Executive Summary of the Thesis

Pulsed Laser Deposited Boron Thin films as Model Systems for studies in Magnetic Confinement Fusion

Laurea Magistrale in Nuclear Engineering - Ingegneria Nucleare

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1. Introduction

The global effort to achieve fusion energy production has intensified in recent years, driven by the promise of abundant and clean energy. The main route pursued by the international community relies on the development of magnetic confinement devices, namely tokamaks and stellarators, capable of confining a plasma in which the deuterium–tritium fusion reaction can take place. The maximum expression of this collective endeavour is the ITER project, a large-scale full tungsten (W) tokamak designed to reach a factor of merit Q, defined as the ratio between the produced fusion power and the external power injected into the plasma, greater than 10. Operation is currently scheduled to begin in 2035. Several technical challenges remain to be solved before first plasma. From the materials perspective, the recent choice of W as the ITER first wall material instead of beryllium mitigates issues related to mechanical degradation under cyclic loads and hazardous handling during construction. However, this selection requires the adoption of techniques to reduce the oxygen content inside the tokamak vessel, due to its ability to enhance tungsten sputtering during start-up and potentially lead to radiative collapse. Boronization is the deposition, through different systems and most commonly Glow Discharge Boronization (GDB), of a thin boron film on the wall of the device [1]. The boron layer acts as an oxygen getter thanks to the highly negative formation energy of its oxides.

Numerous studies have been conducted on different tokamaks and stellarators to achieve a comprehensive understanding of deposited layers in terms of thickness, uniformity, morphology, chemical composition, fuel permeation, and the impact of boron on redeposited materials. From post-mortem analyses, in situ diagnostics, and computational simulations, it can be inferred that the average GDB boron layer, in regions close to the glow discharge cathodes, is typically hundreds of nanometres thick and consists of an amorphous, compact film with a controlled oxygen content of approximately 10%, high surface uniformity, and low carbon contamination. In addition, redeposited material constitutes a highly complex environment, where the morphology and composition of each layer, involving W, B, O, and possibly nitrogen, may vary substantially. In parallel with experimental activities performed directly on fusion devices, the Model System approach has been developed, mainly targeting Plasma Surface Inter-

action (PSI) studies. By adopting different fabrication techniques, it is possible to produce numerous mock-up samples representative of first wall coatings, such as boron layers and redeposited systems, under laboratory conditions. This strategy enables thorough characterisation of each specimen prior to plasma exposure, typically carried out in linear plasma devices capable of operating over a broad range of plasma parameters. A second characterisation after exposure allows direct comparison with pristine films and provides valuable benchmarks for simulation tools.
The thesis activity focuses on the first stage of the Model System life cycle, namely the fabrication of boron coatings. To address the increasing demand for mock-up samples from laboratories across Europe, an optimisation of the existing nanosecond pulsed laser deposition (ns-PLD) system was performed, together with an extension of its operational range, particularly regarding morphology control, oxygen fraction tuning, and nitrogen incorporation. The work can be divided into three main activities. First, under deposition conditions comparable to state-of-the-art samples [2], a study of the ablation mechanism was carried out, focusing on the influence of production parameters on deposition rate and droplet formation, the latter being the primary drawback of PLD deposited films. This activity was conducted in parallel with the development of an original Python program, `PLDSim`, devoted to the analysis of the ablation profile in order to reduce target overconsumption and improve utilisation uniformity. Second, the effects of inert Ar or He background pressure on boron films were investigated, with particular attention to morphology and elemental fraction variations. Finally, the feasibility of nitrogen incorporation into boron films was explored through Reactive Pulsed Laser Deposition.

2. Methods

The thesis objectives were pursued at the Micro and Nanostructured Materials Laboratory (NanoLab), Politecnico di Milano, through the implementation of deposition processes, sample characterisation, and computational analysis of the acquired data.

2.1. Production

Nanosecond pulsed laser deposition (ns-PLD), a physical vapour deposition technique, is particularly suitable for the fabrication of boron Model Systems due to its versatility. It enables the growth of highly compact films, while the introduction of inert gases allows controlled modification of morphological features. The use of a reactive gas, such as nitrogen, makes it possible to tailor film composition. For boron deposition, PLD offers a significant advantage over alternative techniques, providing deposition rates on the order of 10 nm/min, compared with approximately 0.1 nm/min typically achieved by RF magnetron sputtering. The main drawback of the technique lies in its limited lateral uniformity and the impact of droplets on surface homogeneity. The system employs a Continuum-Quantronix Powerlite 8010 pulsed Q-switched Nd:YAG laser, delivering 5-7 ns pulses at the fundamental wavelength $\lambda = 1064\,\text{nm}$. In this work, the second harmonic at $\lambda = 532\,\text{nm}$ was used. The laser beam impinges on the boron target at an angle of 45° inside a vacuum chamber, inducing vaporisation and, under certain conditions, explosive boiling. When a background gas is introduced, collisions within the plasma plume confine the ablated species and reduce their kinetic energy before they reach the substrate, positioned at a target-substrate distance d_{TS}. Higher background pressure and larger d_{TS} favour the formation of less compact and more porous films. The deposition process is monitored by Optical Emission Spectroscopy (OES), enabling qualitative assessment of species energy moderation and the effectiveness of Reactive Pulsed Laser Deposition.

2.2. Characterization

Scanning Electron Microscopy (SEM) was performed using a Zeiss GeminiSEM 40, enabling morphological inspection of both film surface and cross-section, as well as thickness measurements. The X-ray radiation generated by the electron beam, combined with an Oxford Instruments silicon drift detector, enabled Energy Dispersive X-ray Spectroscopy (EDX) to determine elemental fractions and, through subsequent data processing, to estimate film density. Raman spectroscopy was carried out using a Renishaw InVia micro-Raman spectrometer with an excitation wavelength $\lambda_g = 514\,\text{nm}$, providing information on chemical bonding and the possible presence of crystalline phases.

2.3. Computational work

A droplet detection procedure was implemented by integrating high-contrast SEM imaging, ImageJ software, and dedicated Python code. This approach enabled automated analysis of nano- and micro-scale structures formed on the surface of compact films. In addition, the EDDIE [3] program, based on a reference-free approach to electron probe microanalysis, was employed to process EDX data and extract film density values.

3. Results

3.1. `PLDSim`

Within the framework of deposition optimisation, the development of `PLDSim` was primarily motivated by the absence of a tool capable of describing the ablation profile and, consequently, evaluating the most suitable target motion. The Python code, equipped with a graphical user interface, takes as input the drive profile of the motor system and, accounting for the target geometry and laser optical path, computes the pulse impact region at each time step. By superimposing the contributions over an entire deposition, the program generates several diagnostics, including a heat map representing the cumulative engraving effect of the laser on the target. An initial simulation campaign revealed that the most commonly adopted drive profile produced a concentric ring pattern resulting from the combination of symmetric motion and the discrete stepwise operation of the motor system, as shown in Figure 1.a. To mitigate this issue, an asymmetric motion was introduced and adopted for all depositions performed during the thesis. This modification significantly reduced pattern formation and improved ablation uniformity, as illustrated in Figure 1.b. The software further indicated that, even at maximum angular velocity, consecutive laser pulses could partially overlap within the same region of the target. A second simulation campaign, conducted through a trial-and-error approach, led to the definition of a revised motion profile that avoids this behaviour by introducing off-axis ablation and further enhances uniformity, as shown in Figure 2.

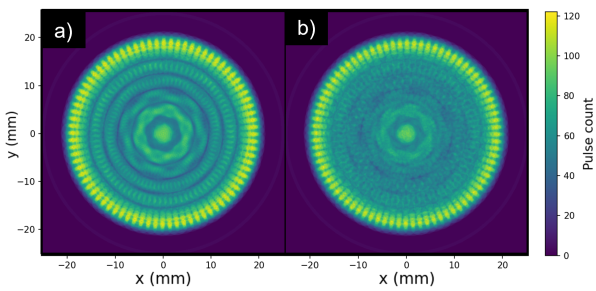

Figure 1: Heat map obtained using: a) standard configuration; b) asymmetric configuration

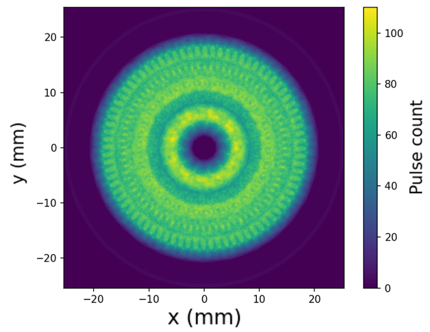

Figure 2: Heat map produced by the adjusted off-axis drive profile.

3.2. In-vacuum deposition of compact films

The first investigation related to the impact of the ablation mechanism on in-vacuum deposition was carried out by evaluating the effect of target replacement and different ablation configurations. Similar to state-of-the-art deposition parameters were adopted, namely average pulse energy $E_p = 650$ mJ, spot size $A_s = 8.8\,\text{mm}^2$, fluence $F = 7.11\,\text{J}\,\text{cm}^{-2}$, base pressure $P < 5 \times 10^{-3}$ Pa, and target-substrate distance $d_{\text{TS}} = 9$ cm. SEM imaging confirmed that surface uniformity was substantially improved by employing a pristine target and an asymmetric motion configuration, compared with a consumed target and a single-velocity configuration. A second study addressing spot size variation is now presented. Experimental evidence of a positive effect on the deposition rate was obtained by increasing A_s from 8.8 mm^2 to 11.1 mm^2, resulting in a 27% increase in deposition rate from $R_p = 11.0\,\text{nm}\,\text{min}^{-1}$ to $R_p = 14.0\,\text{nm}\,\text{min}^{-1}$. A possible explanation for this behaviour is that the combined effect of a larger ablated area and a reduced plume divergence angle compensates for the lower laser penetration associated with the reduced fluence. The elemental fractions of boron and oxygen, as well as the film density, appeared largely unaffected. Depositions performed at higher base pressure confirmed the pronounced sensitivity to oxygen incorporation.

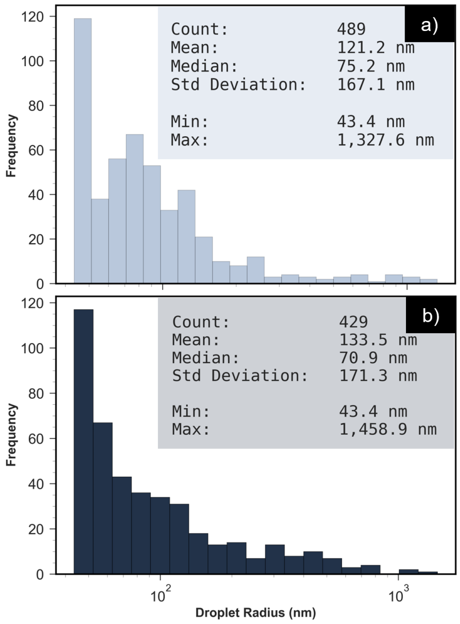

Figure 3: Droplets analysis of samples deposited with $A_s = 8.8$ mm^2 (a) and 11.1 mm^2 (b)

An analysis conducted using the droplet identification system, based on high contrast SEM imaging, enabled comparison of the density and size distribution of droplet-related nano- and micro-structures on the film surface. No significant variation in droplet density was observed as a function of spot size, while a slight increase in the average structure size was detected, as shown in Figure 3. This observation does not preclude the use of either film configuration as a Model System.

3.3. Deposition under inert background gas influence

A first experimental campaign investigated the effect of different argon pressures ($P = 1, 2, 3, 5, 10$ Pa) at fixed $d_{\mathrm{TS}} = 9$ cm, $A_s = 8.8\ \mathrm{mm}^2$, and nearly constant pulse energy $E_p = 630$ mJ. Proper energy moderation of the ablated species was verified by Optical Emission Spectroscopy. Three distinct regimes were identified, as displayed in Figure 4. For $P < 2$ Pa, compact and uniform films were obtained, with a reduced deposition rate compared to in-vacuum conditions. For $P > 2$ Pa, very thin layers in the 100-200 nm range were produced. These films were non-uniform and characterised by surfaces covered with aggregates, including needle-like structures, flakes, clusters, and filamentary formations. Visual inspection after deposition revealed a rapid loss of the mirror-like appearance, followed by gradual development of an opaque superficial layer. The sample deposited at $P = 2$ Pa exhibited intermediate behaviour. The investigation of a shorter target-substrate

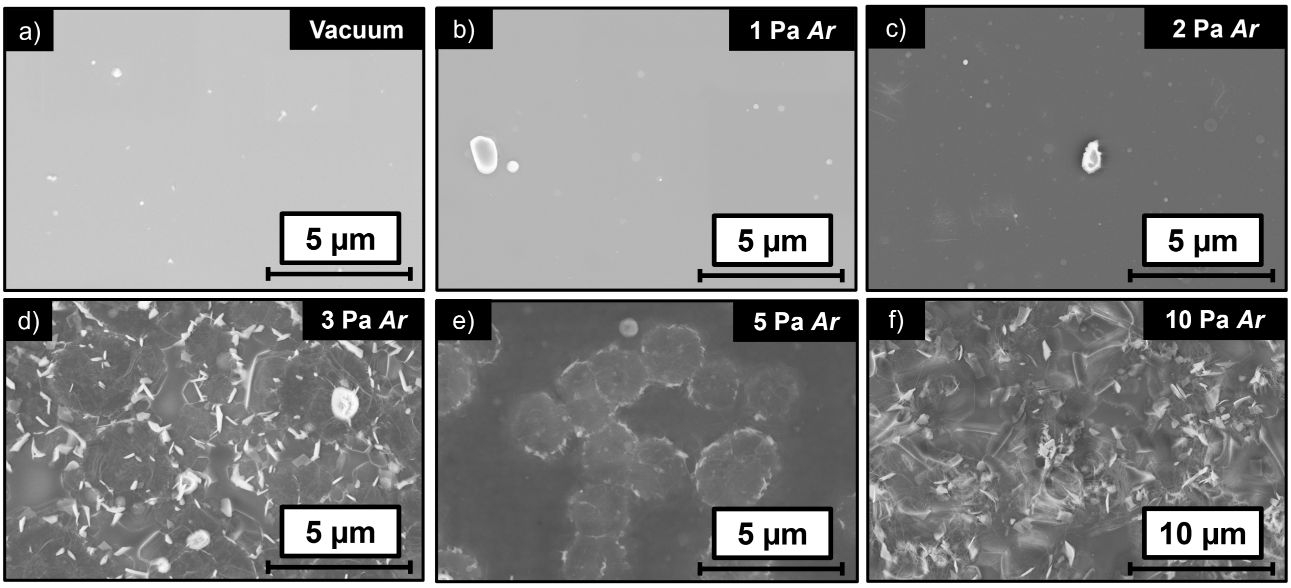

Figure 4: Boron films obtained through Ar pressure swipe at $d_{\mathrm{TS}} = 9$ cm

distance, $d_{\mathrm{TS}} = 7$ cm, provided evidence of porous internal structures at $P = 5$ Pa. However, channelling cracks and pronounced chemical instability were also observed. Another study, adopting helium, was conducted to evaluate the effect of inert gas mass, given its smaller mass difference with respect to boron, which results in higher energy loss per scattering event and more pronounced forward scattering.

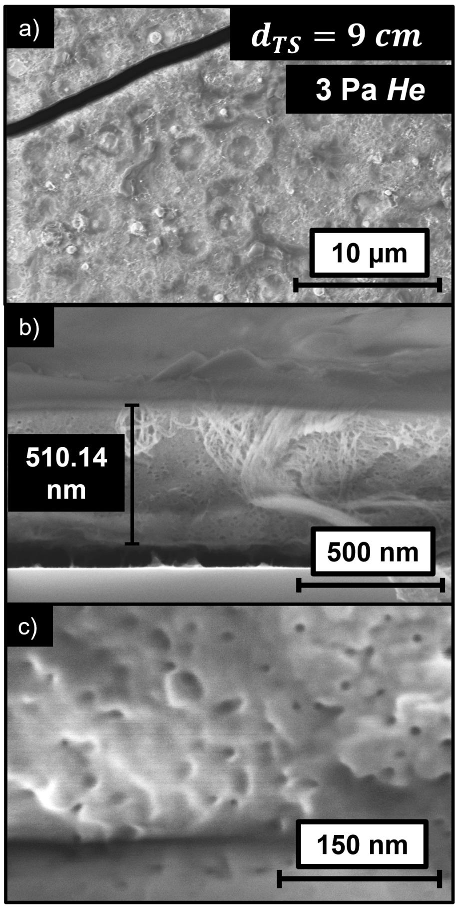

Figure 5: SEM images of film deposited at $P_{\mathrm{He}} = 3$ Pa and $d_{\mathrm{TS}} = 9$ cm: a) planar view; b) cross-section view; c) high magnification of nanostructure

Three combinations of pressure and d_{TS} were investigated. The sample deposited at $d_{\mathrm{TS}} = 7$ cm and $P_{\mathrm{He}} = 1$ Pa exhibited transitional behaviour, with more developed surface structures. Samples produced at $d_{\mathrm{TS}} = 9$ cm and $P_{\mathrm{He}} = 1$ and 3 Pa (Figure 5) showed porous cross-sections, chemical instability, cracking, and, at higher pressure, partial delamination. These films appear to consist of clusters that aggregate into a cohesive layer with clear evidence of voids. The void size is on the order of a few tens of nanometres, as observable in Figure 5.c, indicating relatively dense cluster packing.

Following bibliographical evidence [4], the chemical evolution of these films can be described as a three-step process. Initial oxidation of boron to B_2O_3, likely initiated during deposition and completed upon air exposure, is followed by formation of orthoboric acid H_3BO_3 through reaction with atmospheric moisture. Subsequent partial evaporation of boric acid, due to its low surface tension, further contributes to film evolution. EDX and EDDIE analyses, although qualitative due to the non-uniform morphology of porous films, indicate that the introduction of an inert background gas significantly increases oxygen content and reduces density, from approximately 2.5 $\mathrm{g\,cm^{-3}}$ for compact films to values below 2 $\mathrm{g\,cm^{-3}}$ for porous samples. A shorter d_{TS} leads to an overall density increase. Helium exerts a stronger influence on film composition than argon. Samples exhibiting higher chemical instability show an increased B/O ratio, consistent with boric acid evaporation. Raman spectroscopy enabled the identification of characteristic phonon peaks of $\mathrm{H_3BO_3}$, although strong fluorescence hindered clear observation of O-H and B-H vibrational modes. Mechanical instability, manifested as cracking and delamination, is attributed to tensile residual stresses generated during deposition. These stresses are primarily associated with the high concentration of structural defects, such as micropores, voids, and, in the case of boron PLD, droplets, which promote interatomic interactions and stress accumulation within the film.

3.4. Deposition under N_2 background gas influence

A preliminary study was carried out using three different nitrogen pressures, $P_{\mathrm{N_2}} = 5, 10, 20$ Pa, resulting in the deposition of chemically stable films with thicknesses on the order of one micron, as observable in Figure 6. Optical Emission Spectroscopy allowed identification of nitrogen de-excitation peaks, indicating the effective formation of reactive nitrogen species capable of bonding with boron during film growth. For all samples, SEM analysis revealed an apparently smooth surface composed of densely packed nanometric aggregates forming a highly compact layer. The films exhibited pronounced

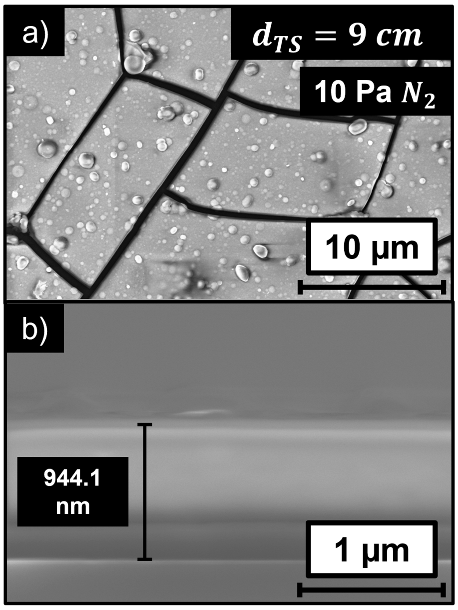

Figure 6: SEM images of film deposited at $P_{\mathrm{N}_2} = 3$ Pa and $d_{\mathrm{TS}} = 9$ cm: a) planar view; b) cross-section view

charging effects, consistent with dielectric behaviour. Channelling cracks were observed in each case. EDX measurements combined with EDDIE analysis indicated a density in the range $\rho = 1.65$–$1.85\,\mathrm{g/cm^3}$, lower than the density of amorphous boron nitride reported in the literature, $\rho = 2.1\,\mathrm{g/cm^3}$. This discrepancy can be attributed to the high oxygen content, approximately 45% for all samples, while nitrogen incorporation remains limited to about 10%. Despite the relatively low nitrogen fraction, the demonstrated capability of nitrogen to stabilise films containing a high concentration of B-O bonds represents a significant result.

4. Conclusion

The thesis activity, conducted within the framework of Model Systems for boronization and re-deposited materials on the first wall of magnetic confinement fusion (MCF) devices, consolidates the role of ns-PLD as a versatile technique for boron film production in fusion research.
The development and implementation of `PLDSim`, specifically designed for the ns-PLD system at NanoLab, enabled control of the ablation process and more efficient target utilisation. Combined with the enhanced uniformity achieved through the adoption of a pristine target, and the experimental evidence of an increased deposition rate with comparable nano- and macro-structures obtained by enlarging the laser spot size, the system now allows efficient in-vacuum production of compact boron films that meet the requirements for Model Systems representative of standard boronization coatings. By adjusting the inert gas background pressure (Ar and He) and the target-substrate distance d_{TS}, a systematic investigation of morphological modifications was carried out. Evidence of a porous-like internal structure was observed for $P_{\mathrm{Ar}} = 5$ Pa at $d_{\mathrm{TS}} = 7$ cm and for $P_{\mathrm{He}} = 1,3$ Pa at $d_{\mathrm{TS}} = 9$ cm. All samples exhibiting such morphology showed pronounced chemical instability upon air exposure. The oxidation process and boric acid formation were analysed by Raman spectroscopy, and possible mitigation strategies were discussed, also in relation to the mechanical instability observed in the porous films. Finally, the capability of the technique to produce boron films with controlled nitrogen incorporation of approximately 10% was demonstrated. Although these samples still present mechanical instability, they exhibit chemically inert behaviour upon air exposure.
Future developments of this work include the mechanical and chemical stabilisation of porous and nitrogen-incorporated films, the investigation of compositional thresholds governing oxygen uptake and boric acid formation, particularly under hydrogenic conditions relevant to MCF devices, and the implementation of physically based ablation models within `PLDSim`.

References

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