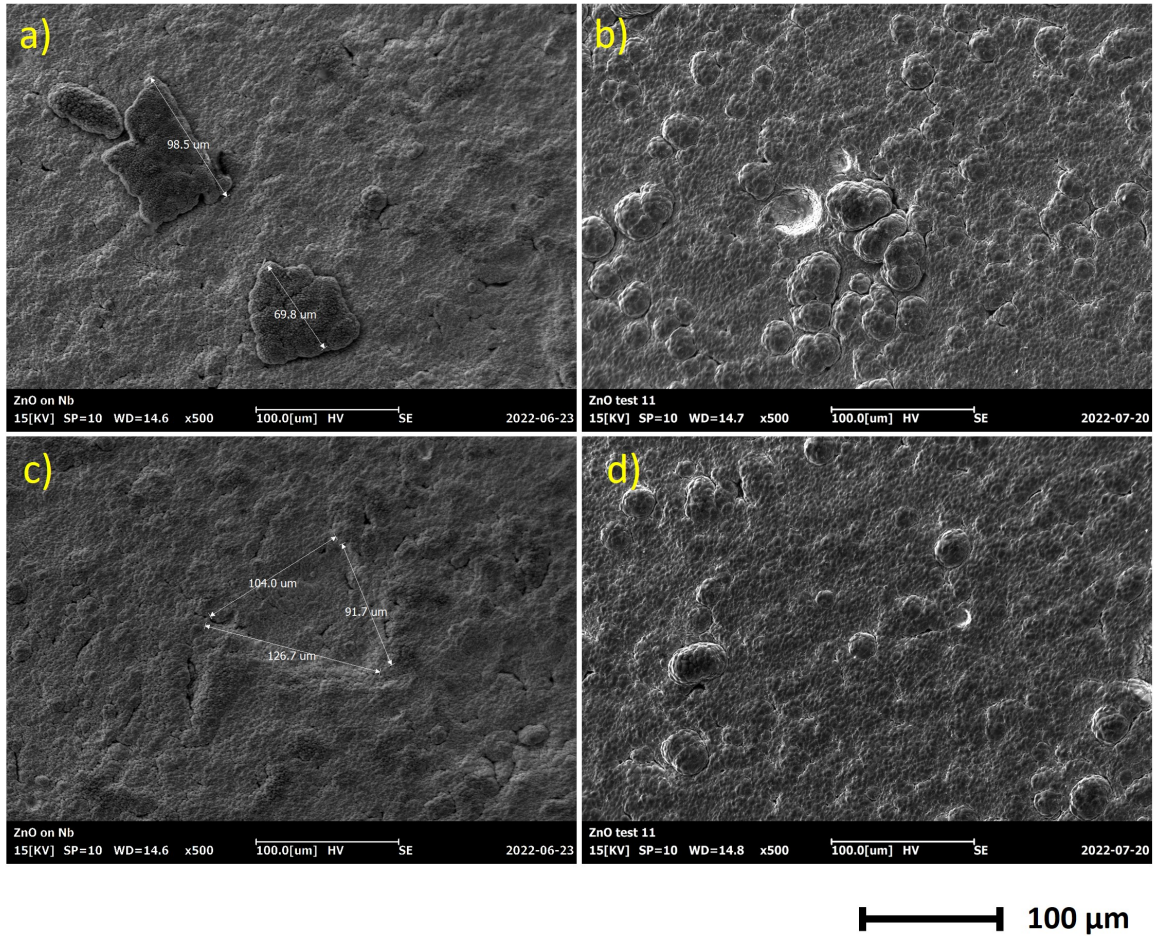


Figure 6.18: Defects on the surface of produced solid targets: a and c - Target 1; b and d - Target 2.

A metallurgical cross-section analysis was performed to evaluate the adhesion of ZnO on the actual substrate material (Nb). The ZnO was sputtered on Nb coin using the optimised parameters for 130 min. Then, the coin was cut by sparkerosion in the LNL mechanical workshop. The cross-section surface was polished using a lapping machine with different abrasive papers (1000 to 3 μm). As a result, the SEM micrographs in Figure 6.19 revealed a mechanical adhesion between the ZnO and the Nb coin. The sample preparation for the cross-section analysis could be improved in future.

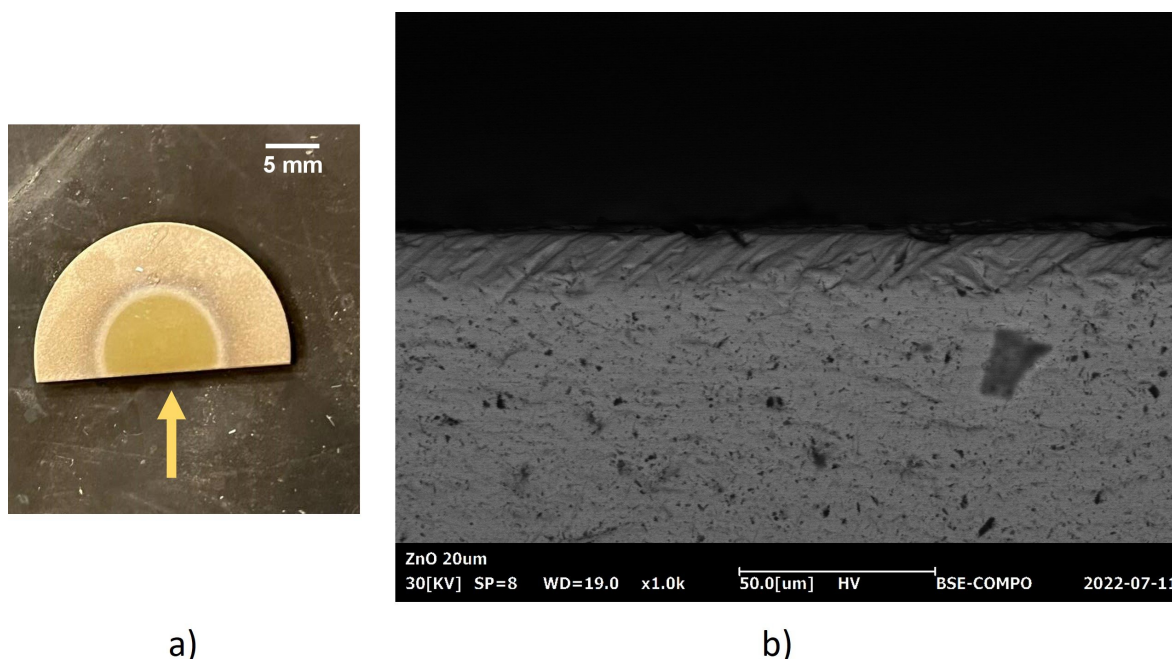


Figure 6.19: Cross-section SEM analysis of ZnO on Nb coin (test ZnO-9).

6.3.2 COMPOUND EVALUATION

The XRD analysis was performed for ZnO film on Nb and quartz samples to confirm the formation of the stoichiometric ZnO. The results are shown in Figure 6.20 and were compared to the diffractogram of ZnO powder.

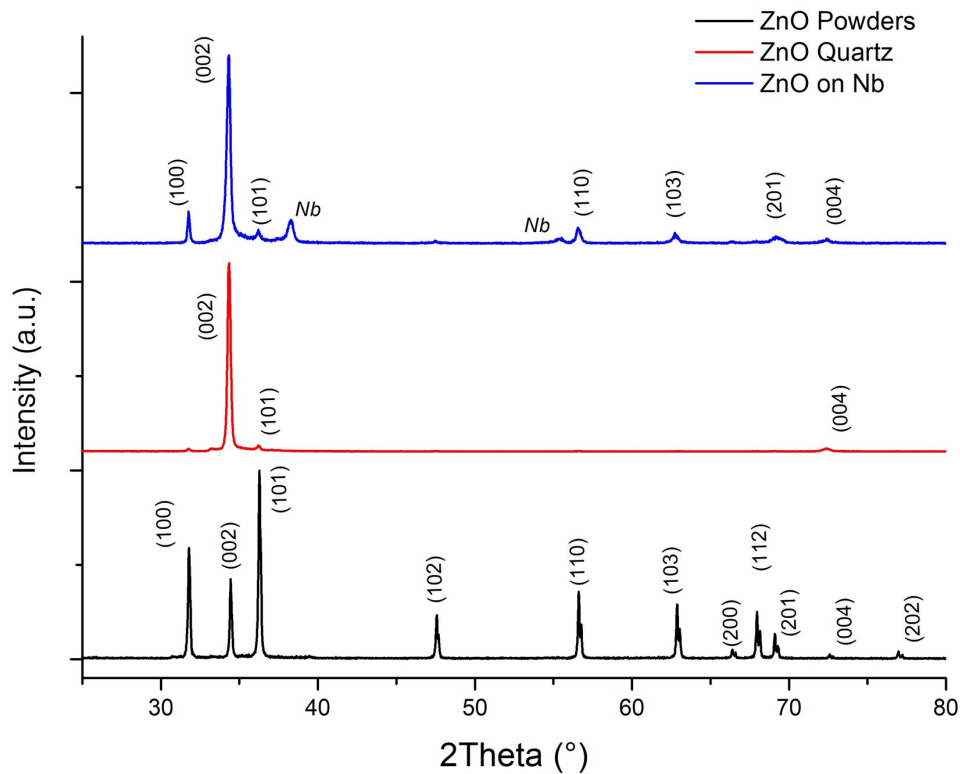


Figure 6.20: Diffractograms of ZnO films sputtered onto Nb and quartz substrates compared to the diffractogram of ZnO powder, used for target sintering production.

The evaluation of the obtained diffractograms in HighScorePlus software (Panaytical) confirms the formation of the ZnO film without metallic Zn contamination, despite possible Zn cathode evaporation suggested by increasing deposition rate in the lengthy process. However, in the diffractogram of ZnO onto Nb, the Nb peaks are visible due to the high penetration depth of the X-rays in the chosen instrument configuration. The diffractogram obtained from the ZnO on the quartz sample supports the results.

It is important to note that sputtering processes typically exhibit preferential film growth. In our case, the higher peak is attributed to the low energy needed for the formation of the (002) plane, which could be assigned to the hexagonal ZnO wurtzite phase with the *c*-axis perpendicular to the substrate surface, as reported in several works [86, 97].

Crystallite sizes were calculated from the Scherrer formula: $D = \frac{K\lambda}{\beta \cos \theta}$. Based on the calculation, the crystalline size of ZnO onto Nb coin is appear to be ~ 30 nm.

6.3.3 THERMO-MECHANICAL IRRADIATION TEST

The produced ZnO targets were tested under the cyclotron beam as a final step. The thermo-mechanical stability of the sputtered targets was evaluated with two irradiation runs (energy of 19 MeV) at 10 and 20 μA for 5 minutes. Irradiation parameters are shown in Table 6.4. The density was calculated according to the Equation 3.4.

Table 6.4: Nat-ZnO targets characteristics and thermo-mechanical irradiation results.

Target	thickness [μm]	Mass [mg]	Relative density [%]	Irradiation current [μA]	Irradiation time [min]	Result
Target 1	20	6.3	72	10	5	excellent
Target 2	30	9.1	70	20	5	excellent

Visual control of the targets after each irradiation was carried out. The photos of the targets before and after the irradiation are shown in Figure 6.21.

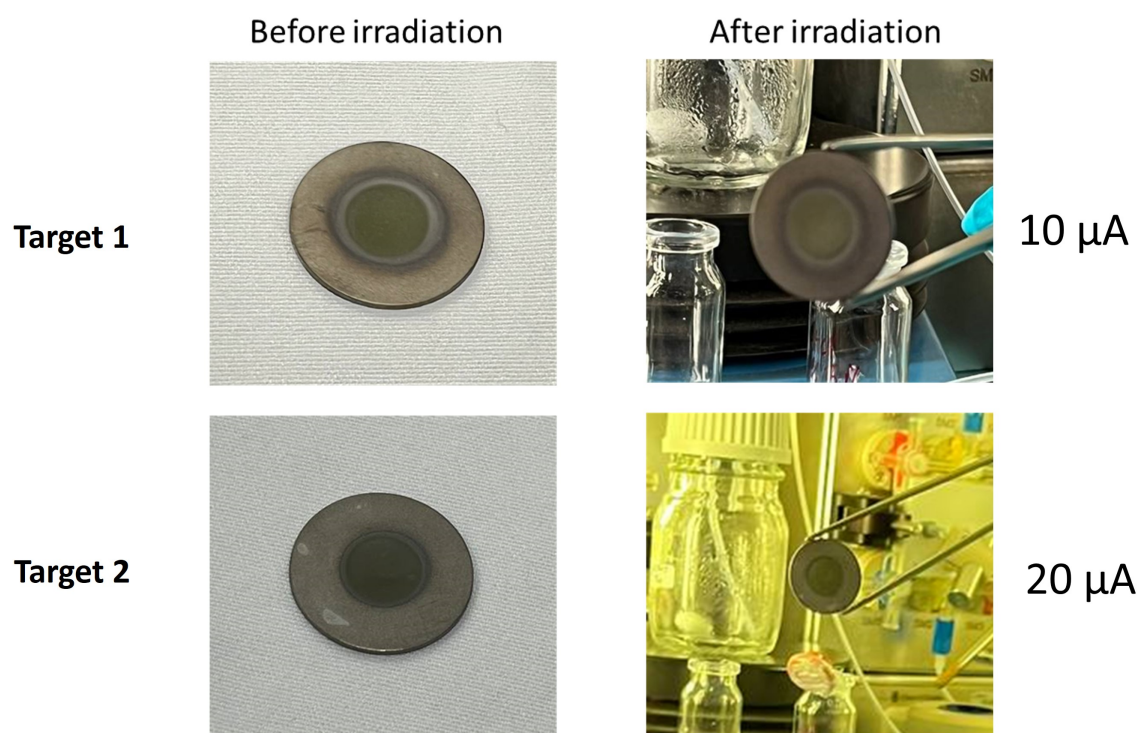


Figure 6.21: nat-ZnO sputtered solid targets: before (left) and after (right) the irradiations under the 19 MeV proton beam of the TR19 ASCI cyclotron (Negrar, Verona, Italy).

After the irradiation tests, the sputtered targets showed no signs of delamination or cracking. These outcomes can be explained by high adhesion performance, facilitating efficient heat exchange during irradiation to dissipate the heat power proportional to the current deposited on the target.

Regarding the density, despite the bulk material being preferable for maximising radionuclidic yield, it could make the future dissolution step more complicated and slower. Thus, the density on the level 90-95% is a good compromise between the requirements [10]. In our case, the relative density reached 70% of the bulk, probably due to the presence of the flakes and droplets. Nevertheless, the integrity of our targets after the irradiation tests was confirmed by visual inspection. However, defects in the deposition should be minimised to avoid detrimental effects (detachment or delamination) during the irradiation.

6.4 CR DEPOSITION WITH IM CONFIGURATION

In the case of Cr deposition, buying the foil of the needed dimension or the Cr tube to produce the Cr cathode was inconvenient. However, it was decided to sputter a thin Cr layer onto a copper cylindrical cathode by standard planar magnetron deposition to evaluate the possibility of depositing Cr with IM. In this way, the Cu cathode works as the recovering shield, as was mentioned in Section 5.

Figure 6.22 shows the Cr cathode preparation. The copper cylinder was placed in the vacuum chamber, as shown in Figure 6.22 A. In this process, the deposition of Cr was performed on a cylindrical cathode and together with a sample holder for experiments, described in Section 5.4.1.

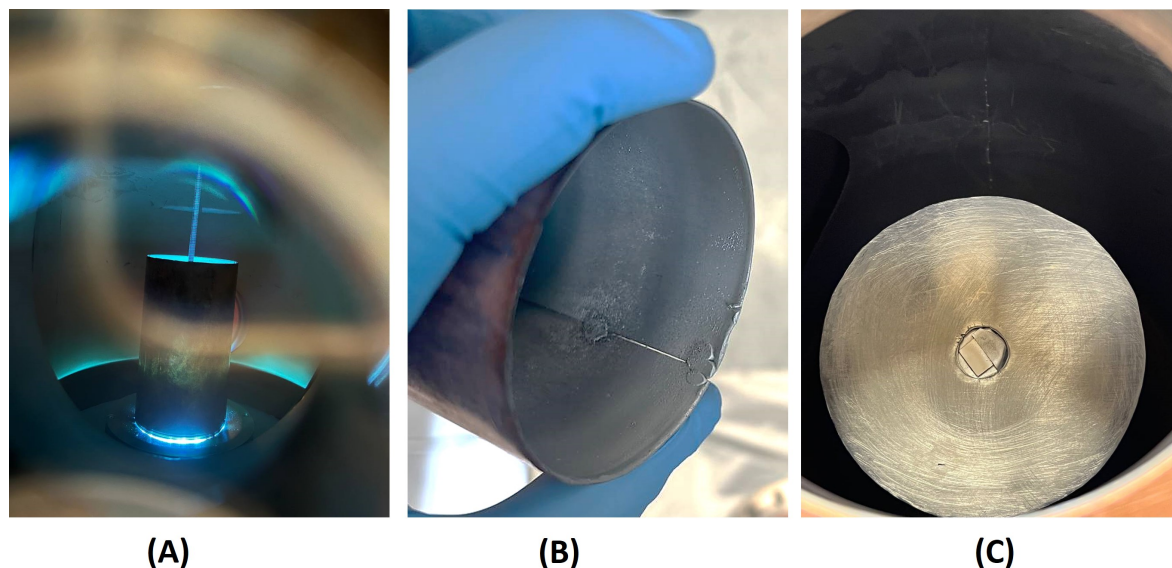


Figure 6.22: Preparing of the cylindrical Cr cathode: (A) sputtering process using a planar magnetron source, (B) Cr deposits inside the cylindrical cathode, (C) protective bottom cover deposited with Cr layer.

The Cr deposition on the Cu cylindrical cathode was performed for 170 minutes from one side and 240 minutes from another, with parameters shown in Table 5.7. Estimating the deposited layer thickness is challenging due to the absence of precise measurements. However, considering that the exposed area of the cylinder to deposition was approximately four times larger than the sample holder area and noting that nearly twice the material was deposited on the recovering shield, a rough estimate suggests that in a 240-minute deposition, where $70\ \mu\text{m}$ were deposited on the sample holder, at least $30\ \mu\text{m}$ was deposited on the cylindrical area.

Figure 6.22 B shows the chromium deposition on the internal cylindrical area. In addition, to prevent any Cu contamination, Cr was sputtered onto a protective covering as was described before (see Figure 6.22 C). The Cr deposition was performed for 40 minutes with 1 A, depositing around $2\text{--}3\ \mu\text{m}$.

Figure 6.23 shows the deposition of chromium film using an inverted magnetron configuration. Figure 6.23 B shows how the sample holder is placed inside the IM source, while Figure 6.23 C display the deposition process with plasma emission.

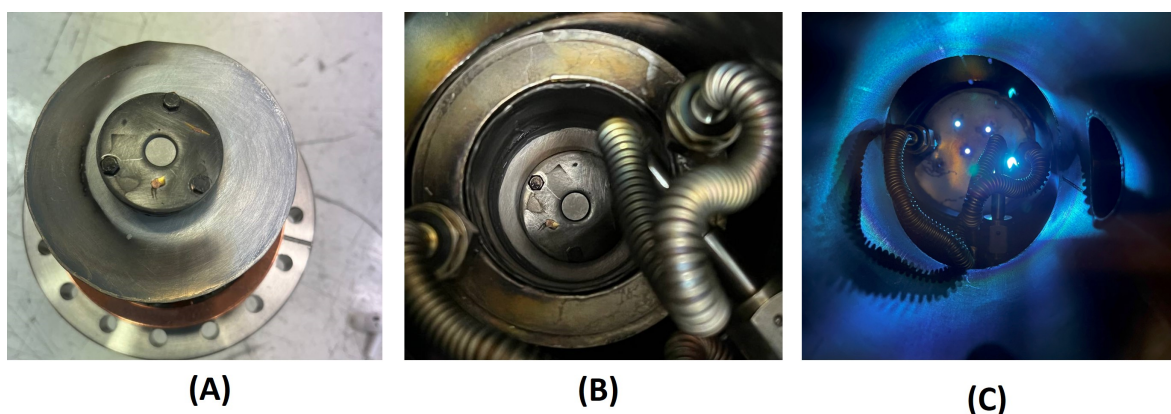


Figure 6.23: Chromium deposition setup with IM configuration: (A) Sample holder with Cr protective cover, (B) sample holder inside the IM, in the vacuum chamber, (C) plasma emission during the deposition process.

The deposition parameters are presented in Table 6.5. The experiments were constrained by the thin layer deposited on the copper cathode.

Table 6.5: Inverted magnetron sputtering parameters of Cr deposition: coil current 7A and working pressure $1.2 \cdot 10^{-2}$ mbar.

Target	Current [A]	Voltage [V]	Time [min]	Dep. rate [nm/min]
Cr-IM-1	0.5	347-308	15	50
Cr-IM-2	1	485-457	75	100

The first test was done for 15 minutes, with 0.5 A. As a result, a Cr deposition of 800 nm was deposited. The following deposition was done for 75 minutes to grow a thicker Cr film. As a result, a $7.3 \mu\text{m}$ Cr film was deposited. The manufactured chromium target has an interesting optical characteristic, as shown in Figure 6.24. At 90 angles, the deposition colour is black, while at low angles, it seems greyer.

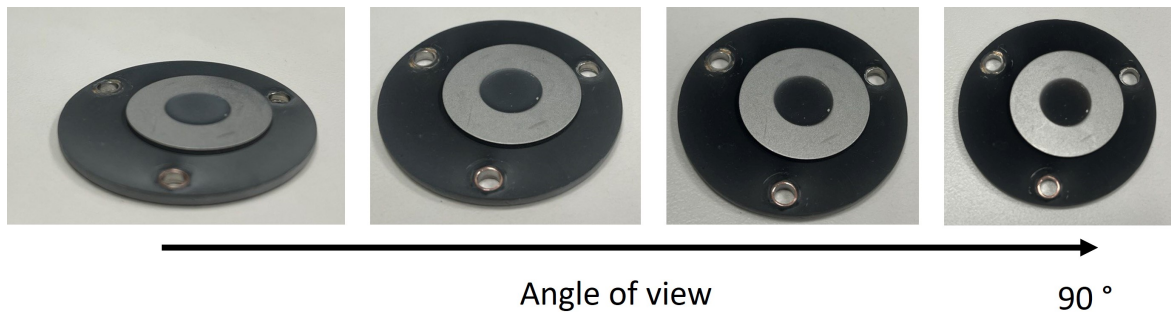


Figure 6.24: First Cr solid target prototype, deposited with IM configuration.

The morphological analysis shows the characteristics of chromium structure. Figure 6.25 shows that the deposition is not uniform, with different cracks presented. Thus, the film's adhesion is low, and it was easily scratched out.

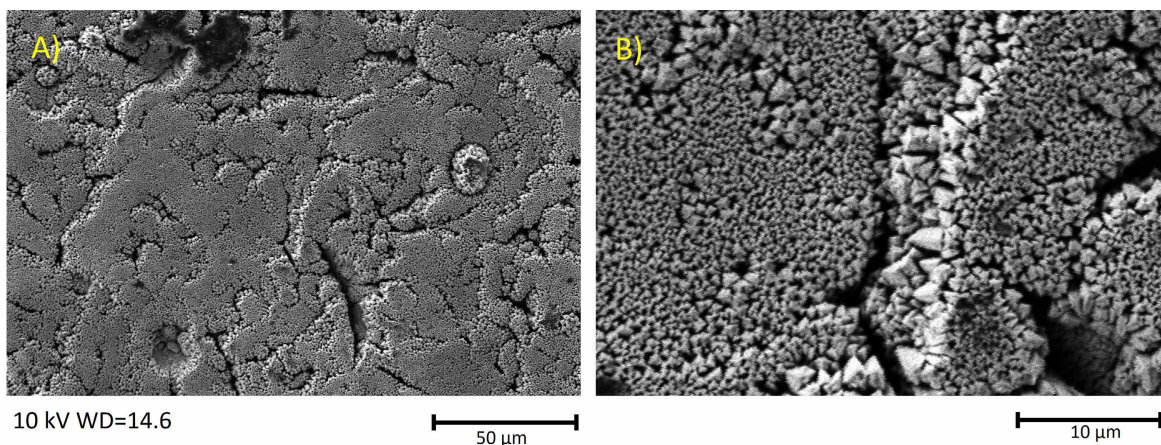


Figure 6.25: SEM morphological analysis on Cu coating deposited on Nb disks.

Figure 6.26 shows the EDS spectrum of Cr deposition on the Nb disk in two regions. As can be noticed, a low percentage of Cu (up to 2.5 % in atomic concentration) is present in the coating. Moreover, some areas are notably contaminated with carbon by unclear origin.

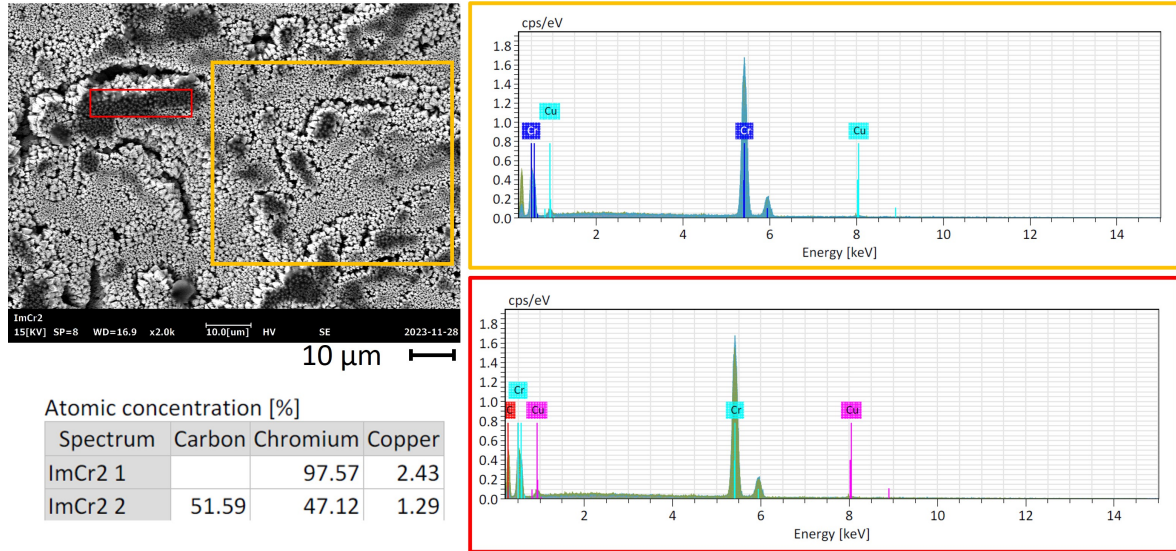


Figure 6.26: Results of EDS analysis of Cr-IM-2 deposition surface areas.

These preliminary results demonstrate the potential for self-preparation of a cylindrical cathode and potential chromium deposition with the inverted magnetron configuration. Further experiments are required to assess possible deposition enhancements with a more controlled cathode preparation.

6.5 CONCLUSIONS

This work demonstrates the feasibility of an inverted magnetron prototype dedicated to solid target manufacturing aimed at radioisotope production for nuclear medicine applications. The material-saving approach described in this work can be exploited for different applications where costly materials are used.

The first two ^{nat}ZnO onto Nb targets were obtained, which can be a starting material for the interesting theranostic ^{67}Cu radionuclide production. The study demonstrates the ability to grow an oxide film of 20-30 μm within two hours. The XRD analysis confirms the absence of Zn contaminants in the film and shows a preferable (002) crystal growth.

The maximum deposition rate achieved in this work was 200 nm/min , which is almost ten times higher than reported in the work [82], where the authors address the importance of a high sputtering rate.

Additionally, the targets exhibited acceptable thermo-mechanical properties during short irradiation beam runs. Although the irradiation tests were successful, it is essential to note that the target thickness must be at least 500 μm for the proper isotope production [50]. Therefore, the results are the first step in further investigating the magnetron sputtering technique, particularly the inverted magnetron source.

7

Discussion and future works

The magnetron sputtering technique has proven successful in manufacturing yttrium solid targets. While physical vapour deposition (PVD) techniques are commonly employed for film deposition, achieving substantial film thickness presents challenges. Nevertheless, this study attained thicknesses of up to $210\ \mu m$.

Additionally, irradiation and Zr-89 production assessments indicate that the final Y5.0 batch achieved a level comparable to bulk yttrium foils. Notably, this dissertation demonstrates that sputtered targets can reach comparable, and even higher, values of saturation yield compared to foil and SPS targets, as discussed by Cisternino et al. [9], ranging from $6.654\ \text{MBq}/\mu\text{Ah}$ (Y5.4) to $15.801\ \text{MBq}/\mu\text{Ah}$ (Y5.7).

Examining Zr-89 production, sputtering targets exhibit advantages in easy handling in hot cells, reducing dissolution time, and facilitating efficient thermal power exchange. However, it is crucial to recognise the limitations of this technique, notably inevitable material losses during deposition, which can reach up to 70%. When considering the low material efficiency of the sputtering cathode (around 27%) and the effective sample holder area, the overall material efficiency of the process is even lower. Challenges in employing this technique include difficulty reaching thicknesses higher than $300\ \mu m$ due to yttrium's tendency to oxidize. This necessitates yttrium coating deposition within a single sputtering cathode without a vacuum break. Nevertheless, by adjusting deposition time or other parameters, sputtering methods enable rapid optimisation in the thickness range.

This dissertation demonstrates that the recovery shield approach can be viable for a single deposition but is not recommended for serial production. Conversely, the proposed inverted magnetron approach addresses the described limitations and challenges. The study reveals minimal material losses in metallic deposition with a Cu cathode, optimising cathode utilisation efficiency. Additionally, cathode preparation can be accomplished using a thin material foil, a more feasible approach for isotopically enriched materials than a bulk thick planar sputtering cathode.

In this dissertation, it was impossible to realise an axial sample holder approach, shown in Figure 7.1A. It is believed that adopting this approach would lead to greater success. In Figure 7.1B, the dedicated sample holder concept was designed to suit the existing inverted magnetron prototype. This dissertation suggests that such an approach can significantly upgrade solid target production.

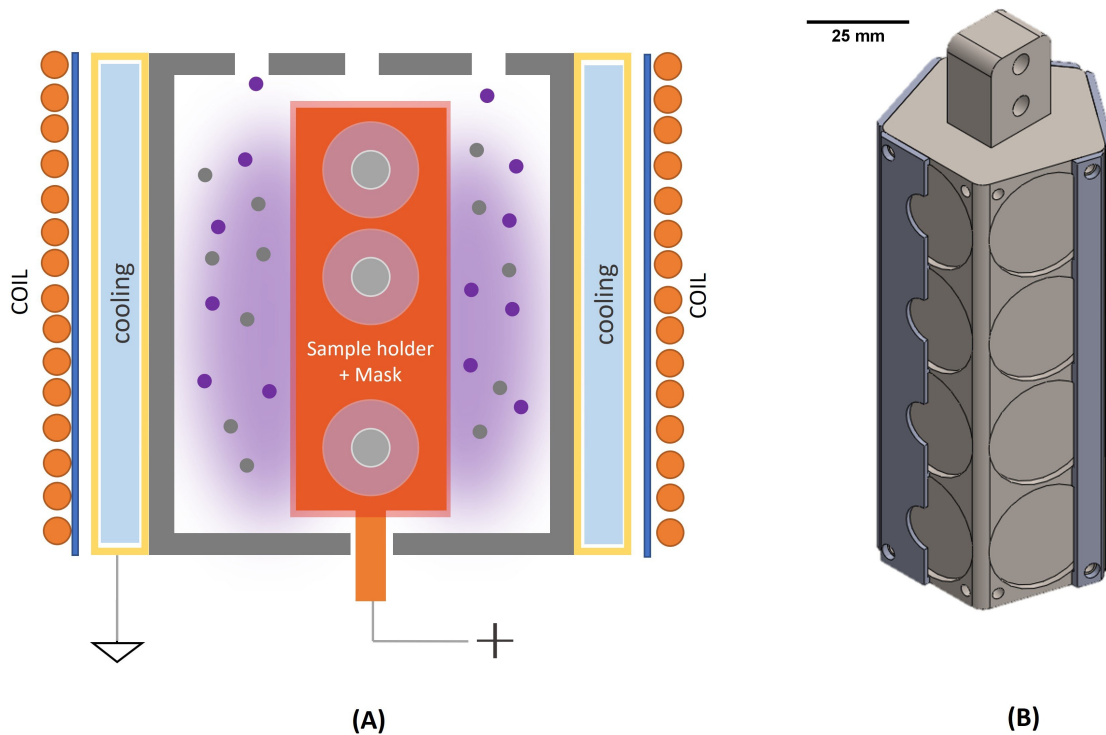


Figure 7.1: The multi-target deposition approach: (A) scheme of the deposition process with inverted magnetron source and (B) a pentagon sample holder concept design, with dedicated masks for 20 targets manufacturing.

The whole deposition system must be upgraded and optimised to study this configuration, including the vacuum chamber and coil. However, as was suggested in the dissertation, the deposition properties of film sputtered on axial and horizontal positions can be different.

If the axial deposition does not satisfy the coating requirements, another approach can also be suggested. The double-side deposition approach, shown in Figure 7.2, can allow depositing two solid targets in one deposition run. This modification can not significantly improve the efficiency of the technique. Still, it can allow to evaluate the influence of the sample holder position (top/bottom) and collect enough statistical data.

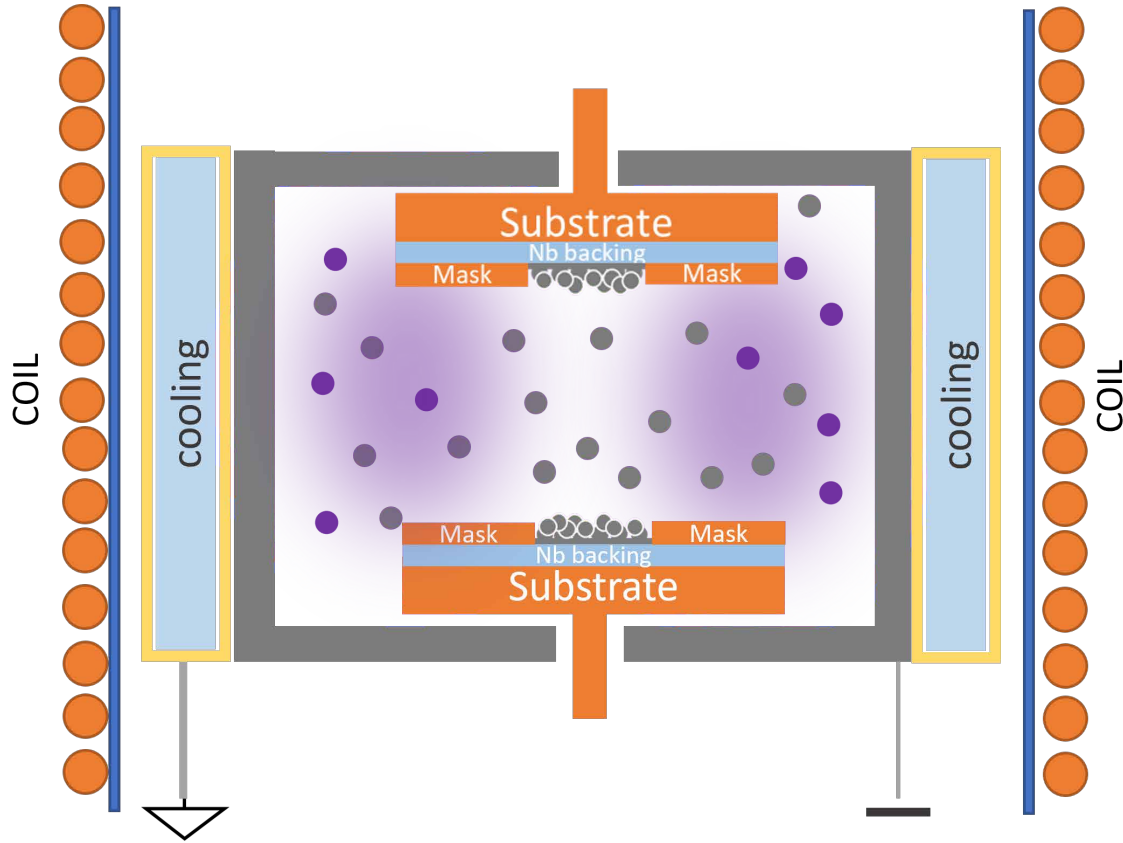


Figure 7.2: Scheme of the double-side deposition approach for inverted magnetron configuration.

This dissertation shows the successful utilisation of a reactive sputtering process for the inverted magnetron configuration. However, it was shown that such a process can produce a higher amount of powder and flakes, which will result in higher material losses. The reactive sputtering must be considered for solid target manufacturing only if the compound cathode is unavailable or cannot be realised in cylindrical form.

This dissertation underscores that sputtering deposition is time-consuming, especially for thick films. Despite the deposition process typically taking hours or a maximum of 1-2 days, the overall deposition process could span one working week, as demonstrated in the manufacturing of yttrium solid targets. These findings suggest that a multi-target preparation strategy is essential to enhance the method's effectiveness.

Utilising isotopically enriched material is challenging for magnetron sputtering techniques due to the high material loss problem and the fact that such materials are primarily available in powder form. In contrast, alternative techniques, such as various sintering processes and electrochemical deposition, can operate with limited material for target production. Furthermore, the recovery process, standard in radioisotope production, is more likely to recover material in powder form.

Despite the acknowledged limitation, magnetron sputtering can still be considered for solid target manufacturing. While growing deposition over $300\text{ }\mu\text{m}$, as needed for radionuclide production, can be challenging, the "thinner" deposition for nuclear cross-section studies can benefit from the technique. Furthermore, the sputtering technique exhibits fewer limitations regarding substrate shapes and materials, allowing the deposition of thick films on substrates with advanced or complex surfaces.

General conclusion

Different magnetron sputtering approaches were investigated during this research for cyclotron solid target manufacturing, focusing on its material efficiency.

The standard planar magnetron DC deposition was used to manufacture yttrium solid targets. The coating process protocol was upgraded with the baking procedure to ensure pure and dense yttrium coatings were deposited. Among twenty-one produced yttrium targets, sixteen were irradiated and tested for ^{89}Zr production, showing a significant improvement in saturation yield. All irradiated targets demonstrated remarkable resilience under high power loads, exhibiting no signs of delamination or damage.

The last deposition batch shows the possibility of reaching a significant thickness: $210\ \mu\text{m}$ thick yttrium coating for a central sample holder position. The other six solid targets in this batch reach $115\ \mu\text{m}$. Different strategies, such as lowering the working distance or increasing the working current, are studied and suggested to improve the deposition thickness further. The new sample holder design was suggested for improving the uniform thickness distribution among the targets in one deposition run.

The ^{89}Zr isotope holds significant interest for immuno-PET studies, and its production using monoisotopic yttrium solid targets provides a robust foundation for future magnetron sputtering evaluations.

This work demonstrates a recovering shield deposition approach, which allows the evaluation of material dissipation in both the magnetron and diode sputtering deposition processes. A novel protective shield was meticulously designed and used for material efficiency investigation by the weighting method.

The results indicated a promising avenue for a substantial recovery of cathode material during sputtering processes, applicable to both magnetron and diode sputtering options. The strategic utilization of such a recovering shield demonstrated the potential to reduce material losses from an initial 70% down to a remarkable 10%. Despite the drawback of a specific cathode erosion, the magnetron sputtering method emerged as the preferred choice for radiopharmaceutical applications due to its high deposition rate and final coating properties.

Moreover, this dissertation shows the feasibility of thick film deposition, surpassing $200\text{ }\mu\text{m}$. This capability is particularly significant for radiopharmaceutical applications, specifically in producing cyclotron solid targets, highlighting the versatility and potential of sputtering methods. As a result, one $70\text{ }\mu\text{m}$ thick chromium solid target was manufactured, utilising a recovery shield approach.

Furthermore, it was for the first time proposed the utilisation of an inverted magnetron (IM) for solid target manufacturing, as a material-efficient sputtering configuration. The design idea and simplified version of IM are presented in detail. Although the proper material efficiency study was not feasible, the approach shows no significant material losses outside the magnetron volume.

The inverted magnetron prototype was used for metallic copper deposition and reactive zinc oxide sputtering deposition. The first two ^{nat}ZnO onto Nb targets were obtained. ^{nat}ZnO can be used as a starting material for theranostic ^{67}Cu . Its production in a sufficient amount for pre-clinical and clinical tests is limited by the lack of a suitable target that can withstand the high proton beam current. For this reason, the development of innovative target manufacturing technologies is fundamental.

This study demonstrates the ability to grow an oxide film of $20\text{-}30\text{ }\mu\text{m}$ within two hours. Additionally, the targets exhibited acceptable thermo-mechanical properties during short irradiation beam runs. The XRD analysis confirms the absence of Zn contaminants in the film and shows a preferable (002) crystal growth. The maximum deposition rate achieved in this work was 200 nm/min , almost ten times higher than reported in the literature.

Resource-saving approaches have become a common practice in optimising many industrial processes. The results of this study are the first step in further investigating the magnetron sputtering technique, particularly the inverted magnetron source, as a material-saving technique. The approach described in this work can be exploited for different applications where costly materials are used.

The optimisation and future deployment of magnetron sputtering techniques will be continued in the framework of the CUPRUM-TTD (67/64CU PRoduction and Use in Medicine _Target Technology Development) INFN project.

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