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1. Chimie des Interactions Plasma-Surface (ChIPS), Faculté des Sciences, Université de Mons.
2. Institut d'Electronique de Microélectronique et de Nanotechnologie–Site de Valenciennes (IEMN–UMR CNRS 8520), Université Polytechnique Hauts-de-France.

**Relation procédé–plasma–propriétés des matériaux lors du
dépôt de couches minces de titanate de bismuth sodium par
pulvérisation cathodique magnétron**

JURY

Prof. Stéphanos KONSTANTINIDIS	UMONS	Co-promoteur
Prof. Denis RÉMIENS	UPHF	Co-promoteur
Prof. François RENIERS	ULB	Rapporteur
Prof. Christophe CIBERT	Unicaen	Rapporteur
Prof. Carla BITTENCOURT	UMONS	Examinatrice
Prof. Kristiaan TEMST	KU Leuven	Président du jury/Examinateur

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Doctoral School :

Doctoral School University of Mons.

Doctoral School Polytechnique Hauts-de-France (ED PHF n°635).

Research unit:

1. Plasma-Surface Interaction Chemistry Laboratory (ChIPS), Faculty of Sciences, University of Mons.
2. Institute of Electronics, Microelectronics and Nanotechnology–Valenciennes site (IEMN–UMR CNRS 8520), Université Polytechnique Hauts-de-France.

**Process-Plasma-Material Properties Relationship in the
Deposition of Bismuth Sodium Titanate Thin Films by
Magnetron Sputtering**

JURY

Prof. Stéphanos KONSTANTINIDIS	UMONS	Co-supervisor
Prof. Denis RÉMIENS	UPHF	Co-supervisor
Prof. François RENIERS	ULB	Rapporteur
Prof. Christophe CIBERT	Unicaen	Rapporteur
Prof. Carla BITTENCOURT	UMONS	Examiner
Prof. Kristiaan TEMST	KU Leuven	President of the jury/Examiner

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General introduction

The inorganic ferroelectric piezoelectric materials are an important class of materials due to their precise control of deformation in the pm range and the feasibility of their growth in nanostructured formats. Their thin films are very interesting because they are compatible with the current microelectronics industry and have numerous applications, including MEMS-based devices. The $\text{Pb}(\text{Zr}_{1-x}\text{, Ti}_x)\text{O}_3$ or PZT is currently considered the industry leader due to its compositional versatility for use as both a piezoelectric sensor and actuator. However, the presence of carcinogenic Pb in its composition underscores the need to explore its alternatives. $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT) is a promising candidate for actuator applications; however, its film synthesis by the widely used magnetron sputtering technique presents challenges. Morphological challenges comprise the formation of large NaO_x surface defects, which compromise the film's suitability for device applications. Compositional challenges include the excess deposition of Bi during film growth and the sublimation-driven loss of Na during post-annealing, thereby forming bismuth titanate secondary phases alongside the primary BNT phase, ultimately reducing the overall ferroelectric and piezoelectric performance.

The work described in this thesis concerns our findings on the above-stated issues in BNT thin films grown by magnetron sputtering using powder targets. These challenges were investigated thanks to plasma diagnostics and surface analysis of the powder targets and the deposited films for selected deposition conditions, complemented by the sputtering and transport simulations to better understand the target-plasma-film chemistry correlation. The manuscript is overall divided into four chapters:

- First chapter focuses on the literature review about the state of Pb-free inorganic piezoelectric materials and their thin films. It also explores literature on magnetron sputtering, plasma processes, and thin film growth. Finally, it provides a detailed review of the sputter-deposited BNT films and their concerning challenges.
- Second chapter presents the materials and methods used in the experimentations, data processing, and results presentation. It also introduces the Monte Carlo codes used for the target sputtering and transport processes.
- Third chapter presents a detailed study of target surface conditioning, where the compositions of the target surface, plasma ions, and as-deposited films were analyzed to monitor the stabilization of the target surface. The surface composition of the conditioned targets was subsequently recorded and used as input for the sputtering simulations presented in the following chapter.
- Fourth chapter describes the growth of BNT films using conditioned targets. Simulations were performed to predict the composition and average kinetic energy of the deposition flux arriving at the substrate. The plasma ion chemistry together with the film composition before and after annealing were systematically investigated to better understand the correlation between the target-plasma-film chemistry, as well as the origin of morphology- and composition-related issues in BNT thin films.
- Fifth chapter offers an overall summary of the main findings of this work and discusses possible directions for future research on this subject.

Chapter 1 Sputter Deposited BNT Thin Films:

Fundamentals and Challenges

This chapter provides an overview of the fundamental principles of piezoelectric effects and materials, with a focus on current progress in Pb-free thin film-based piezoelectric microactuators. It further outlines the essential concepts of the sputtering process, plasma chemistry, and thin film growth mechanisms. Finally, it reviews the state of the art in depositing $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT) thin film by Magnetron sputtering, highlights the key challenges encountered, and presents a strategy for their systematic investigation.

1.1 Piezoelectric Effects

The term ‘Piezoelectricity’ originates from two Greek words: “Piezein”, which means pressure, and “Elektron”, which means electricity. It refers to the ability of certain electrical insulating materials to generate an electric charge across them when subjected to mechanical stress, as illustrated in Figure 1-1 (a). The piezoelectric effect was first observed by Abbé René-Just Haüy in 1817, but formally studied by the brothers Jacques and Pierre Curie in 1880. During their experiments with crystals like quartz, tourmaline, and Rochelle salt, they demonstrated that mechanical stress can be converted into electric charges ¹. The following year, reciprocity of the piezoelectric effect was theoretically predicted by Gabriel Lippmann ² and experimentally confirmed by the Curie brothers ³, as illustrated in Figure 1-1 (b). Further, many studies were conducted to develop a better understanding of the relationship between crystallinity and piezoelectric effects ⁴. Piezoelectricity is typically defined as the linear coupling between electrical and mechanical energies; however, its bi-directional conversion is not entirely efficient. Piezoelectric materials that demonstrate a higher ‘direct’ piezoelectric effect usually tend to have

lower ‘inverse’ piezoelectric performance and vice versa. It is generally measured by the piezoelectric charge or strain coefficients (d or d^*), where d_{33} and d_{31} represent the generated electric charge in 1D (out-of-plane) and 2D (in-plane) fashion, respectively. The ‘Soft Piezoelectrics’ describe the materials having a prominent direct piezoelectric effect, while ‘Hard Piezoelectrics’ designates those with a higher inverse piezoelectric effect, which are used in the ‘Sensors’ and ‘Actuators’ applications, respectively. The first practical application of piezoelectric effects was demonstrated by Paul Langevin in 1917 during WWI by developing Quartz-based Sonar technology ⁵. Later in 1947, Roberts *et al.* discovered that polycrystalline BaTiO₃ ceramics have about 100 times higher piezoelectricity as compared to quartz crystals when poled under higher voltages ⁶. In 1954, Jaffe *et al.* found that the piezoelectric efficiency of PbZrO₃–PbTiO₃ (PZT) solid solution ceramics is around double compared to that of the BaTiO₃ ceramics ⁷. The discovery of oxide-based high-quality piezoelectric ceramics, followed by the development of their nanostructures, such as thin films, paved the way for their applications across various fields, including microelectronics, biomedicine, energy harvesting, and aerospace.

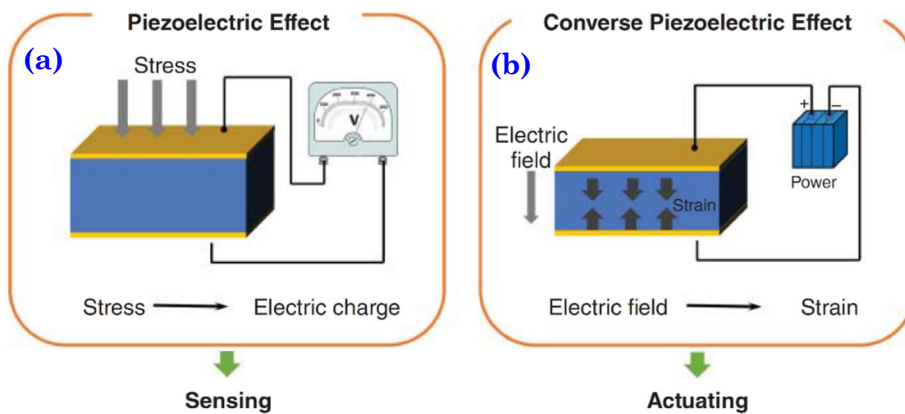


Figure 1-1: Schematic illustration of the Piezoelectric effects, (a) Direct piezoelectric effect used by sensors, (b) Inverse piezoelectric effect used by actuators ⁸.

1.1.1 Piezoelectric Materials

Generally, certain types of crystalline materials exhibit strong piezoelectric character. There are 32 categories of 3D crystalline structures, of which 11 are centrosymmetric and 21 are non-centrosymmetric. When the latter type of structures (except the cubic class 432) are subjected to external pressure, electric dipoles appear across them along with the physical deformation. Among the 20 non-centrosymmetric piezoelectric crystalline structures, only 10 types are ferroelectric, exhibiting spontaneous polarization, referred to as polar point groups. Pure piezoelectric materials exhibit electric charges only under mechanical pressure, with lower piezoelectric coefficients, and have fixed positions of the electric dipoles. On the other hand, Ferroelectric piezoelectric materials exhibit spontaneous polarization and possess higher piezoelectric coefficients that can be reversed when subjected to strong external electric fields⁸. Such ferroelectric piezoelectric crystalline materials are indeed the subject of this thesis. The categorical framework of non-centrosymmetric crystalline materials is shown in Figure 1-2.

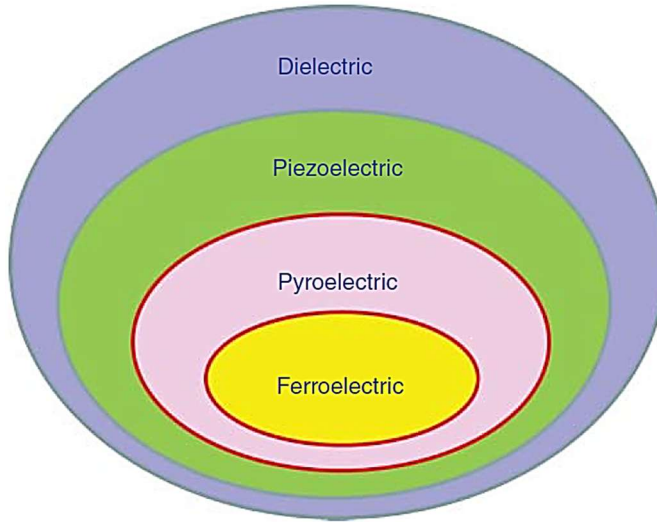


Figure 1-2: Schematic illustration of non-centrosymmetric crystalline classes and the relationship among them. All ferroelectric materials

possess dielectric character, but a limited number of dielectric materials can have ferroelectric characteristics ⁸.

On the nanoscale (order of 10–100 Å), ferroelectric materials are composed of tiny ‘polar domains’ which are separated by the ‘domain walls’. A strong electric voltage, in the range of kV, is used to align those polar domains in one direction to highlight their overall ferroelectric character, called the process of ‘Poling’. However, in an unpoled state, the bulk ceramics are electrically neutral on the macroscale due to the overall directions of the polar domains, which almost cancel out the net charge. Those polar domains can be rearranged in a chosen direction when the material is poled by a sufficiently strong electric field (E , kV). However, the overall polarization (P) shows a hysteresis cycle, as shown in Figure 1-3. When the E field is applied to the material, it deforms in the direction of the electrical gradient, showing a mechanical strain due to the re-orientation of its polar domains, which can reach a maximum up to a ‘Saturation Polarization’ (P_s). Later, when the E field is removed, the polar domains partially revert but mostly sustain their new course, demonstrating a ‘Remnant Polarization’ (P_r). The P_r can be eliminated by applying an opposite E field of a certain amplitude, called the ‘Coercive Electric Field’ (E_c). The Curie Temperature (T_c) is an important parameter of the piezoelectric materials, beyond which they become ‘Paraelectric’ and their P_r disappears, resulting in a linear P - E hysteresis whose slope indicates the permittivity of the material ⁹. Another critical parameter is the Depolarization Temperature (T_d), which is usually lower than the T_c and demonstrates the Anti-ferroelectric character. Applying the E field in the temperature window of $T_d - T_c$, half of the tiny ferroelectric domains switch their polarity in the opposite direction to the other half, which leads to the cancellation of polarization on the macroscale and produces a double hysteresis loop.

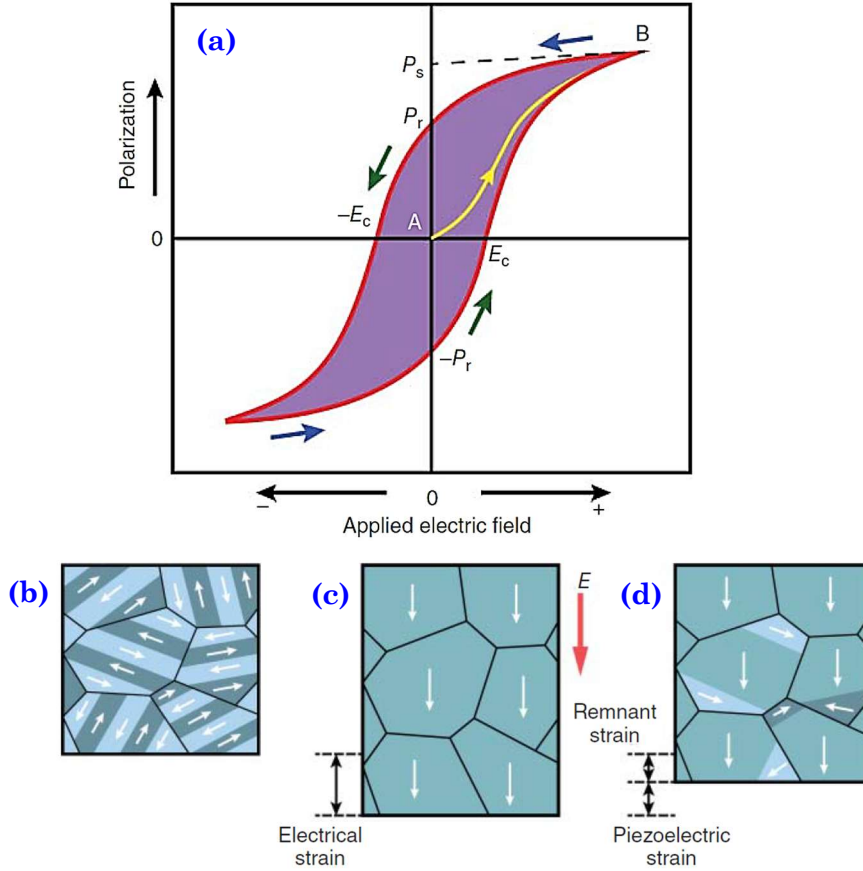


Figure 1-3: Schematic illustration of (a) the P - E hysteresis loop and the Poling process, showing the alignment of ferroelectric domains and the resultant strains under an electric field. (b) virgin state (c) saturation state (d) remnant state ⁸.

1.1.2 Perovskite Crystal Structure

Following its discovery by Gustav Rose in 1839, the Perovskite crystal structure has demonstrated superior functional properties across a range of applications, including superconductivity, magnetism, photovoltaics, catalysis, thermoelectricity, ferroelectricity, and piezoelectricity ¹⁰. The versatile perovskite structure can exhibit multiple symmetry variants depending on the material composition, cation sizes, temperature, and external pressure. These structures include Cubic ($Pm\bar{3}m$, paraelectric), Tetragonal ($P4mm$, ferroelectric), Orthorhombic

(*Pbnm*, centrosymmetric but prone to distortions so ultimately a ferroelectric), Rhombohedral (*R3c*, ferroelectric), Hexagonal (*P3c1*, multiferroic), Monoclinic (*Cm*, ferroelectric), and Triclinic (*P1*, metastable but potentially ferroelectric). The general formula of perovskite structure is ABX_3 , and the Goldschmidt tolerance factor governs its stability ($0.88 < t < 1.05$) that depends upon the ionic radii (R_A, R_B, R_X) and the difference in the ions' electronegativities, as shown below in Equation 1.1.

$$t = \frac{R_A + R_X}{\sqrt{2}(R_B + R_X)} \quad (1.1)$$

The cubic perovskite structure, with a tolerance factor close to 1, generally has a larger 'A-site' cation like Ba^{2+} , Pb^{2+} , Bi^{3+} on the cube corners, a smaller 'B-site' cation like Zr^{4+} , Ti^{4+} , Nb^{5+} on the cube center, and 'X-site' anion like Cl^{-} , Br^{-} , I^{-} , O^{2-} on the cube's face centers, alongside the existence of each 'A' cation at the central position of a cuboctahedral cavity composed of eight ' BX_6 ' octahedrons. When the ionic radii or electronegativity differences shift within the Goldschmidt tolerance limit, the cubic structure can distort into lower-symmetry forms (e.g., tetragonal, orthorhombic, or rhombohedral). These distortions are the source of non-centrosymmetry in the crystalline structure of perovskites, which create electric dipoles in the unit cells and enable their ferroelectric character, as shown in Figure 1-4.

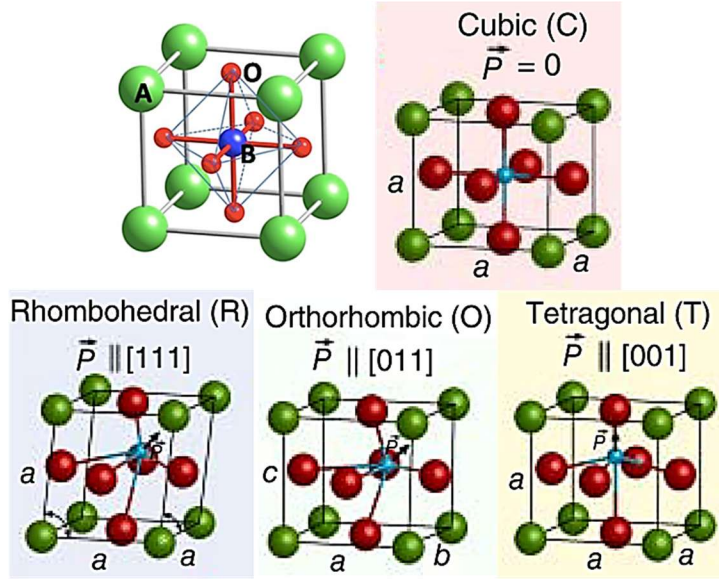


Figure 1-4: Schematic illustration of the Perovskite structure in Non-polar (Cubic) and Polar formats (Rhombohedral, Orthorhombic, and Tetragonal) ⁸.

1.1.3 Lead-based Materials: $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$

Among the ferroelectric piezoelectric ceramics, BaTiO_3 was the first to be discovered ⁶; however, it has a comparatively lower Curie temperature ($T_c \sim 130^\circ\text{C}$), which limits its utility across a range of applications ¹¹. The PZT [$\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$], a solid solution of rhombohedral PbZrO_3 (antiferroelectric) and tetragonal PbTiO_3 (ferroelectric) phases with a Morphotropic Phase Boundary (MPB), was soon discovered to have piezoelectric efficiencies double as that of the BaTiO_3 and T_c above 300°C , which swiftly captured most of the piezoelectric market and is still the leader today ^{7, 12}. The MPB is the composition-driven transition region in a solid solution where two crystallographic phases (e.g., rhombohedral and tetragonal) coexist, leading to enhanced piezoelectric characteristics. At the MPB composition, both phases coexist with minimal temperature dependence—

demonstrating the excellent temperature stability of PZT ceramics—as shown in the phase diagram in Figure 1-5.

The PZT has demonstrated excellent piezoelectric properties, like the electrostrain of 0.57% under an electric field of 2 kV/mm in ceramic form ¹³ and an even higher electrostrain of 0.9% under an electric field of 200 kV/cm, with a d_{33}^* of 450 pm/V in a 4-micron thick film grown by the Pulsed laser deposition (PLD) technique ¹⁴. Besides the existence of MPB, the composition of PZT piezoceramics can also be easily adapted to ‘soft’ and ‘hard’ piezoelectric applications through substitution and doping, making them ideal for use as sensors, actuators, and transducers. However, PZT is facing significant environmental concerns as it contains a large amount of Pb, which is being banned globally. For instance, the European Union’s directives: Waste Electrical and Electronic Equipment (WEEE) and Restriction on the use of certain Hazardous Substances (RoHS) in electrical and electronic equipment, alongside the regulations by North America, Japan, South Korea, and China, which allow merely 0.1 wt% usage of Pb ⁸.

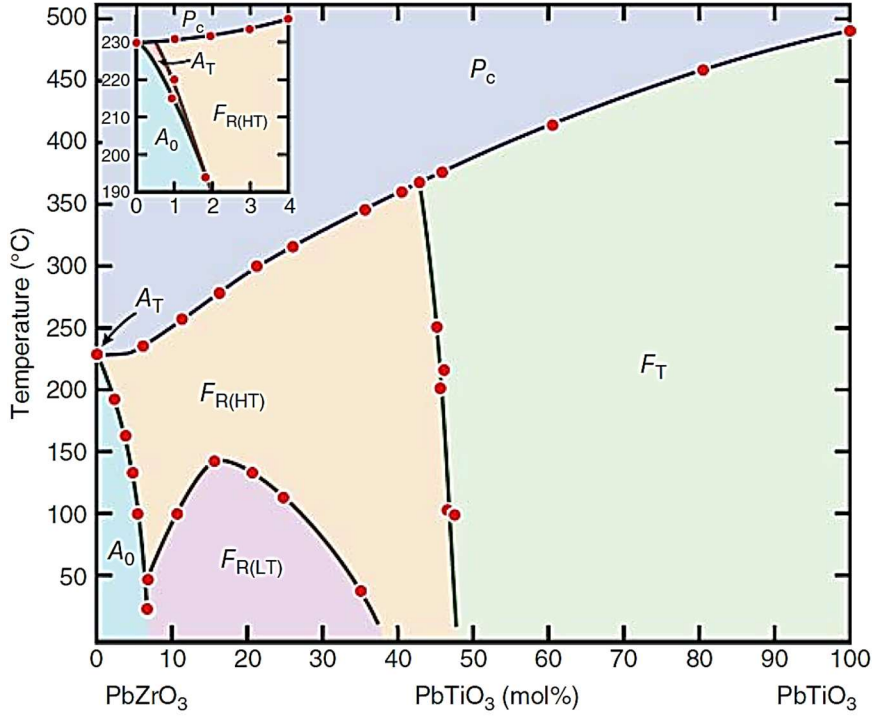


Figure 1-5: Phase diagram of the PZT ceramic material system. A_0 , A_T , $F_{R(LT)}$, $F_{R(HT)}$, P_C , and F_T represent the antiferroelectric phase of $PbZrO_3$, antiferroelectric-tilted phase, low-temperature rhombohedral ferroelectric phase, high-temperature rhombohedral ferroelectric phase, cubic paraelectric phase, and tetragonal ferroelectric phase, respectively

12.

1.1.4 Lead-Free Materials: $(K_{0.5},Na_{0.5})NbO_3$

The $(K_{0.5},Na_{0.5})NbO_3$ or KNN piezoceramics were discovered by Jaeger *et al.* back in 1962, showing a higher dielectric constant ' ϵ ' of 420 and piezoelectric constant ' d_{33} ' of 160 pC/N along with a T_C of $\sim 200^\circ\text{C}$ ¹⁵. Similar to the PZT, KNN also has MPB between the ferroelectric $KNbO_3$ and antiferroelectric $NaNbO_3$ phases; however, it gained very little attention onwards due to the difficulties during sintering caused by the evaporation-based losses of K and Na. Later in 2004, Saito *et al.* sparked interest by demonstrating the d_{33} of 416 pC/N in the highly oriented (001) crystallographic textured KNN-based piezoceramics ¹⁶. Tao *et al.* demonstrated further enhanced piezoelectric properties of non-textured

KNN-based ceramics with a d_{33} of 650 ± 20 pC/N by stabilizing a multiphase Rhombohedral-Orthorhombic-Tetragonal (*R-O-T*) system through doping of multiple elements ¹⁷. Li *et al.* further improved the piezoelectric performance of textured KNN-based piezoceramics [(K,Na)(Nb,Sb)O₃-CaZrO₃-(Bi,K)HfO₃] and achieved the so far highest d_{33} of 704 pC/N and d_{33}^* of 980 pm/V ¹⁸. A list of some essential studies on KNN-based ceramics is provided on the following pages, while the phase diagram of the KNN-based material system and the evolution of its piezoelectric coefficient are given in Figures 1-6 and 1-7, respectively.

The development of a reliable and industry-compatible fabrication protocol for KNN thin films deposition has also been explored in detail. Wakasa *et al.* deposited 2-micron thick polycrystalline KNN films with preferred c-axis orientation on a Pt/Ti/Si/SiO₂/Si substrate at a growth temperature of 680°C by RF magnetron sputtering in Ar and O₂ mixed gas atmosphere and demonstrated a d_{31}^* of -53.5 pm/V at 20 V_{pp} ¹⁹. Li *et al.* deposited 600 nm thick c-axis oriented KNN films on LaNiO₃ (LNO)/Si substrate at a growth temperature of 550°C in a mixed gas environment of Ar and O₂ (4:1) at ~10 mTorr pressure by sputtering a stoichiometric ceramic target. The films annealed by Rapid Thermal Annealing (RTA) in an O₂ ambient at 750°C with an LNO counter electrode demonstrated ϵ_r of 899 at 1 kHz, d_{33} of 58 pm/V, P_r of 12 $\mu\text{C}/\text{cm}^2$ ²⁰. Kim *et al.* followed the sputtering route and deposited 330 nm thick, (100)-oriented KNN films on Sr₂Nb₃O₁₀/Pt/Si at a growth temperature of 350°C in a mixed gas environment (Ar:O₂ = 4:1) at a pressure of 10 mTorr and 100W RF power. The as-deposited films were annealed at 300°C under a 50 Torr oxygen ambient, which achieved ϵ_r of 278 with a loss of 1.7% at 100 kHz, d_{33}^* of 175 pm/V, P_r of 17.7 $\mu\text{C}/\text{cm}^2$, and E_c of 120 kV/cm ²¹. Sumitomo Chemicals Japan has recently commercialized KNN piezoelectric thin film wafers with KNN layers up to 4 microns thick, exhibiting piezoelectric properties

comparable to those of PZT films. To conclude, (001) texturing, MPB formation, and carefully designed post-processing are promising pathways for high-performance piezoelectric KNN-based ceramics and films.

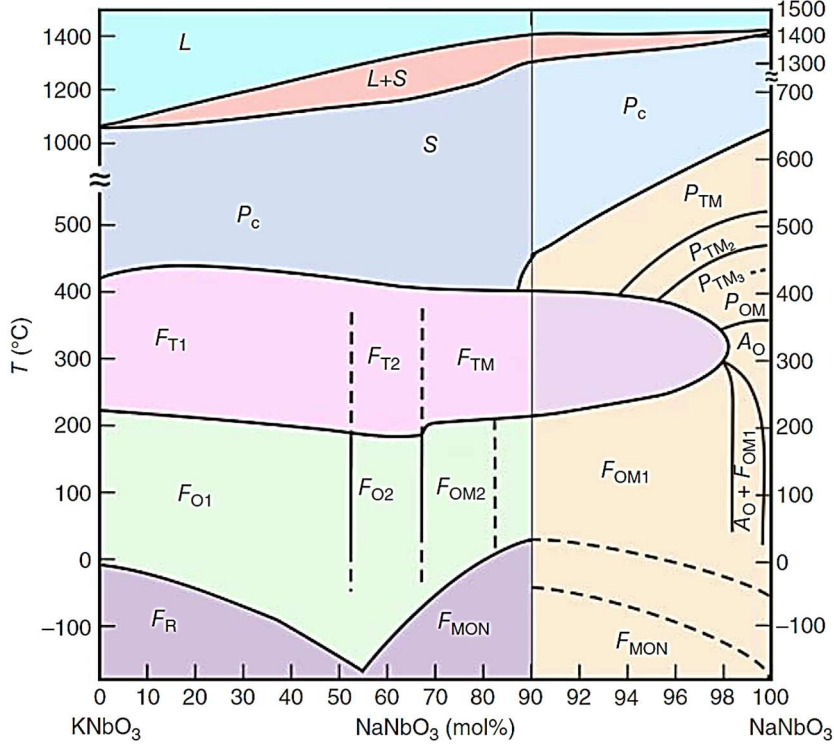


Figure 1-6: Phase diagram of the KNN ceramic material system. The F, A, P, L, and S represent ferroelectric, anti-ferroelectric, paraelectric, liquid, and solid phases, respectively. The subscripts R, O, C, and T represent rhombohedral, orthorhombic, cubic, and tetragonal crystalline phases ²².

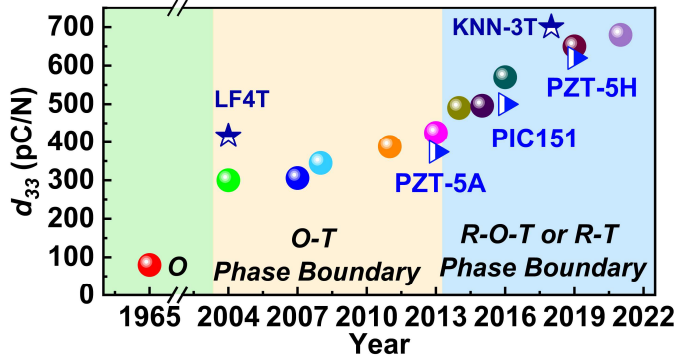


Figure 1-7: Evolution of d_{33} in KNN and PZT-based ceramics w.r.t. crystalline phases. O, T, and R represent the orthorhombic, tetragonal, and rhombohedral crystalline phases. Their combinations denote the MPB amongst various phases ²³.

1.1.5 Lead-Free Materials: $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$

Following its discovery by Smolenskii *et al.* in 1961 ²⁴, Bismuth sodium titanate ($\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$, BNT) has garnered considerable attention as a promising Pb-free perovskite piezoelectric material, particularly due to its potential to replace PZT in Microactuator applications ²⁵. It shows a strong ferroelectric character with a P_r of $38 \mu\text{C}/\text{cm}^2$, E_c of $73 \text{ kV}/\text{cm}$, ϵ_r of $500 - 700$ (dielectric loss of $0.04 - 0.05$), and d_{33} of $70 \text{ pC}/\text{N}$ ²⁶ alongside a moderately high T_C of 320°C and a T_D around 230°C ²⁷. Due to difficulties in sintering caused by the loss of evaporated Na, BNT ceramics usually have Bi-secondary phase formation, resulting in relatively lower piezoelectric properties ($d_{33} \sim 100 \text{ pC}/\text{N}$) ²⁸. Nonetheless, cation substitution at the A and/or B sites has been extensively explored to enhance the properties of BNT piezoceramics ²⁹. Takenaka *et al.* substituted the A-site (Bi, Na) of BNT ceramics with Ba by composing a solid solution of $(1-x)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ -(x) BaTiO_3 , which demonstrated the MPB of rhombohedral BNT and tetragonal BT phases at 6 mol% BaTiO_3 , similar to that of the PZT. The 0.94BNT-0.6BT resulted in enhanced piezoelectric properties ($d_{33} 125 \text{ pC}/\text{N}$, $k_{33} 55\%$) with decreased temperature ranges ($T_C 288^\circ\text{C}$, $T_D 130^\circ\text{C}$), phase diagram shown in Figure

1-8²⁹. Sasaki *et al.* composed a similar solid solution of $(1-x)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ - $(x)\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ having the MPB between rhombohedral BNT and tetragonal BKT phases at 16-20 mol% $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ ³⁰. The solid solutions like BNT-BKT and BNT-BT-BKT ceramics have demonstrated superior piezoelectric properties (d_{33} : 144 – 231 pC/N, d_{33}^* : 250 – 1400 pm/V) and (d_{33} : 170 – 298 pC/N, d_{33}^* : 314 – 857 pm/V), respectively^{31, 32}. In summary, MPB can further enhance the piezoelectric performance of the BNT-based ceramics. A comparison of various piezoelectric material systems, in terms of performance and temperature ranges, is shown in Figures 1-9 and 1-10.

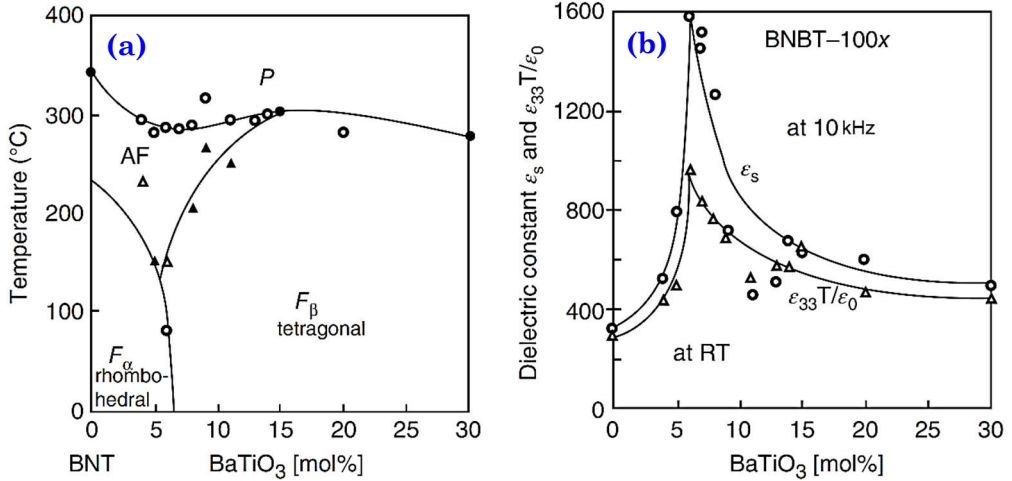
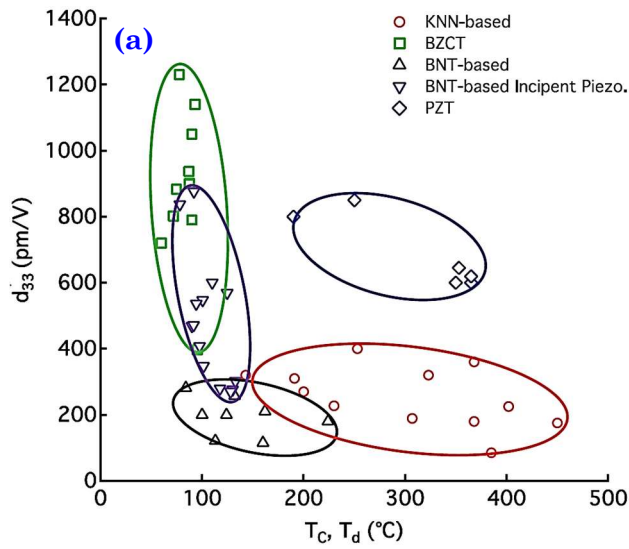
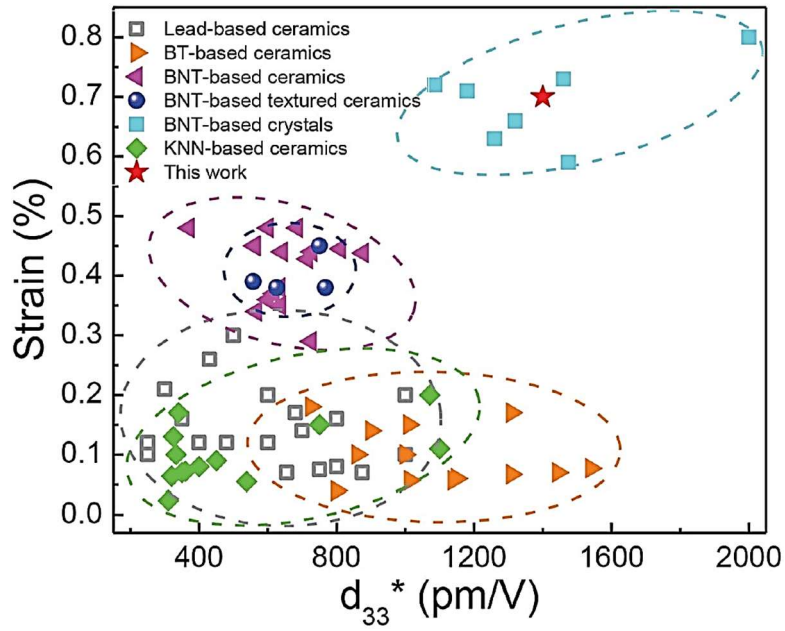


Figure 1-8: Takenaka *et al.* proposed (a) Phase diagram of $(1-x)\text{BNT} - (x)\text{BT}$ system. The terms F, AF, and P describe the ferroelectric, anti-ferroelectric, and paraelectric phases (b) Correlation of the dielectric properties with the material composition, showing the best BNT-BT system performance around 6 mol% BaTiO_3 ²⁹.



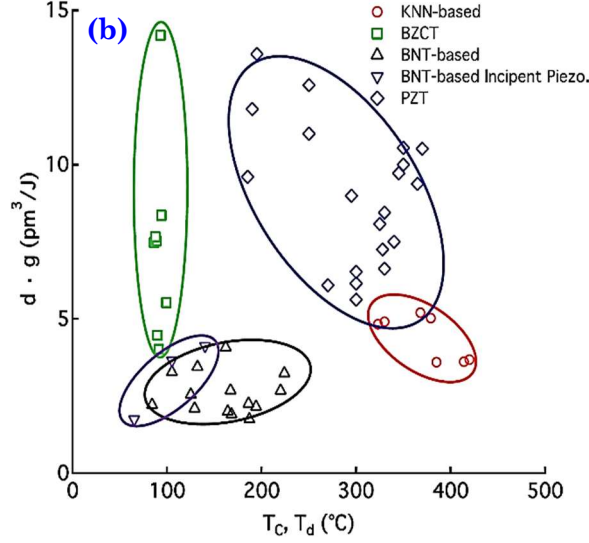


Figure 1-10: (a) The d_{33}^* Vs depolarization temperature ranges of various piezoelectric materials (BZCT: (Bi,Zn)(Co,Ti)O₃) (b) The product of piezoelectric strain coefficient (d) and the piezoelectric voltage coefficient (g) as a function of depolarization temperature. In both scenarios, BNT-based ceramics show moderate efficiencies ³¹.

1.2 BNT Thin Films: Growth Techniques

The growth of BNT films has been achieved through various routes, which can be divided into two main categories: solution chemistry synthesis and Vacuum-based deposition.

1.2.1 Solution Chemistry Synthesis

The solution chemistry route can be commonly described as a technique in which precursors exist in a solution phase, precipitating into a film format on the substrate's surface after solvent evaporation. It comprises methods such as sol-gel, Chemical Solution Deposition (CSD), and Metalorganic Decomposition (MOD), among others. Generally, Sol-gel spin-coating is the most studied solution chemistry technique for synthesizing BNT and BNT-based thin films. In the sol-gel process, metal precursors, typically organic salts, are dissolved in organic solvents along with catalysts and water, under continuous stirring and heating. The

catalysts facilitate the hydrolysis reaction, which forms an extended network of metal hydroxides, marking the completion of the sol preparation. This sol is then spin-coated onto the substrate surface, followed by an annealing step at 200–300 °C to evaporate the solvents and water, and to densify the precursors into M–O–M bonds. To achieve greater film thickness, the spin-coating and low-temperature annealing steps are repeated. Finally, a high-temperature post-annealing treatment ($\geq 500^\circ\text{C}$) is performed to promote long-range crystallization within the film

³⁴.

Although the sol-gel method allows for easier control over composition in terms of doping, the resultant films are not only porous but also deficient in Bi and Na due to their high volatility caused during post-annealing. The imbalance of the composition is compensated either by increasing the concentration of Bi and/or Na in the sol preparation phase or by performing the crystallization at comparatively lower temperatures for longer durations ³⁵⁻⁴¹. The BNT films synthesized by the sol-gel method generally don't show a very high piezoelectric response $<50 \text{ pm/V}$ ⁴²⁻⁴⁴ due to the inherent porosity issues, however, BNT-based derivatives have shown some impressive results. Li *et al.* synthesized (100) oriented BNT–BT–ST $[\text{0.755Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{--}0.065\text{BaTiO}_3\text{--}0.18\text{SrTiO}_3]$ films by the sol-gel technique on $\text{LaNiO}_3/\text{Pt}(111)/\text{Ti}/\text{SiO}_2/\text{Si}$ substrate and demonstrated a piezoelectric response of the film as $d_{33,f}$ of 140 pm/V ⁴⁵. Xu *et al.* doped Mn inside the BNT-SBT $[(0.8)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{--}(0.2)(\text{Sr}_{0.7}\text{Bi}_{0.2-0.1})\text{TiO}_3\text{--}1\text{mol\% Mn}]$ by the sol-gel method and synthesized BNT-SBT thin films on $\text{Pt}(111)/\text{Ti}/\text{SiO}_2/\text{Si}$ substrate, showing a $d_{33,f}$ of $\sim 144 \text{ pm/V}$ ⁴⁶. Furthermore, Chen *et al.* achieved an impressive $d_{33,f}$ of $\sim 159 \text{ pm/V}$ from BNT-BKT $[\text{Bi}_{0.5}(\text{Na}_{0.85}\text{K}_{0.15})_{0.5}\text{TiO}_3]$ films synthesized by the sol-gel method ⁴⁷. Below is a list of essential works on BNT thin film growth using various solution chemistry techniques.

Structure and Composition	Synthesis Technique	Thickness (nm)	ϵ_r	P_r ($\mu\text{C}/\text{cm}^2$)	E_C (kV/cm)	$d_{33,f}$ (pm/V)	Ref.
Si/LaNiO ₃ (100)/Bi _{0.5} Na _{0.5} (Ti _{0.98} Fe _{0.02})TiO ₃ (100)	Sol-gel	300	485	27.6	60	19.6	48
Si/SiO ₂ /Ti/Pt/poly-(Bi _{0.5} Na _{0.5})TiO ₃	Sol-gel	520	277	8.3	200	24.8	49
Si/Pt/poly-0.89(Bi _{0.5} Na _{0.5})TiO ₃ – 0.11BaTiO ₃	Sol-gel	260	164	1.6	85	29	42
Si/SiO ₂ /TiO ₂ /Pt/poly-(Bi _{0.5} Na _{0.5})TiO ₃	Sol-gel	350	425	9	46	47	44
Si/SiO ₂ /TiO _x /Pt/poly-(Bi _{0.5} Na _{0.5})TiO ₃ – 1 mol% Mn	CSD	500	-	44	165	50-60	35
Si/SiO ₂ /TiO ₂ /Pt/poly-(Bi _{0.5} Na _{0.5})TiO ₃	CSD	600	-	5	52	67	50
Si/SiO ₂ /TiO _x /Pt/poly-(72.5 mol% BNT– 22.5 mol% BKT–5 mol% Bi(Mg _{0.5} Ti _{0.5})O ₃	CSD	270	620	12	51	75	51
Si/SiO ₂ /Ti/Pt(111)/poly- (0.94)Bi _{0.5} Na _{0.5} TiO ₃ -(0.06)BaTiO ₃	Sol-gel	200	440	12	87	83	52
Si/SiO ₂ /Ti/Pt/poly-(0.94)Bi _{0.5} Na _{0.5} TiO ₃ - (0.06)BaTiO ₃	MOD	230	504	24	103	94	53

Si/Pt/poly-0.92(Bi _{0.5} Na _{0.5})TiO ₃ – 0.08BaTiO ₃	Sol-gel	65	243	0.87	220	100	⁵⁴
Si/SiO ₂ /TiO ₂ /Pt/poly- 0.755(Bi _{0.5} Na _{0.5})TiO ₃ –0.065BaTiO ₃ – 0.18SrTiO ₃	Sol-gel	-	630	-	-	140	⁵⁵
Si/SiO ₂ /Ti/Pt(111)/poly-0.8(BNT)– 0.2(Sr _{0.7} Bi _{0.2-0.1})TiO ₃ – 1 mol% Mn	Sol-gel	310	570	11.4	56	144	⁴⁶
Si/SiO ₂ /Ti/Pt(100)/poly- Bi _{0.5} (Na _{0.85} K _{0.15}) _{0.5} TiO ₃	Sol-gel	680	-	38	315	158.9	⁴⁷

Table 1-1: Dielectric, ferroelectric, and piezoelectric performance of BNT-based films deposited by Solution Chemistry techniques

1.2.2 Vacuum-based Deposition

Film growth in a high-vacuum, solvent-free environment typically yields pure, uniform, and dense thin films. For BNT, two methods are predominantly reported: pulsed laser deposition (PLD) and magnetron sputtering. In PLD, short, high-energy laser pulses ablate the target, producing a plume of species that traverse the vacuum (or a controlled gas) and condense on an opposing substrate. The substrate is commonly heated to the film's crystallization temperature to promote epitaxial growth when lattice matching is favorable. Although PLD is considered a promising technique (illustrated in Figure 1-11), conventional PLD systems have their limitations. For example, the transport of ejected elements is very directional, limiting the compositional control over large substrate areas. Another problem is the re-evaporation of arriving species on the substrate surface due to continuous substrate heating, which causes different losses for each element, resulting in element-specific compositional imperfections in the film. Wang *et al.* used the PLD technique to grow 0.94BNT-0.06BT films doped with 0.5 mol% CeO₂ and 0.5 mol% La₂O₃, demonstrating a piezoelectric efficiency of 31 pm/V⁵⁶. In another study, Wang *et al.* further enhanced the piezoelectric response of the BNT-based films by using the Bi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}TiO₃ composition, achieving a value of 64 pm/V⁵⁷. Jin *et al.* used 0.5 mol% Mn doping in the 0.935BNT–0.065BT film, which decreased the leakage currents and resulted in a higher piezoelectric efficiency of 92 pm/V⁵⁸. Song *et al.* used a highly crystalline (001)-oriented SrTiO₃ substrate for the deposition of c-axis oriented BNT films and achieved a significant piezoelectric efficiency of 145 pm/V⁵⁹. Recently, Ishihama *et al.* demonstrated that the polycrystalline (1-x)(Bi_{0.5}Na_{0.5})TiO₃–xBaTiO₃ (x = 0.2–0.5) film composition with a thickness of 2 microns can reach a piezoelectric coefficient greater than 220 pm/V⁶⁰.

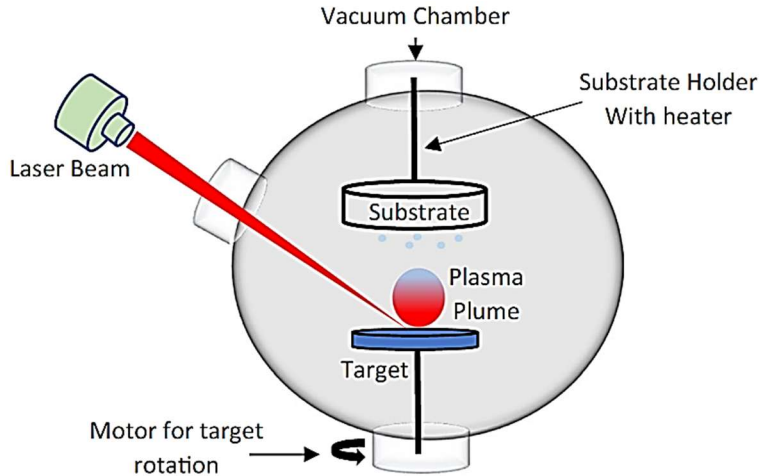


Figure 1-11: Schematic illustration of the PLD process ⁶¹.

Magnetron sputtering is another important vacuum-based deposition technique, where energetic ions (e.g., Ar⁺) eject target atoms that condense on a substrate, enabling the formation of large-area, uniform coatings with usually very good process control. Unlike PLD, it is widely used in microelectronics and is therefore employed here for the growth of BNT thin films. Nevertheless, reports on sputtered BNT are limited due to the scarcity of commercial BNT targets and the challenges of in-house target fabrication and process optimization. The first notable study on BNT piezoelectric films sputter deposition was carried out by Quignon *et al.*, in which they achieved a significant 80 pm/V efficiency by growing a 750 nm thick polycrystalline BNT film ⁶². Hamieh and Kossman *et al.* followed up on the work but were unable to exceed the 60 pm/V efficiency due to the hindrance of growing thicker films beyond 500 nm, resulting from the formation of sodium oxide surface defects that rupture during post-annealing, thereby destroying the film ⁶³⁻⁶⁵. However, Tanaka *et al.* managed to achieve 200 pm/V efficiency by growing 2 μm thick, c-oriented 0.93BNT – 0.07BT with 1 at.% Mn doping using the magnetron sputtering technique ⁶⁶. Below is a list of essential works on BNT thin film growth using PLD and sputtering techniques.

Structure and Composition	Synthesis Technique	Thickness (nm)	ϵ_r	P_r ($\mu\text{C}/\text{cm}^2$)	E_C (kV/cm)	$d_{33,f}$ (pm/V)	Ref.
(LaAlO ₃) _{0.3} (Sr ₂ AlTaO ₆) _{0.35} (001)/CaRuO ₃ (001)/0.94(Bi _{0.5} Na _{0.5})TiO ₃ – 0.06BaTiO ₃ – 0.5 mol% CeO ₂ – 0.5 mol% La ₂ O ₃ (001)	PLD	380	-	29.5	74	31	⁵⁶
Si/SiO ₂ (100)/LaNiO ₃ (100)/Bi _{0.5} Na _{0.5} TiO ₃ (100)	Sputtering	350	470	3.3	60	56	⁶³
Si(100)/LaNiO ₃ (100)/Bi _{0.5} Na _{0.5} TiO ₃ (100)	Sputtering	400	545	4	65	57	⁶⁷
Si/SiO ₂ /Ti/Pt/poly-[Bi _{0.5} (Na _{0.7} K _{0.2} Li _{0.1}) _{0.5}]TiO ₃	PLD	350	-	13.9	25	64	⁵⁷
Si/SiO ₂ /TiO _x /Pt(111)/poly-(Bi _{0.5} Na _{0.5})TiO ₃	Sputtering	750	520	12	125	80	⁶²
Si/SiO ₂ /Ti/Pt/0.935BNT – 0.065BT(001) – 0.5 mol% Mn	PLD	380	110 0	11.3	65	92	⁵⁸
SrTiO ₃ (001)/La _{0.5} Sr _{0.5} CoO ₃ (001)/Bi _{0.5} Na _{0.5} TiO ₃ (001)	PLD	250	559	15.6	47	145	⁵⁹
Si(100)/SiO ₂ /Ti/Pt(111)/LSMO/poly-0.94BNT – 0.06BT	PLD	400	568	13.98	110	-	⁶⁸
Si/SiO ₂ /TiO ₂ /Pt/poly-0.92(Bi _{0.5} Na _{0.5})TiO ₃ – 0.08BaTiO ₃	PLD	530	820	22	120	-	⁶⁹

Si(100)/SiO ₂ /Ti/Pt(111)/poly- 0.94(Bi _{0.5} Na _{0.5})TiO ₃ – 0.06BaTiO ₃	PLD	950	572	25.19	60	-	70
MgO(110)/Pt(110)/0.91(Bi _{0.5} Na _{0.5})TiO ₃ – 0.09BaTiO ₃ (110)	Sputtering	3000	120 0	20	27	-	71
Si(100)/Ir/LaNiO ₃ (100)/c-0.93BNT – 0.07BT – 1 at.% Mn	Sputtering	2000	726	13.3	-	200	66
Si/SiO _x /TiO ₂ /Pt/poly-(1-x)(Bi _{0.5} Na _{0.5})TiO ₃ – xBaTiO ₃ (x = 0.2 – 0.5)	PLD	2000	110 0	18	60	>220	60

Table 1-2: Dielectric, ferroelectric, and piezoelectric performance of BNT-based films deposited by Vacuum-based techniques

1.3 Sputtering Process: An Overview

Sputtering is the process of ejecting surface atoms from a target via momentum transfer from bombarding fast particles. When high-energy positive ions (≥ 100 eV), e.g., those extracted from a plasma and accelerated by an applied negative bias strike the target, collision cascades are initiated within the material's sub-surface region. These cascades may propagate to the surface, causing the ejection of atoms if their energy exceeds the target's surface binding energy. This process is accompanied by the emission of secondary electrons, photons, surface phonons, and recoils, along with partial implantation of the bombarding ions into the target, as illustrated in Figure 1-12. Most of the energy of the bombarding ions (80–90%) is dissipated in target heating, while only ~10–20% is transferred to the sputtered species. These species travel through the background gas, eventually undergoing energy and charge transfer processes that influence their energy and angular distribution before reaching the surfaces to be coated.

The sputtering yield (Y) is a crucial parameter defined as the number of sputtered atoms per incident bombarding ion, which depends on several factors related to both the target and the incident ions. For the target, the atom's mass (m_t), surface binding energy (E_b), density (ρ_t), crystallographic orientation, etc., play an important role. For the incident ions, their energy (E_i), mass (m_i), and angle of incidence (θ) are critical. For instance, the E_b of most elements ranges from 1–10 eV, so the incident ions must possess higher energies to initiate the sputtering process. The highest Y is typically achieved at an incidence angle (θ) of 60° – 70° relative to the surface plane due to maximum momentum transfer. Additionally, ions with higher charge states, such as Ar^{2+} , receive twice greater acceleration compared to lower charge state ions like Ar^{1+} .

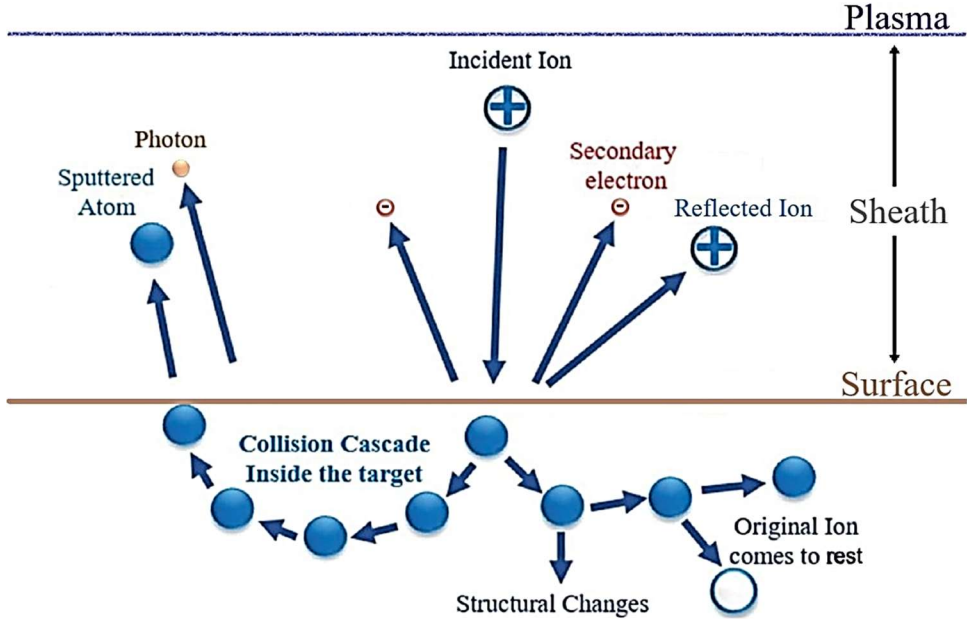


Figure 1-12: Graphical illustration of the incident ion–target surface interaction, which can reflect, implant, cause electron/photon emissions, and initiate a collision cascade resulting in sputtering of atom(s) ⁷².

The extended form of Sigmund's theory ⁷³ describes the relationship between those parameters and the angular distribution of sputtering yield $Y(\theta)$, as shown in Equation 1.2.

$$Y(\theta) = \frac{\alpha}{E_b} \cdot \frac{\rho}{m_t} \cdot \frac{4m_i m_t}{(m_i + m_t)^2} \cdot Z_i Z_t \cdot E_i \cdot \cos^{-n} \theta \quad (1.2)$$

Where α is the proportionality constant (0.1–1), $\frac{4m_i m_t}{(m_i + m_t)^2}$ is the energy transfer efficiency factor, Z_i and Z_t are the atomic numbers of incident ions and target atoms respectively, and $\cos^{-n} \theta$ (n : 1.5–2.5) is the angular distribution of the sputtered atoms. At low incident ion energies (100–500 eV), the angular distribution of sputtered atoms is dependent on the mass ratio of incident ions and target atoms. The distribution approaches a cosine shape at the mass ratio of ~ 1 . However, it becomes under-cosine when the ratio is significantly less than 1 and over-cosine when it is far greater than 1, as illustrated in Figure 1-13 ⁷². The angular

distribution of sputtered species can change during the transport based on the number of collisions they face. The original angular distribution remains conserved, typically up to a few centimeters away from the target's surface when the discharge pressure is very low (≤ 1 mTorr). However, it generally becomes broader with an increase in the number of collisions, resulting from an increase in working pressure and/or an increase in the target-to-substrate distance ^{74, 75}.

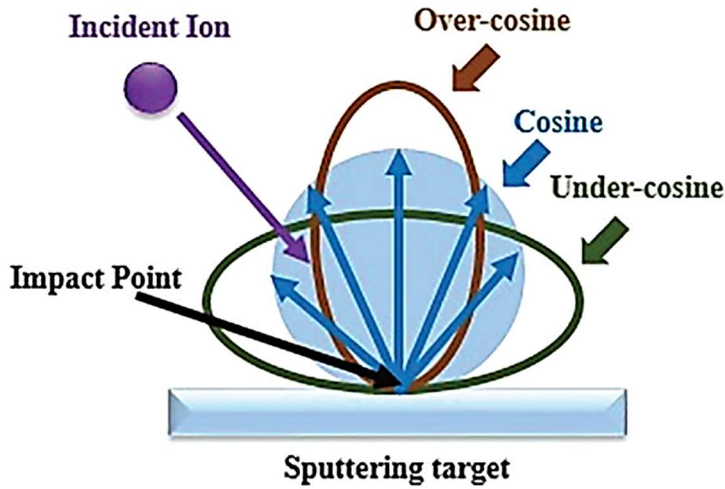


Figure 1-13: Graphical illustration of the sputtered atom's angular distribution – Cosine law ⁷².

1.3.1 Electrical Discharges

In a lab environment, the sputtering process is carried out inside an electrically grounded metallic chamber, under low-pressure conditions (1–50 mTorr), with a controlled flow of electric current through a gas medium. The background gas breaks down to form a weakly ionized plasma whose charge density is a small fraction of the overall neutral gas density ($n_i \sim 10^{-4} n_g$, n_i : number of ions, n_g : number of gas atoms). The target is mounted on the cathode, and positive ions are bombarded onto it, resulting in sputtering of the target's surface alongside secondary electron (SE) emission, etc. Secondary electrons are necessary to sustain the plasma by creating new positive ions from the neutral background gas,

thereby continuing the process of sputtering. These electrons can be easily lost to the grounded chamber walls and that indeed happens in the very beginning because the thermal velocity of electrons $(eT_e/m)^{1/2}$ is at least 100 times higher than that of the ions $(eT_i/M)^{1/2}$ due to $\frac{m}{M} \ll 1$ and $T_e \gg T_i$ (m , T_e : mass and temperature of the electrons, M , T_i : mass and temperature of the ions), which can risk the sustainability of plasma. Although plasma is quasi-neutral on the macroscopic scale, it still possesses a global positive potential called the Plasma potential (V_p). On the other hand, surfaces inside an electrical discharge can either be connected to ground or left floating, having a surface potential (V_s). Positive ions from the gas phase accelerate towards the surfaces by the plasma–surface potential difference ($\Delta V = V_p - V_s$) that appears in the sheath region, playing an essential role in the ion-surface interaction. If the surface is disconnected from the ground, i.e., floating, the surface potential is named as floating potential (V_f). Finally, the target’s surface possesses a high negative self-bias (V_{bias}), which results in a greater potential difference ($\Delta V = V_p - V_{bias}$, ≥ 100 eV), causing the sputtering phenomenon. In low-pressure electrical discharges, collisions between the charged particles (ions/ e^-) and the neutral gas atoms play a critical role because they facilitate the ionization of the background gas (e.g., Ar) that continues the sputtering process ($e^- + \text{Ar} \rightarrow \text{Ar}^+ + 2e^-$).

The negative bias voltage at the target’s surface ($\geq 100\text{V}$) accelerates positive gas ions (e.g., Ar^+ , Ar^{2+}) toward the target’s surface, which not only performs the processes of sputtering and emission of SE but also embeds some of these ions into the target’s surface. In the case of insulating targets, the embedded positive ions induce a net positive surface charge, which can accumulate if not promptly neutralized. This eventually counteracts the negative self-bias voltage of the target’s

surface and halts the sputtering process. Upon further buildup of the positive charge, the resulting electric field may exceed the target material's dielectric breakdown limit, prompting a sudden influx of electrons from the plasma. This event, known as arcing, can cause localized surface damage to the target, eject micron-sized particulates that can contaminate the film, and degrade the power supply ⁷⁶. The controlled neutralization of such a positive charge on the target's surface relies on the plasma electrons for non-conductive ceramic targets.

Radio frequency (RF, 13.56 MHz) power supplies are generally utilized for insulating targets. The target surface neutralization is achieved using plasma electrons during the 'positive' or zero half-cycle, making it ideal for sputtering our insulating BNT targets. The RF generator is coupled to the magnetron cathode using a matching network, ensuring effective power transfer and protection of the generator itself. As the target's sheath oscillates, the plasma ions and electrons respond differently because of the significant difference in their respective masses, thermal velocities, and the plasma frequency. The plasma electrons respond almost instantly to the oscillating target sheath, whereas the positive ions experience nearly a DC-like sheath, resulting in the continuous bombardment of the target's surface, thereby promoting the surface sputtering.

1.3.2 Magnetron Sputtering

Conventional sputtering requires high gas pressures (≥ 100 mTorr) to sustain the plasma because the mean free path of the SE for ionization is too large at lower pressures, resulting in their rapid loss to the chamber walls and compromising the overall ionization efficiency. The mean free path (*MFP*) of electrons and ions can be calculated using Equation 1.3.

$$MFP = \frac{k_B T}{\sqrt{2} \pi d^2 P} \quad (1.3)$$

Where k_B is Boltzmann's constant (8.62×10^{-5} eV/K), T is the temperature, d is the collision cross-section, and P is the gas pressure. Higher gas pressure also reduces the films' purity, deposition rates, and adhesion, leading to increased porosity due to increased gas-phase scattering of the sputtered atoms. To avoid all those problems, the mean free path of SE is decreased by incorporating a toroidal (closed-loop) magnetic field (B) above the target's surface that traps electrons in a complex trajectory, preventing them from quickly escaping to enhance the ionization efficiency. The magnetic field is typically created by incorporating permanent magnets inside the cathode, resulting in a dense plasma region near the target surface. The sputtering erodes the target surface in a non-uniform fashion by creating a ring-shaped sputtering region called the 'Racetrack', as illustrated in Figure 1-14.

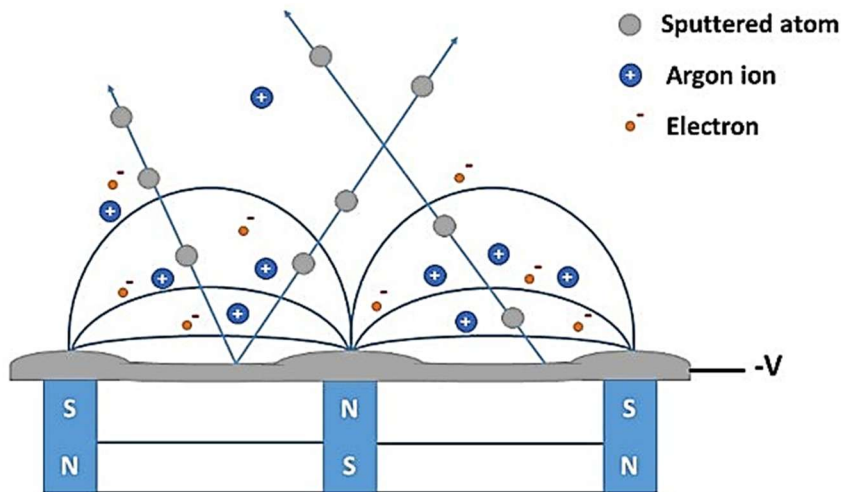


Figure 1-14: Schematic illustration of a typical Magnetron sputtering cathode, highlighting the eroded 'racetrack' region on the target's surface (side view) ⁷⁷.

The configuration of magnets results in either a so-called balanced or unbalanced magnetron, where the magnetic field lines form a closed loop in the former type. In contrast, a partially open field structure emerges in the latter case, as illustrated in Figure 1-15. The total strength

of the central and outer magnetic poles is equal in a ‘conventional’ balanced magnetron, resulting in SE trapping near the target surface, highly efficient ionization of the gas, and dense localized plasma formation. Sputtered species that escape the dense plasma contribute to the depositions. On the other hand, an unbalanced magnetron has one of the magnetic poles stronger than the other, allowing the plasma to extend farther than the balanced magnetrons. The unbalanced magnetrons can be subdivided into two types: those with a stronger central pole (Type I) and those with a stronger outer pole (Type II). The Type-I unbalanced configuration allows plasma flux to reach farther horizontally outward to the target. The Type II unbalanced configuration extends plasma flux exclusively toward the substrate, promoting ion bombardment during the film growth. Nonetheless, a balanced magnetron cathode is used throughout this thesis.

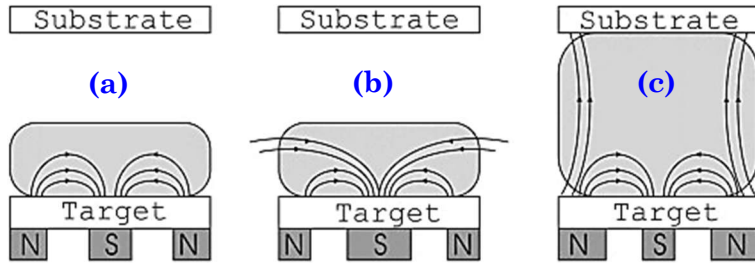


Figure 1-15: Schematic illustration of (a) Balanced, (b) Unbalanced Type I, and (c) Unbalanced Type II magnetrons ⁷⁸.

1.3.3 Powder Targets

The loosely packed powders have been explored as sputtering sources in the R&D sector, referred to as the "Powder targets", which can either be simply cold-pressed crystallized powders or moderately heated during the pressing to increase their overall density ⁷⁹. Such targets are interesting because their composition can be easily adapted for the deposition of complex ‘multi-element’ thin films. However, they suffer from limitations like lower structural integrity, increased surface

roughness and porosity, higher impurity levels, and reduced thermal conductivity compared to their dense counterparts. The powder targets generally have elevated surface temperatures, along with higher discharge voltages at a constant current, compared to the dense targets. The elevated surface temperature stems from the lower thermal conductivity of powder targets, which is a result of their porous nature, and the fact that these pores are filled with vacuum ⁸⁰. On the other hand, the inherently higher surface roughness of powder targets facilitates the re-capture of some SE, contributing to the increase in discharge voltages ⁸¹.

The effective sputtering yield of powder targets can be similar to or different from the dense targets because of the two competing effects: the “locally inclined” surfaces in powder targets enhance the sputtering yield, while the overall surface roughness increases the re-capture of sputtered atoms, resulting in the lowering of the sputtering yield ⁸². Zhu *et al.* sputtered $\text{Ba}(\text{Sn}_{0.15}\text{Ti}_{0.85})\text{O}_3$ powder targets using RF magnetron plasma and concluded that nanosized powder achieves higher deposition rates in comparison to the micron-sized powders as a result of lower surface roughness ⁸³. The angular distribution of sputtered species from powder targets is usually broader than their dense counterparts because the local surface normals are randomly oriented across the rough powder surface, causing the sputtered atoms to be ejected at a wider range of angles rather than preferentially along the global surface normal, as shown in Figure 1-16 (a). In the case of multi-element targets, the surface composition changes during the initial sputtering period until it reaches a steady state, known as the ‘target conditioning’. Early in this phase, elements with higher sputtering yields dominate the film composition; however, their concentration on the target’s surface decreases over time, resulting in a reduction of their deposition flux. Meanwhile, the surface

exposure of lower sputtering yield elements increases, enhancing their flux, which leads to the equilibrium surface composition, as illustrated in Figure 1-16 (b).

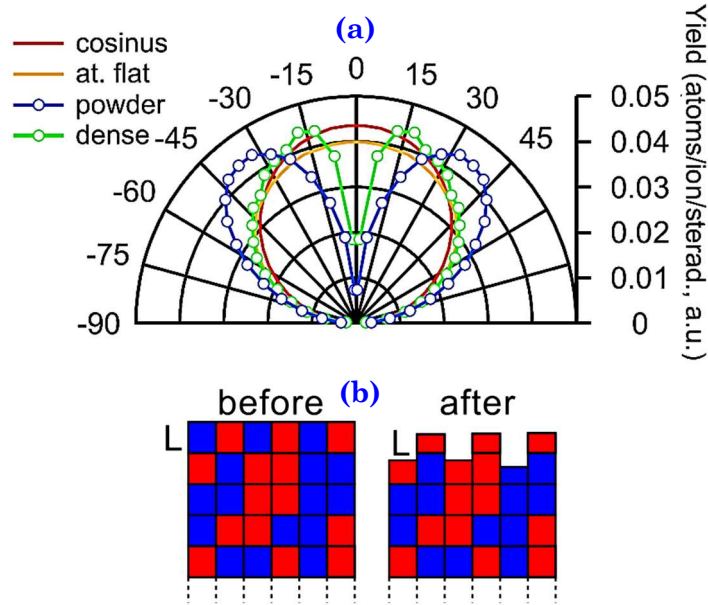


Figure 1-16: (a) Simulation of sputtered atom ejection profiles from single-element targets shows variations based on surface type: orange for atomically flat, green for dense, blue for powder, and red for the reference cosine distribution. (b) Graphical representation of a mixed powder target before and after conditioning, consisting of hypothetical square-shaped particles with dimension L . The blue material has a higher sputtering yield than the red, causing the initial 50/50 surface composition to shift to an equilibrium of 20/80 by the end of the conditioning cycle ⁷⁹.

1.4 Plasma Chemistry and Ion Energy Distribution Function (IEDF)

In sputtering discharges, plasma chemistry and ion energy distributions critically affect film growth characteristics. The IEDF, in particular, governs how ions deposit, their likelihood of re-evaporation, and their contribution to surface diffusion or adatom mobility on the substrate, i.e. via momentum transfer. While various diagnostic methods

exist to probe plasma chemistry and IEDFs, Mass spectrometry (MS) is especially suited for complex systems—such as those using powder-based, multi-element targets—because it enables identification of multiple ion species and measurement of their energy distributions. The plasma chemistry is primarily shaped by gas-phase reactions that occur before species reach the substrate, which are described in the following subsections.

- Ionization ($e^- + X \rightarrow X^+ + 2e^-$): It is the primary process that forms and sustains plasma, in which a high-energy electron collides with a neutral atom or molecule (X), transferring enough energy to eject one of its electrons and produce a positive ion (X^+). The process overall results in one positive ion and two electrons. The examples of ionization processes in BNT plasma inside an Ar discharge would be the formation of Ar^+ , Bi^+ , Na^+ , Ti^+ , and O^+ ions, where neutral Ar atoms come from the background gas, and the other neutral atoms (Bi, Na, Ti, and O) are sputtered from the target. The reverse reaction, i.e. neutralization ($X^+ + e^- \rightarrow X$), occurs on the walls in such low pressure discharges.
- Dissociation ($e^- + X_2 \rightarrow X + X + e^-$): It is another vital process that contributes to the plasma chemistry, mainly when a reactive gas (e.g., O_2 , N_2 , Cl_2) is also supplied alongside the Ar to the sputtering discharge. In this process, a high-energy electron collides with a neutral diatomic molecule (X_2), breaking the molecular bond, producing two neutral atoms ($X + X$) and a scattered electron. One example of the dissociation process in BNT plasma inside an Ar discharge would be the formation of neutral O atoms from sputtered oxygen-bearing molecules from the target, e.g., TiO , NaO , and BiO molecules.

- Attachment ($e^- + X \rightarrow X^-$): In this process, an electronegative atom or molecule (X) captures a free electron to form a negative ion (X^-), which reduces the electron density of plasma. This means that fewer electron-impact ionization events will occur, resulting in a mixture of positive and negative ions, unlike electropositive plasmas, which typically contain mostly positive ions and electrons. Example of the attachment process in BNT plasma is the formation of O^- ions from sputtered O that capture free electrons during transport. The O^- ions can also be emitted from the target surface originally as negative ions, followed by their acceleration via the target sheath potential, i.e., hundreds of eV ⁸⁴. These fast negative oxygen ions may influence the film growth ⁸⁵.
- Charge-exchange ($X^+ + Y \rightarrow X + Y^+$): If the densities of X and Y species are high enough (pressure ≥ 10 mTorr), this reaction occurs in the sheath region which promotes the broadening of IEDFs and the angular distribution of ions before reaching the surfaces. In this process, a positive ion (X^+) transfers its charge to a neutral specie (Y) during the collision, creating a neutral specie (X) and a positive ion (Y^+). The newly formed positive ion (Y^+) traveling with low kinetic energy (essentially thermal) prior to the reaction, is accelerated in the sheath region toward the surface, therefore creating a low-energy signal in the IEDF. Besides, the non-collided population of original incoming ions (X^+) ‘ballistically’ passes through the sheath region because their energy remains primarily conserved. In the case of BNT plasma, such reactions can occur, e.g., between Ar^+ ions and Ar atoms, and Ar^+ ions and other atoms whose gas-phase density is high enough.
- Excitation ($e^- + X \rightarrow X^* + e^-$) and De-excitation ($X^* \rightarrow X + h\nu$): In these reactions, a free electron transfers part of its energy to a

neutral atom or molecule (X) which becomes excited (X^*). The de-excitation produces radiation, forming the visible glow in plasmas, where each line corresponds to a specific species and transition that is essential for Optical emission spectroscopy (OES) based plasma diagnostics. In the case of BNT plasma, some of the examples of such reactions would be the excitation and de-excitation of sputtered Bi, Na, Ti, and O, while emitting OES lines at 293.83 nm, 298.90 nm, 302.46 nm, and 306.77 nm (Bi I), doublet at 589.0 + 589.6 nm (Na I), 398.2 nm and other lines around 445–592 nm (Ti I), and triplet at 777 nm and another at 844 nm (O I). Besides, Ar is also very much studied using its OES lines such as Ar I at 415.86 nm, 420.07 nm, and 427.75 nm, or 750.39 nm.

1.5 Growth of Sputter-Deposited Films

Film formation is driven by the condensation of sputtered species (neutrals and ions) on a substrate, with the growth mechanism governed by the plasma parameters, substrate bias, and temperature. Transport of the film-forming species toward the substrate critically depends on their collision rate in gas-phase, which primarily depends on the gas pressure and target–substrate distance. Unlike the neutrals, ions are accelerated in the sheath in front of substrate by the plasma–surface potential drop; arriving with higher kinetic energy and can promote, e.g., the film densification or crystallization through momentum transfer ^{74, 75}. Sputtered species lose most of their kinetic energy upon reaching the substrate through inelastic surface interactions (heat), leading to physical or chemical adsorption, or re-evaporation if the binding energy is insufficient ⁸⁶. The diffusion of adatoms on the substrate surface depends on their residual energy, recoil energy from newly arriving species, thermal energy from the substrate, and local binding energy gradients at surface steps and grain boundaries. Adatoms migrate toward lower-

energy sites, stabilizing into nucleation centers where islands form. The neighboring islands/nuclei merge over time, resulting in the formation of a continuous film. Higher adatom mobility and extended diffusion lengths favor the formation of larger islands with lower nucleation densities, resulting in smoother, denser, partially crystalline, and well-adhered films. In contrast, lower adatom mobility and restricted diffusion result in numerous, but smaller, islands, leading to rough, porous, and amorphous films with poorer adhesion. Moderate adatom mobility and diffusion lengths lead to columnar growth^{87, 88}, where competitive grain growth occurs due to limited surface diffusion. These films exhibit intermediate roughness, density, and adhesion, with a partially amorphous or nanocrystalline structure.

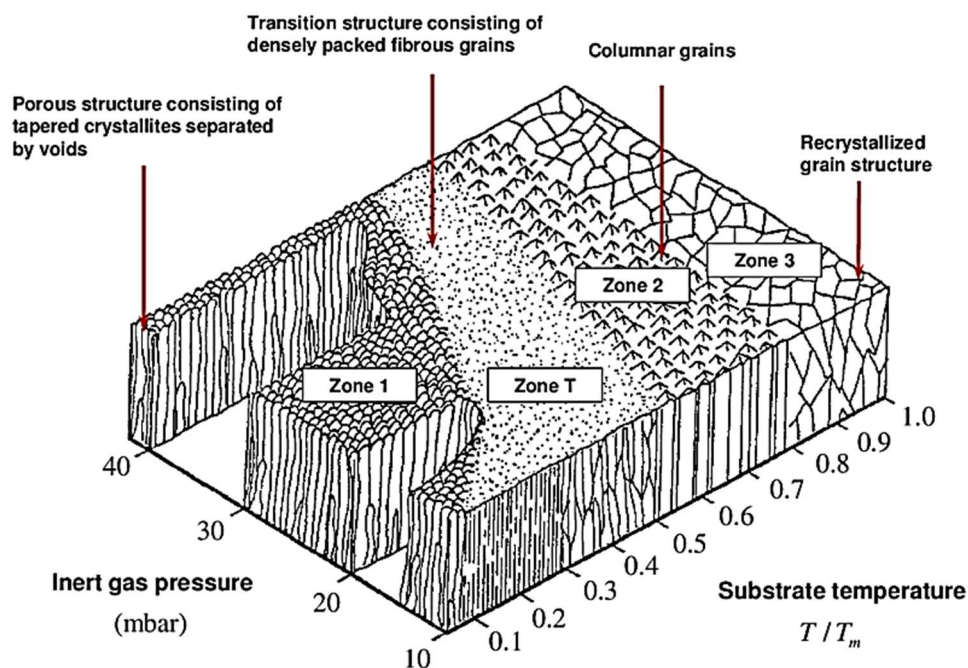


Figure 1-17: Thornton's model of film structure as a function of the gas pressure and substrate temperature. At low substrate temperatures and high pressure (Zone 1), films form as porous structures due to limited atom mobility. Slightly higher temperatures or lower pressure (Zone T) result in denser, fibrous grains. At moderate temperatures (Zone 2), columnar grains develop, while high

temperatures (Zone 3) produce dense, recrystallized structures through enhanced atomic diffusion ⁸⁷.

In one of the earlier models ‘Thornton's Structure Zone Model’ (SZM) shown in Figure 1-17, thin film microstructure is categorized into distinct zones—Zone 1, Zone T, Zone 2, and Zone 3—based on the homologous temperature (the ratio of substrate temperature to the melting point of the film material: T/T_m) and the sputtering gas pressure. Zone 1 features porous, fibrous structures formed at low temperatures and high pressures due to the limited mobility of adatoms. Zone T (transition zone) exhibits dense, columnar grains resulting from increased adatom mobility at moderate temperatures and pressures. Zone 2 features large, columnar grains with faceted surfaces, characteristic of high temperatures and low pressures, where surface diffusion is dominant. Finally, Zone 3 is characterized by equiaxed, recrystallized grains formed at higher substrate temperatures and lower pressures, where bulk diffusion dominates and grain growth is maximized. However, such recrystallization may also be influenced by impurities released in the chamber at elevated temperatures, such as the desorption of H₂O molecules from the chamber walls ⁸⁹.

1.6 State of the Art in Sputter Deposition of BNT Films

Magnetron sputtering is the most widely used vacuum-based technique in the microelectronics industry for depositing thin films. However, a limited number of studies address the deposition of BNT films via the sputtering route due to the lack of commercially available BNT targets and the challenges of in-house fabrication of targets and optimization of the deposition process. Watanabe *et al.* were the first to use RF magnetron sputtering for BNT films deposition. Using powder-based cold-pressed targets whose composition was Bi_{0.5}Na_{0.75}TiO₃, thus with an excess of Na, along with a growth temperature of 500°C on

Pt(100)/MgO(100) substrates, they obtained 500 nm thick, c-axis oriented $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT) films⁹⁰. Zhou *et al.* deposited 170 nm thick polycrystalline BNT films with (110) preferred orientation, using a stoichiometric $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ ceramic target on an unheated Pt/Ti/SiO₂/Si substrate. Following the formation of the Bi-secondary phase ($\text{Bi}_2\text{Ti}_2\text{O}_7$) alongside the BNT during the post-annealing at 700°C, the BNT ceramic powder was added inside the furnace to compensate for the loss of volatile elements like Na by creating their dense vapors, finally the pure BNT phase was realized. However, oxygen vacancies were still present and were causing the dielectric losses^{91, 92}. Wu *et al.* deposited 60 nm thick polycrystalline BNT films with a (111) prominent direction on a Pt/TiO₂/SiO₂/Si substrate at a growth temperature of 650°C using a ceramic BNT target and employed it as a template for the growth of BiFeO_3 thin film⁹³. Quignon *et al.* used a Bi-deficient cold-pressed mixture powder target $\text{Bi}_{0.55}\text{NaTi}_2\text{O}_x$ composed of Bi_2O_3 , TiO_2 , $\text{Na}_2\text{Ti}_3\text{O}_7$ powders, and an unheated Pt(111)/TiO_x/SiO₂/Si substrate for the deposition of (110) oriented 750 nm thick BNT films. Post-annealing was performed at 675°C in an O₂ ambient (25 mTorr), and a d_{33} of 80 pm/V was achieved⁶². Hamieh *et al.* deposited 350 nm thick, (100)- oriented BNT films on a $\text{LaNiO}_3(100)/\text{SiO}_2/\text{Si}$ substrate at a growth temperature of 200°C, employing a stoichiometric $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ cold-pressed mixture powder target. Following the post-annealing at 650°C for 60 minutes in ambient air, and demonstrated d_{33} of 56 pm/V^{63, 64}.

Kruzina *et al.* used a ceramic BNT target to deposit 250 nm thick polycrystalline BNT films with a (110) preferred orientation at a growth temperature of 200°C on a Pt/sitall substrate. The BNT films were annealed at 700°C for 45 minutes in the presence of ceramic BNT powder to compensate for the loss of volatile elements, such as Na⁹⁴. Employing the deposition protocol of Hamieh *et al.*⁶⁴, Moolayil *et al.* deposited 400

nm thick (100) oriented BNT films on $\text{LaNiO}_3(100)/\text{Si}$, demonstrating a slight increase in the piezoelectric coefficient $d_{33\max}$ of 57 pm/V ⁶⁷. Kossman *et al.* also employed the protocol of Hamieh *et al.* and deposited 450 nm thick (100)-oriented BNT films, demonstrating enhancements in both electrical and piezoelectric properties, with a d_{33} value of 60 pm/V ⁶⁵. Harigai *et al.* used a stoichiometric $(1-x)\text{BNT}-(x)\text{BT}$ target ($0.1 > x > 0.5$), $\text{Pt}(100)/\text{MgO}(100)$ substrate with a growth temperature of 700°C , and deposited up to 3 microns thick (100) orientated 0.93BNT-0.07BT films ⁹⁵. Adachi *et al.* followed the work and employed a stoichiometric $(1-x)\text{BNT}-(x)\text{BT}$ target ($0.05 > x > 0.15$) with 0.2 at.% Mn additive to deposit a 3 microns thick (110) orientated 0.91BNT-0.09BT on a $\text{Pt}(110)/\text{MgO}(110)$ substrate at a growth temperature of 700°C ⁹⁶. In both studies, in-situ crystallization of the films is likely occurring because there is no mention of post-annealing, while XRD (X-ray diffraction)- based crystallinity is reported. A key observation across all magnetron sputter depositions is that pure c-axis-oriented BNT films were only possible when the base layer itself was c-axis oriented and the substrate was heated during BNT film growth, potentially due to increased adatom mobility and the existence of a c-axis-oriented growth template. In (001) or c-oriented films, ferroelectric domains are more likely to undergo 90° and 180° switching, leading to higher piezoelectric strain coefficients. However, in (111)-oriented films, domain motion is more restricted due to the complex multi-domain configurations, which reduces the effective piezoelectric response. A list of the key deposition and post-deposition parameters reported across those studies is provided in Table 1-3.

Noteworthy, the sputtered BNT thin films are prone to *in-situ* formation of sodium oxide surface defects and compositional imbalances, specifically Bi excess during film growth and sublimation-driven loss of Na during the high-temperature post-annealing. The formation of sodium

oxide surface defects on BNT thin films was first observed by Hamieh *et al.*⁶³. The deposition of excess Bi in sputtered BNT films was also initially reported by Hamieh *et al.*⁶⁴ and has since been documented in subsequent studies^{65, 67}. Zhou *et al.* first identified the compositional imbalance of the BNT films based on the evaporation of volatile elements during the high-temperature post-annealing.^{91, 92}, which was later followed by Kruzina *et al.*⁹⁴. The sodium oxide surface defects generally rupture during the post-annealing of BNT films, rendering them unsuitable for device applications. The compositional imbalance creates an excess of Bi, resulting in the formation of Bi secondary phases, i.e., bismuth titanates, alongside the formation of BNT primary phase. Such bismuth titanate phases compromise the ferroelectric/piezoelectric performance of the BNT phase, hence limiting the overall performance of BNT film-based devices.

Watanabe <i>et al.</i> 2001 ⁹⁰	Reference
11.11	Power (W/cm ²)
Ar : O ₂ = 9 : 1	Background Gas
3	Pressure (mTorr)
Ceramic powder: Bi _{0.5} Na _{0.75} TiO ₃	Target Composition
5.5	Target-Substrate Distance (cm)
Pt(100)/ MgO(100)	Substrate Type
500	Growth Temperature (°C)
-	Temperature (°C)
-	Duration (min)
-	Environment
500nm, Pure (100) orientated (Bi _{0.5} ,Na _{0.5})TiO ₃	Film Thickness (nm), Crystalline orientation

Harigai <i>et al.</i> 2010 ⁹⁵	Wu <i>et al.</i> 2009 ⁹³	Zhou <i>et al.</i> 2004-05 ^{91, 92}
-	-	2.5
Ar : O ₂	Ar : O ₂ = 7 : 1	Ar
6	10	10
stoichiometric (1 – x)BNT – (x)BT target (0.1 > x > 0.5)	Ceramic: composition unknown	Ceramic: Bi _{0.5} Na _{0.5} TiO ₃
-	-	-
Pt(100)/MgO(100)	Pt(111)/TiO ₂ /SiO ₂ /Si	Pt/Ti/SiO ₂ /Si
700	650	-
-	-	700
-	-	60
-	-	O ₂ with BNT powder assistance
2.5 – 3.0 μm, Pure (100) orientated 0.93BNT-0.07BT	60nm, (110) preferred Polycrystalline (Bi _{0.5} ,Na _{0.5})TiO ₃	170nm, (110) preferred Polycrystalline (Bi _{0.5} ,Na _{0.5})TiO ₃

Quignon <i>et al.</i> 2012 ⁶²	Adachi <i>et al.</i> 2011 ⁹⁶
13.12	-
Ar	Ar : O ₂
10	-
Cold-pressed mixture powder: Bi _{0.55} NaTi ₂ O _x	stoichiometric (1 – x)BNT – (x)BT target (0.05 > x > 0.15) – 0.2 at.% Mn
8	-
Pt(111)/TiO _x /SiO ₂ /Si	Pt(110)/MgO(110)
Unheated	700
675	-
60	-
O ₂ : 25 mTorr	-
750nm, (110) preferred Polycrystalline (Bi _{0.5} ,Na _{0.5})TiO ₃	3.0 μm, (110) orientated 0.91BNT-0.09BT

Kruzina <i>et al.</i> 2021 ⁹⁴	Hamieh <i>et al.</i> 2020-21 ^{63, 64}
3.2	13.12
Ar	Ar
7.5	10
Ceramic: composition unknown	Cold-pressed mixture powder: $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$
-	8
Pt(111)/sitall	$\text{LaNiO}_3(100)/\text{SiO}_2/\text{Si}$
200	200
700	650
45	60
Air with BNT powder assistance	Ambient air
250nm, (110) preferred Polycrystalline $(\text{Bi}_{0.5}, \text{Na}_{0.5})\text{TiO}_3$	350nm, Pure <i>c</i> -axis orientated $(\text{Bi}_{0.5}, \text{Na}_{0.5})\text{TiO}_3$

Moolayil <i>et al.</i> 2024 ⁶⁷	Kossman <i>et al.</i> 2022 ⁶⁵
13.12	13.12
Ar	Ar
10	10
Cold-pressed mixture powder: Bi _{0.5} Na _{0.5} TiO ₃	Cold-pressed mixture powder: Bi _{0.5} Na _{0.5} TiO ₃
8	8
LaNiO ₃ (100)/Si	LaNiO ₃ (100)/SiO ₂ /Si
200	200
650	650
60	60
Ambient air	Ambient air
400nm, Pure <i>c</i> -axis orientated (Bi _{0.5} ,Na _{0.5})TiO ₃	450nm, Pure <i>c</i> -axis orientated (Bi _{0.5} ,Na _{0.5})TiO ₃

Table 1-3: Magnetron sputter deposition of BNT-based films: A critical review

1.6.1 Formation of Sodium Oxide Surface Defects

Sputtering Na-based targets often results in the formation of sodium oxide surface defects in deposited films, a phenomenon observed across various material systems. Horwat *et al.* reported this by depositing $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ (NASICON) films using Na-containing targets, where sodium oxide surface defects were evident on the as-deposited films. They attributed the sodium migration to the electrical diffusion of Na^+ ions from the interior of the film toward its surface, driven by the plasma-substrate potential variations during film growth and the Na^+ ion superconductivity characteristic of the NASICON material ⁹⁷. Similarly, Mansfield *et al.* observed this behavior on the surface of as-deposited Na-doped Mo films obtained by the sputtering of Na-containing targets ⁹⁸. Lee *et al.* further reported the formation of sodium oxide surface defects during the post-annealing of Na_xCoO_2 thin films deposited by sputtering of Na-based targets. The Na_xCoO_2 as-deposited films did not have sodium oxide surface defects; however, they started appearing once the film's post-annealing temperature reached 650°C , suggesting the thermal diffusion of Na^+ ions to be responsible for their migration towards the surface and forming sodium oxide defects by reacting with the atmospheric oxygen ⁹⁹.

Hamieh *et al.* also reported the formation of sodium oxide surface defects on the BNT films during their growth on unheated substrates by sputtering $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ mixture-powder targets. They attributed these defects to variations in the plasma-substrate potential, which drove diffusion of Na^+ ions toward the film surface, where they reacted with the oxygen and formed sodium-oxide defects. However, this process accelerated during the film's post-annealing at 650°C , indicating the occurrence of thermal diffusion and additional Na^+ ion migration towards the film surface, which resulted in the rupture of those defects (shown in Figure 1-18), rendering the films unsuitable for device applications.

However, sodium oxide surface defects neither formed during film deposition once the growth temperature was elevated by 50°C (150°C–200°C), nor did their formation activate later during the post-annealing of films ⁶³. In summary, if sodium oxide defects form on the film's surface during the sputter-deposition process, electrical diffusion of Na⁺ ions will be the potential origin. However, if such defects form or increase during the post-annealing process, thermal diffusion of Na⁺ ions will likely be the mechanism.

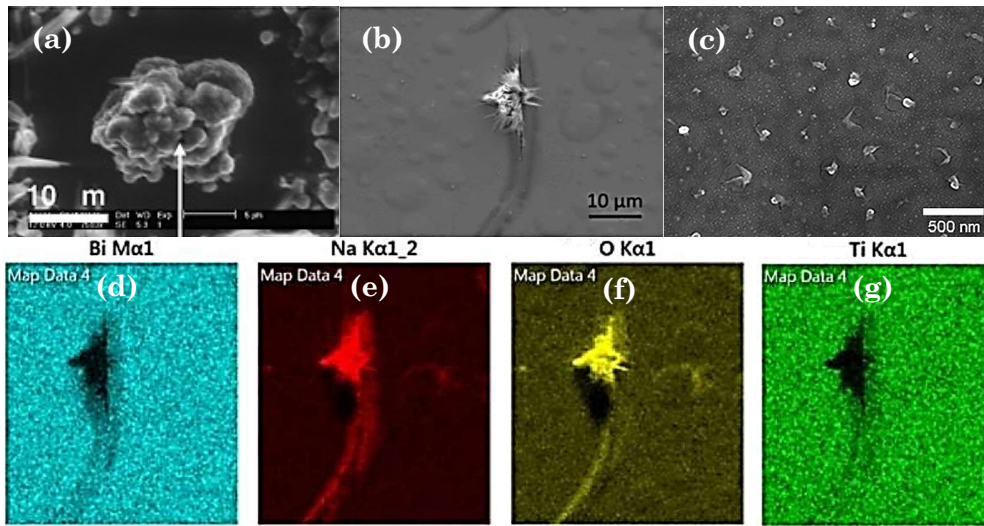


Figure 1-18: Scanning electron microscopy (SEM) images of sodium oxide surface defects on (a) NASICON (the scale bar is 1 micron, but the authors did not mention what they are referring to by the '10 m') ⁹⁷, (b) BNT ⁶³, (c) Na_xCoO₂ ⁹⁹ films, and (d–g) elemental mapping of BNT's sodium oxide defects using Energy Dispersive X-ray spectroscopy (EDX) technique.

1.6.2 Excess of Deposited Bi

Sputtering Bismuth-based targets typically results in film growth with an excess of Bi in their composition, which causes the formation of undesired Bi-secondary phases, such as bismuth titanate in the case of BNT films, compromising the functional properties of the primary phase. This phenomenon suggests a possible correlation between the sputtering

process and the Bi excess present in the grown films. Westwood *et al.* observed that heavier and more energetic sputtered species, such as Bi atoms in our process, experience minimal scattering and are transported in a direction perpendicular to the target surface, resulting in their relative excess inside the growing film. Conversely, species with masses comparable to or lower than that of the background gas, such as O, Na, and Ti atoms in our case, would undergo significant scattering during transport, leading to their thermalization and a diffusion-dominant process of deposition, resulting in their comparatively reduced concentration within the films ⁷⁴. Depla *et al.* also demonstrated similar trends in a detailed study based on the Monte Carlo simulation code ‘SiMTRA’ (Simulation of Metal Transport), which allows modeling of the sputtered species transport in the gas phase ⁷⁵. Both studies provide insights into the distinct transport mechanisms governed by the mass and energy of sputtered species, which can dictate the composition of growing films. These mechanisms may potentially explain the excess bismuth observed in sputter-deposited BNT films. Also, the excess of Bi can be controlled by manipulating its sticking coefficient, which is very sensitive to the growth temperature, as reported in the literature ¹⁰⁰. Zilko *et al.* found that a 30°C increase in growth temperature (from 135°C to 165°C) re-evaporates half the flux of impinging Bi species during the deposition of $\text{InSb}_{1-x}\text{Bi}_x$ alloy films ¹⁰¹. Similarly, Iljinas *et al.* demonstrated a sevenfold reduction in the thickness of Bi_2O_3 films with a 50°C increase in growth temperature (from 450°C to 500°C) ¹⁰². Hamieh *et al.* reported a 30% excess of Bi in BNT films compared to the target’s composition. Increasing the growth temperature by 50°C (from 150°C to 200°C) and thereby re-evaporating excess Bi resulted in the deposition of stoichiometric $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ films ⁶³.

1.6.3 Sublimation-driven Loss of Na during Post-Annealing

As stated above, post-deposition annealing of the as-deposited BNT films is required for 1h at 650–700°C to attain their long-range crystalline ordering, which is necessary to enable the ferroelectric/piezoelectric character of BNT material. However, alkali metal ions such as Na⁺ exhibit higher thermal mobility within the semi-crystalline and low-density solids, often leading to their sublimation during annealing¹⁰³. Thermal stimulation is highly effective, even causing trace amounts of alkali metals to migrate along the thermal gradient. Feng *et al.* reported the thermal diffusion of residual sodium (10–170 ppm) toward the surface of sol-gel synthesized TiO₂ powder within a temperature range of 300–600°C¹⁰⁴. Similarly, Jakubczyk *et al.* observed ~25% sodium loss during annealing of the sol-gel synthesized NaCo₂O₄ powder at 950°C, which was reduced to below 10% by pre-coating the NaCo₂O₄ powder with a thin NaOH layer to enrich sodium concentration before annealing¹⁰⁵. Dargham *et al.* synthesized BNT thin films by sol-gel spin-coating technique and used 20 mol% extra sodium precursor to compensate for the Na loss during annealing at 700°C⁴⁴. Madani *et al.* noted up to 33% sodium and potassium loss during the annealing of KNN thin films in a temperature range of 750–900°C, deposited at room temperature via sputtering. To address this, they increased the concentration of Na and K inside the target, enhancing the transfer of these elements onto the substrate during film growth¹⁰⁶. In another study, Chen *et al.* sputtered KNN films at a growth temperature of 300°C, finding almost no potassium and only trace amounts of sodium in the films. They partially compensated for this loss by annealing the films in a Na/K-rich vapor atmosphere (3:1 ratio) at 700°C¹⁰⁷. For BNT thin films, sodium loss is primarily reported in the case of solution synthesized films, where the evaporation of solvents create diffusion pathways for Na

sublimation during annealing; however, there is a lack of data on this issue for vacuum-grown BNT films.

Zhang *et al.* employed Molecular dynamics (MD) simulations to calculate the activation energy for Na^+ ions migration inside the BNT material and found it to be higher than 2 eV, which far exceeds the usual annealing temperatures; however, those simulations were performed on pure crystalline BNT phase ¹⁰⁸. On the other hand, Thao *et al.* reported that the diffusion of sodium atoms inside the sodium silicate glasses increases with the decrease of overall crystallinity due to the formation of more pathways for Na migration, based on the MD simulations and experimental data ¹⁰⁹. Therefore, the loss of Na during annealing of ‘poorly crystallized’ as-deposited BNT films leads to the compositional imbalance, i.e., excess of Bi, resulting in the formation of undesired Bi-based secondary phases. Zhou *et al.* indeed observed the formation of Bi-secondary phases during the post-annealing of magnetron sputtering-deposited BNT films in an O_2 ambient, which they attributed to the volatility and eventual loss of Bi, addressing this by using ceramic BNT powder-assisted annealing. However, it was indeed caused by the volatility and loss of Na because the activation energy of Bi^{3+} (4 eV) is twice that of Na^{1+} (2 eV) ^{91, 92}. Recently, Kruzina *et al.* also reported this challenge for sputter-deposited BNT films and used sodium vapor-assisted ambient during annealing at 700°C to compensate for its sublimation-driven loss ⁹⁴.

1.7 Summary, Research Questions, and Proposed Strategy

Piezoelectric materials play a crucial role in modern electronics and electromechanical applications, with perovskite-based ferroelectrics being the preferred choice due to their superior functional properties. Among them, $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ (BNT) has gained increasing attention as a

Pb-free alternative to traditional $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ (PZT) ceramics, offering high polarization, strong piezoelectric response, and environmental sustainability. However, the industrial-scale integration of BNT thin films via RF magnetron sputtering presents significant challenges, particularly in controlling the stoichiometry and surface morphology. During the film deposition, sodium oxide surface defects form and excess Bi is incorporated, while Na loss becomes prominent during post-deposition annealing. This study therefore aims to identify the root causes of the described issues and propose strategies to optimize the synthesis process for high-quality piezoelectric BNT films via the RF magnetron sputtering technique. To reach this goal, a detailed analysis of target-plasma-film chemistry is proposed. The conceptual framework of this thesis is represented in Figure 1-19.

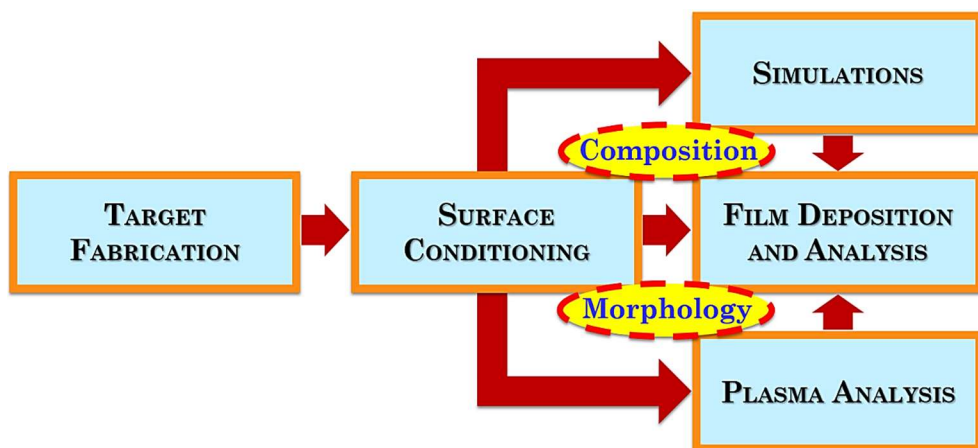


Figure 1-19: Conceptual framework of the thesis, integrating the conditioned target surface composition, sputtering and transport simulations (TRIM, SiMTRA), and film composition analysis to investigate bismuth titanate secondary phase formation in crystallized BNT films. Simultaneously, correlations between target surface composition, plasma ion chemistry, and film morphology are used to explain the NaO_x surface defects formation during growth in BNT films.

Chapter 2 Materials and Methods

2.1 Experimental Setup

This chapter introduces all the experimental means employed during this thesis work. This includes the sputtering assembly as well as the plasma and materials characterization tools. The simulation tools (TRIM and SiMTRA) used for the target's sputtering and species transport are introduced.

2.1.1 Sputtering Chamber

The sputtering chamber was sourced from Kurt J. Lesker and featured a stainless-steel body with a cylindrical geometry, measuring 40 cm in length and 20 cm in diameter, as depicted in Figure 2-1. The chamber's body was connected to an electrical ground and was pumped by a primary pump, 'DUO 10 MC', and a turbo molecular pump, 'HiPace 350', both from Pfeiffer Vacuum. The pressure was monitored by a wide-range gauge, 'WRGDS-NW35', from Edwards, while the gas flow was regulated by 'FC-R7700CD' flow meters from the Aera Analog Series, both with an error margin of $\leq 2\%$. The magnetron cathode, based on permanent magnets, had a diameter of 3 inches and was connected to the chamber in an upward-facing direction via a DN100CF flange. The minimum feasible distance between the target's surface and the mass spectrometer's orifice was 16 cm, while up to a minimum of 4 cm distance was attainable between the target and substrate surfaces. The substrate is brought in front of the target by a transfer arm. The latter is moved out of the deposition chamber and parked inside a load-lock chamber located on the left hand side of the main chamber to load/unload the sample. The magnetic field of the magnetron cathode was a 'balanced' type magnetron cathode having ~ 80 mT magnetic field strength with a perpendicular reach of 4 cm. A capacitively-coupled RF power supply 'RFX-600' with the

matching unit ‘ATX-600’, both from Advanced Energy, were used to power up the discharge.

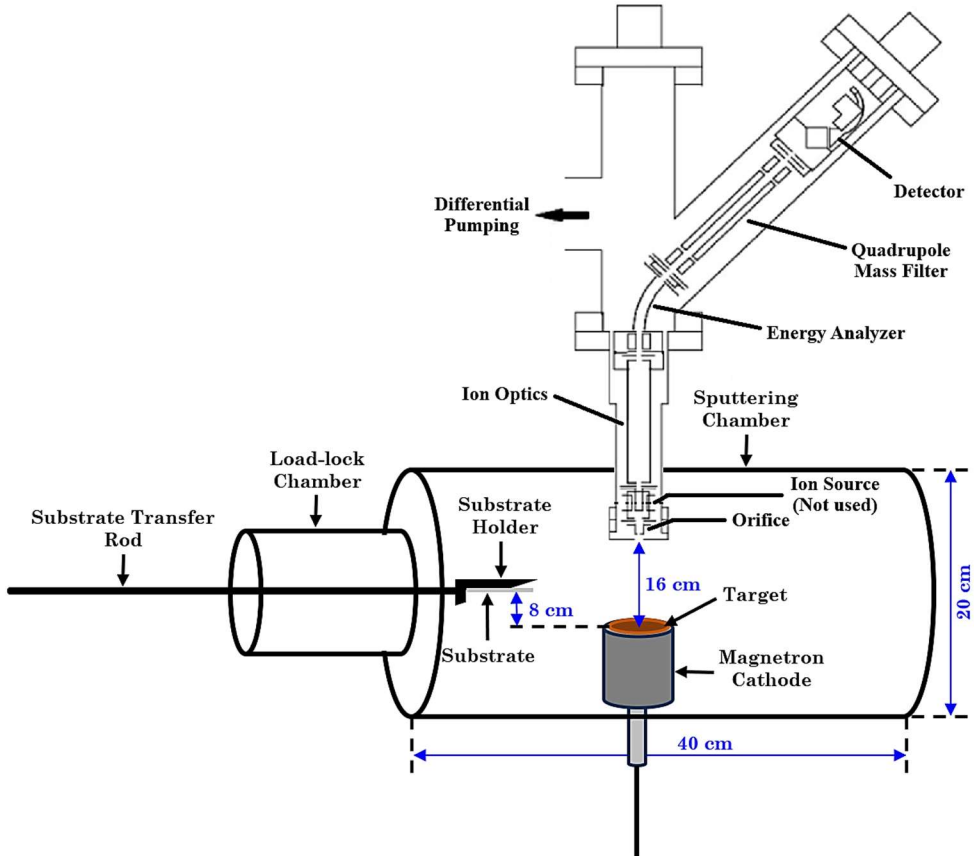


Figure 2-1: Illustration of the sputtering chamber and mass spectrometer assembly, where the mass spectrometer is facing the target's center and the load-lock chamber is located on the left-hand-side of the deposition chamber.

2.1.2 Targets Fabrication

Cold-pressed mixture-powder ‘BNT’ targets having a 3-inch diameter and 3 mm thickness were used in this thesis work. The Bi_2O_3 , $\text{Na}_2\text{Ti}_3\text{O}_7$, and TiO_2 powders, sourced from Neyco, were used as precursors, which had an identical particle size of 325 mesh (~44 microns) and a purity of 99.9 %. Two main target compositions were employed:

$\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT50.50) and $\text{Bi}_{0.35}\text{Na}_{0.5}\text{TiO}_{2.8}$ (BNT35.50), having compositions based on Equation 2.1.

$$\left(\frac{x}{2}\right)\text{Bi}_2\text{O}_3 + \left(\frac{y}{2}\right)\text{Na}_2\text{Ti}_3\text{O}_7 + (z)\text{TiO}_2 = (\text{Bi}_x\text{Na}_y)\text{Ti}_{1.5y+z}\text{O}_{1.5x+3.5y+2z} \quad (2.1)$$

Initially, all the precursors were weighed, mixed in Isopropyl alcohol (IPA), and ball-milled inside a planetary ball mill for ~12 hours, followed by at least 24 hours of drying at 70°C. Next, the mixture of powders was pressed into a 3-inch mold using a uniaxial pressure of 20-25 mt for four hours. Finally, the cold-pressed powder target was bonded to a Cu plate using silver paste, followed by drying at 70°C for several hours. An average of ~33 g of mixture powder was used in each target, resulting in a density of 2.3 g/cm³. Freshly prepared targets are depicted in Figure 2-2 (a, b) alongside the one during sputtering (c).

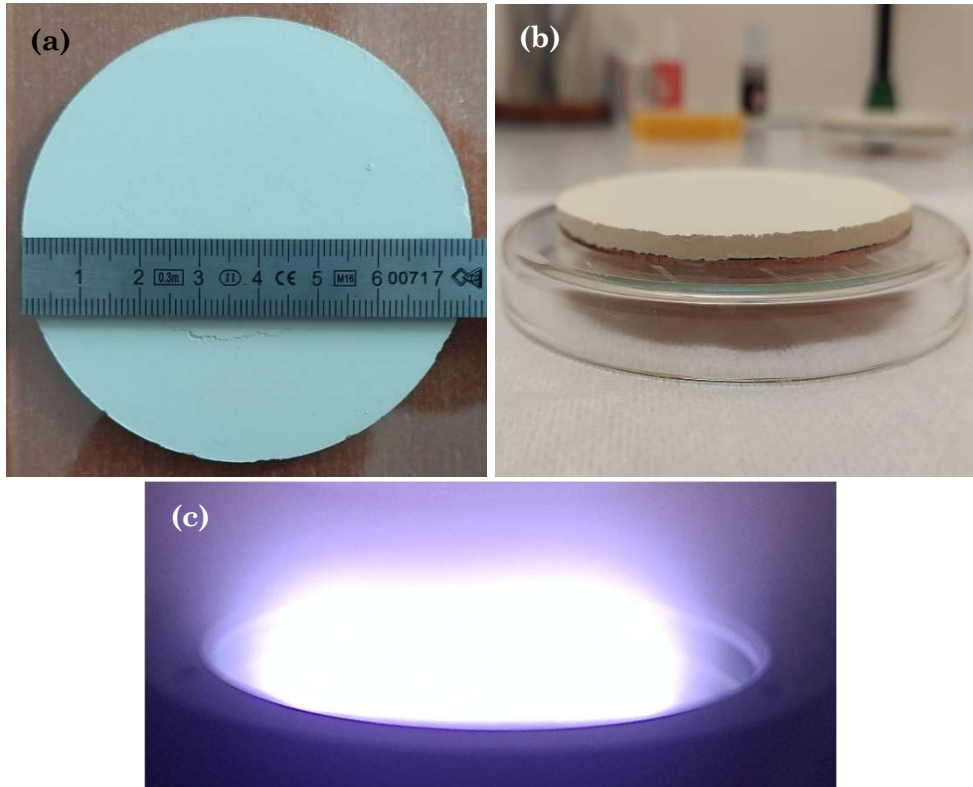


Figure 2-2: Typical pristine BNT powder target (a) top view, (b) side view, and (c) during sputtering.

2.1.3 Films Deposition

We deposited films on $3.81 \times 2 \text{ cm}^2$ Si substrates, with the longer dimension chosen to match the 3.81 cm radius of the 3-inch diameter target, allowing for spatially resolved composition analysis across the full radial extent of the deposition flux. After the film deposition, the substrate was divided into three equal ‘1.27 cm’ radial zones, center: 0–1.27 cm, middle: 1.27–2.54 cm, and edge: 2.54–3.81 cm, where each zone was separately characterized. In each zone, three EDX measurements were performed—one at the zone’s midpoint and two at positions offset by $\pm 0.5 \text{ cm}$ —and the average value was reported. This scheme is illustrated in Figure 2-3 below.

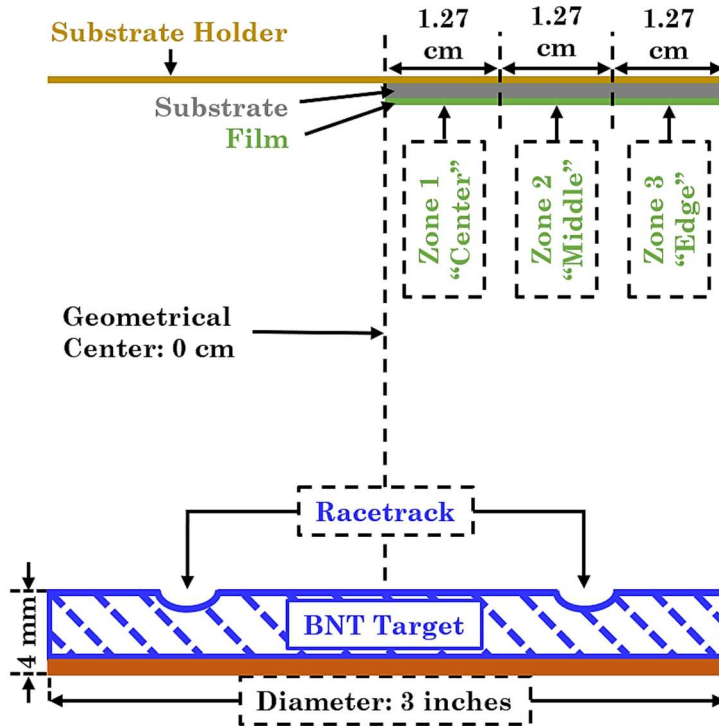


Figure 2-3: Side view of a $3.81 \times 2 \text{ cm}^2$ Si substrate's division into three equal '1.27 x 2 cm² zones: Center (0–1.27 cm), Middle (1.27–2.54 cm), and Edge (2.54–3.81 cm), corresponding to the plasma flux from a 3-inch

BNT target. This zonal scheme is consistently employed throughout the thesis to analyze film composition and morphology.

2.2 Characterization Techniques

2.2.1 Structural Analysis

The X-ray Diffraction (XRD) is a non-destructive analytical technique used to analyze the crystalline structure, phase composition, and lattice parameters of materials. A source directs X-rays of Angstrom wavelength onto the sample, where they experience constructive and destructive interferences with the crystalline planes inside the sample (interplanar distance also in Angstrom), following Bragg's law ($n\lambda = 2d\sin\theta$, λ : X-ray wavelength, d : interplanar distance). The diffracted beam passes through a monochromator before reaching the detector to suppress the K_β and other unwanted radiations, allowing only the K_α radiation to pass through, thereby enhancing the accuracy of diffraction measurements. In this thesis, the Grazing Incident-angle X-ray Diffraction (GIXRD) technique was employed, utilizing a Panalytical Empyrean (HTK-2000N) XRD machine with a Cu K α source ($\lambda = 1.5406$ Å). The source voltage was fixed at 45 kV with a current of 30 mA, and the X-ray angle relative to the samples was 2°.

2.2.2 Morphological Analysis

The surface morphology of targets and films was characterized using a 'Hitachi SU8020 Field emission gun' Scanning electron microscope (SEM) at 10 kV. It operates by focusing a beam of electrons onto a sample, where interactions with the surface generate Secondary Electrons (SE), Backscattered Electrons (BSE), and characteristic X-rays. The SE and BSE signals are detected to produce detailed images with a nanometer-scale resolution. The thickness of as-deposited films was measured using a probe profilometer 'Dektak XT' from Bruker employing a 2-micron-sized tip.

2.2.3 Compositional Analysis of Targets

The compositional characterization of pristine targets was performed using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), with an error margin of ≤ 2 wt%. The ICP-OES analysis was carried out by Ms. Alice Belfiore from Materia Nova using the ‘Optima 7300dv’ system. Briefly, the ‘mixture BNT’ powder was dissolved into an equimolar mixture of HCl, HNO₃, and HF acids and converted into an aerosol, which was then introduced into a high-temperature Ar plasma (6000–7000 K). In principle, the high-energy plasma breaks the aerosol molecules and releases individual atoms, which then excite and relax, producing optical emissions. Those optical emissions are detected and quantified for each element available in the sample, except oxygen. The elemental mapping of targets was performed by the Energy Dispersive X-ray Spectroscopy (EDX) using the ‘Thermo Scientific Noran System 7’ detector, while 10 kV electron beam was used during the samples scanning. The X-ray Photoelectron Spectroscopy (XPS) based ‘surface’ analysis was performed for the compositional analysis of conditioned targets, having an average sampling depth in the range of a few nm. The XPS analysis (error margin ≤ 1 at.%) was performed by Mr. Xavier Noirfalise from Materia Nova, using the Genesis (Physical Electronics) system. The pressure in the analysis chamber was typically 2×10^{-6} Pa, and the data were collected using Mg radiation at 1253.6 eV. The photoelectrons were collected at a take-off angle of 90° (normal detection) to the sample surface plane. For all samples, an Ar profile is made using a Gas cluster ion beam (GCIB) at 20 kV and 20 nA with a sputtered area of 2×2 cm². The profiles are performed with a step of 1 min, where the elements are analyzed with a pass energy of 27 eV (high-resolution spectra) at each step. Atomic compositions were derived from peak areas using photoionization cross-sections calculated by

Scofield *et al.* (110), corrected for the dependence of the escape depth on the kinetic energy of the electrons, and corrected for the analyzer transmission function of the spectrometer. Atomic compositions were derived from the peak areas after a Shirley background subtraction (111) to isolate the true photoelectron peaks.

2.2.4 Compositional Analysis of Plasma

The plasma ion composition was analyzed by a quadrupole mass spectrometer ‘EQP-1001’ from Hiden Analytical Ltd (Figure 2-4), which was connected to the sputtering chamber by a DN100CF flange with a 100-micron-sized orifice, facing the target’s center. It was differentially pumped by a primary pump ‘nXDS15i’ and a turbo molecular pump ‘Std Exch EXT 75DX’ while its pressure was monitored by a high/ultra-high vacuum gauge ‘AIM-XL-MSEAL’, all from Edwards. The base vacuum of the mass spectrometer was $\sim 1 \times 10^{-7}$ Torr, which increased to $\sim 1 \times 10^{-6}$ Torr during the analysis. During the films deposition, argon pressure was fixed at 10 mTorr along with a target–substrate distance of 8 cm. However, the target–orifice distance equals 16 cm, so the Ar pressure was reduced to 5 mTorr to have an identical product of pressure (P) and target–orifice or target–substrate distance (D), with $P \times D = 80$ mTorr.cm. The $P \times D$ parameter governs the number of collisions during transport in the gas phase, thereby affecting both the population of ions detected and to some extent also their energies upon reaching the MS orifice (and the substrate) ¹¹⁰. During the time-resolved plasma ion composition analysis, the mass spectrometry (MS) scans were conducted at 50-minute intervals, with each measurement averaging ~ 10 minutes in duration, corresponding to a scan rate of one per hour. Mass spectrometry is an analytical technique used to determine the gas-phase composition and the relative abundance of plasma ions by measuring their mass-to-charge

ratios (m/q). Energy-resolved mass spectrometry extends this capability by also measuring the Ion Energy Distribution Functions (IEDFs).

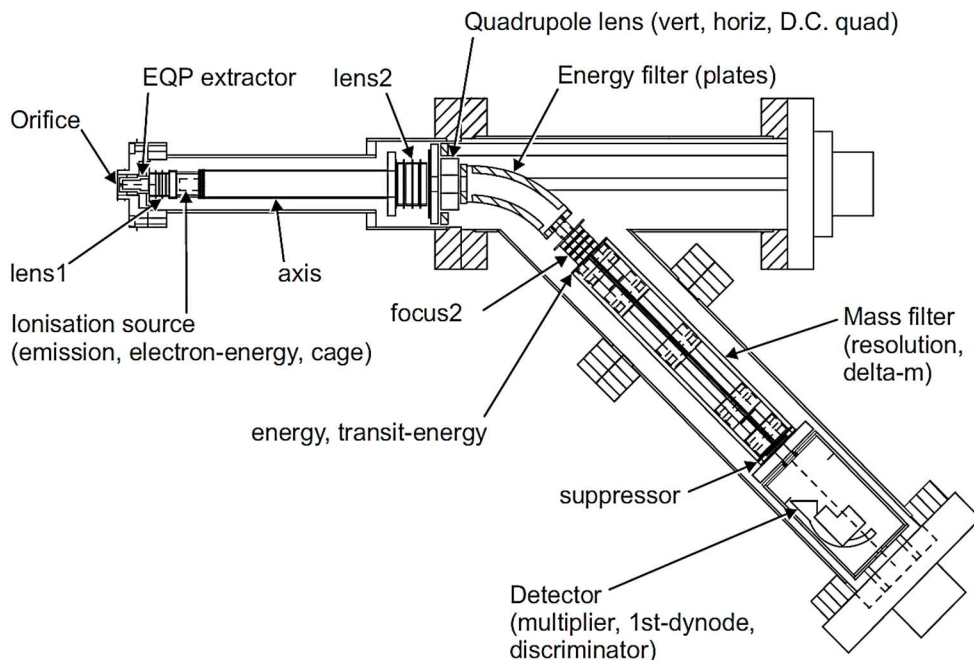


Figure 2-4: Schematic diagram of the HAL's EQP 1001 Mass Spectrometer.

The EQP 1001 consists of four key stages (Figure 2-4):

- Ion optics stage (orifice, lens 1, axis, lens 2): Selects the polarity of incoming ions (positive or negative ions) and focuses the ion beam along the MS optical axis.
- Electrostatic energy analyzer stage (quadrupole lens, energy filter, focus2): Filters out neutral species, allowing only ions with specific kinetic energies to pass through.
- RF quadrupole mass filter stage (resolution, delta-m): Separates ions based on their mass-to-charge ratio, transmitting one m/q at a time.
- Secondary electron multiplier (SEM) detector stage (multiplier, 1st-dynode, discriminator): Converts the incoming ion current to

electrons for software-based generation of mass spectra and IEDFs.

The plasma ion chemistry was determined by the target-derived elemental ion ratios ($\frac{Bi}{Ti}$, $\frac{Na}{Ti}$, and $\frac{Bi}{Na}$), where O was excluded from the discussion because it can also originate from the residual IPA (C_3H_8O) and water molecules in the BNT targets. Water can also outgas from the chamber walls. The elemental ion ratios were calculated in four steps. First, the IEDF of each detected ion specie ($j^{1+} = Bi^{1+}, Na^{1+}, Ti^{1+}, BiO^{1+}, TiO^{1+}$) was integrated to obtain its total intensity (Eq. 2.2). Second, the total ion intensity of each element was obtained by summing the intensities of all ions of that element (e.g., Bi ions = $Bi^{1+} + BiO^{1+}$), as expressed in Eq. 2.3. Finally, the elemental ion ratios were calculated according to the Eqs. 2.4–2.6.

$$I_{j^{1+}} = \int IEDF_{j^{1+}}(E)dE \quad (2.2)$$

$$I_j = I_{j^{1+}} + I_{jo^{1+}} + I_{jo_2^{1+}} + \dots \quad (2.3)$$

$$\left(\frac{Bi}{Na}\right) = \frac{I_{Bi}}{I_{Na}} \quad (2.4)$$

$$\left(\frac{Bi}{Ti}\right) = \frac{I_{Bi}}{I_{Ti}} \quad (2.5)$$

$$\left(\frac{Na}{Ti}\right) = \frac{I_{Na}}{I_{Ti}} \quad (2.6)$$

2.2.5 Compositional Analysis of Films

The film's compositional analysis is an important aspect of this work and was primarily performed by the Energy Dispersive X-ray Spectroscopy (EDX) using the 'Thermo Scientific Noran System 7' detector, embedded inside the SEM machine. A 10 kV electron beam was consistently used during the EDX measurements, while the elemental quantification was performed using the lines: Ti La at 0.455, O Ka at

0.525, Na K α at 1.041, Bi M α at 2.42, and Ti K α at 4.508 keV. To enable the spatially-resolved compositional analysis, films were deposited on strip-shaped substrates, measuring 3.81 x 2 cm², matching the radius of 3-inch BNT targets, and were divided after film deposition into three equal zones of 1.27 x 2 cm²: center (0–1.27 cm), middle (1.27–2.54 cm), and edge (2.54–3.81 cm), as shown in Figure 2-5. In each zone, three EDX measurements were performed: one at the zone's midpoint and two at the positions offset by ± 0.5 cm over the substrate length, and the average value was reported.

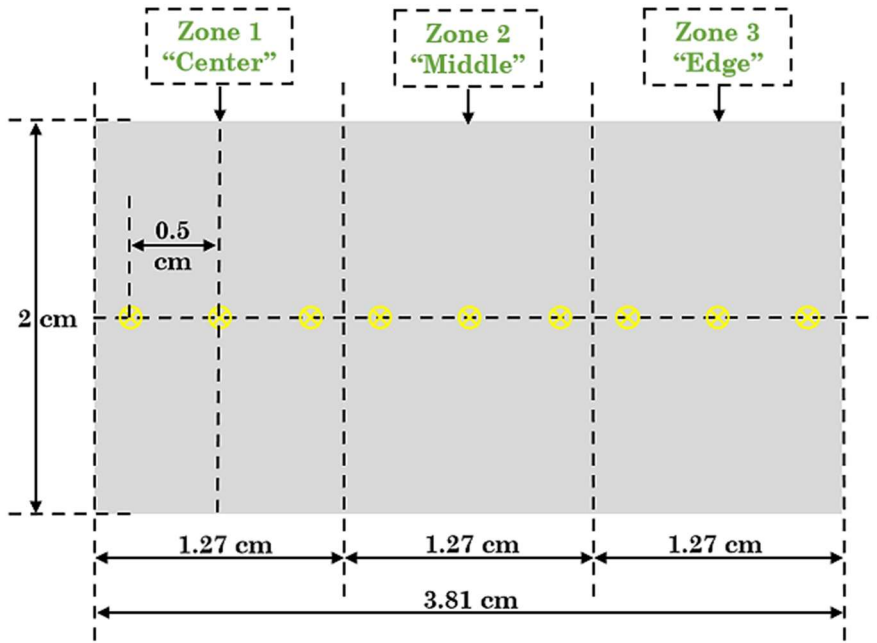


Figure 2-5: Front view of the substrate, highlighting the division of zones and the approximate composition measurement points.

In ABO₃ perovskites such as Bi_{0.5}Na_{0.5}TiO₃, the crystal structure consists of a 3-D framework of corner-sharing TiO₆ octahedra, with Ti⁴⁺ cation residing at the cube center (B-site), Bi³⁺ and Na¹⁺ cations sharing the cube corners (A-site), while O²⁻ anions occupying the cube's face centers (O-site), as shown below in Figure 2-6.

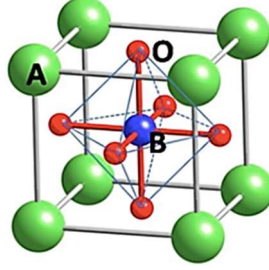


Figure 2-6: Schematic illustration of the cubic perovskite crystal structure.

The composition of BNT films is determined using the cation ratios normalized to Ti, e.g., $\frac{Bi}{Ti} = \frac{Na}{Ti} = 0.5$ alongside the $\frac{Bi}{Na} = 1$, with the oxygen content implicitly assumed through the ABO_3 stoichiometry¹¹¹⁻¹¹³. This convention allows direct valuation of A-site non-stoichiometry and enables the identification of Bi- or Na-rich (or deficient) compositions. In contrast, the O quantification by EDX relies on a low-energy X-ray signal of Ka line at ~ 0.525 keV, which is strongly affected by absorption within the sample, detector-window effects, and surface contamination (e.g., carbon). As a result, only cation ratios will be used to characterize the chemistry of the BNT films. Despite its ease of use, the EDX accuracy in elemental quantification is not optimal, and its error can reach up to several at.%, especially for the lighter elements like Na and O in our case. To enhance the accuracy of EDX-based cation ratios, some films were also analyzed by the “heavy-ion” hybrid Elastic recoil detection analysis–Rutherford backscattering spectrometry (hybrid ERDA-RBS) and the average calibration factors were determined ($k = 1.2 \pm 0.4$, $l = 1.1 \pm 0.4$, and $m = 0.9 \pm 0.2$), according to the following equations:

$$\left(\frac{Bi \text{ at\%}}{Na \text{ at\%}}\right)_{Hybrid \text{ ERD-R}} = k \left(\frac{Bi \text{ at\%}}{Na \text{ at\%}}\right)_{EDX} \quad (2.7)$$

$$\left(\frac{Bi \text{ at\%}}{Ti \text{ at\%}}\right)_{Hybrid \text{ ERD-R}} = l \left(\frac{Bi \text{ at\%}}{Ti \text{ at\%}}\right)_{EDX} \quad (2.8)$$

$$\left(\frac{\text{Na at}\%}{\text{Ti at}\%}\right)_{\text{Hybrid ERD-RBS}} = m \left(\frac{\text{Na at}\%}{\text{Ti at}\%}\right)_{\text{EDX}} \quad (2.9)$$

The procedure employed to determine these calibration factors is detailed in the Appendix C of this thesis. These calibration factors are applied to all the EDX-based film compositions throughout this thesis. Hybrid ERDA-RBS analysis of BNT films was performed by Mr. Karim-Alexandros Kantre at IMEC (Belgium) using the ‘6SDH-1 (MAX 2 MV)’ ERD accelerator from National Electrostatics Corporation. A high-energy and heavy ion beam of 12.601 MeV $^{79}\text{Br}^{6+}$ was employed as the primary projectile and directed onto the sample at a grazing incidence angle, inducing elastic collisions and recoil of target atoms. In this hybrid approach, RBS involves the detection of backscattered primary ions and provides accurate quantification of heavy elements such as Bi. In contrast, ERDA relies on the detection of forward-emitted recoiled target atoms, enabling sensitive analysis of light- and medium-mass elements, including O, Na, and Ti, within the same measurement. The energy detection and analysis of recoiled atoms were used to extract quantitative elemental depth profiles and to determine absolute atomic areal densities, reported in units of 10^{15} atoms/cm². Depth information was obtained directly from the energy loss of the recoiled species, while statistical uncertainties were derived from the detected event counts. The experimental geometry consisted of a 40° scattering angle and a 15° sample tilt, optimizing the detection of recoiled atoms while minimizing geometrical and spectral distortions (see Figure 2-7).

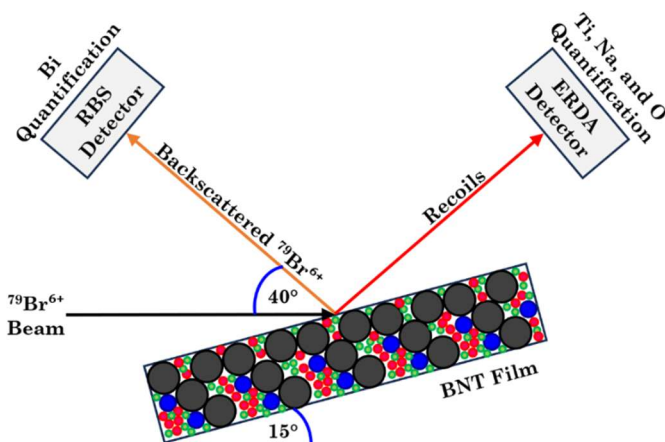


Figure 2-7: Schematic illustration of the hybrid ERDA-RBS analysis of BNT films.

2.3 Modelling and Simulations

The Monte Carlo simulation codes ‘TRIM’ (Transport of Ions in Matter) ^{114, 115} and ‘SiMTRA’ (Simulation of Metal Transport) ^{75, 82} were used for the target’s sputtering and species transport in the gas phase, respectively. For this purpose, the ‘surface erosion profile’ of the conditioned target was first analyzed by an optical profilometer ‘VR 6000’ from *Keyence*, and the XPS technique characterized its composition. The surface erosion profile was then converted into a 2D probability plot, having the precise location, geometry, and composition of the racetrack. In the TRIM simulations, a 100 nm thickness of the target was sputtered using 99999 Ar ions bombarding the target’s surface at 0° angle of incidence, i.e., normal incidence. TRIM code supports the sputtering simulations of multi-element targets, whereas the SiMTRA code is a binary tool that can handle the transport simulations of only a single element’s sputtered atoms through the background gas. Therefore, the resultant sputtering profile (energy and direction of sputtered atoms) from TRIM code was broken down into four parts to create individual files for each element (Bi, Na, Ti, O). Next, the individual files were submitted to the SiMTRA code one by one, and their transport profiles towards all

the surfaces inside the sputtering chamber were computed, including the substrate, which measured $3.81 \times 2 \text{ cm}^2$. The 2D deposition profiles of each element on the substrate's surface were then converted into individual line graphs along the substrate's length by adding the number of deposited atoms across the substrate's width at each length point. Finally, the four 'line' deposition profiles for the individual elements were normalized to get a combined graph, showing the probable impinging flux composition across various locations on the substrate (see Figure 2-5), i.e., Center (0 – 1.27 cm), Middle (1.27 – 2.54 cm), and Edge (2.54 – 3.81 cm) zones.

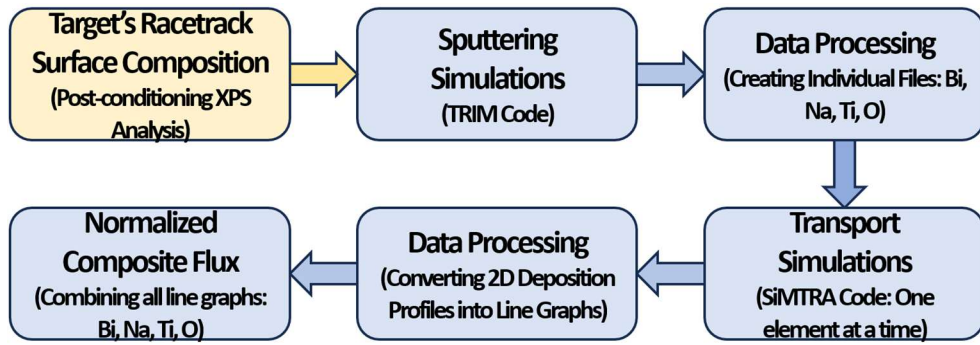


Figure 2-8: An overview of the simulation scheme and data processing.

2.4 Scheme of Experiments

The central theme of this thesis was to investigate the relationship between target-plasma-film chemistries and the realization of crystalline $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ films with the proper stoichiometric composition, ideally without sodium oxide surface defects. The following strategy was employed to conduct the experiments.

- i. Initially, the pristine BNT powders are characterized by ICP-OES and EDX techniques to determine their chemical compositions.
- ii. The pristine targets are pre-conditioned by continued sputtering for ~10 h at an applied power density of 2.19 W/cm^2 under 10

mTorr Ar pressure using an RF discharge, followed by their XPS-based surface analysis.

- iii. The elemental composition of conditioned targets' racetrack surface is used as the 'actual' composition for the sputtering simulations using the 'TRIM' code, followed by the modeling of species transport via the 'SiMTRA' code.
- iv. Next, the conditioned targets were sputtered continuously for ~8 h at an applied power density of 2.19 W/cm², under 10 mTorr Ar pressure (P) and a target-substrate distance (D) of 8 cm (P x D = 80 mTorr.cm) for film deposition. For mass spectrometry analysis, a reduced Ar pressure of 5 mTorr and an extended target-orifice distance of 16 cm were used due to system constraints. The intention was to maintain the P x D parameter at 80 mTorr cm, which results in a similar number of collisions for the sputtered species during their gas-phase transport and ensures the same deposition flux composition during film growth and plasma diagnostics experiments. The objective was to investigate, in a time-resolved manner, whether the plasma and film chemistries of a conditioned target evolve over the ~8 h deposition period.
- v. The mass spectrometer was tuned only once at the start of the sputtering process for each target, and the same tuning parameters were used for the whole 8–10 h sputtering period, to be able to track the plasma evolution from the 'initial state'. The MS scan took around 10 minutes on average and was performed once at the end of each hour, allowing hourly based time-resolved plasma composition analysis.
- vi. The Si substrates were cleaned with acetone to remove organic contaminants, rinsed with Isopropyl alcohol (IPA) to displace

residues, and dried with N₂ gas. To track the hourly evolution of the film composition, each film deposition lasted 50 minutes (with 10 minutes reserved for substrate loading and unloading), followed by EDX analysis, resulting in hourly based time-resolved film composition analysis.

- vii. Afterwards, the films were annealed in ambient air inside a conventional lab furnace at 700°C for 1 h with a ramp up and down of 3°C/minute.
- viii. Finally, the composition of annealed films was again characterized by EDX whose results calibrated by hybrid ERDA-RBS technique, along with the GIXRD analysis for the crystallinity evaluation of the films. The surface morphology of films was also recorded using SEM, both before and after the annealing.

2.5 Summary

This chapter describes the various experimental methods employed in achieving the goals of this thesis. A multi-faceted approach is implemented, including the target's chemistry analysis, plasma diagnostics, and characterization of the film's composition and structure. Techniques such as EDX, ICP-OES, and XPS are employed for analyzing the target's surface chemistry, mass spectrometry is used for detecting plasma-phase species, and EDX (calibrated by hybrid ERDA-RBS analysis) are used for analyzing film composition. The GIXRD is used to assess the crystallinity and phase stability of the films. Additionally, TRIM and SiMTRA codes are employed to simulate the transport of target atoms towards the substrate, providing deeper insight into the observed experimental trends.

Chapter 3 Study of the Conditioning Period using Pristine Targets

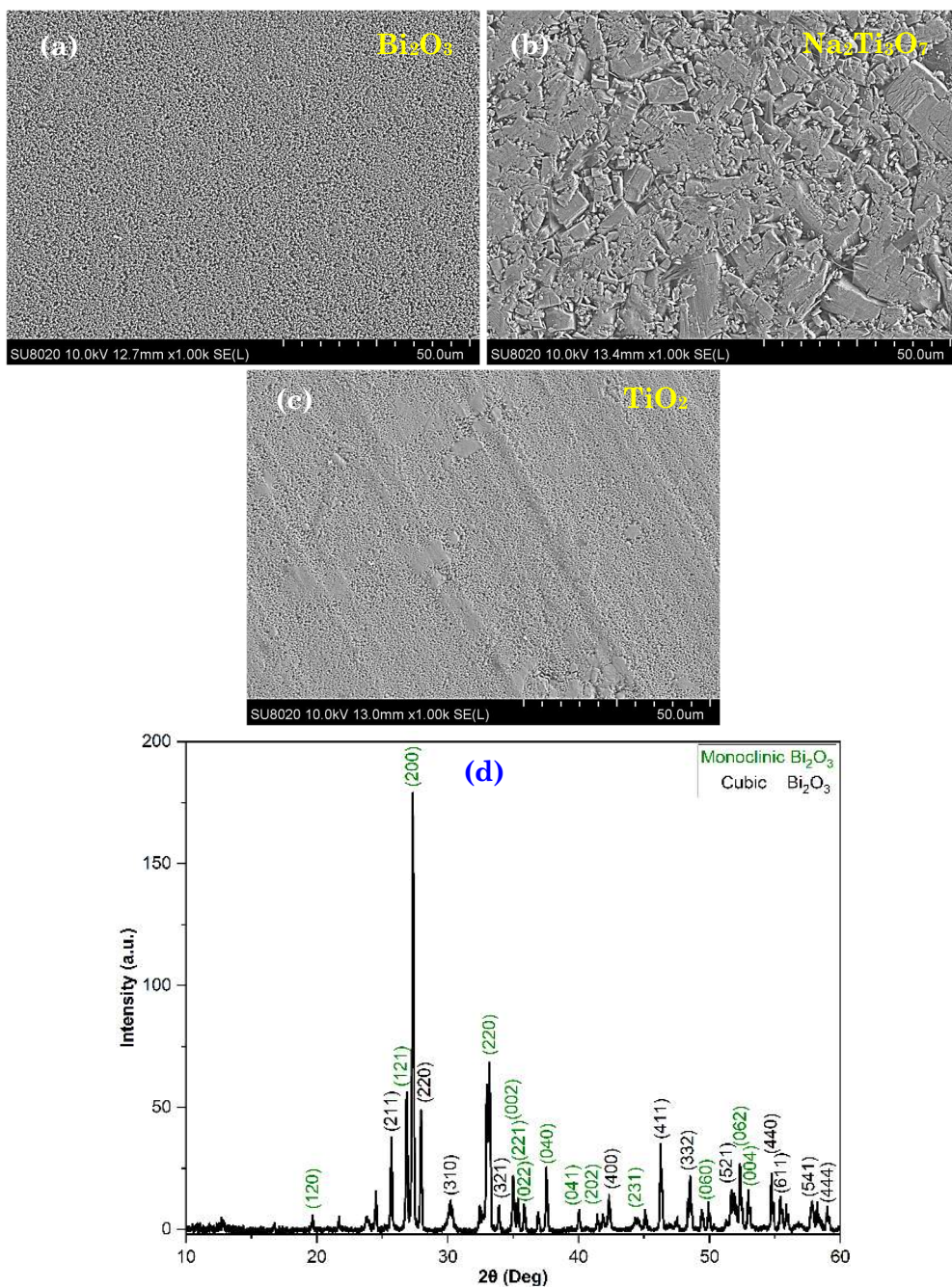
Following the strategy proposed by Hamieh *et al.* who worked on it at UPHF^{63, 64}, the pre-conditioning of the powder-based multi-element BNT targets is initially performed for 10 h at a power density of 2.19 W/cm² and 10 mTorr Ar pressure, in order to stabilize the target surface composition, ensuring a reproducible film composition from the onset of deposition. Therefore, the current chapter focuses on the evolution of pristine BNT targets' surface characteristics during this pre-conditioning period. It also presents the associated plasma ion chemistry, as recorded by mass spectrometry, and film composition analysis. The post-conditioning surface composition of the targets, particularly in the racetrack region, is also recorded for use as input to sputtering and transport simulations in the film deposition studies discussed in the next chapter.

3.1 Characterization of the precursors and pristine BNT targets

3.1.1 Characterization of the precursor powders

Hamieh *et al.* deposited BNT thin films primarily using stoichiometric Bi_{0.5}Na_{0.5}TiO₃ (BNT50.50) targets after the targets had undergone surface conditioning. The as-deposited films grown in the middle radial region (1.27–2.54 cm, Figure 2-3, p. 44) of unheated 3-inch diameter substrates exhibited a ~3 at.% excess of Bi^{63, 64}. To address the excess of bismuth, we have proposed a 2.5 at.% Bi-deficient Bi_{0.35}Na_{0.5}TiO_{2.8} (BNT35.50) target composition for investigation. As described in Section 2.1.2, the precursors used for the targets' fabrication were Bi₂O₃, Na₂Ti₃O₇, and TiO₂ powders. The top-view SEM and XRD data

acquired for the pristine powders used to fabricate our sputtering targets are shown in Figure 3-1.



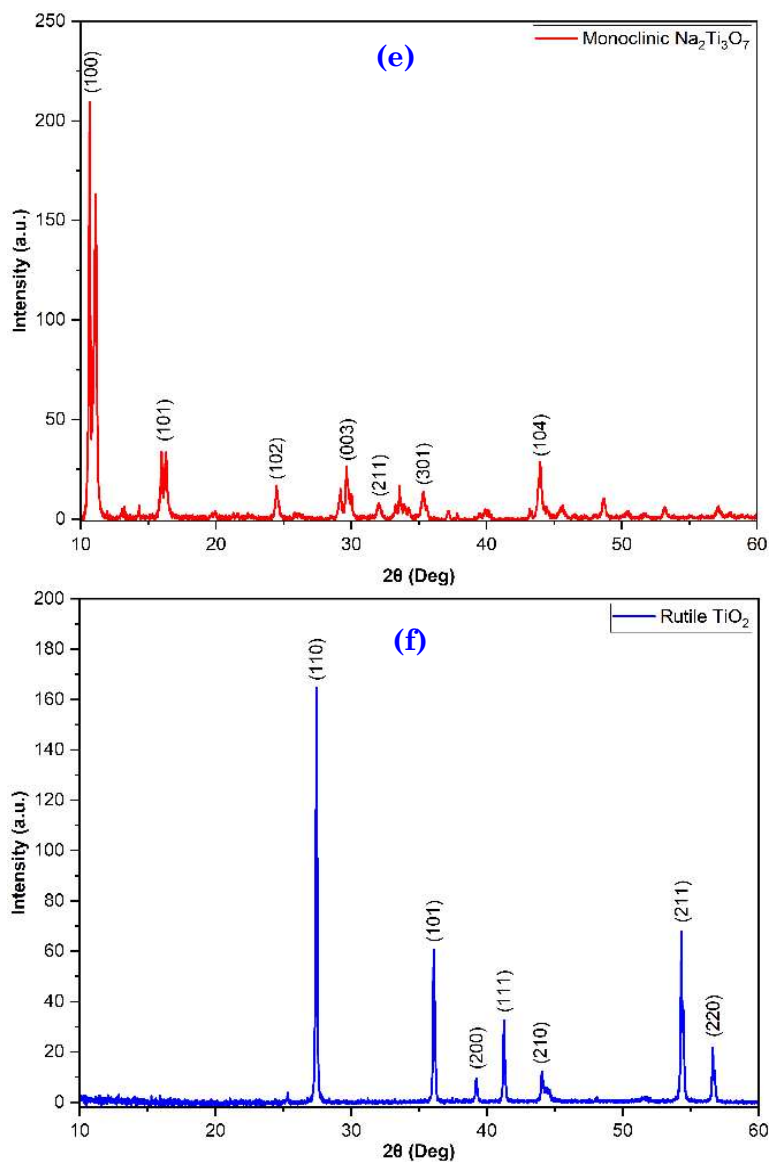


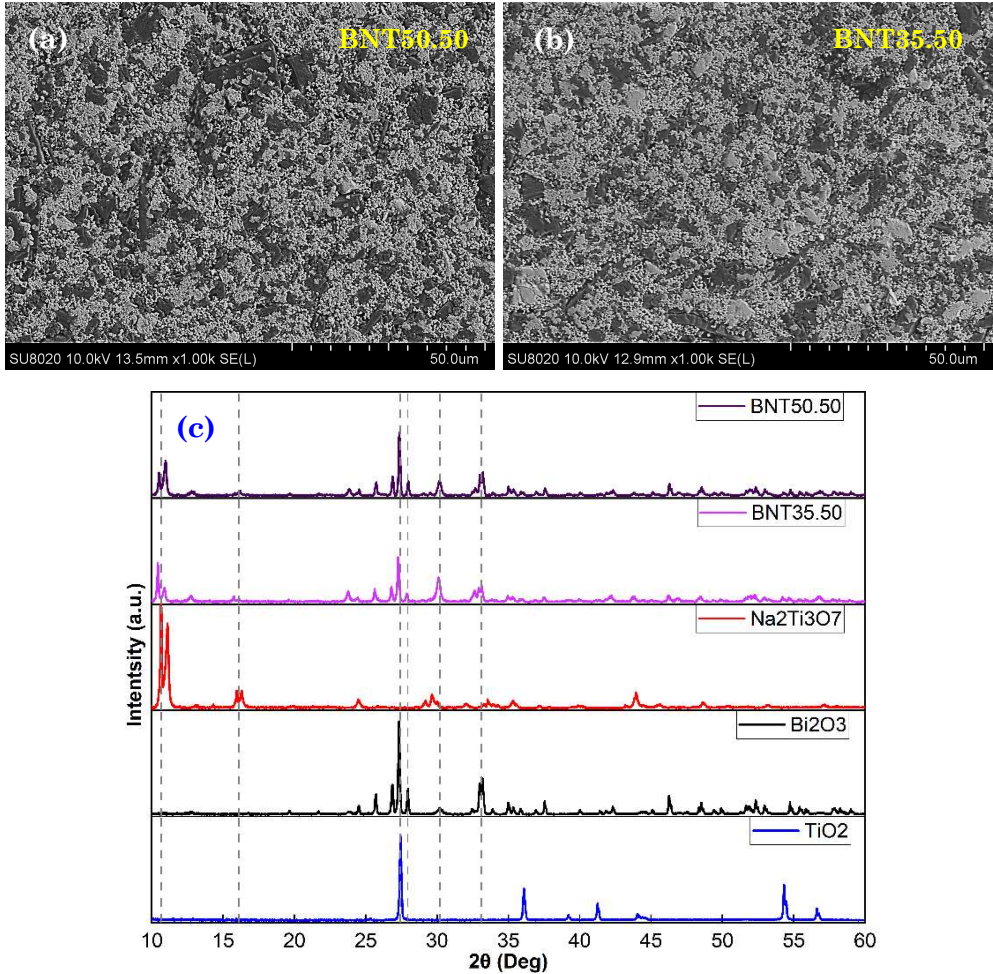
Figure 3-1: SEM top-view images and XRD patterns of precursor powders used in the fabrication of BNT targets: (a, d) Bi_2O_3 , (b, e) $\text{Na}_2\text{Ti}_3\text{O}_7$, and (c, f) TiO_2 .

The powder's particle size plays a critical role in the sputtering process, as it influences the target's surface morphology, the target erosion rate, and consequently the film deposition conditions. Zhu *et al.* demonstrated that sputtering $\text{Ba}(\text{Sn}_{0.15}\text{Ti}_{0.85})\text{O}_3$ powder targets with RF magnetron plasma yields higher deposition rates when using nanosized powders compared to micron-sized ones, primarily due to the reduced surface roughness of finer powders⁸³. Despite the similar mesh ratings in our case, SEM micrograph analysis combined with the ImageJ tool calculated that the Bi_2O_3 and TiO_2 powders were significantly finer than the $\text{Na}_2\text{Ti}_3\text{O}_7$, with average grain sizes of 0.5 μm , 1 μm , and 11.5 μm , respectively. Besides, all the precursor powders were crystalline: TiO_2 and $\text{Na}_2\text{Ti}_3\text{O}_7$ had rutile and monoclinic phases^{116, 117}, respectively, while the Bi_2O_3 had both monoclinic (α) and cubic (β) phases¹¹⁸. The presence of metastable β - Bi_2O_3 phase, which is stable only in the 727°C–824°C range, suggests the Bi_2O_3 powder was quenched.

3.1.2 Characterization of the pristine powder targets

The surface morphology of pristine BNT targets is depicted in Figure 3-2 (a, b), where Bi_2O_3 , $\text{Na}_2\text{Ti}_3\text{O}_7$, and TiO_2 phases are evident in both of the mixture compositions, i.e., BNT50.50 and BNT35.50. The XRD patterns of both target compositions are shown in Figure 3-2 (c) along with the diffractograms of pristine powders, presented for reference, highlighting the ‘mixture’ nature of both compositions as the characteristic peaks of all individual precursors are present in both cases. Up to 30% relative decrease in the intensity of the Bi_2O_3 phase is evident in the Bi-deficient BNT35.50 composition compared to BNT50.50, reflecting its 25% lower Bi_2O_3 content. The EDX-based elemental mapping, as depicted in Figure 3-2 (d–i), reveals that the larger dark particles correspond to the $\text{Na}_2\text{Ti}_3\text{O}_7$, while the smaller bright particles specify the Bi_2O_3 and TiO_2 . The ICP-OES analysis of both BNT

compositions confirm close agreement with their nominal elemental concentrations. For BNT50.50 ($\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$) composition, the ideal elemental ratios are $\frac{\text{Bi}}{\text{Na}} = 1$ and $\frac{\text{Bi}}{\text{Ti}} = \frac{\text{Na}}{\text{Ti}} = 0.5$, where the measured values, $\frac{\text{Bi}}{\text{Na}} = 0.92 \pm 0.06$, $\frac{\text{Bi}}{\text{Ti}} = 0.50 \pm 0.02$, and $\frac{\text{Na}}{\text{Ti}} = 0.54 \pm 0.03$, showed very good consistency with the desired composition. For BNT35.50 ($\text{Bi}_{0.35}\text{Na}_{0.5}\text{TiO}_{2.8}$) composition, the expected atomic ratios are $\frac{\text{Bi}}{\text{Na}} = 0.7$, $\frac{\text{Na}}{\text{Ti}} = 0.5$, and $\frac{\text{Bi}}{\text{Ti}} = 0.35$, while the measured values, $\frac{\text{Bi}}{\text{Na}} = 0.71 \pm 0.05$, $\frac{\text{Na}}{\text{Ti}} = 0.61 \pm 0.04$, and $\frac{\text{Bi}}{\text{Ti}} = 0.43 \pm 0.03$, again demonstrated good agreement with the intended stoichiometry.



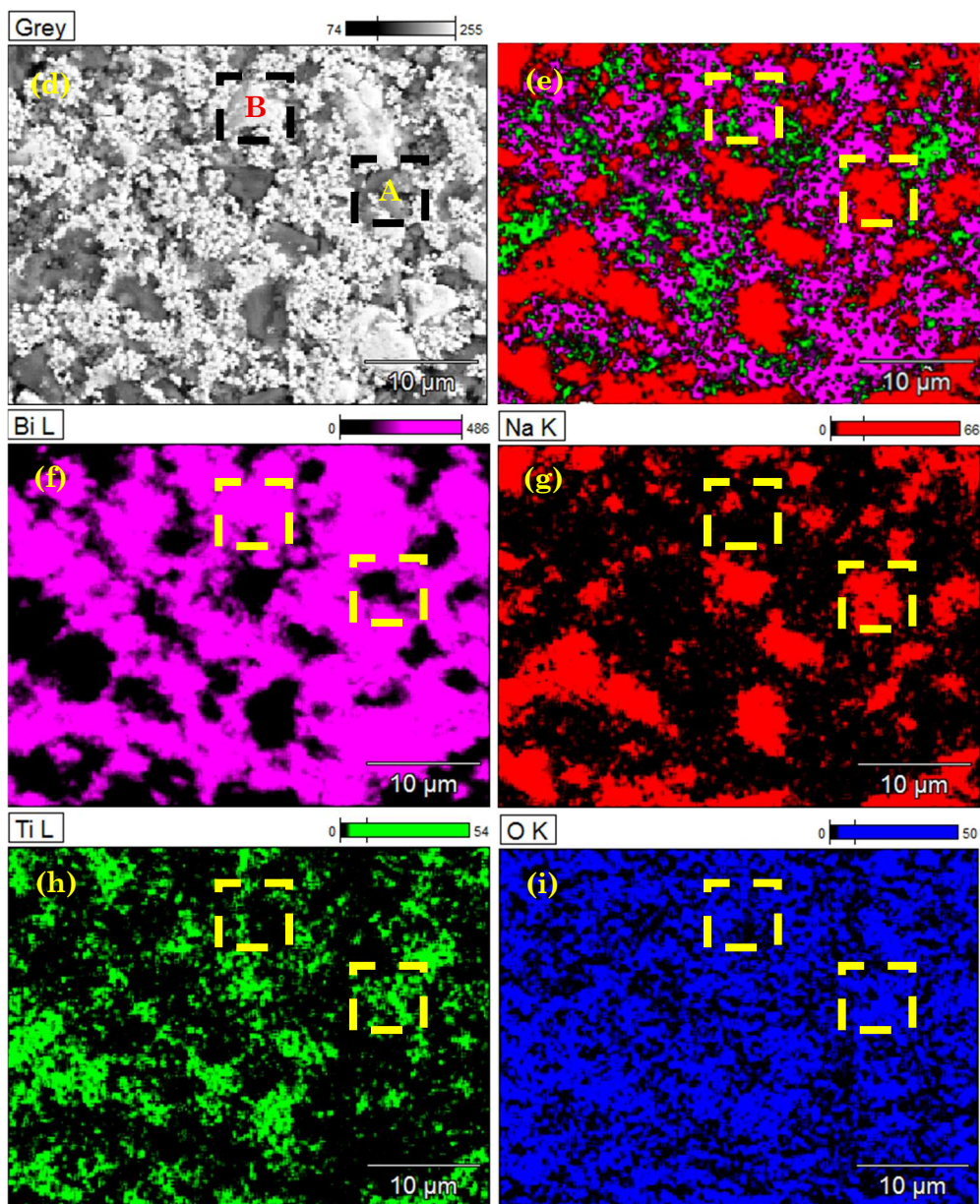


Figure 3-2: SEM micrographs of pristine powder targets (a) BNT50.50, (b) BNT35.50, and (c) XRD analysis of BNT powders with precursor references. (d–i) EDX elemental maps of BNT50.50 target surface, including (e) a superimposed Bi–Na–Ti elemental map highlighting the elements present at analysis spots A and B.

3.2 Plasma ion chemistry at 2.19 W/cm² and 80 mTorr.cm

To monitor the evolution of plasma ion chemistry, mass spectrometry (MS) analysis was carried out throughout the conditioning period. The mass spectra of both BNT50.50 and BNT35.50 plasmas during the final hour of conditioning are shown in Figure 3-3, while the detected ions are listed in Table 3-1.

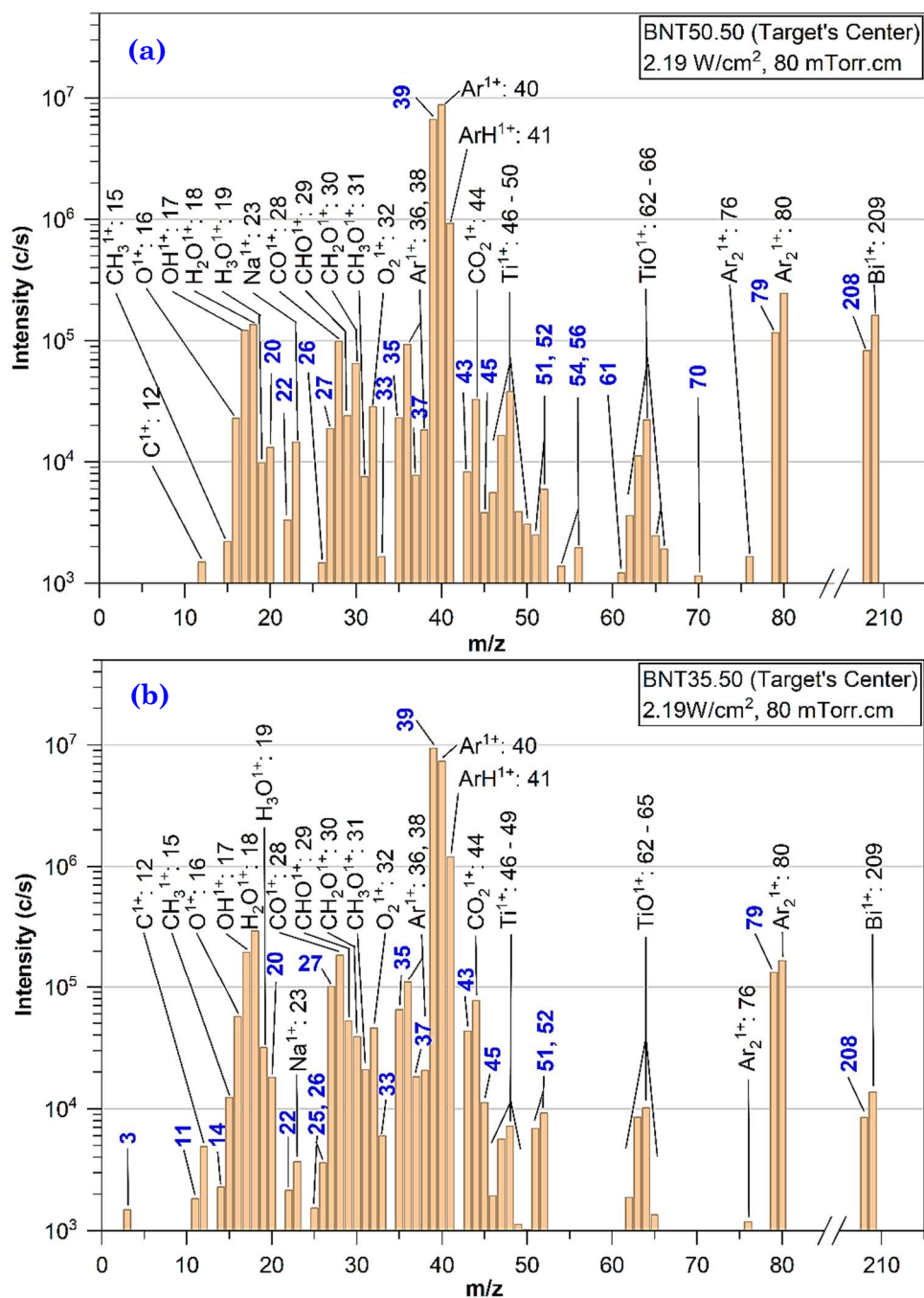


Figure 3-3: Mass spectra of (a) BNT50.50 and (b) BNT35.50 sputtering plasmas during the final hour (~10th h) of conditioning.

m/z ratio	ion	m/z ratio	ion
12	C ¹⁺	16	O ¹⁺
17	OH ¹⁺	18	H ₂ O ¹⁺
19	H ₃ O ¹⁺	23	Na ¹⁺
26	C ₂ H ₂ ¹⁺	28	CO ¹⁺
29	CHO ¹⁺	30	CH ₂ O ¹⁺
32	O ₂ ¹⁺	36, 38, 40	Ar ¹⁺
41	ArH ¹⁺	44	CO ₂ ¹⁺
46–50	Ti ¹⁺	62–66	TiO ¹⁺
76, 80	Ar ₂ ¹⁺	209	Bi ¹⁺

Table 3-1: List of ions detected in both the BNT50.50 and BNT35.50 sputtering plasmas.

The OH¹⁺, H₂O¹⁺, and H₃O¹⁺ ions likely originate from water molecules desorbing from the walls of MS and sputtering chamber. The C¹⁺, CO¹⁺, CO₂¹⁺, C₂H₂¹⁺, CHO¹⁺, and CH₂O¹⁺ ions presumably derive from the residual molecules of carbon dioxide inside the chamber and the residue IPA (C₃H₈O) in targets, which was added into the precursor powders during the target's fabrication. The argon-based ions (Ar¹⁺, ArH¹⁺, and Ar₂¹⁺) obviously originate from the background Ar gas. The oxygen ions (O¹⁺ and O₂¹⁺) originate from the sputtering of Bi₂O₃, Na₂Ti₃O₇, and TiO₂ precursor powders, water molecules, and the residual IPA (C₃H₈O) in targets. The sodium ions (Na¹⁺) are sputtered from the Na₂Ti₃O₇, titanium ions (Ti¹⁺ and TiO¹⁺) arise from both the Na₂Ti₃O₇ and TiO₂, and the Bi¹⁺ ions originate only from the Bi₂O₃ powder.

There is always an additional peak on the left side of every major peaks, e.g., 15 next to 16 (O¹⁺), 22 next to 23 (Na¹⁺), 31 next to 32 (O₂¹⁺), etc., which is caused by an instrumental artifact. To assess this possibility, metallic Ti and Bi targets were reactively sputtered in an Ar/O₂ discharge. As shown in Figure 3-4, both of the mass spectra similarly exhibit these

additional peaks which suggests that the peak broadening is indeed happening. The remarkably high intensity of Bi^{1+} peak (209 u) might reflect the concurrent sublimation/evaporation of Bi during sputtering, driven by the high power density of 4.93 W/cm^2 applied during that measurement. The Bismuth target was found to be partially melted after the experiment. However, the disappearance of the carbon-related peaks observed in Figure 3-3 confirms that IPA used during BNT targets preparation affects the plasma ion chemistry.

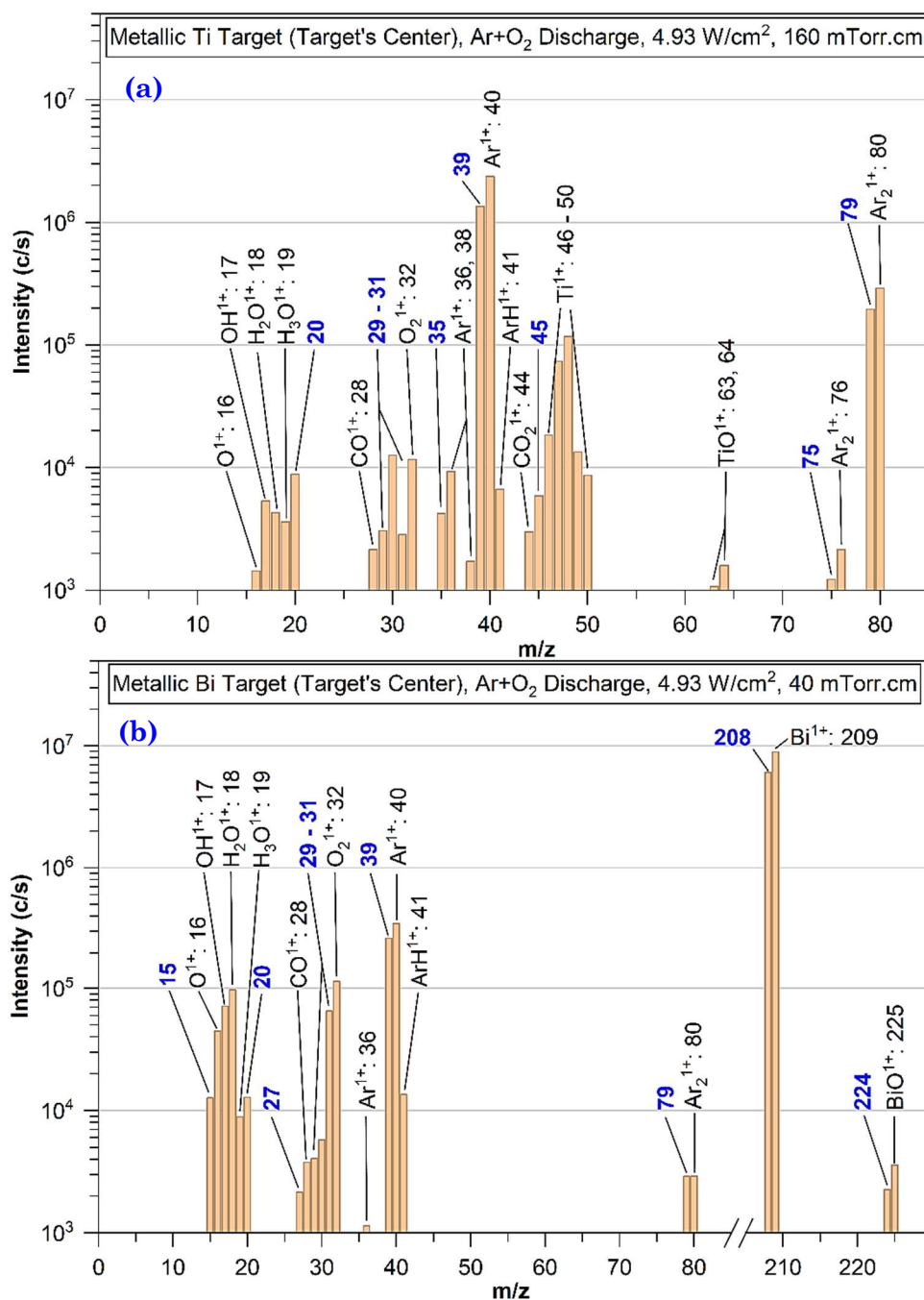


Figure 3-4: Mass spectra of sputtering plasmas from (a) metallic Ti and (b) metallic Bi targets in Ar/O₂ discharges.

Besides, there are still other unidentified peaks ($m/z = 3, 14, 20, 25, 33, 51, 52, 54, 56, \text{ and } 70$), which may arise from peak broadening or

from impurities originating from the target and the MS–sputtering assembly. Among the secondary peaks, 39 m/z seems significant which could in theory be assigned to the NaO^{1+} ion. The literature lacks data on the mass spectrometry analysis of $\text{Na}_2\text{Ti}_3\text{O}_7$ sputtering plasma; however, Na-based compounds have been studied in the framework of sputtering or other gas phase processes. Wiens *et al.* sputtered Na_2SO_4 using a 3 keV Ar^+ ion beam and performed Time-of-flight mass spectrometry (ToF-MS) analysis. They found that Na (23 u) is the most abundant sputtered specie, having over an order of magnitude higher intensity than NaO (39 u) and Na_2O (62 u) ¹¹⁹. Similarly, Dukes *et al.* sputtered various sodium silicates ($\text{NaAlSi}_3\text{O}_8$, $(\text{Na,Ca})\text{AlSi}_3\text{O}_8$, $(\text{K,Na})\text{AlSi}_3\text{O}_8$) using a 4 keV He^+ ion beam, followed by mass spectroscopy analysis. They also found that the intensity of Na^{1+} ion (23 m/z) was likewise over an order of magnitude higher than that of the NaO^{1+} ion (39 m/z); however, no conclusions were drawn for Na_2O^{1+} ion (62 m/z) because their measurements were limited only up to 50 m/z ¹²⁰. Together, these studies highlight that sputtering of Na-based complex oxides predominantly emits Na (23 u), with NaO (39 u) and Na_2O (62 u) as minor constituents. One can reasonably expect a similar trend for the $\text{Na}_2\text{Ti}_3\text{O}_7$ containing BNT sputtering plasma as well, suggesting that 39 m/z peak in mass spectra might be a clue for the presence of NaO^{1+} molecule, even though the peak at 39 m/z is overlapped by the intense peak of Ar^{1+} ion (40 m/z). The IEDFs of various target-derived ions are shown below in Figure 3-5, which were recorded during the last hour of conditioning period.

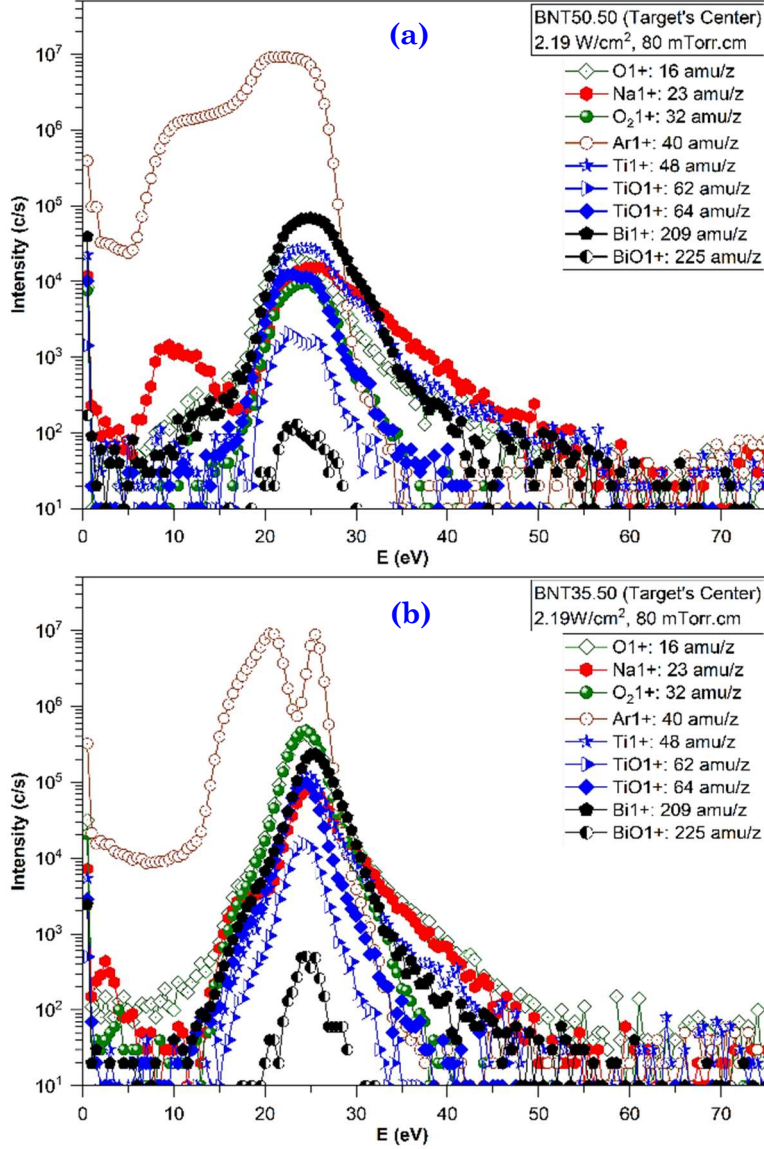


Figure 3-5: Mass spectrometry-based IEDFs of selected ions in (a) BNT50.50 and (b) BNT35.50 plasmas during the final conditioning hour ($\sim 10^{\text{th}}$ h).

The plasma potential (V_p) for both plasmas was found to be ~ 25 V, as determined from the maximum of Ar^{1+} (40 m/z) IEDF with the MS orifice electrically grounded ¹²¹. Accordingly, all IEDFs exhibit maxima near 25 eV, consistent with this plasma potential. The target-derived atomic ions (Bi^{1+} , Na^{1+} , Ti^{1+} , and O^{1+}) exhibit high-energy tails (i.e., $E > 25$

eV), characteristic of sputtered species and the so-called Sigmund-Thomson distribution ¹²²⁻¹²⁴. On the other hand, the Ar^{1+} IEDF shows a marked low-energy shoulder (i.e., $E < 25$ eV), which is usually attributed to the resonant charge exchange reactions occurring inside the sheath. The condition for this reaction to occur is that the sheath is large enough and that the collision frequency is significant; the colliding species are in rather large concentration in the gas phase. It can be understood that this condition is fulfilled for the argon gas ions. Broadening of the IEDF can also be induced in RF discharges because of the oscillating (RF) sheath ¹²⁵. Particularly, the Na^{1+} ion also show a secondary low-energy peak for both target compositions. This low energy peak (which is more pronounced in the case of BNT50.50 target compared to BNT35.50) ¹²⁶, suggests the existence of a substantial population of Na atoms in the gas phase. Since the sputtering simulations suggest lower transport of Na (1328–1333 atoms) towards the MS orifice compared to that of the Ti (1486–1496 atoms) and Bi (1505–1544 atoms), it is reasonable to assume that sputtering is not the only process responsible for the production of gaseous Na atoms in our experiments.

During the sputtering process, most of the incoming argon ion energy is converted into heat, which can drive the target surface to very high temperatures ¹²⁷. Cormier *et al.* observed that the surface of a metallic Ti target can reach temperatures as high as 870 °C, despite the active water cooling of cathode ¹²⁸. The temperature could rise even further when sputtering loosely packed insulating powder targets, such as the BNT targets studied here, due to their inherently lower thermal conductivity relative to dense metallic targets used in Cormier’s experiments ⁷⁹. Becker *et al.* showed that $\text{Na}_2\text{Ti}_3\text{O}_7$ decomposes in air to $\text{Na}_2\text{Ti}_6\text{O}_{13}$ and Na_2O at $\sim 800^\circ\text{C}$, followed by further decomposition into TiO_2 and Na_2O above 1110°C ¹²⁹, during which Na_2O gets sublimated due

to its higher vapor pressure. This decomposition process is expected to occur at relatively lower temperatures under low-pressure conditions, such as those found in an electrical discharge like ours. Furthermore, according to Hildenbrand et al, the vapor pressure of Na_2O is 5.21×10^{-7} atm (0.4 mTorr) at 710°C . The later increased more than fivefold to 2.81×10^{-6} atm (2.13 mTorr) at 783°C , releasing atomic Na and O gases ¹³⁰. In line with the target surface temperatures reported in the literature ¹²⁸ and the studies of Becker and Hildenbrand et al, one can suspect that the BNT target surface reaches very high temperatures during sputtering (for several hours), thereby emitting Na species from the target's surface through both the sputtering and sublimation processes. In the estimated target surface temperature range of $\sim 800^\circ\text{C}$, the sublimated Na neutrals will have a maximum K.E. of up to 0.1 eV compared to the sputtered species having peak K.E. of ~ 25 eV. This leads to a substantial flux of low-energy Na neutrals (≤ 0.1 eV), a fraction of which is ionized via charge-exchange reactions with Ar^{1+} ions in the sheath in front of MS orifice (or the substrate). The resulting Na^{1+} ions are subsequently re-accelerated within the sheath but experience only a fraction of the full plasma-orifice potential drop, thereby contributing to a distinct low-energy component in the Na^{1+} IEDF, as observed. However, the charge exchange reactions between Na (23 u) and Ar^{1+} (40 u) are expected to be relatively inefficient due to both the mass mismatch and the large ionization potential difference (Na = 5.14 eV, Ar = 15.76 eV), leaving the majority of sublimated Na atoms in the neutral state. It is therefore expected that the gas phase contains a large amount of Na neutrals, “invisible” during the mass spectrometry analysis, which can incorporate in the growing film.

In BNT50.50 plasma, the low-energy (≤ 10 eV) ion fraction is about 7% of the total Na^{1+} ions population, whereas in the BNT35.50 plasma, it is reduced to $\sim 1\%$. This suggests that the population of low-energy Na

atoms is likely much lower in BNT35.50 plasma compared to BNT50.50, which has further decreased the charge exchange reactions between Na (23 u) and Ar (40 u) species in the sheath of MS orifice (and the substrate). This implies a reduced decomposition of $\text{Na}_2\text{Ti}_3\text{O}_7$ into Na_2O , possibly due to the lower surface temperature of the BNT35.50 target compared to BNT50.50. Zaremba *et al.* investigated the solid-state reaction between Bi_2O_3 and TiO_2 at atmospheric pressure using differential thermal analysis (DTA) and reported an exothermic event at $\sim 600^\circ\text{C}$, marking the formation of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$; however, the enthalpy of reaction was not quantified¹³¹. Similarly, Wisniewski *et al.* used differential scanning calorimetry (DSC) to study a $\text{Bi}_2\text{O}_3\text{--TiO}_2\text{--SiO}_2\text{--Nd}_2\text{O}_3\text{--Al}_2\text{O}_3$ glass-ceramic at atmospheric pressure and observed a narrow exothermic peak at 680°C corresponding to the crystallization of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ from the amorphous glass; the enthalpy of reaction was likewise not quantified¹³². Both of those studies operate within the presumed ‘sputtering-induced’ surface temperature range ($\sim 700\text{--}800^\circ\text{C}$) of the BNT targets, supporting the likelihood of Bi_2O_3 and TiO_2 reacting to form $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ on the target’s surface. As this is an exothermic reaction so it likely contributes additional heat, further elevating the target surface temperature. This additional heat supply could potentially play an important role as according to Hildenbrand et al, the vapor pressure of Na_2O increases more than fivefold from 0.4 to 2.13 mTorr when the temperature increases from 710 to 783°C , releasing atomic Na and O gases¹³⁰. In BNT35.50 target, the 25% reduction in Bi_2O_3 content would proportionally decrease the formation of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, resulting in a relatively lower surface temperature. This reduction in temperature would moderately suppress the decomposition of $\text{Na}_2\text{Ti}_3\text{O}_7$ along with the subsequent sublimation of Na neutrals. As a result, fewer Na atoms are present in the plasma phase, diminishing the already inefficient charge-exchange reaction with Ar^{1+} , as

reflected by the reduced population of Na^{1+} ions in BNT35.50 plasma (i.e., ~1%) compared to that of the BNT50.50 (i.e., ~7%). The evolution of target-derived elemental ion ratios ($\frac{\text{Bi}}{\text{Ti}}$, $\frac{\text{Na}}{\text{Ti}}$, and $\frac{\text{Bi}}{\text{Na}}$) during conditioning is illustrated in Figures 3-6.

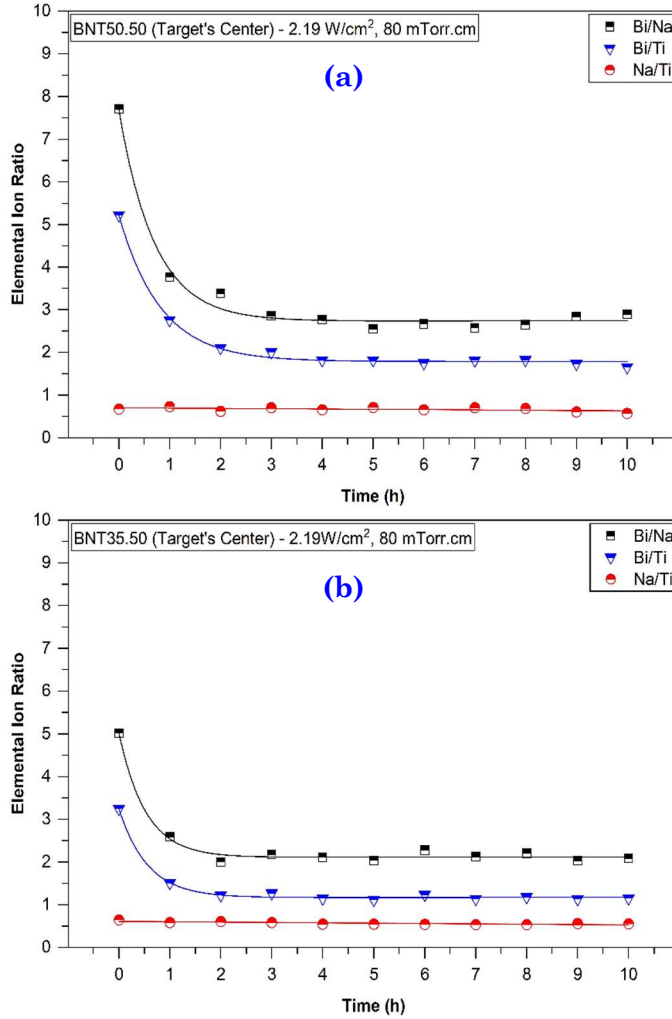


Figure 3-6: Mass spectrometry-based time-resolved elemental ion ratios in (a) BNT50.50 and (b) BNT35.50 plasmas during 10 h conditioning period.

Overall, both plasmas exhibit similar trends with higher Bi-related ratios in the start of conditioning which declines and stabilizes after a few

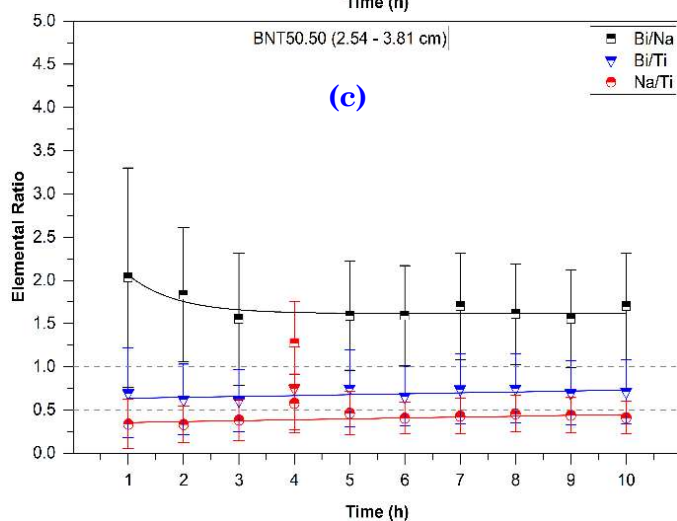
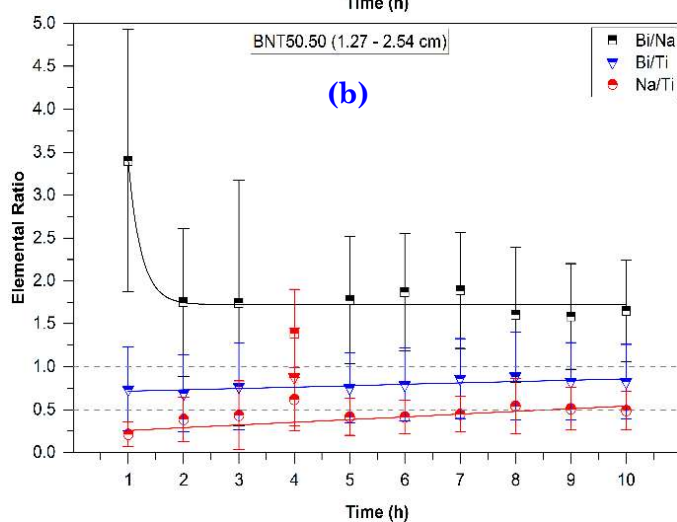
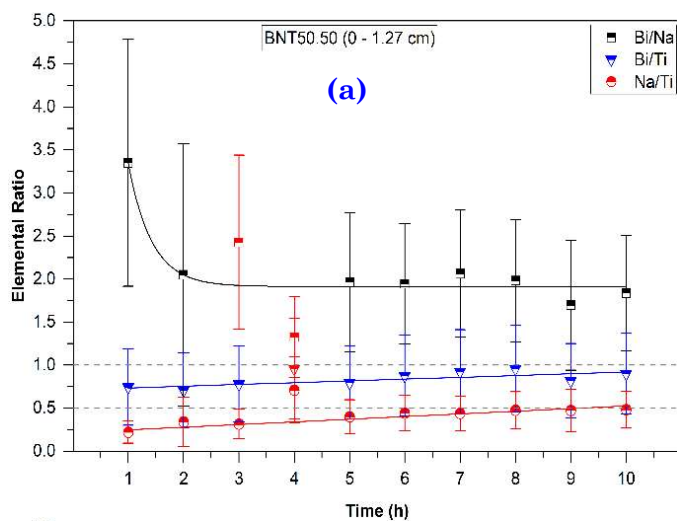
hours of sputtering. In contrast, the $\frac{Na}{Ti}$ ratio remains steady throughout the conditioning period. The initially high intensity of Bi-based signal in gas phase can be attributed to the lower backscattering of sputtered Bi (209 u) atoms by Ar (40 u) gas due to the significant difference in their masses. In contrast, lighter atoms like Ti (48 u) Na (23 u), and O (16 u) are efficiently backscattered and redeposited on targets surface, reflected as their relatively lower intensities in the gas phase. This causes a decrease in Bi concentration on the targets surface which is progressively replaced by lighter elements such as Ti, Na, and O. After the initial few hours (BNT50.50: ~4 h, BNT35.50: ~2 h), the targets surface composition apparently stabilizes with a decreased Bi concentration as indicated by lower Bi-based intensity ratios. In addition, the overall intensities of Bi-based ratios are higher in BNT50.50 plasma compared to BNT35.50, which can be attributed to 25% excess of Bi_2O_3 in the pristine BNT50.50 targets compared to BNT35.50. The $\frac{Na}{Ti}$ intensity ratio is very close in both cases because their contents are also closely similar in both sputtering targets.

In summary, the evolution of plasma ion chemistry from BNT50.50 and BNT35.50 targets was examined over a ~10 h conditioning period using mass spectrometry. The Bi-based ratios were higher in the beginning of conditioning period, which declined and stabilized after a few hours of sputtering (BNT50.50: ~4 h, BNT35.50: ~2 h). Notably, the low-energy secondary peak in the Na^{1+} (23 m/z) IEDF suggests additional emission process from the target surface, likely originating from the sputtering-induced heating of the target which lead to the decomposition of $Na_2Ti_3O_7$ into Na_2O , that subsequently sublimates and releases Na and O neutrals. Depending on the overall population of such low-energy Na neutrals and the re-evaporation processes occurring on substrate's

surface, this might lead to the deposition of excess Na within the as-deposited films and/or contribute to the formation of NaO_x surface defects in the BNT thin films.

3.3 Evolution of deposited films chemistry at 2.19 W/cm² and 80 mTorr.cm

To record the evolution of film composition during the continuous ~10 h conditioning period, films were deposited on Si (100) substrates. Each film deposition lasted 50 minutes, with ~10 minutes for loading and unloading the substrates, yielding 10 individual films, one representing each hour of the conditioning period. The target-substrate distance was 8 cm, and the Ar pressure was 10 mTorr; hence $P \times D = 80 \text{ mTorr.cm}$, as used in the MS experiments. The films composition is described in elemental ratios, where the desired stoichiometric Bi_{0.5}Na_{0.5}TiO₃ composition should have $\frac{Bi}{Na} = 1$ and $\frac{Bi}{Ti} = \frac{Na}{Ti} = 0.5$. Notably, the EDX based elemental ratios are calibrated using the hybrid ERDA-RBS based elemental ratios (details are described in Section 2.2.5, pp. 48–51). The final space-resolved composition of hourly deposited films is shown in Figure 3-7 (a–f).



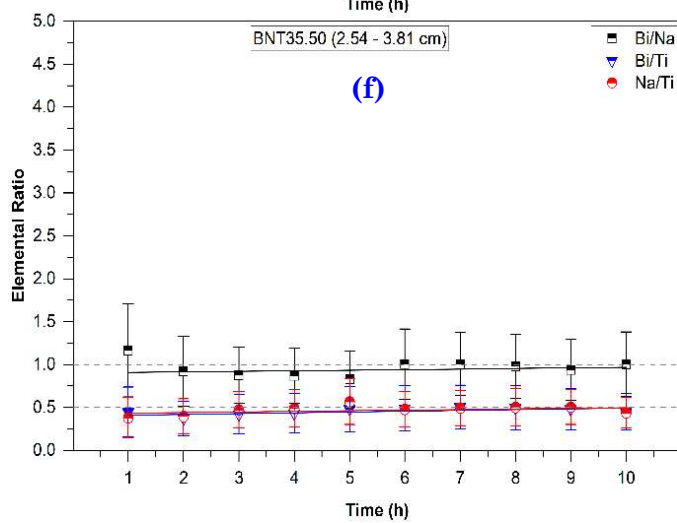
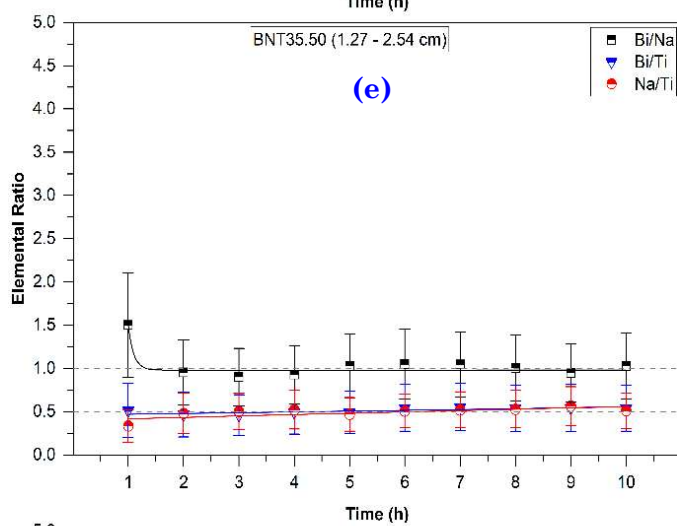
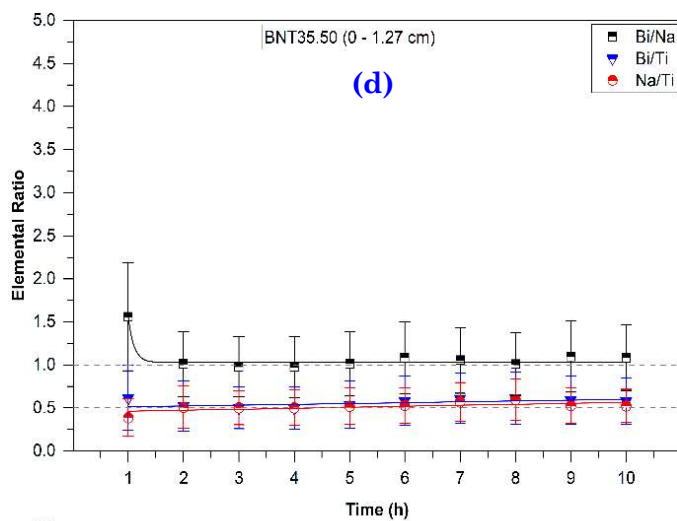


Figure 3-7: Time-resolved compositional profile of hourly deposited films during 10 h conditioning period using (a–c) BNT50.50 and (d–f) BNT35.50 targets. Dashed lines highlight the desired elemental ratios of

$$\frac{Bi}{Na} = 1 \text{ and } \frac{Bi}{Ti} = \frac{Na}{Ti} = 0.5.$$

Overall, the Bi content and so the $\frac{Bi}{Na}$ ratio of films is significantly higher during the initial conditioning hours across both of the targets which sharply decreases and relatively stabilizes afterward, potentially highlighting the evolution of target surface composition with a lowering concentration of Bi. This trend could be attributed to the lower backscattering of sputtered Bi (209 u) atoms by the Ar (40 u) gas due to a large difference in their masses, causing a decrease of its relative concentration on the targets surface over time. In contrast, lighter atoms like Ti (48 u), Na (23 u), and O (16 u) are efficiently backscattered and redeposited on targets surface, resulting in their increased concentration and ultimately leading to the stabilization of targets surface composition. After the initial few hours (BNT50.50: ~5 h, BNT35.50: ~2 h), the average $\frac{Bi}{Na}$ ratio relatively stabilizes but remains much higher in BNT50.50 films, due to the 25% excess of Bi_2O_3 in pristine BNT50.50 targets compared to the BNT35.50, where it has nearly the ideal value of 1 across the whole substrate. The mean $\frac{Bi}{Ti}$ ratio also remains higher in BNT50.50 films, due to the inherent Bi excess of its targets in comparison to the BNT35.50 films, which have nearly ideal value of 0.5 throughout the conditioning period. Finally, the average $\frac{Na}{Ti}$ ratio of BNT50.50 films reaches the desired value of 0.5 during the final hours of conditioning while the BNT35.50 films have the ideal value throughout the conditioning period.

Spatially after stabilization, the average $\frac{Bi}{Na}$ ratio remains higher in the center zone of substrate (BNT50.50: 1.9 ± 0.7 , BNT35.50: 1.1 ± 0.4) with a decreasing trend towards the edges (BNT50.50: 1.6 ± 0.6 ,

BNT35.50: 0.9 ± 0.4), showing more significance in the BNT50.50 films, due to the inherent Bi excess of BNT50.50 targets. The general spatial distribution could be again ascribed to the relatively lower scattering of sputtered ‘heavy’ Bi atoms during the transport through Ar gas towards the substrate compared to the lighter Ti, Na, and O atoms, resulting in a plasma flux with higher Bi concentration in its center compared to the edges. Similarly, the mean $\frac{Bi}{Ti}$ ratio stays higher in the center zone of substrate (BNT50.50: 0.9 ± 0.5 , BNT35.50: 0.6 ± 0.3) with a decreasing trend towards the edges (BNT50.50: 0.7 ± 0.4 , BNT35.50: 0.4 ± 0.2). Finally, the average $\frac{Na}{Ti}$ ratio also remains higher in the center zone of substrate (BNT50.50: 0.5 ± 0.2 , BNT35.50: 0.5 ± 0.2) with a decreasing trend towards the edges (BNT50.50: 0.4 ± 0.2 , BNT35.50: 0.4 ± 0.2). The film thickness profiles showed an increasing trend over time, as shown in Figure 3-8 (a, b). Spatially, the thickness profile follows that of typical sputtered films on static substrates, with greater thickness at the center which decreases toward the edges (Table 3-2).

Film Deposition Rates (nm/min)			
	Center (0–1.27cm)	Middle (1.27–2.54cm)	Edge (2.54–3.81cm)
BNT50.50	3.1 ± 0.1	2.4 ± 0.0	2.0 ± 0.0
BNT35.50	3.0 ± 0.0	2.3 ± 0.0	1.9 ± 0.1

Table 3-2: Deposition rates of films from BNT50.50 and BNT35.50 targets during the conditioning period.

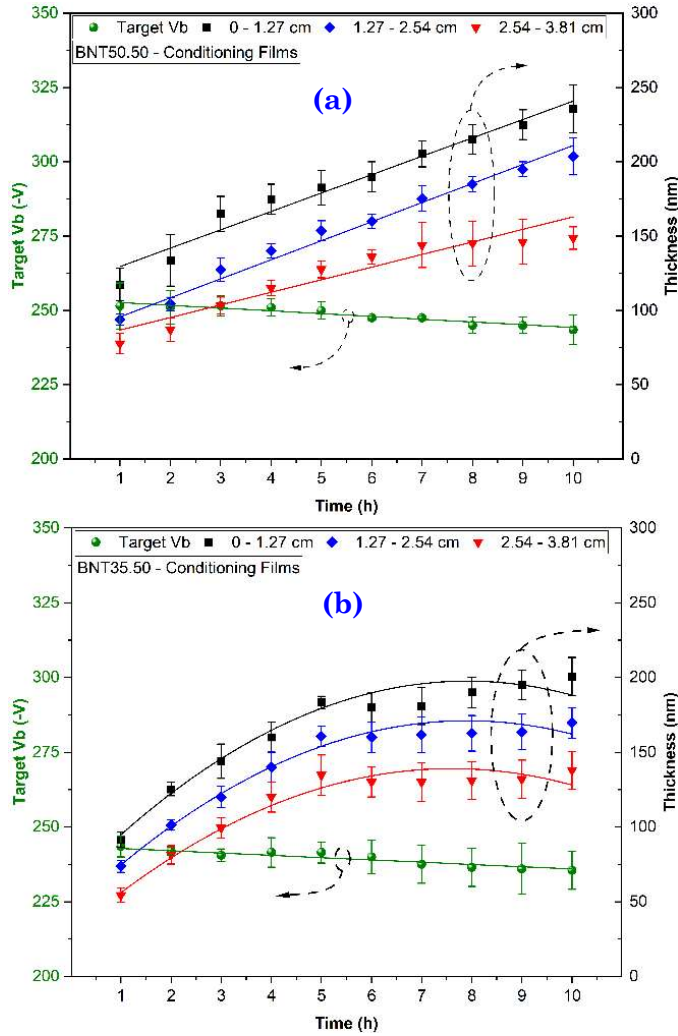


Figure 3-8: Hourly deposited film thickness profiles and target self-bias voltage of (a) BNT50.50 and (b) BNT35.50 targets.

The time-resolved negative self-bias voltage (V_b) of both types of BNT targets are also shown in Figure 3-8, which were initially in the range of -255 V to -245 V and gradually dropped to a less negative range of -240 V to -235 V by the end of conditioning period. This shift is attributed to sputtering-induced erosion of the target's racetrack, occurring at an average rate of $\sim 5.7 \mu\text{m/h}$ for BNT targets (see Section 3.4 for details). This reduces the distance between the eroded surface and the cathode's magnets, thereby strengthening the magnetic field and

enhancing electrons confinement near the target surface. The resulting increase in ionization efficiency raises the discharge current, leading to a less negative V_b . Under the constant applied power, this does not significantly alter the average sputtering rate, as the lower bombarding ion energy (related to the target voltage) is offset by a higher ion flux (determined by the discharge current) despite the change in negative self-bias voltage. The surface morphology of as-deposited films during the conditioning period, using both types of targets, is shown in Figure 3-9, highlighting regions within each zone that exhibit relatively more surface defects.

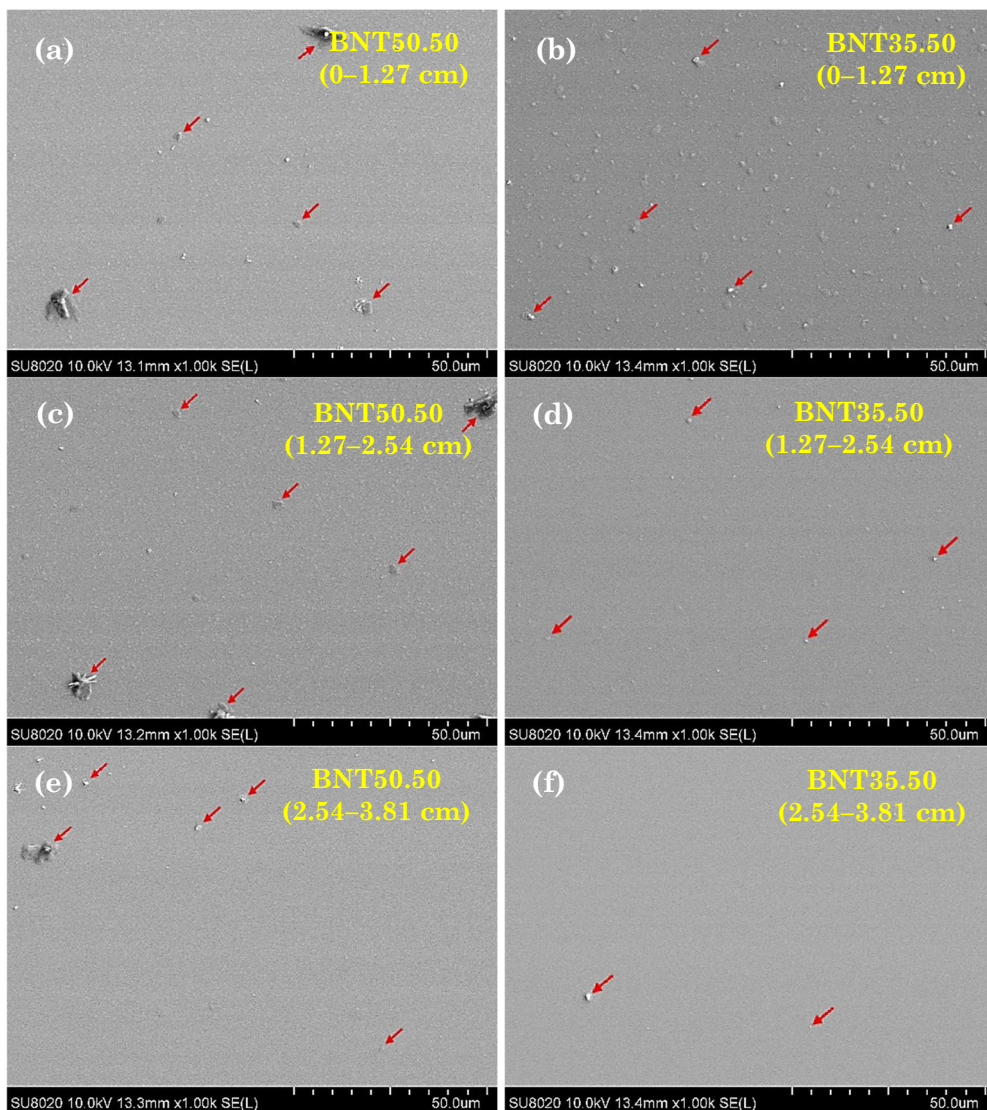


Figure 3-9: SEM surface morphology of as-deposited films from (a, c, e) BNT50.50 and (b, d, f) BNT35.50 targets during the conditioning period. Red arrows indicate NaO_x surface defects across the different zones of substrate.

Overall, the NaO_x surface defects are evident everywhere, with elemental mappings provided in Figures 3-10 (BNT50.50) and 3-11 (BNT35.50). The occurrence of these defects might correlate with the abundance of sublimated low-energy Na species in the gas phase, as evidenced by the secondary low-energy peak of Na^{1+} ions (23 m/z) observed

in both plasmas during MS analysis (see Figure 3-5). The average size of these surface defects is larger in the films of BNT50.50 target ($\sim 6 \mu\text{m}$) than in those from the BNT35.50 ($\sim 1 \mu\text{m}$), which correlates with the population of low-energy Na^{1+} ions ($\leq 10 \text{ eV}$) that is $\sim 7\%$ in BNT50.50 plasma compared to the $\sim 1\%$ in BNT35.50. This supports our hypothesis about the lower population of sublimated low-energy Na neutrals ($\leq 0.1 \text{ eV}$) in BNT35.50 plasma compared to the BNT50.50. Our observed defect sizes are generally consistent with reported defect sizes in sodium-containing sputter-deposited thin films such as BNT ($\leq 10 \mu\text{m}$)⁶³, NASICON ($\sim 2 \mu\text{m}$)⁹⁷, and Na_xCoO_2 ($\sim 0.2 \mu\text{m}$)⁹⁹, with defect shapes remaining diverse and without preferred morphology. The global defect density is higher in the center zone of substrate and decreases towards the edge for both targets, following the film thickness profile over a static substrate. However, the literature does not provide critical data on the defect density distribution in thin films across different substrate zones.

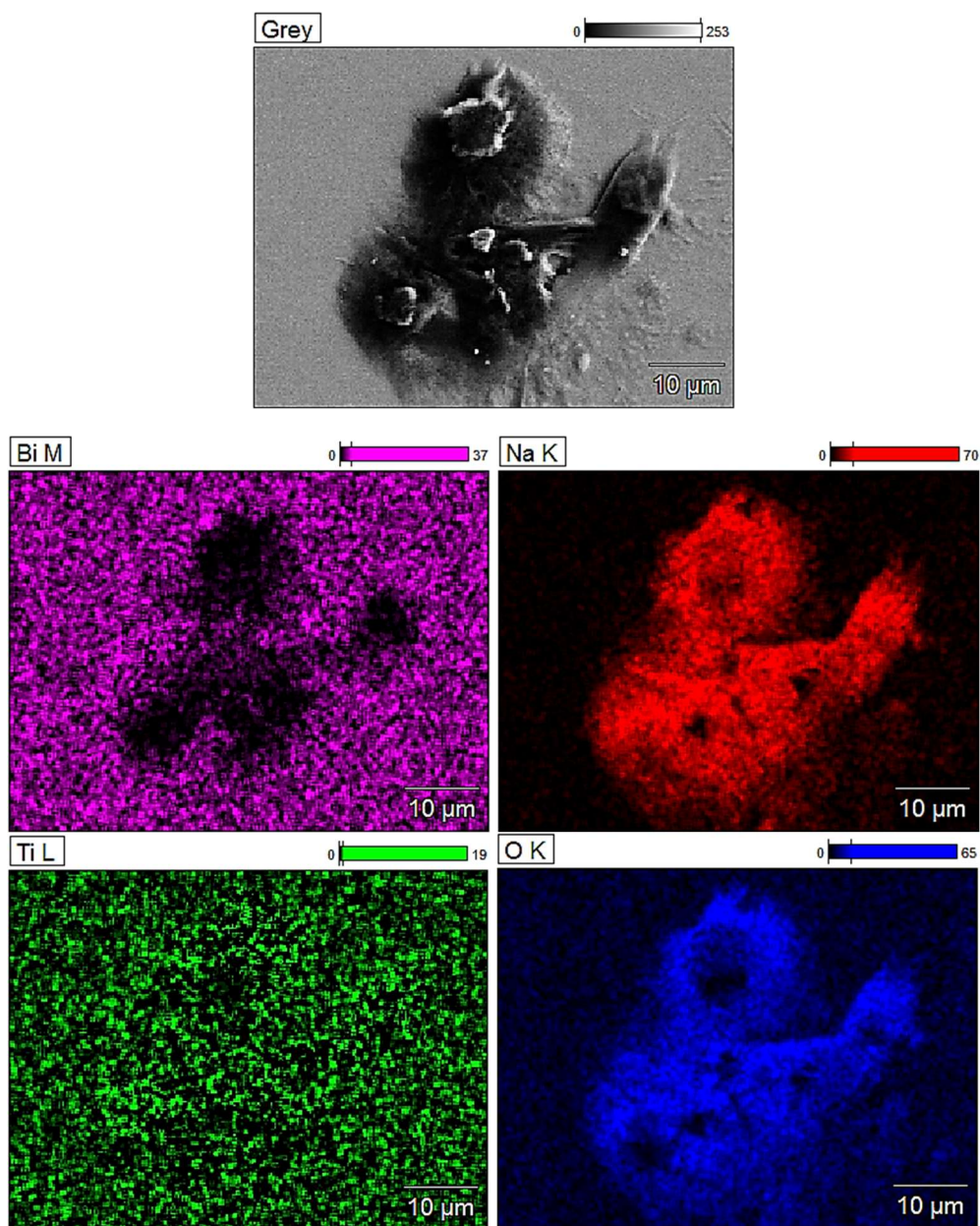


Figure 3-10: EDX elemental maps of NaO_x surface defect on a BNT50.50 target-based film.

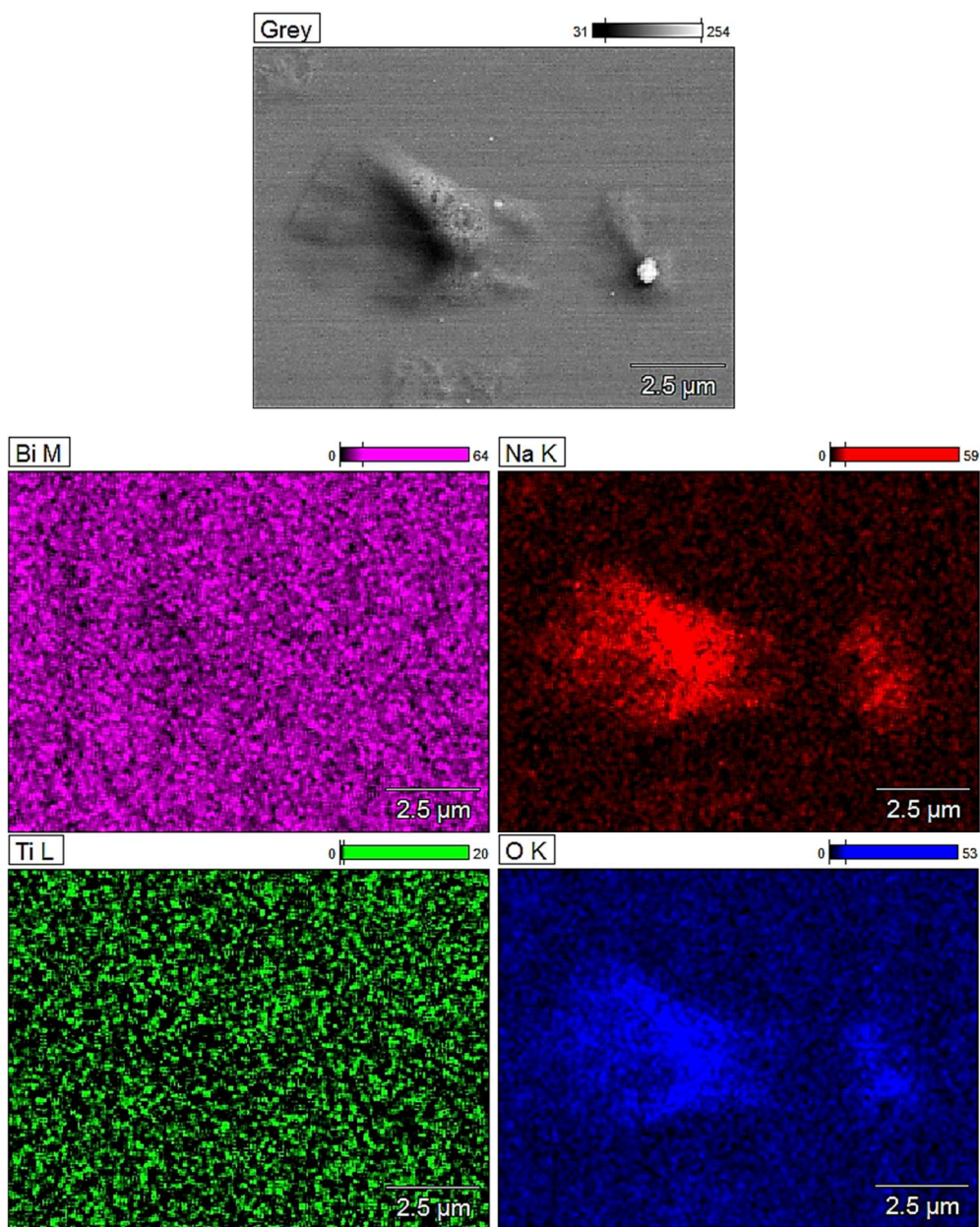


Figure 3-11: EDX elemental maps of a NaO_x surface defect on a BNT35.50 target-based film.

In summary, the films composition suggests that the surface of both targets stabilizes as a result of ~10 h conditioning, however, the BNT35.50 target stabilizes much faster (~2 h) compared to the BNT50.50

(~5 h). The $\frac{Bi}{Na}$ ratio and the content of bismuth is higher in both BNT50.50 and BNT35.50 films during the initial conditioning hours, followed by a decline and relative stabilization. This is attributed to the lower backscattering of sputtered Bi atoms by the Ar gas compared to the lighter Ti, Na, and O atoms which causes a decrease of Bi concentration and an increase of the lighter elements on the targets surface, leading to then target surface composition stabilization. Afterwards, the Bi content still stays higher in case of the BNT50.50 films, owing to the 25% excess of Bi_2O_3 in the pristine BNT50.50 targets. The as-deposited films by both BNT50.50 and BNT35.50 targets exhibit micron-sized NaO_x surface defects, which might originate from the abundance of sublimated low-energy Na neutrals and the appearance of a secondary low-energy peak in the Na^{1+} IEDFs. The average size of surface defects is larger in the films of BNT50.50 target (~6 μm) than in those of the BNT35.50 (~1 μm), which associates with the population low-energy Na^{1+} ions in the plasma, that is ~7% in BNT50.50 plasma compared to the ~1% in BNT35.50. The global defect density is highest at the center of substrate and decreases toward the edges.

3.4 Surface characterization of the conditioned targets

The surfaces of conditioned targets, mainly the racetrack region, were analyzed to track the evolution in their composition and morphology in response to the ~10 h conditioning period. The surface of a conditioned BNT50.50 target analyzed by 2D/3D optical profilometry is presented in Figure 3-12(a), which has a gray colored appearance in contrast to the yellow surface of the pristine target, as shown in Figure 3-12(b). A significant amount of the redeposition is evident in the center of the target, highlighted by an increased surface roughness in the 2D profile, as shown in Figure 3-12(a). The surface erosion profile was mainly recorded

to locate the racetrack position, which was found to be 2.25 cm away from the target's center. Although the target's radius was 3.81 cm, the edge was positioned 2.95 cm away from the center because some of the edge area was under the metallic ring (that holds the target) and was not subjected to the sputtering process. A schematic illustration of target's radial zones based on the optical profilometry is shown in Figure 3-12 (c).

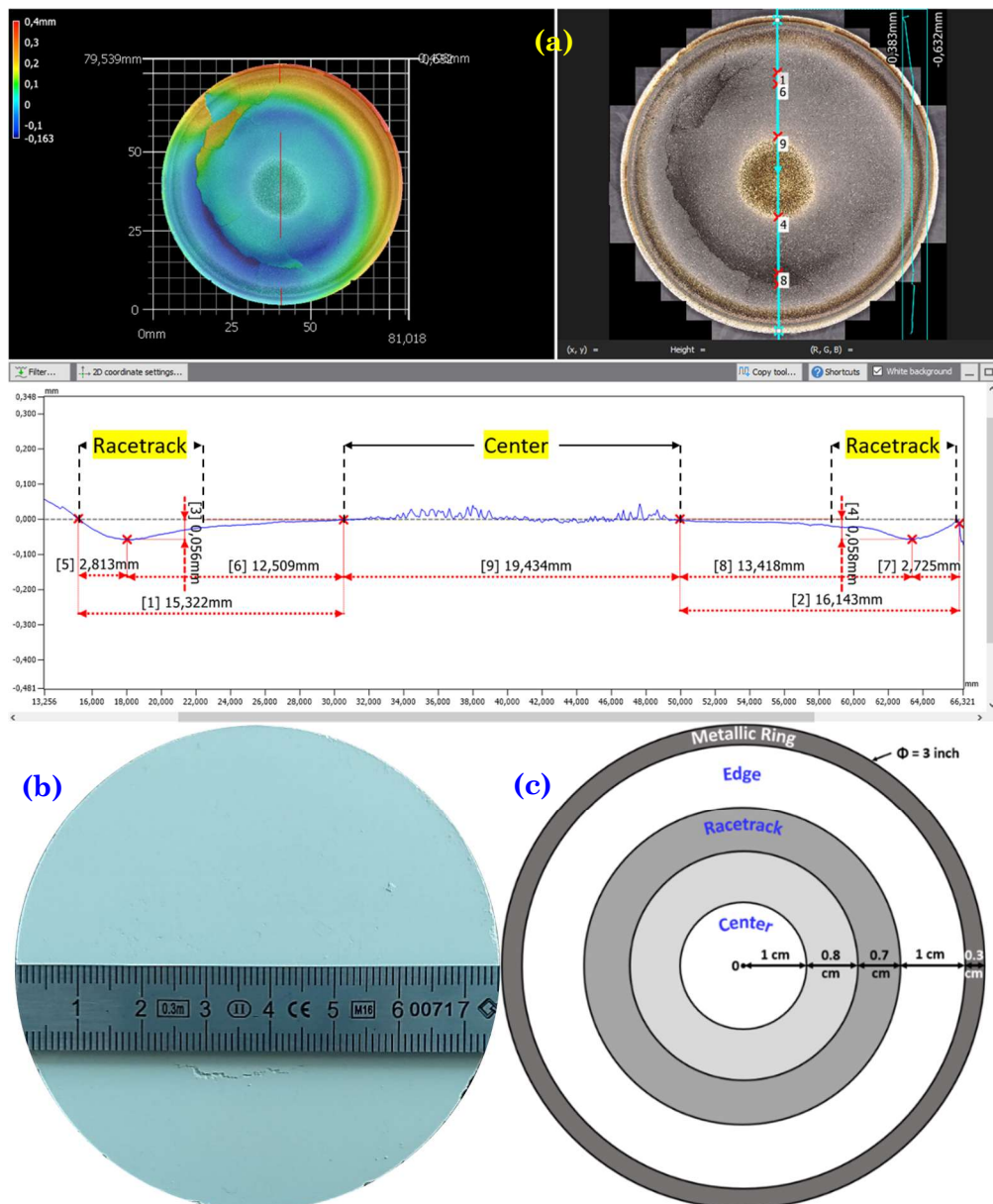


Figure 3-12: (a) Surface erosion profile of a typical BNT target after ~10 h conditioning, highlighting the position of racetrack from the target center; redeposition is evident as increased surface roughness in the central region. (b) Pristine BNT target. (c) Schematic of the target zonal distribution based on optical profilometry, where the outer 0.3 cm radial zone stays underneath the metallic clamp ring.

Over the ~10 h conditioning period, the targets' racetrack eroded up to ~57 microns (erosion rate ~5.7 $\mu\text{m/h}$), while the average film deposition rates were 149.3 ± 1.5 nm/h for the BNT50.50 target and 142.7 ± 1.6 nm/h for the BNT35.50 target. Thus, only ~3% of the sputtered material contributed to film growth, while the remaining ~97% was either deposited on other surfaces, including redeposition onto the target, or removed by continuous pumping. To determine the evolution of targets 'top surface' composition in response to the conditioning, XPS analysis was performed, and the results are shown in Figure 3-13. The racetrack composition represents the 'true' conditioned surface, as it is the primary sputtering hotspot and will be later used in the sputtering simulations.

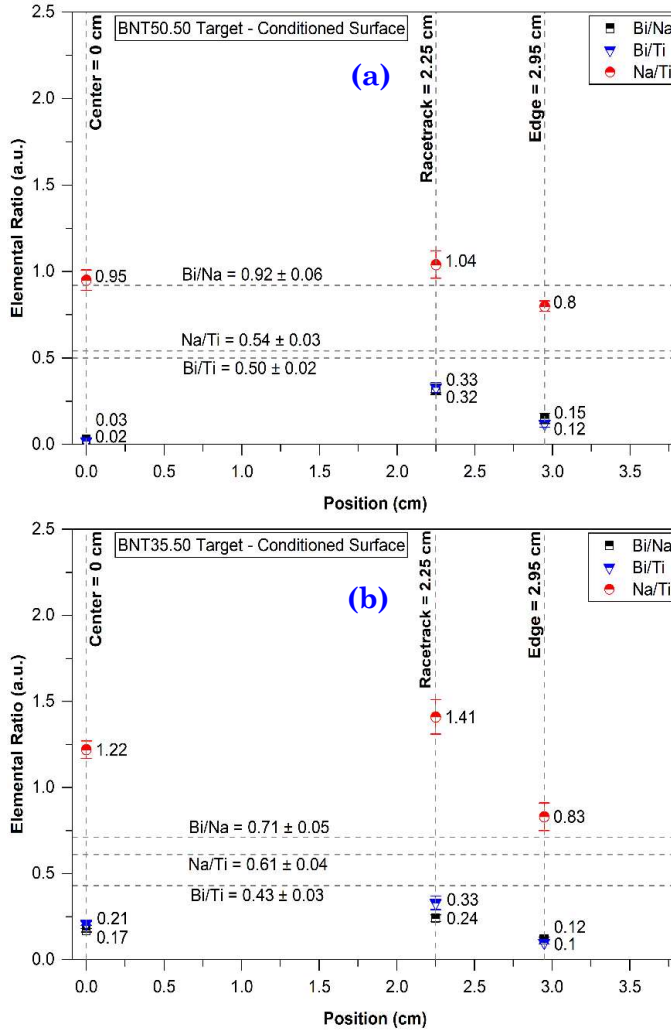


Figure 3-13: XPS-derived top-surface compositions of conditioned targets (a) BNT50.50 and (b) BNT35.50. Horizontal dashed lines represent the pristine compositions, and vertical dashed lines mark the different zones of the target.

At the racetrack's surface, both the $\frac{Bi}{Na}$ and $\frac{Bi}{Ti}$ ratios have significantly lowered which is attributable to the Bi depletion from there because its sputtered flux experiences weaker backscattering owing to its greater atomic mass (209 u) than that of the background Ar gas (40 u)¹³³. This is in agreement with the films composition which showed a significantly higher Bi content during the initial conditioning hours,

followed by a steeper decline and relative stabilization (Figure 3-7, p. 72–74). In contrast, the $\frac{Na}{Ti}$ ratio has nearly doubled which can be ascribed to the likely strong backscattering of Na by the background gas and its enhanced redeposition, given that its atomic mass (23 u) is nearly half to that of Ar (40 u) ¹³⁴. The center and edge regions also exhibit significant Na redeposition that covers much of the surface, leading to a substantial attenuation of the Bi signal, as reflected by $\frac{Bi}{Na}$ and $\frac{Bi}{Ti}$ ratios that are even further lower than those in the racetrack region. Consistently, their $\frac{Na}{Ti}$ ratios are also lower than those of the racetrack, indicating that Na redeposition is more dominant in the racetrack than in the center and edge regions. The SEM images in Figure 3-14 (c–h) show the resulting surfaces of both targets after the conditioning compared to their pristine state (a–b).

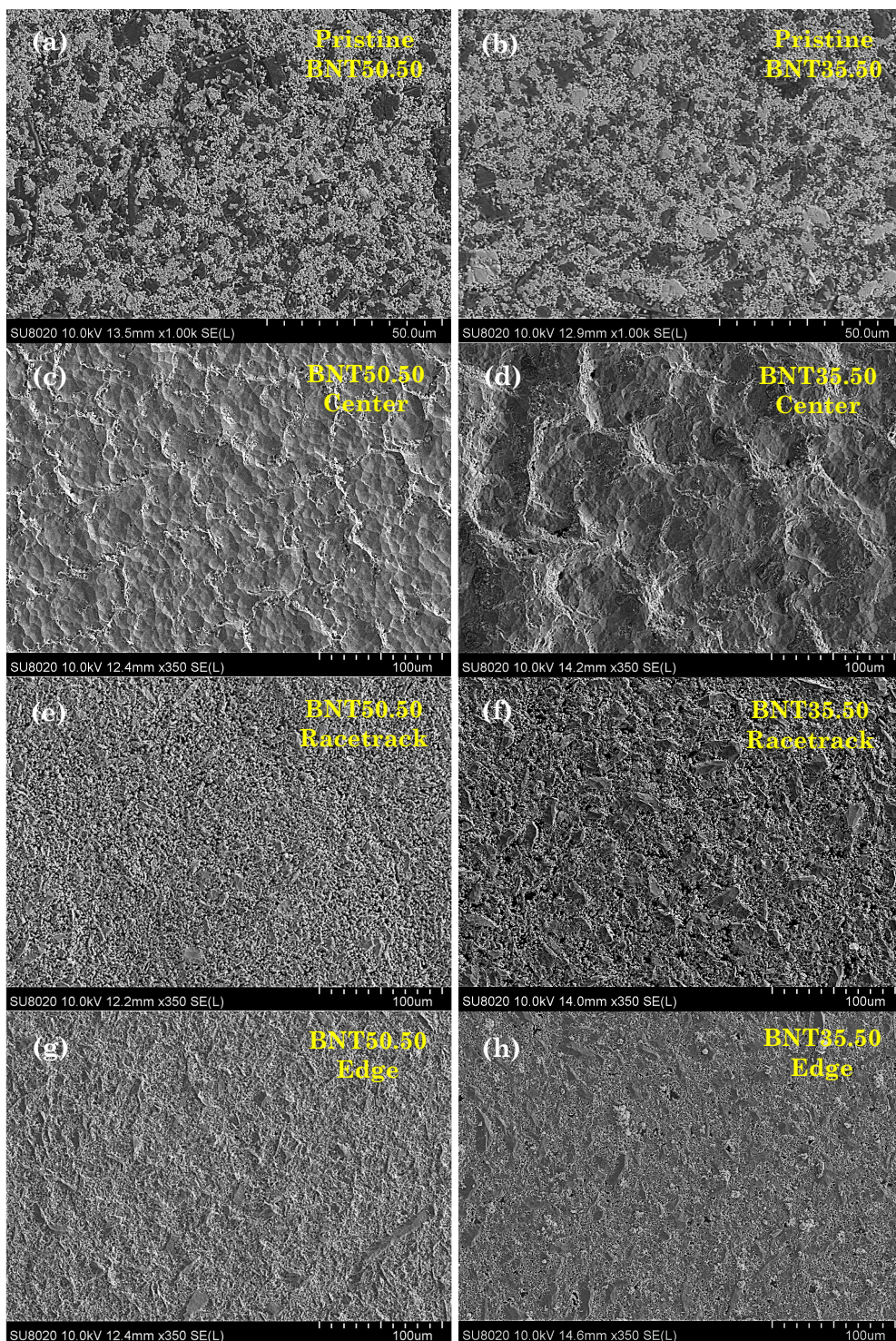


Figure 3-14: SEM images of BNT50.50 and BNT35.50 targets showing (a, b) pristine surfaces. Conditioned surfaces: (c, d) center, (e, f) racetrack, and (g, h) edge regions.

On the pristine targets surface, there was a clear distinction between the larger dark $\text{Na}_2\text{Ti}_3\text{O}_7$ particles and the finer bright Bi_2O_3 and TiO_2 particles, which now mainly exists at the racetrack and edge regions of the conditioned targets. The surface morphology of the center regions in both targets shows significant evolution compared to the pristine state, consistent with the 2D profilometry (Figure 3-12a), which reveals increased roughness due to the redepositions. The edge region also exhibits a higher density than the racetrack, again confirming the redepositions, which is in agreement with compositional data (Figure 3-13). The EDX elemental mapping of a BNT50.50 target surface is shown in Figures 3-15, 16, and 17; to assess the effects of conditioning on its elemental composition. In the pristine state, the surface of BNT targets exhibits overlap between Ti and Na maps, consistent with the presence of $\text{Na}_2\text{Ti}_3\text{O}_7$ particles, and a distinct Bi map corresponding to Bi_2O_3 particles (Figure 3-2d–i, p. 60). After conditioning, this trend only exists at the racetrack region, while there is no convincing overlap between the Ti and Na maps, nor a distinction from the Bi map, in the center and edge regions of the target surface.

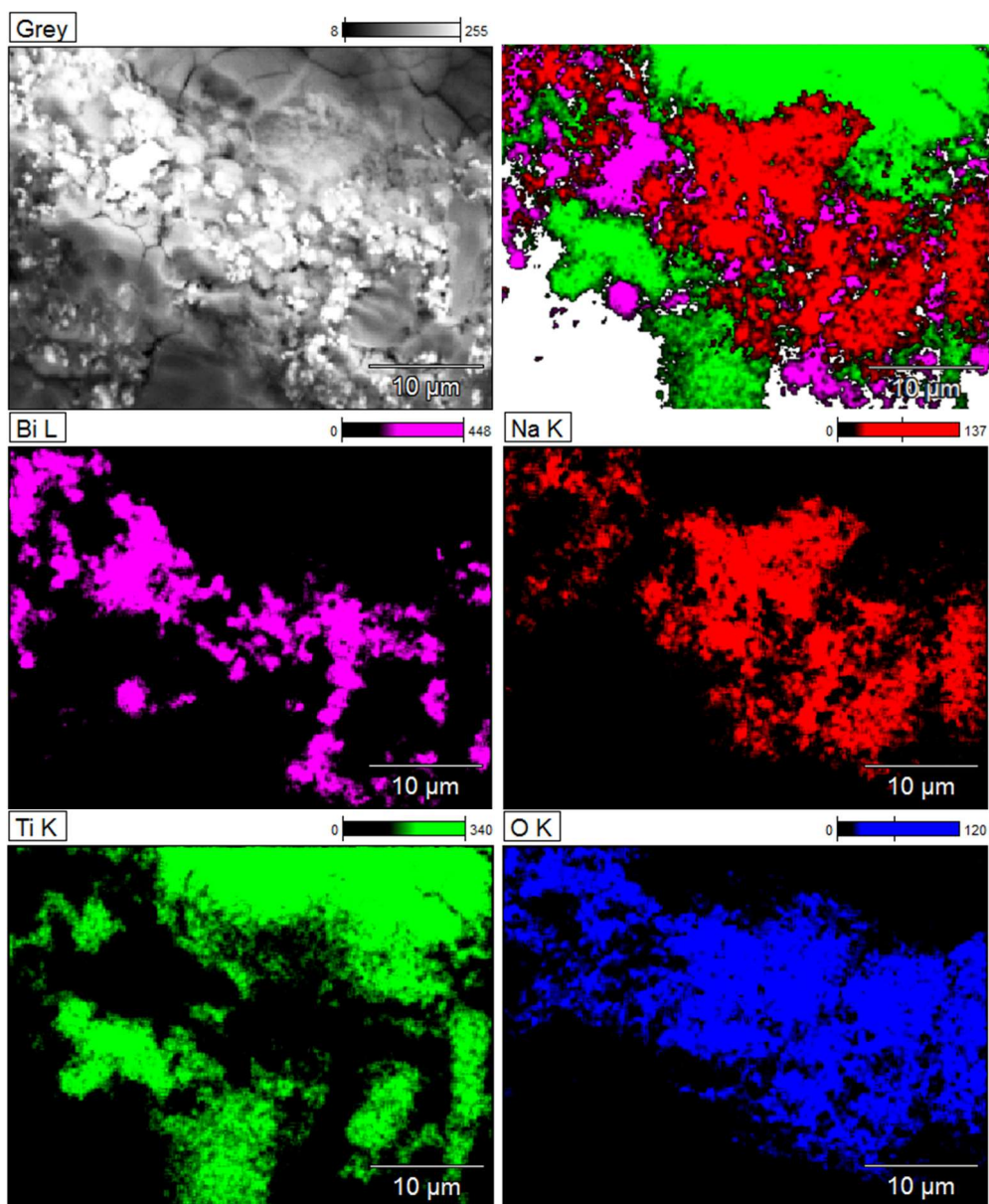


Figure 3-15: EDX elemental maps of the center region of a conditioned BNT50.50 target, with a superimposed map of the Bi–Na–Ti elemental distribution.

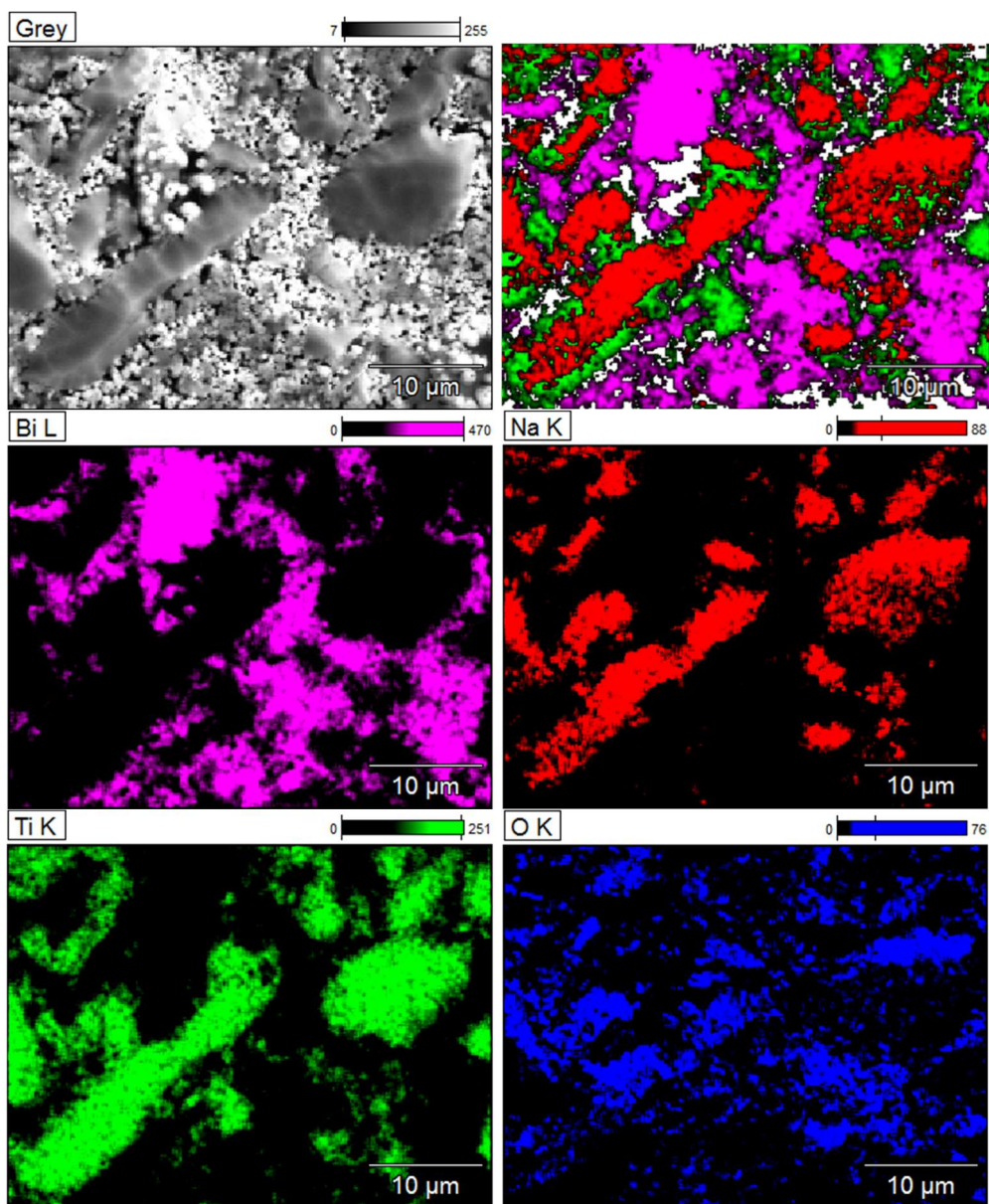


Figure 3-16: EDX elemental maps of the racetrack region of a conditioned BNT50.50 target, with a superimposed map of the Bi–Na–Ti elemental distribution.

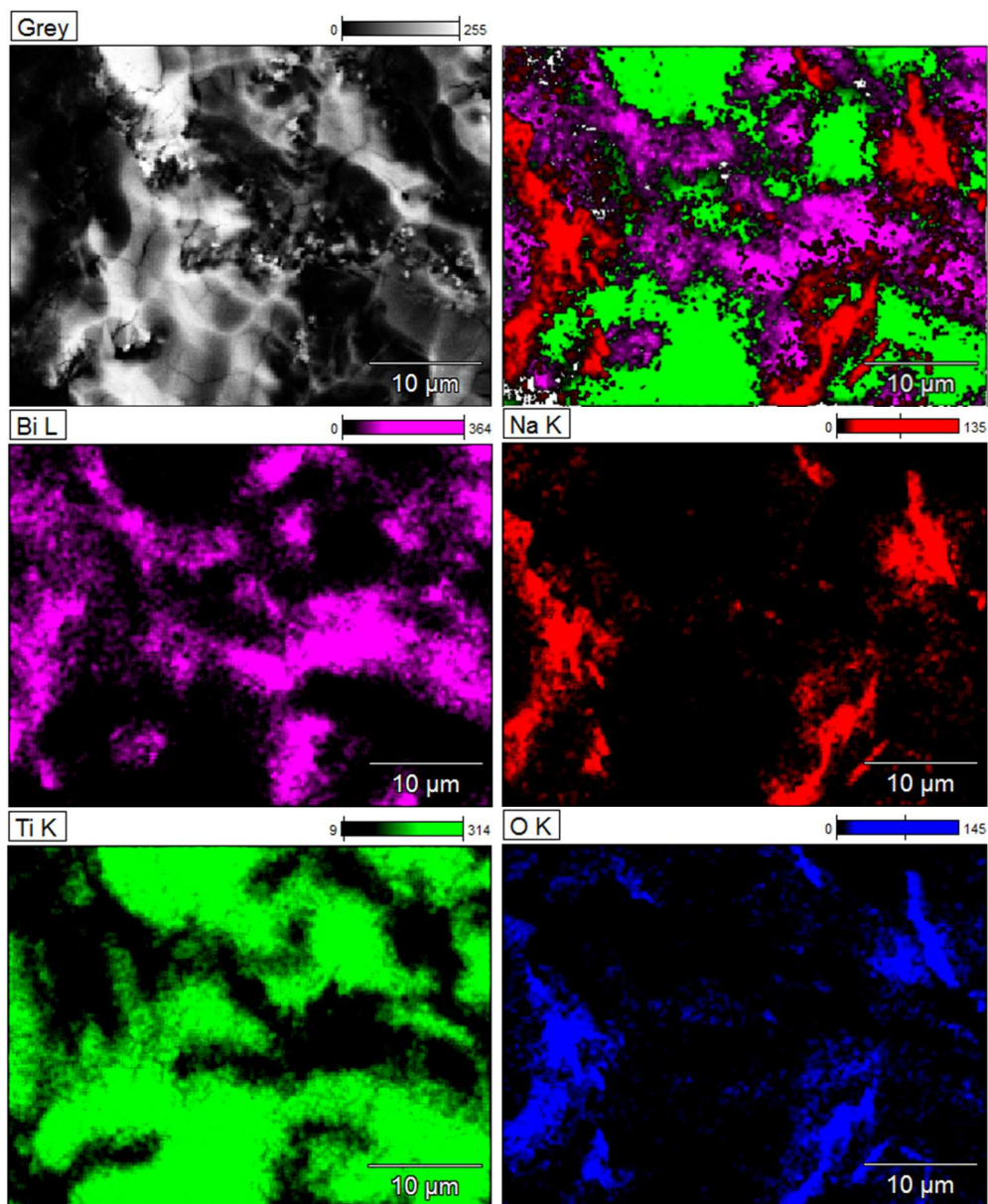


Figure 3-17: EDX elemental maps of the edge region of a conditioned BNT50.50 target, with a superimposed map of the Bi–Na–Ti elemental distribution.

In summary, the surfaces of both types of targets have significantly evolved as a consequence of the ~10 h conditioning. The racetrack region has lost a significant amount of Bi and gained even greater amount of Na

across both of the target compositions. This trends is also in agreement with the films composition, showing initially higher Bi content followed by its decline and relative stabilization over time. The redeposition of Na was much higher at the racetrack compared to center and edge regions of the targets.

3.5 Summary

This chapter presented the analysis of pristine BNT targets and the evolution of their surfaces in response to the conditioning period. Two target compositions were studied: stoichiometric $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT50.50) and 25% Bi_2O_3 deficient $\text{Bi}_{0.35}\text{Na}_{0.5}\text{TiO}_{2.8}$ (BNT35.50). The surfaces of targets were conditioned by continued sputtering for 10 h at 2.19 W/cm^2 power density and 10 mTorr Ar pressure following the procedure implemented at UPHF. During the conditioning, plasma initially exhibited higher $\frac{\text{Bi}}{\text{Na}}$ and $\frac{\text{Bi}}{\text{Ti}}$ ion ratios which declined and stabilized after a few hours of sputtering (BNT50.50: ~ 4 h, BNT35.50: 2 h). This could be ascribed to the lower backscattering of heavy Bi species by incoming Ar^+ ions compared to the other sputtered species that are evidently lighter (i.e., Ti and Na etc.), which get efficiently redeposited on the target surface. This causes the evolution of target surface composition which finally stabilizes with a significant reduction in Bi content while a tremendous increase in the Na concentration. Inside the as-deposited films, $\frac{\text{Bi}}{\text{Na}}$ ratios were also higher during the initial conditioning hours, followed by a decrease and a relative stabilization (BNT50.50: 5 h, BNT35.50: 2 h), reflecting the impact of Bi content on the stabilization of target surface composition. Similarly, their $\frac{\text{Bi}}{\text{Ti}}$ and $\frac{\text{Na}}{\text{Ti}}$ ratios gradually evolved and stabilized over comparable timescales. Therefore, both the plasma ion chemistry and the as-deposited film composition indicate that the target surface composition reaches a steady state after ~ 5 h

(BNT50.50) and ~2 h (BNT35.50) of continued sputtering at 2.19 W/cm² and 10 mTorr Ar.

The target surface temperatures were estimated to reach around 800°C during sputtering, sufficient to decompose Na₂Ti₃O₇ into Na₂O and titanium based oxides. The higher vapor pressure of Na₂O at these temperatures leads to its sublimation into low-energy Na and O neutrals, a small portion of which is detected as the low-energy secondary peak in Na¹⁺ (23 m/z) IEDFs. These sublimated low-energy Na atoms (≤ 0.1 eV) potentially lead to the formation of NaO_x surface defects in the films. The average size of surface defects is larger in the films of BNT50.50 target (~6 μ m) than in those of the BNT35.50 (~1 μ m), which suggests the lower population of sublimated Na atoms in the BNT35.50 plasma compared to the BNT50.50. Given the presumed sputtering-induced target surface temperature range of ~800°C, Bi₂O₃ and TiO₂ likely react to form Bi₄Ti₃O₁₂ on the target surface. This reaction is exothermic and contributes additional heat, thereby further elevating the target surface temperature. This additional heat supply could potentially play an important role as the vapor pressure of Na₂O increases more than fivefold from 0.4 to 2.13 mTorr when the temperature increases from 710 to 783°C. As the BNT35.50 composition contains 25% less Bi₂O₃, its surface temperature will correspondingly be lower than that of BNT50.50, leading to a smaller population of Na neutrals. This assumption is also supported by analyzing the IEDFs and the population of low-energy (≤ 10 eV) Na¹⁺ ions, that is ~7% in BNT50.50 plasma compared to the ~1% in BNT35.50 plasma. Defects were most pronounced in the center zone of substrate and decreased toward the edges, consistent with the film's thickness profile. However, one should not overlook that the substrate might be subjected to bombardment by high-energy negative ions like O⁻ emitted by the target. These ions are known to induce changes in the film properties, in

particular on the film section located in front of the racetrack from which they are predominantly emitted. This intensified bombardment by oxygen ions having a kinetic energy of the order of the target sheath potential might also play a role in the formation mechanism of NaO_x defects. Therefore, dedicated plasma analysis studies should be carried out to determine their impact.

Chapter 4 Effects of Sputtering Conditions on BNT Film Properties

This chapter presents the deposition of BNT films using conditioned targets under the deposition parameters selected to fit with Hamieh's strategy. A typical issue of this process is the appearance of bismuth titanate secondary phases, leading to poor piezoelectric performance. On the other hand, the formation of NaO_x surface defects renders the films unsuitable for device applications. These questions are investigated thanks to the mass spectrometry-based plasma diagnostics and surface analysis of the deposited films under selected deposition conditions, in order to better understand the target-plasma-film chemistry correlation. In particular, we studied the influence of target composition (Section 4.1), target-substrate distance (Section 4.2), and sputtering power density (Section 4.3) on the film's crystalline composition and microstructure.

4.1 Influence of the target composition on film properties

In this section, conditioned BNT50.50 and BNT35.50 targets are used to deposit films according to the process parameters employed by Hamieh *et al.* at UPHF, and the impact of target composition on film properties is investigated.

4.1.1 Sputtering of cond. BNT50.50 target at 2.19 W/cm² and 80 mTorr.cm

Following the work of Hamieh *et al.* ^{63, 64}, conditioned BNT50.50 targets were sputtered continuously for 8 h at a power density of 2.19 W/cm², under 10 mTorr Ar pressure, with an 8 cm target-substrate distance ($P \times D = 80$ mTorr.cm). Complementary simulations of target sputtering and gas-phase transport of the sputtered species were

performed, and the plasma ion chemistry, as well as the composition and morphology of the as-deposited and annealed films, were analyzed.

Simulations of target sputtering and transport processes

The Monte-Carlo simulation codes TRIM^{114, 115} and SiMTRA^{75, 82} were combined to determine whether sputtered material transport through the gas phase could, by itself, lead to compositional inhomogeneities in the as-deposited films. At a power density of 2.19 W/cm² and P x D of 80 mTorr.cm, the mean self-bias (V_{bias}) of BNT50.50 targets was around -230 V and the plasma potential (V_p) was approximately 25 V. The plasma potential was determined from the Ar¹⁺ (40 m/z) IEDF's peak, while the orifice of mass spectrometer was electrically grounded¹²¹. This corresponds to a potential difference in the cathode sheath ($E_{Ar+} = V_{bias} + V_p$) and an ion energy of around 250 eV, which was used in the sputtering yield calculations by the TRIM code. The measured target density of 2.3 g/cm³ was also used as input in the simulations. Furthermore, the XPS-derived top-surface composition of BNT50.50 target's racetrack region (Figure 3-13a, pp. 83–84) was used as an input for TRIM simulations. Overall, the sputtering yields rise with the increasing incident ion energy from 100–500 eV (see Figure 4-1). Bismuth (209 u), being the heaviest element, shows the lowest sputtering yield (0.02–0.06 atoms/ion), while oxygen (16 u), as the lightest element, has the highest yield (0.15–0.62 atoms/ion).

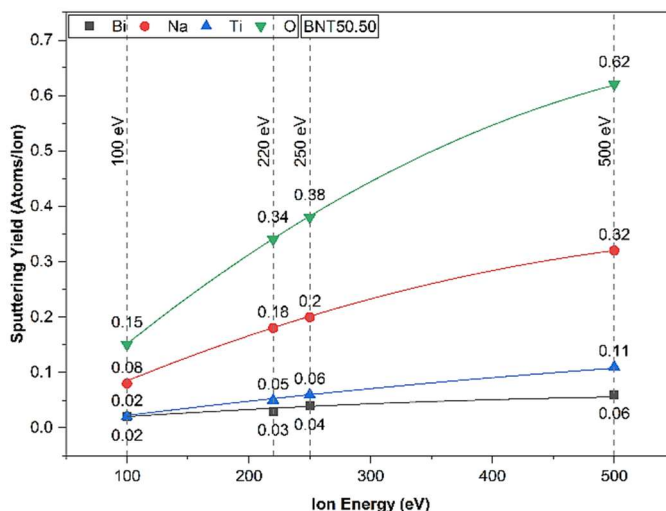


Figure 4-1: TRIM-simulated sputtering yields from the conditioned BNT50.50 target as a function of Ar^{1+} ion energy (100–500 eV).

The TRIM code models only surface sputtering and typically assumes targets to be amorphous and dense solids, whereas the BNT targets used here consist of loosely packed crystalline powders. In the sputtering process, crystallinity can influence a target's sputtering yield, with dense atomic planes yielding higher rates than the less dense planes¹³⁵. However, sputtering yields are often dominated by surface atom binding energy and knock-on processes in the low-energy regime (near threshold: tens to a few hundred eV)^{73, 136, 137}. The TRIM code calculates sputtering yields based on binary collisions between the incident ions and the individual neutral atoms, treating the target as a collection of isolated atoms. It does not account for the molecular bonds or chemical effects, nor the sublimation of surface species, so it only predicts the ejection of single neutral atoms, not molecules or clusters. However, the mass spectrometry analysis of BNT plasmas confirmed the presence of molecular species such as O_2^{1+} , TiO^{1+} , etc. (Figure 3-3, p. 61), some of which can originate from the sputtering process; therefore TRIM code likely underestimates the sputtering yields from our BNT targets. Furthermore, the effective

sputtering yield of powder targets can differ from that of dense targets due to two competing effects: surface inclination enhances sputtering, while roughness-induced re-capture of sputtered species reduces the net yield⁸². In general, nanometer-sized particles favor the yield enhancement, while larger micrometer-sized particles tend to decrease the effective yield due to the increased surface roughness⁸³. The precursor powders used in the fabrication of BNT targets have average particle sizes of 0.5 μm for Bi_2O_3 , 1 μm for TiO_2 , and 11.5 μm for $\text{Na}_2\text{Ti}_3\text{O}_7$. Theoretically, TRIM may underestimate the sputtering yields for the Bi, Ti, and O from finer Bi_2O_3 and TiO_2 powders and overestimate it for Ti, Na, and O from the coarser $\text{Na}_2\text{Ti}_3\text{O}_7$; however, these opposing effects may balance out each other due to the likely increased surface roughness resulting from the mixed powder composition of BNT targets (Figure 3-2, pp. 59–60). Notably, the TRIM code also provides outputs such as the angular distribution and energy of the sputtered species as they leave the target surface. This information is particularly important for calculating the spatial distribution of the sputtered species in the gas phase and as they reach the substrate surface. A key limitation of SiMTRA is that it calculates only the deposition flux arriving at the substrate and does not account for the eventual re-evaporation of atoms after they land on a surface. Based on the TRIM results, the transport of each element was simulated individually using SiMTRA, and the corresponding deposition profiles on a 3.81 cm long substrate were computed for 250 eV Ar^{1+} ion bombardment of the BNT target. The corresponding elemental flux ratios are shown below in Figure 4-2 (details on the data processing are provided in Section 2.3, pp. 52–53).

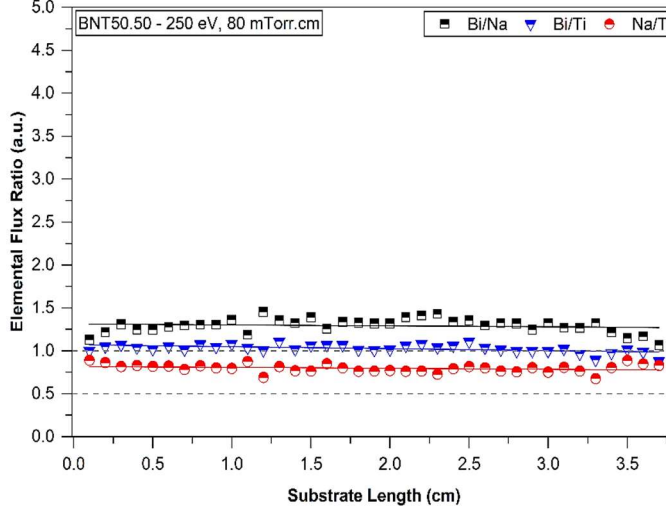


Figure 4-2: SimMTRA-simulated transport of sputtered species from the conditioned BNT50.50 target toward a 3.81 cm long substrate at a target–substrate distance of 8 cm, under 250 eV Ar¹⁺ ion bombardment.

Overall, the average elemental flux ratios ($\frac{Bi}{Na} = 1.3$, $\frac{Bi}{Ti} = 1$, $\frac{Na}{Ti} = 0.8$) exceed the desired stoichiometric film composition ($\frac{Bi}{Na} = 1$, $\frac{Bi}{Ti} = \frac{Na}{Ti} = 0.5$), indicating Bi enrichment and a relative Ti deficiency in the flux arriving at the substrate. Notably, the Bi flux is ~29 at.% higher than that of Na, despite its lower sputtering yield (0.04 atoms/ion) and lower surface concentration on the target (see XPS results in Figure 3.13, p. 83). This behavior is attributed to the lower scattering of heavy Bi species (209 u) in Ar gas (40 u) during transport. In contrast, the Ti flux is ~37 at.% lower than its stoichiometric level (i.e., twice the Na flux), likely due to its relatively lower concentration at the conditioned target surface. Consequently, an excess of Bi and a deficiency of Ti are expected in the as-deposited films, whereas the desired film stoichiometry (Bi_{0.5}Na_{0.5}TiO₃) requires equal Bi and Na contents and twice as much Ti as Na. Besides, the overall deposition flux was higher at the substrate center which decreased by 16% in the middle zone and by 24% at the edge zone, consistent with the typical thickness profile of a sputter-deposited film on

a static substrate. The SiMTRA simulations were extended to target-substrate distances of 4–16 cm to assess the impact of gas-phase collisions on the composition of the arriving flux (Figure 4-3). As the distance (or equivalently the $P \times D$ product) increases, lighter species such as O (16 u) and Na (23 u) undergo stronger gas-phase scattering in Ar, leading to progressive attenuation of their flux at the substrate.

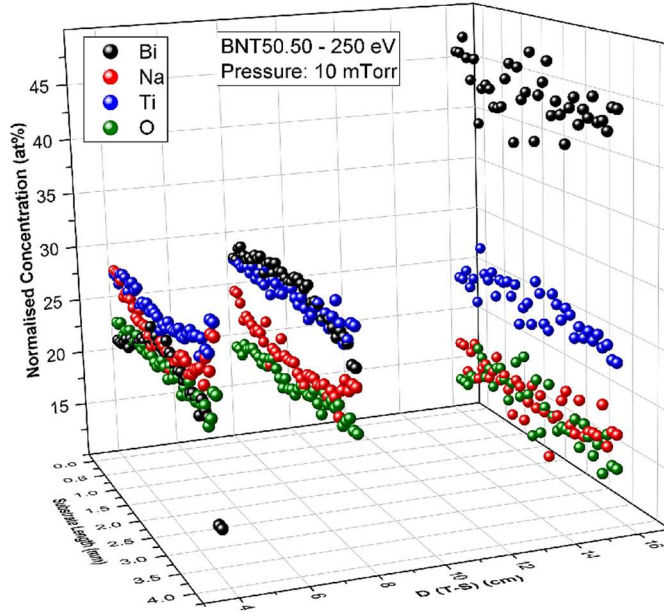


Figure 4-3: SiMTRA-simulated normalized transport of sputtered atoms from the conditioned BNT50.50 target toward a 3.81 cm long substrate for target-substrate distances of 4–16 cm, under 250 eV Ar^{1+} ion bombardment.

Westwood *et al.* experimentally demonstrated this phenomenon at 5 mTorr Ar pressure that heavier Mo atoms (96 u) exhibit a mean free path of ~ 2 cm, whereas lighter O atoms (16 u) have a mean free path below 1 cm due to more frequent collisions with the background gas ⁷⁴. Depla *et al.* reported similar mass-dependent transport behavior using SiMTRA simulations ⁷⁵. In summary, our simulations indicate that BNT films deposited on a static substrate are thicker in the center region, with thickness reductions of $\sim 16\%$ and $\sim 24\%$ in the middle and edge regions,

respectively. In terms of composition, the Bi flux toward the substrate is predicted to be ~29 at.% higher than that of Na, while the Ti flux is ~37 at.% lower than its stoichiometric level, potentially leading to Bi enrichment and Ti deficiency in the as-deposited films.

Evolution of plasma ion chemistry during 8 h of continuous sputtering

At UPHF, Hamieh *et al.* observed the formation of NaO_x surface defects in BNT thin films deposited on unheated substrates by sputtering conditioned BNT50.50 targets at a power density of 2.19 W/cm², 10 mTorr Ar pressure, and target–substrate distance of 8 cm (P x D = 80 mTorr.cm). In contrast, when the substrate was preheated to 200°C and maintained at this temperature, defect formation was delayed, appearing only toward the end of the 4th hour of continuous deposition ^{63, 64}. Therefore, it was decided to monitor the plasma ion chemistry under identical conditions for ~8 h, with particular attention to the evolution of Na-containing ions. The plasma potential (V_p) was found to be ~25 V, determined from the maximum of Ar¹⁺ (40 m/z) IEDF with the MS orifice electrically grounded ¹²¹. The mass spectrum acquired during the final hour (~8 h) of sputtering is shown in Figure 4-4, and the detected ions are listed in Table 4-1.

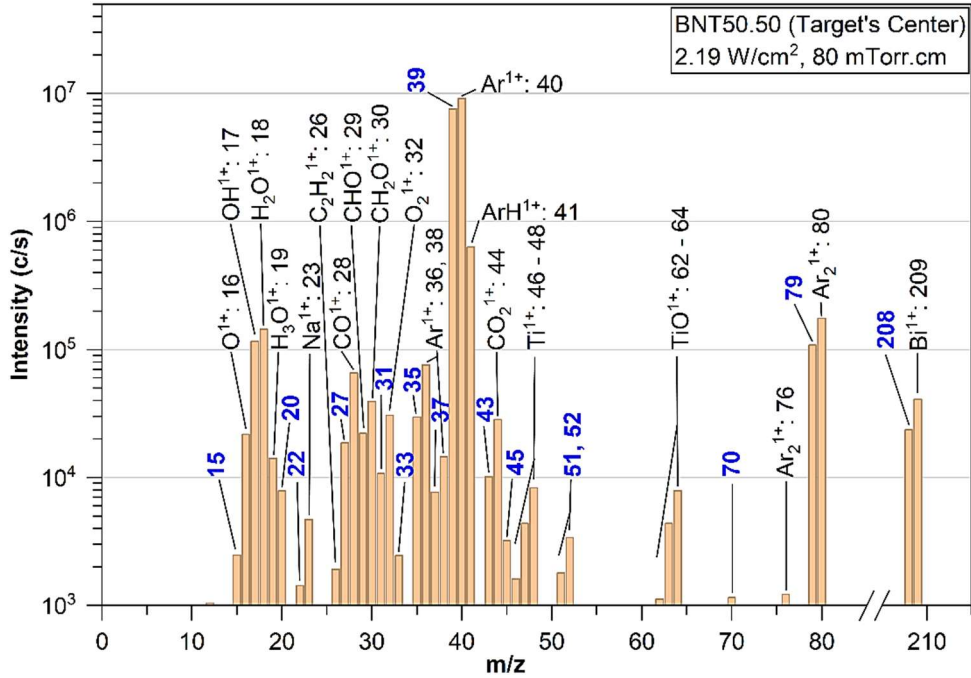


Figure 4-4: Mass spectrum of the plasma from a conditioned BNT50.50 target during the final hour (~8 h) of sputtering.

m/z ratio	ion	m/z ratio	ion
16	O ¹⁺	17	OH ¹⁺
18	H ₂ O ¹⁺	19	H ₃ O ¹⁺
23	Na ¹⁺	26	C ₂ H ₂ ¹⁺
28	CO ¹⁺	29	CHO ¹⁺
30	CH ₂ O ¹⁺	32	O ₂ ¹⁺
36, 38	Ar ¹⁺	40	Ar ¹⁺
41	ArH ¹⁺	44	CO ₂ ¹⁺
46–48	Ti ¹⁺	62–64	TiO ¹⁺
76, 80	Ar ₂ ¹⁺	209	Bi ¹⁺

Table 4-1: List of ions detected ions in the plasma of a conditioned BNT50.50 target.

The OH¹⁺, H₂O¹⁺, and H₃O¹⁺ ions likely originate from water molecules desorbing from the walls of MS and sputtering chamber. The

CO^{1+} , CO_2^{1+} , $\text{C}_2\text{H}_2^{1+}$, CHO^{1+} , and CH_2O^{1+} ions presumably derive from the residual molecules of carbon dioxide inside the chamber and the residue IPA ($\text{C}_3\text{H}_8\text{O}$) in targets, which was added to the precursor powders during the target's fabrication. The argon-based ions (Ar^{1+} , ArH^{1+} , and Ar_2^{1+}) obviously originate from the background Ar gas. The oxygen ions (O^{1+} and O_2^{1+}) originate from the sputtering of Bi_2O_3 , $\text{Na}_2\text{Ti}_3\text{O}_7$, and TiO_2 precursor powders, water molecules and the residual IPA ($\text{C}_3\text{H}_8\text{O}$) in targets. The sodium ions (Na^{1+}) are sputtered from the $\text{Na}_2\text{Ti}_3\text{O}_7$, titanium ions (Ti^{1+} and TiO^{1+}) arise from both the $\text{Na}_2\text{Ti}_3\text{O}_7$ and TiO_2 , and the Bi^{1+} ions originate only from the Bi_2O_3 powder.

There is always an additional peak on the left side of every major peaks, e.g., 15 next to 16 (O^{1+}), 22 next to 23 (Na^{1+}), 27 next to 28 (CO^{1+}), 31 next to 32 (O_2^{1+}), etc. This is caused by an instrumental artifact, which has been discussed in detail inside the Section 3.2 (pp. 61–63). Besides, there are still other unidentified peaks ($m/z = 20, 33, 51, 52$, and 70), which could be caused by this instrumental artifact or may arise from the impurities inside the target and the MS–sputtering assembly. The IEDFs of various target-derived ions are shown below in Figure 4-5, which were recorded during the last hour (~ 8 h) of sputtering period.

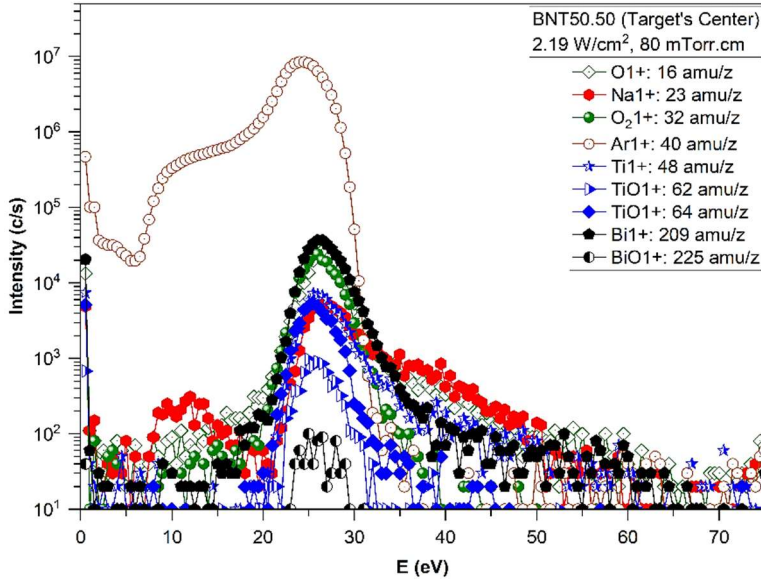


Figure 4-5: Mass spectrometry-based IEDFs of selected ions in the plasma of a conditioned BNT50.50 target during the final hour (~8 h) of sputtering.

The maximum of each IEDF occurs at ~25–27 eV, consistent with the plasma potential (~25 eV) measured with the mass spectrometer orifice electrically grounded. The target-derived atomic ions (Bi^{1+} , Na^{1+} , Ti^{1+} , and O^{1+}) exhibit high-energy tails (i.e., $E > 25$ eV), characteristic of sputtered species and the so-called Sigmund-Thomson distribution¹²²⁻¹²⁴. On the other hand, the IEDF of the Ar^{1+} ions shows a marked low-energy shoulder (i.e., $E < 25$ eV). This low-energy shoulder is usually attributed to the resonant charge exchange reactions occurring inside the sheath. The condition for this reaction to occur is that the sheath is large enough and that the collision frequency is significant; the colliding species are in rather large concentration in the gas phase. It can be understood that this condition is fulfilled for the argon gas ions. Broadening of the IEDF can also be induced in RF discharges because of the oscillating (RF) sheath¹²⁵. The low-energy peak of Na^{1+} ion suggests the existence of a substantial population of low-energy Na neutrals originated by the sublimation from $\text{Na}_2\text{Ti}_3\text{O}_7$ on the target's surface alongside the usual sputtering process

(Section 3.2, pp. 64–68 for details). Notably, the Na^{1+} ion also show a low-energy peak around 10 eV. Since the simulations suggest lower transport of Na (1333 atoms) towards the MS orifice compared to that of the Ti (1496 atoms) and Bi (1505 atoms), it is reasonable to assume that sputtering is not the only process responsible for the production of gaseous Na atoms in our experiments.

Briefly, most of the bombarding ions energy is converted into heat in the near-surface region of the target during sputtering, which can raise its temperature to around 800°C ^{127, 128} and decompose $\text{Na}_2\text{Ti}_3\text{O}_7$ into Na_2O and titanium based oxides ¹²⁹. Owing to its relatively high vapor pressure (~ 0.4 mTorr at 710°C under ambient conditions), Na_2O readily sublimates, releasing neutral Na and O atoms ¹³⁰. This generates a substantial flux of low-energy Na neutrals (≤ 0.1 eV), a fraction of which is ionized via charge-exchange reactions with Ar^{1+} ions in the sheath in front of MS orifice. The resulting Na^{1+} ions are subsequently re-accelerated within the sheath but experience only a fraction of the full plasma–orifice potential drop, thereby contributing to a distinct low-energy component in the Na^{1+} IEDF, as observed. However, the charge exchange reactions between Na (23 u) and Ar^{1+} (40 u) are expected to be relatively inefficient due to both the mass mismatch and the large ionization potential difference (Na = 5.14 eV, Ar = 15.76 eV), leaving the majority of sublimated Na atoms in the neutral state. This is consistent with the observation that only $\sim 8\%$ of the Na^{1+} population constitutes its low-energy fraction (≤ 10 eV). Consequently, the Na^{1+} IEDF indicates the presence of a considerable population of low-energy Na neutrals in the gas phase, which can be incorporated into the growing film and eventually contribute to the formation of NaO_x surface defects. Besides, BiO^{1+} (225 m/z) ions are detected in a very low intensity, likely due to preferential O sputtering from Bi_2O_3 (0.80 atoms/ion) compared to TiO_2 (0.73) and

$\text{Na}_2\text{Ti}_3\text{O}_7$ (0.52), along with the gas-phase dissociation, both of which reduce the detection of intact BiO^{1+} ions. The evolution of target-derived elemental ion ratios ($\frac{\text{Bi}}{\text{Ti}}$, $\frac{\text{Na}}{\text{Ti}}$, and $\frac{\text{Bi}}{\text{Na}}$) during ~8 h of continued sputtering is illustrated in Figures 4-6. The ‘red’ data points in $\frac{\text{Bi}}{\text{Ti}}$ and $\frac{\text{Bi}}{\text{Na}}$ ratios highlight the outliers which were significantly deviating from the general trends of the concerned ratios, so they were excluded from the curve fitting .

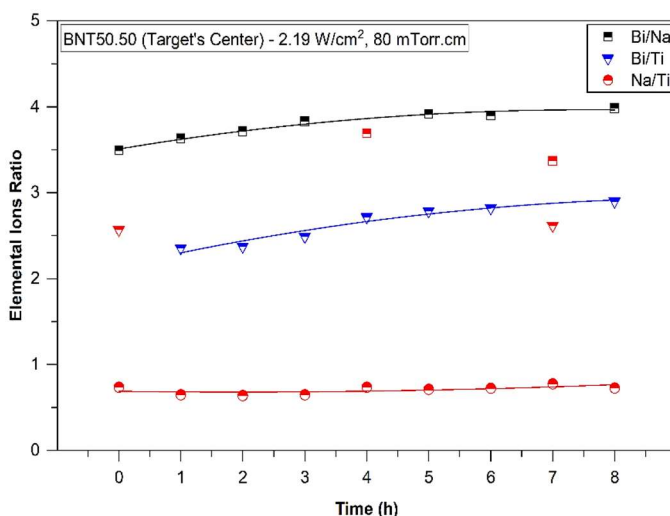


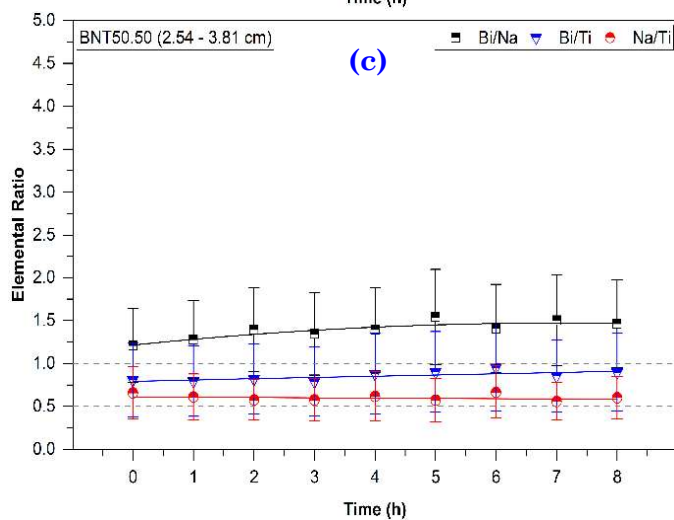
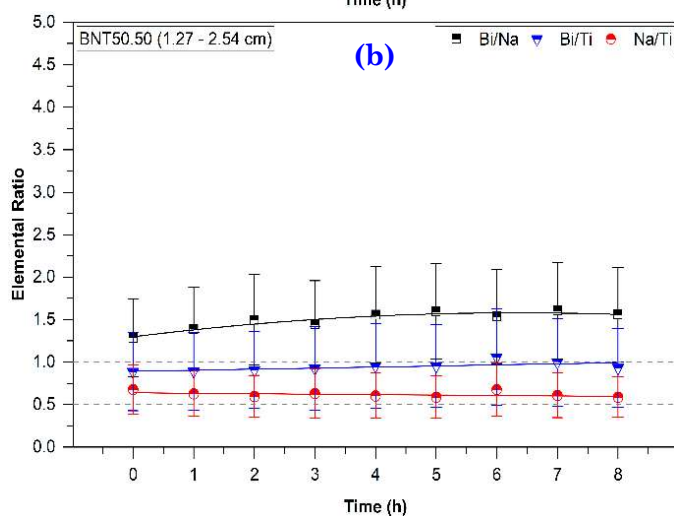
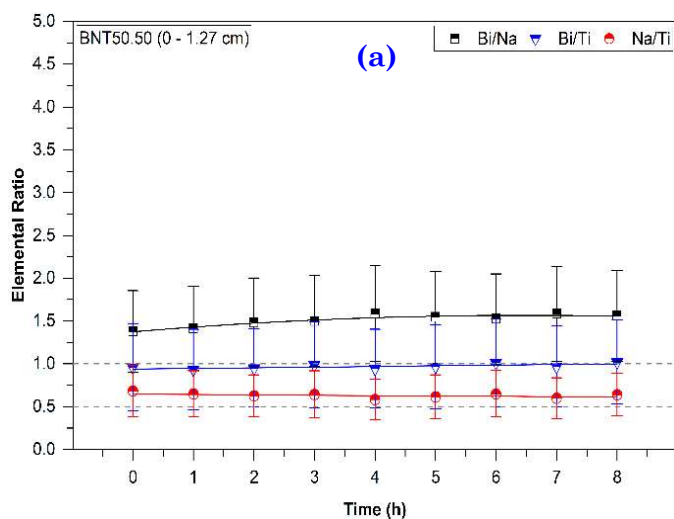
Figure 4-6: Mass spectrometry-based time-resolved elemental ion ratios in the plasma of a conditioned BNT50.50 target during ~8 h of continuous sputtering.

In contrast to the conditioning period, the elemental ion ratios are relatively stable during the ~8 h of continued sputtering. The Bi-related ratios show a rather small increase over time which also stabilizes during the later hours. On the other hand, the intensity of $\frac{\text{Na}}{\text{Ti}}$ ratio remains steady throughout the ~8 h of continued sputtering. In summary, the evolution of the plasma ion chemistry of conditioned BNT50.50 targets was examined over ~8 h of continuous sputtering using mass spectrometry. The elemental ion ratios remain relatively stable throughout this period, in contrast to the conditioning stage, reflecting improved surface stabilization. Notably, the low-energy secondary peak in the Na^{1+} (23 m/z)

IEDF indicates an additional emission pathway from the target surface, likely associated with thermally induced Na sublimation. Depending on the population of these low-energy Na species and their re-evaporation at the substrate, this may contribute to the formation of NaO_x surface defects.

Composition and morphology of as-deposited films

To record the evolution of film composition during ~8 h of continuous deposition using conditioned BNT50.50 targets, films were deposited at hourly intervals on Si (100) substrates. The final space and time resolved, EDX-derived composition of films deposited at hourly intervals, along with their spatially averaged composition, is shown in Figure 4-7.



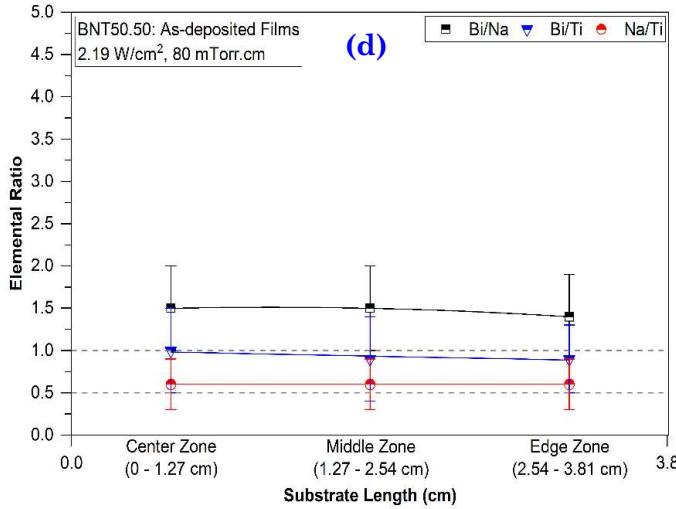


Figure 4-7: (a–c) Time-resolved composition of films deposited at hourly intervals, and (d) spatially averaged composition of these films, using a conditioned BNT50.50 target.

The time-resolved compositional analysis shows slight evolution in the elemental ratios during the first half of the deposition period, indicating a residual progression of the conditioned target surface composition at a reduced rate compared to the conditioning period, followed by stabilization in the latter half of deposition. The spatially averaged composition shows that the $\frac{Bi}{Na}$ ratio exceeds the stoichiometric value of 1, reaching 1.5 ± 0.5 in the center and middle zones while slightly decreasing to 1.4 ± 0.5 at the edge. This trend is consistent with simulations predicting a ~29 at.% higher Bi flux relative to Na arriving at the substrate. The radial variation likely arises from the lower gas-phase scattering of heavy Bi species in Ar compared to the lighter elements like Ti, Na, and O in BNT plasma, leading to a Bi-enriched flux at the plasma center. The quantitative differences between experiment and simulation can be attributed to the limitations of SiMTRA code, which only models the deposition fluxes arriving at a surface while it does not account for the later processes like re-evaporation of atoms after their landing. Similarly,

the average $\frac{Bi}{Ti}$ ratio exceeds its stoichiometric value of 0.5, reaching 1.0 ± 0.5 at the center while decreasing to 0.9 ± 0.4 toward the edge, further indicating Bi enrichment in the films. Finally, the average $\frac{Na}{Ti}$ ratio remains 0.6 ± 0.3 across the substrate, close to the stoichiometric value of 0.5, yet still consistent with the ~37 at.% Ti-deficient flux predicted by transport simulations. The observed excess of Bi typically leads to the formation of Bismuth titanate secondary phases alongside the primary BNT phase, which lowers the overall piezoelectric performances of the BNT film^{63, 64}. The GIXRD technique was used to analyze the crystalline structure of as-deposited films, as shown in Figure 4-8.

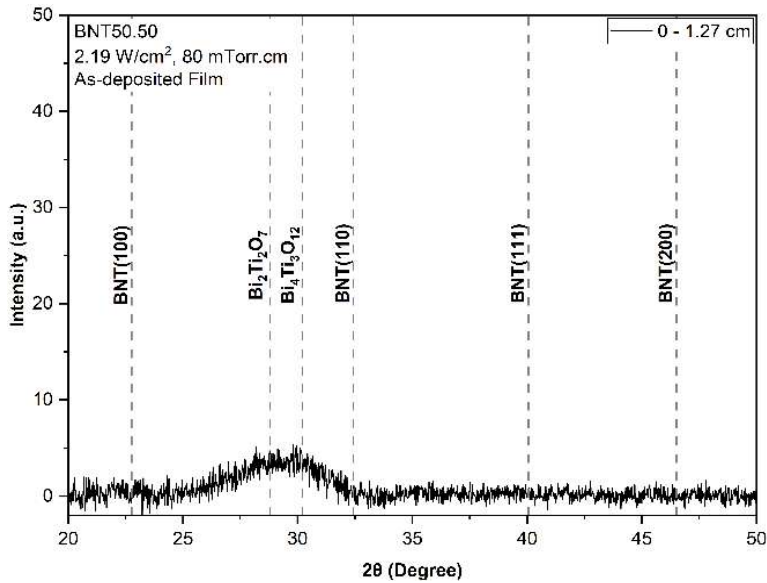


Figure 4-8: GIXRD pattern of the as-deposited film from the center zone of substrate.

The films were predominantly amorphous, consistent with the known crystallization onset of the BNT phase at ~450°C^{63, 64}. However, very weak bismuth titanate-related reflections were detected in films from the center zone, potentially due to the localized heating by an energetic and comparatively higher flux of Bi arriving there. The

measurements were performed at the substrate center, where increased film thickness facilitates the detection from even minor crystallographic features. The time-resolved self-bias voltage of the target and the thickness profile of as-deposited films are shown in Figure 4-9.

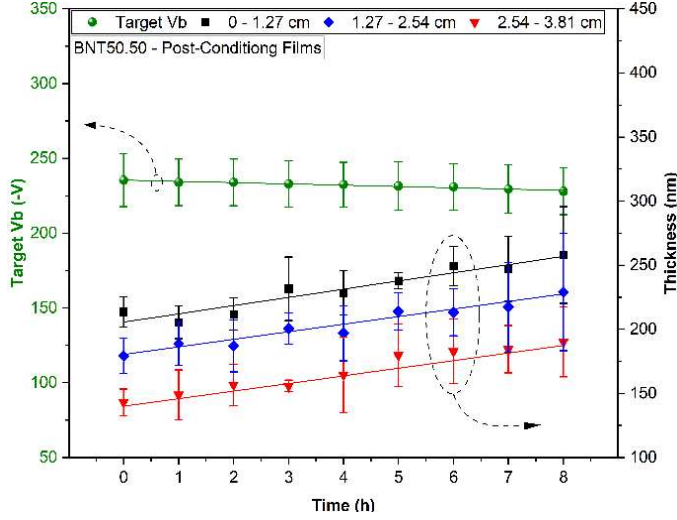


Figure 4-9: Self-bias voltage of the conditioned BNT50.50 targets and the corresponding film thickness profiles across the different zones of substrate.

The self-bias voltage (V_b) of conditioned BNT50.50 targets was decreasing from -236 to -228 V, which arises from the racetrack erosion that brings the surface closer to the magnets, strengthens the magnetic field, and improves electron confinement. The resulting increase in ionization efficiency raises the discharge current, leading to a less negative V_b . Under the constant applied power, this does not significantly alter the average sputtering rate, as the lower bombarding ion energy (related to the target voltage) is offset by a higher ion flux (determined by the discharge current) despite the change in negative self-bias voltage. The time-resolved thickness evolution of films across all three substrate zones shows an overall linear increase. Spatially, the thickness profile follows that of typical sputtered films on static substrates, with maximum

thickness at the center and a gradual decrease toward the edges, consistent with simulations predicting $\sim 16\%$ and $\sim 24\%$ reductions in the middle and edge zones, respectively. Overall, the average deposition rates on the center, middle, and edge zones of substrate are 4.6 ± 0.4 , 4.1 ± 0.4 , and 3.4 ± 0.4 nm/min, respectively. The morphology of as-deposited films across all three zones of the substrate is shown in Figure 4-10, where red arrows and a high-magnification image highlight NaO_x surface defects; the corresponding EDX maps are given in Figure 4-11.

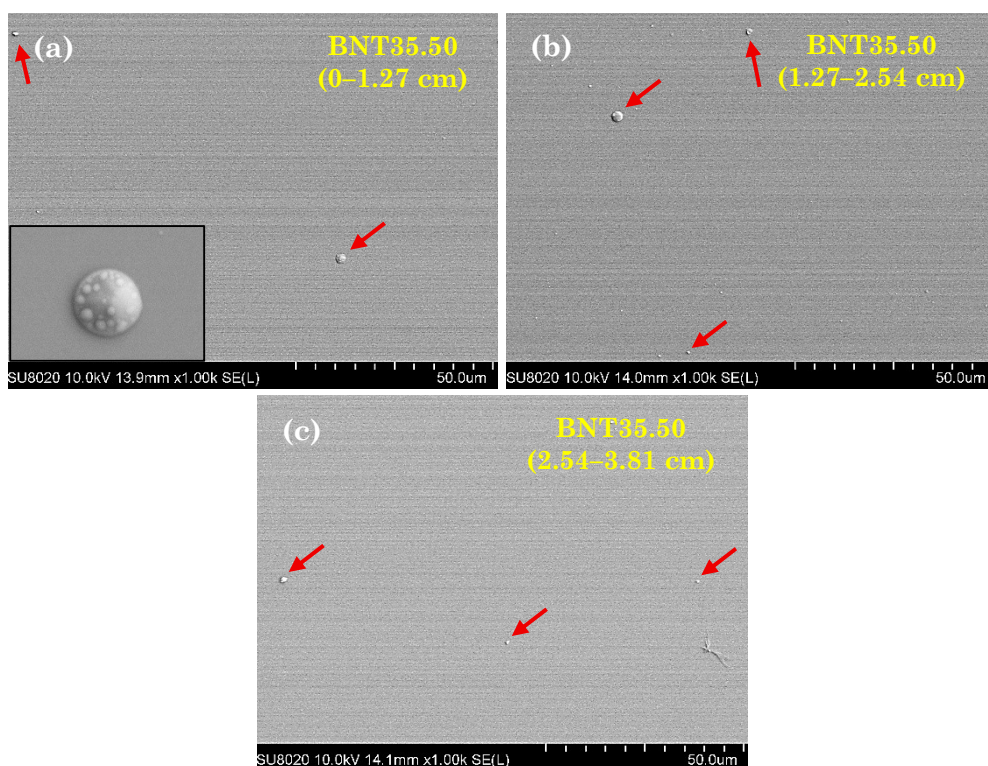


Figure 4-10: Surface morphology of as-deposited films with red arrows indicating NaO_x surface defects; inset: high-magnification image ($5 \times 4 \mu\text{m}^2$ size) of a NaO_x surface defect.

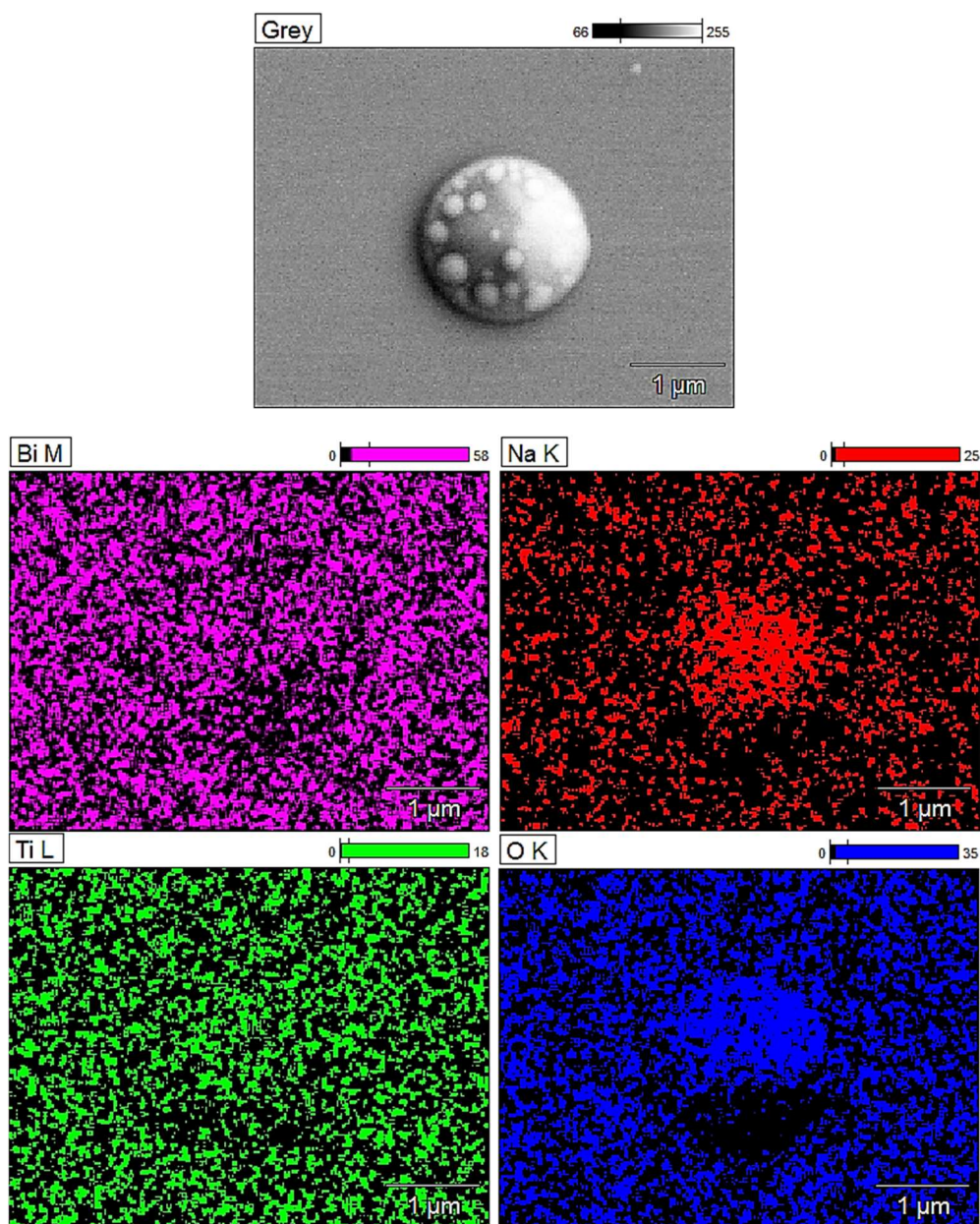


Figure 4-11: EDX elemental maps of a NaO_x surface defect on as-deposited BNT films from the BNT50.50 target.

The formation of those defects is possibly linked to the presence of a large amount of sublimated low-energy Na neutrals, the potential origin of which is discussed earlier (pp. 65–68). The average defect size ($\sim 5 \mu\text{m}$) agrees with the reported values for BNT ($\leq 10 \mu\text{m}$)⁶³, NASICON ($\sim 2 \mu\text{m}$)

⁹⁷, and Na_xCoO₂ (~0.2 μm) ⁹⁹ films, with defect shapes remaining diverse and without preferred morphology. The global defect density is relatively higher in the center zone of substrate and decreases towards the edge, following the film thickness profile over a static substrate. However, the literature does not provide critical data on the defect density distribution in thin films across different substrate zones. In summary, the composition of the as-deposited films shows slight evolution during the first ~4 h of deposition, indicating residual evolution of target surface composition on a smaller scale compared to the conditioning period. Thereafter, all elemental ratios stabilize, suggesting effective surface stabilization and implying that BNT50.50 targets require ~14–15 h of conditioning rather than the previously suggested 10 h. The films were rich in Bi content across the substrate, particularly in the center and middle zones, attributed to reduced gas-phase scattering of Bi relative to lighter species. This excess is reflected in the GIXRD analysis of the center region, where weak bismuth titanate secondary-phase reflections are observed in otherwise amorphous films. The NaO_x surface defects are also formed, consistent with the observations of Hamieh *et al.* for the BNT films growth on unheated substrates ⁶³. The formation of such defects is likely linked to the thermal decomposition of Na₂Ti₃O₇ on target's surface and subsequent sublimation of Na₂O as low-energy (≤ 0.1 eV) Na and O atoms. The flux of sublimated Na atoms predominantly contribute to NaO_x defects formation rather than significantly altering the average composition of films.

Composition and morphology of annealed films

The hourly deposited thin films from conditioned BNT50.50 targets were amorphous, as already shown in Figure 4-8. However, the ferroelectric/piezoelectric character of BNT films requires long-range crystalline ordering, which can be induced by annealing in ambient air at

700°C for 1 h, using heating and cooling rates of 3°C/min^{63, 64}. The effects of annealing on the composition and morphology of BNT films are studied. The spatially-resolved, EDX-derived composition of the annealed films is shown in Figure 4-12.

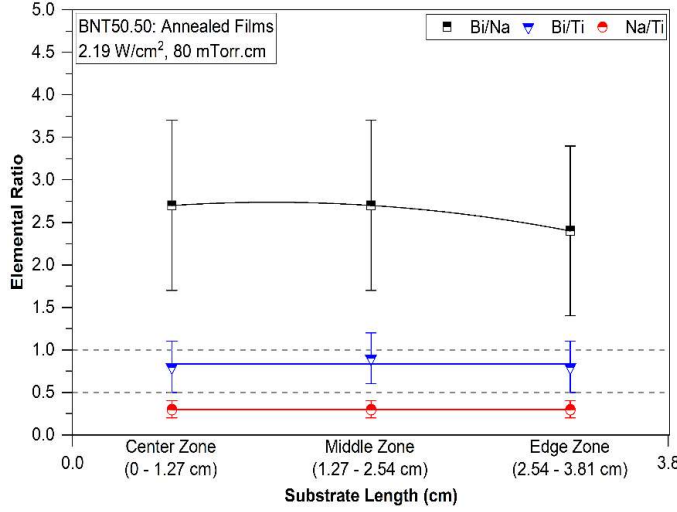


Figure 4-12: Compositional analysis of films deposited from a conditioned BNT50.50 target and annealed at 700°C for 1 h in ambient air.

Overall, approximately 40–50% of Na was lost, with an associated uncertainty of $\pm 20\text{--}30\%$, reflecting the relatively large error margins of the measured elemental ratios. Indeed, the average $\frac{Bi}{Na}$ ratio increased from 1.5 ± 0.5 to 2.7 ± 1.0 in the center and middle, while from 1.4 ± 0.5 to 2.4 ± 1.0 in the edge zone of substrate during the films annealing. Similarly, the average $\frac{Na}{Ti}$ ratio has dropped from 0.6 ± 0.3 to 0.3 ± 0.1 , whereas the $\frac{Bi}{Ti}$ ratio remains nearly unaffected in the range of 0.9–0.8. This is consistent with the observation of Kruzina *et al.*, who reported the sublimation of Na during the annealing of sputter-deposited BNT films at 700°C⁹⁴. Now with reference to the Na content, films have more than

twice as much Bi and Ti available which may lead to the formation of a strong bismuth titanate secondary phase alongside the BNT. The GIXRD analysis of annealed films confirmed the co-existence of bismuth titanate phase(s) alongside the polycrystalline BNT phase with an intense (110) reflection (Figure 4-13).

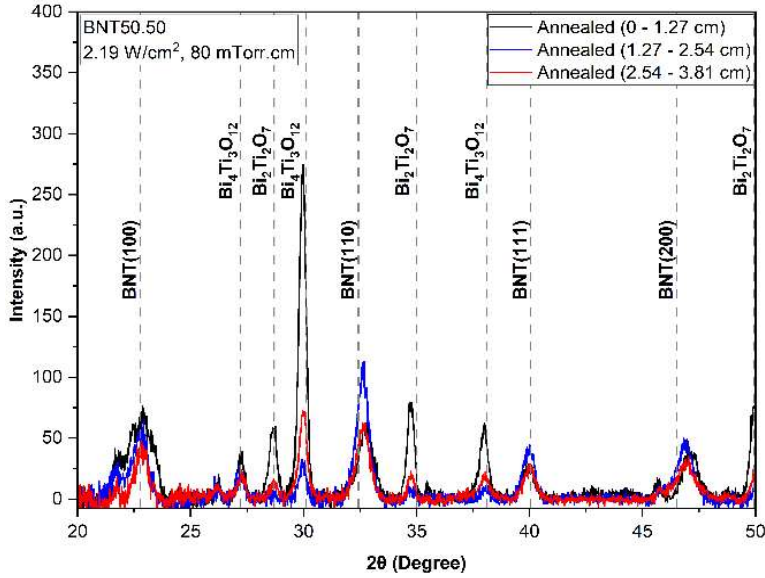


Figure 4-13: GIXRD analysis of films deposited from a conditioned BNT50.50 target and annealed at 700°C for 1 h in ambient air.

Overall, the fractions of both phases account for ~50% each, with the bismuth titanate being more prominent in the center zone, consistent with the compositional analysis of the films. Spatially, the fraction of bismuth titanate phase follows the zonal trend center > edge > middle with phase fractions of 73%, 51%, and 26%, respectively. This trend partially correlates with the Bi distribution, which is highest at the center and decreases toward the edge. The surface morphology of annealed films is shown in Figure 4-14, revealing the effects of NaO_x defect sublimation during annealing; the corresponding EDX maps are presented in Figure 4-15.

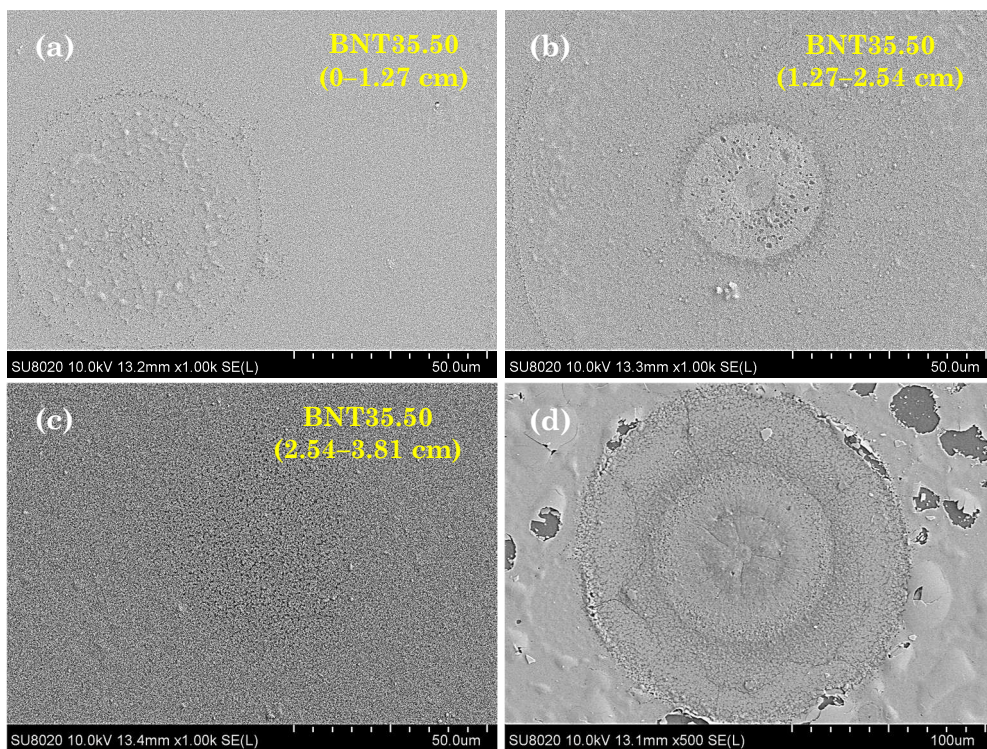


Figure 4-14: (a–c) SEM morphology of annealed BNT50.50 films showing NaO_x defect eruption; (d) resulting surface degradation.

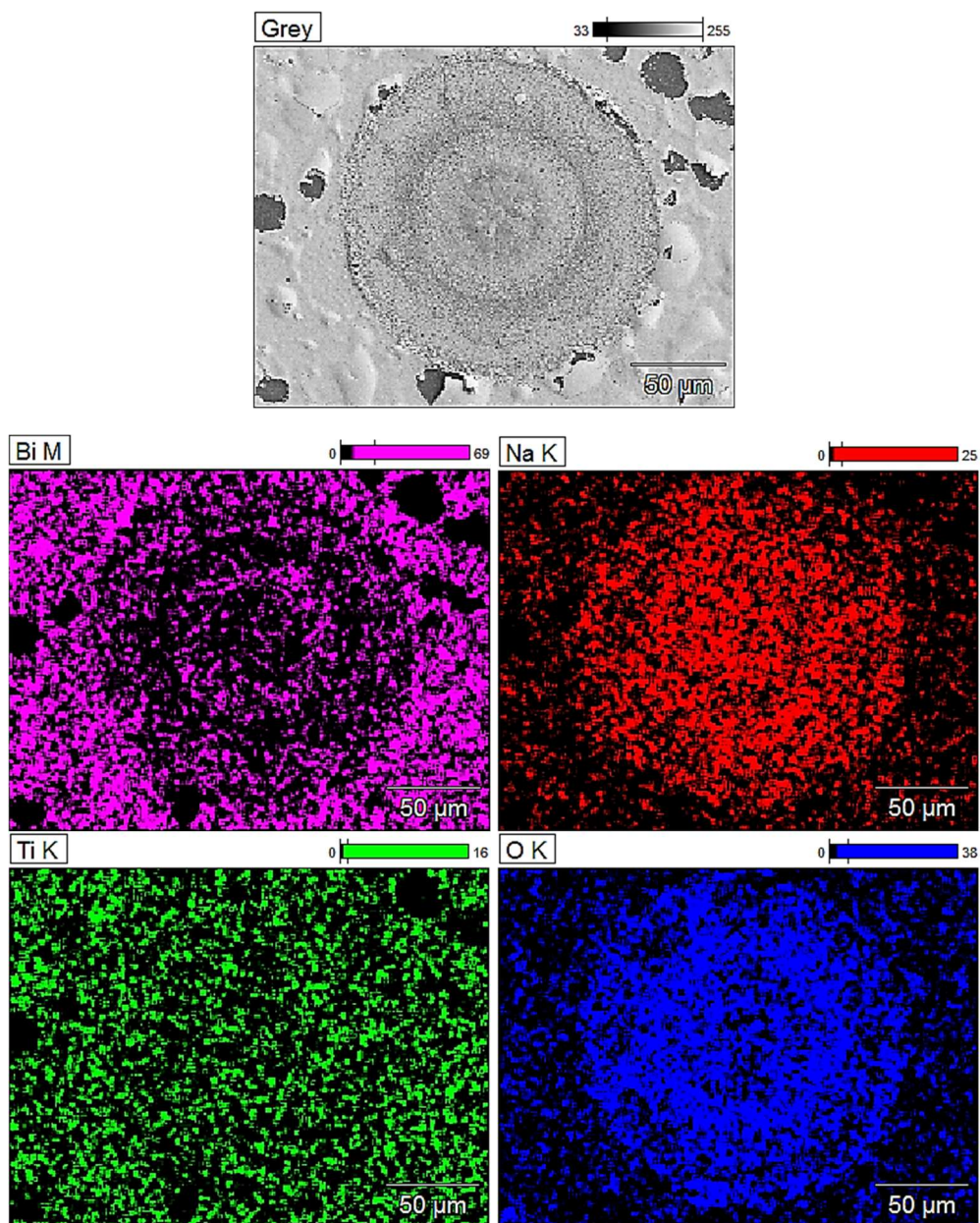


Figure 4-15: EDX elemental maps of a ruptured NaO_x surface defect in annealed films from a BNT50.50 target.

Although the average defect diameter in the as-deposited state was $\sim 5 \mu\text{m}$ (Figure 4-10), rupture of individual defects affects a surface area of $\geq 150 \mu\text{m}$ in the annealed films. In summary, films deposited from BNT50.50 targets lose approximately 40–50% Na through sublimation

during annealing at 700°C ($\pm$ 20–30% uncertainty). Relative to the decreased Na content, Bi and Ti become more than twice as abundant, leading to ~50% BNT and ~50% bismuth titanate crystalline phase fractions. In addition, the rupture of NaO_x surface defects during annealing causes significant surface degradation, rendering the films unsuitable for device applications.

Conclusion

In contrast to the conditioning period, the plasma-phase elemental ion ratios from the conditioned BNT50.50 targets remain relatively stable during 8 h of subsequent sputtering. In the film composition, the elemental ratios ($\frac{Bi}{Na}$, $\frac{Bi}{Ti}$, $\frac{Na}{Ti}$) gradually evolve during the first ~4 h of deposition before stabilizing, indicating that a longer conditioning time of ~14–15 h is required rather than the previously proposed 10 h. The simulations predict a ~29 at.% higher Bi flux relative to Na arrive at the substrate, consistent with the observed $\frac{Bi}{Na}$ ratio of $1.4\text{--}1.5 \pm 0.5$ in the as-deposited films. During film annealing, an average of 40–50% Na is lost due to sublimation, leading to Bi and Ti concentrations up to twice those of Na and to the substantial formation of bismuth titanate secondary phases (~50% phase fraction), which may degrade the piezoelectric performance of BNT films. It was therefore decided to first address the Bi excess by decreasing its concentration in the sputtering target, a change expected to reduce the sputtered Bi flux and thereby eliminate its excess in the as-deposited films. In addition, the target surface temperature is presumed to be sufficiently high to promote the sublimation of Na neutrals, which are likely responsible for the formation of NaO_x surface defects. During annealing, these defects rupture, causing severe surface degradation and rendering the films unsuitable for device applications.

4.1.2 Sputtering of cond. BNT35.50 Target at 2.19 W/cm² and 80 mTorr.cm

Decreasing the Bi concentration in the target is expected to reduce its incorporation into the films during deposition. Therefore, conditioned Bi-deficient BNT35.50 targets were sputtered under identical conditions of 2.19 W/cm² power density and a pressure-distance product of 80 mTorr.cm.

Simulations of target sputtering and transport processes

The Monte Carlo codes TRIM and SiMTRA were used, as described previously, to simulate the target sputtering and species transport, respectively. The top-surface composition of the racetrack region of the conditioned BNT35.50 target (Figure 3-13b, p. 83–84) was used as a representative overall target composition. The target density and Ar¹⁺ ion energy were fixed at 2.3 g/cm³ and 250 eV, respectively. The TRIM-based calculated sputtering yields for incident ion energies in the range of 100–500 eV, are shown in Figure 4-16.

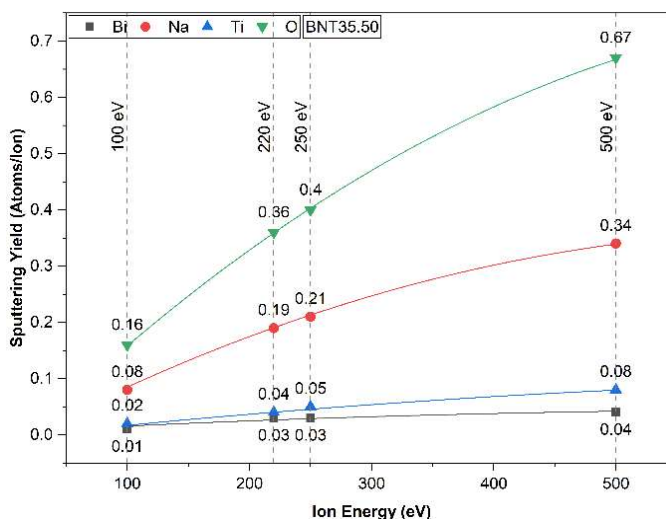


Figure 4-16: TRIM-simulated sputtering yields from the conditioned BNT35.50 target as a function of Ar¹⁺ ion energy (100–500 eV).

Overall, the elemental sputtering yields from the conditioned BNT35.50 target are comparable to those of conditioned BNT50.50 (Figure 4-1, p. 93), except for Bi. At an ion energy of 250 eV, the Bi yield has decreased by 25% to 0.03 atoms/ion in BNT35.50 target compared to that of the 0.04 atoms/ion in BNT50.50. The corresponding elemental flux ratios are shown below in Figure 4-17.

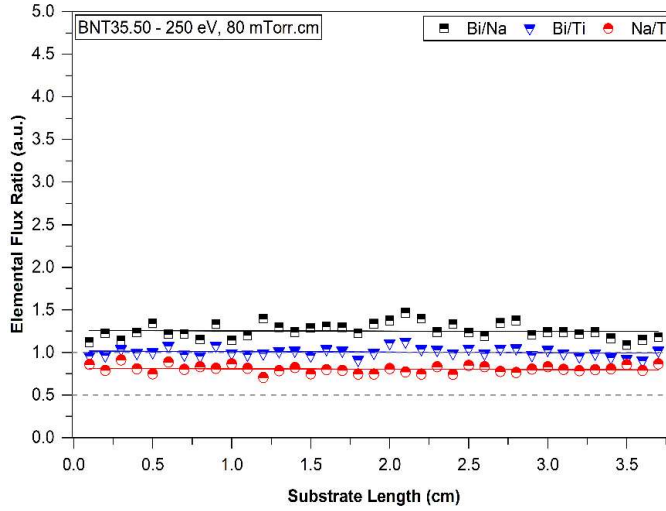


Figure 4-17: SiMTRA-simulated transport of sputtered species from the conditioned BNT35.50 target toward a 3.81 cm long substrate at a target–substrate distance of 8 cm, under 250 eV Ar¹⁺ ion bombardment.

Overall, the average elemental flux ratios ($\frac{Bi}{Na} = 1.2$, $\frac{Bi}{Ti} = 1$, $\frac{Na}{Ti} = 0.8$) exceed the desired stoichiometric film composition ($\frac{Bi}{Na} = 1$, $\frac{Bi}{Ti} = \frac{Na}{Ti} = 0.5$) and are comparable to those of the conditioned BNT50.50 target ($\frac{Bi}{Na} = 1.3$, $\frac{Bi}{Ti} = 1$, $\frac{Na}{Ti} = 0.8$). However, the Bi flux is now 25 at.% higher than that of Na, corresponding to a ~4 at.% reduction relative to BNT50.50 (29 at.%). Consequently, a decreased Bi excess is expected in the as-deposited films, which may facilitate achieving the desired stoichiometry (Bi_{0.5}Na_{0.5}TiO₃) requiring equal Bi and Na contents. The Ti flux is ~38 at.% below its stoichiometric level ($\approx 2 \times Na$), comparable to BNT50.50 (~37

at.%), with no observed impact on as-deposited film composition. The deposition flux is highest at the substrate center and decreases by ~15% in the middle and ~24% at the edge, consistent with a typical sputter-deposited film thickness profile. In summary, reducing the Bi content in the target (BNT35.50 vs BNT50.50) lowers the Bi flux while preserving the overall transport trends, leading to a moderate reduction in Bi excess in the arriving flux and is expected to promote stoichiometric BNT film growth.

Evolution of plasma ion chemistry during 8 h of continuous sputtering

The plasma ion chemistry was analyzed by MS technique under the same working conditions and timing as previously. The mass spectrum acquired during the final hour (~8 h) of sputtering is shown in Figure 4-18, and the detected ions are listed in Table 4-2.

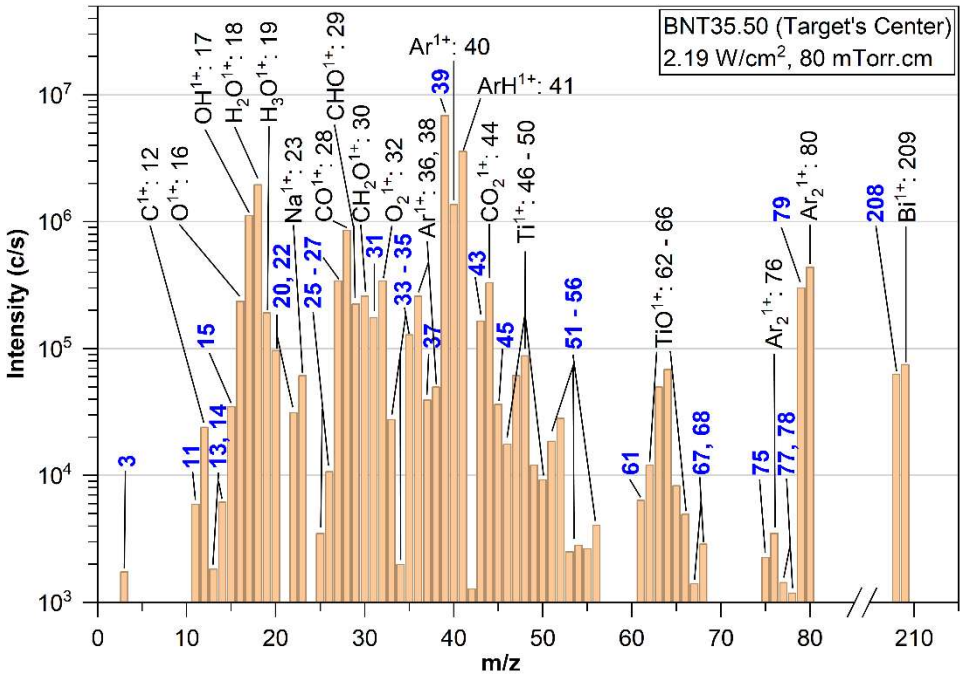


Figure 4-18: Mass spectrum of the plasma from a conditioned BNT35.50 target during the final hour (~8 h) of sputtering.

m/z ratio	ion	m/z ratio	ion
12	C ¹⁺	16	O ¹⁺
17	OH ¹⁺	18	H ₂ O ¹⁺
19	H ₃ O ¹⁺	23	Na ¹⁺
28	CO ¹⁺	29	CHO ¹⁺
30	CH ₂ O ¹⁺	32	O ₂ ¹⁺
36, 38	Ar ¹⁺	40	Ar ¹⁺
41	ArH ¹⁺	44	CO ₂ ¹⁺
46–48	Ti ¹⁺	62–64	TiO ¹⁺
76, 80	Ar ₂ ¹⁺	209	Bi ¹⁺

Table 4-2: List of ions detected ions in the plasma of a conditioned BNT35.50 target.

Overall, the plasma ion chemistry of conditioned BNT35.50 target does not show any significant difference compared to the conditioned BNT50.50 target. The usual target-derived ions like O¹⁺ (16 m/z), O₂¹⁺ (32 m/z), Na¹⁺ (23 m/z), Ti¹⁺ (46–50 m/z), TiO¹⁺ (62–66 m/z), and Bi¹⁺ (209 m/z), along with their secondary peaks 15, 22, 31, 45, 61, and 208 are detected. Those secondary peaks are caused by an instrumental artifact that is discussed in Section 3.2 (pp. 61–63) in detail. Furthermore, the signature of Ar gas, IPA (C₃H₈O), CO₂, and water molecules alongside their secondary peaks were also present in the plasma phase. The IEDFs of various target-derived ions are shown below in Figure 4-19, which are recorded during the last hour (~8 h) of sputtering period.

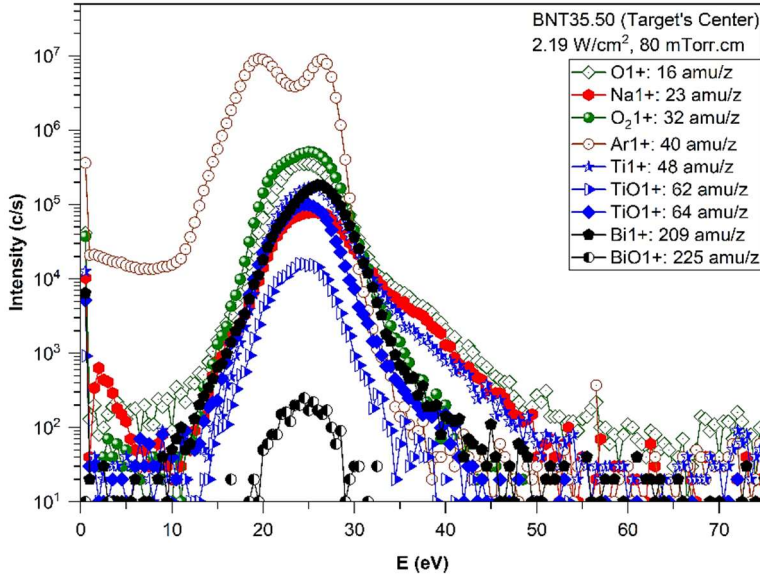


Figure 4-19: Mass spectrometry-based IEDFs of selected ions in the plasma of a conditioned BNT35.50 target during the final hour (~8 h) of sputtering.

The IEDFs of the plasma from conditioned BNT35.50 targets are also largely similar to those of BNT50.50, except for Na^{1+} ions, with comparable peak K.E. of 25–27 eV. The low-energy shoulder of Ar^{1+} and the high-energy tails of target-derived atomic ions (Bi^{1+} , Na^{1+} , Ti^{1+} , and O^{1+}) are also observed. The BiO^{1+} (225 u/e) signal remains weak, consistent with previous observations. Notably, the Na^{1+} ions exhibit a secondary low-energy peak (≤ 10 eV), as observed for BNT50.50; however, its relative population in BNT35.50 is ~1% of the IEDF, compared to ~8% for BNT50.50. This reduction suggests less efficient charge-exchange between low-energy Na neutrals and Ar^{1+} ions in the sheath, likely due to a lower population of sublimated Na atoms. This indicates reduced decomposition of $\text{Na}_2\text{Ti}_3\text{O}_7$ into Na_2O , probably due to a lower surface temperature of the BNT35.50 target compared to BNT50.50. This reduction is attributed to the 25% lower Bi_2O_3 content in BNT35.50 targets, leading to a decreased $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ formation and less exothermic reaction on the BNT35.50 target surface (for details, see Section 3.2, pp.

67–68)). The reduced temperature could only moderately suppress the decomposition of $\text{Na}_2\text{Ti}_3\text{O}_7$, however, it will significantly influence the subsequent sublimation of Na neutrals. According to Hildenbrand et al, the vapor pressure of Na_2O decreases more than fivefold (from 2.13 to 0.4 mTorr) when the temperature drops from 783 to 710°C¹³⁰. Consequently, fewer Na neutrals are present in the plasma phase, further reducing the already less efficient charge-exchange processes with Ar^{1+} , as reflected in the diminished low-energy Na^{1+} ions population (Figure 4-19). The decreased population of Na neutrals may also limit the formation of NaO_x surface defects during the film growth. The evolution of target-derived elemental ion ratios during ~8 h of continuous sputtering is shown in Figure 4-20.

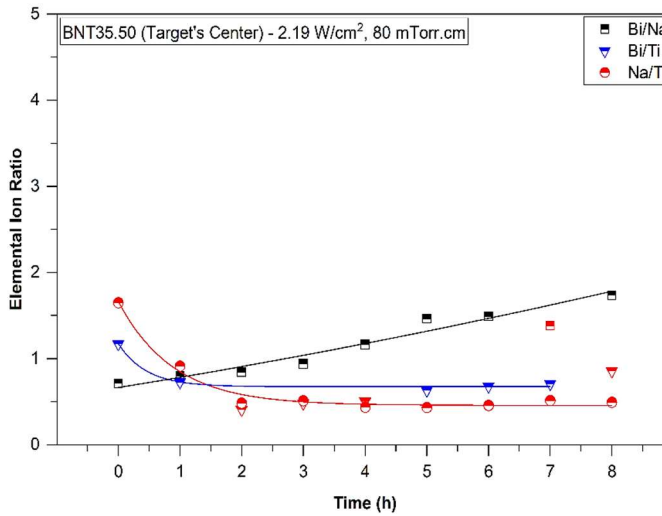


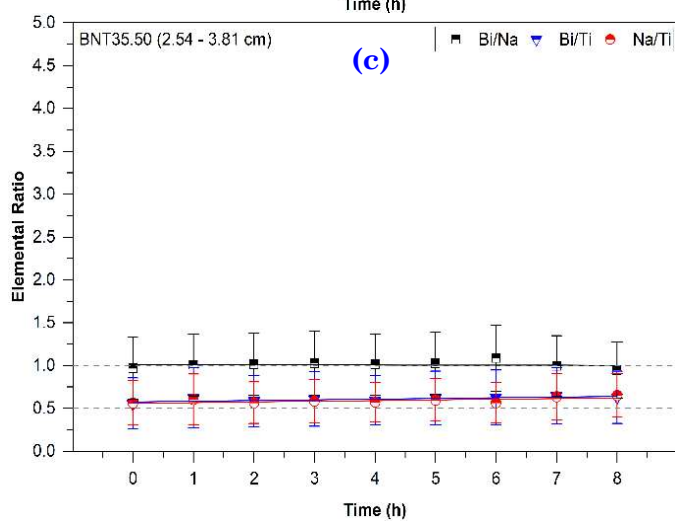
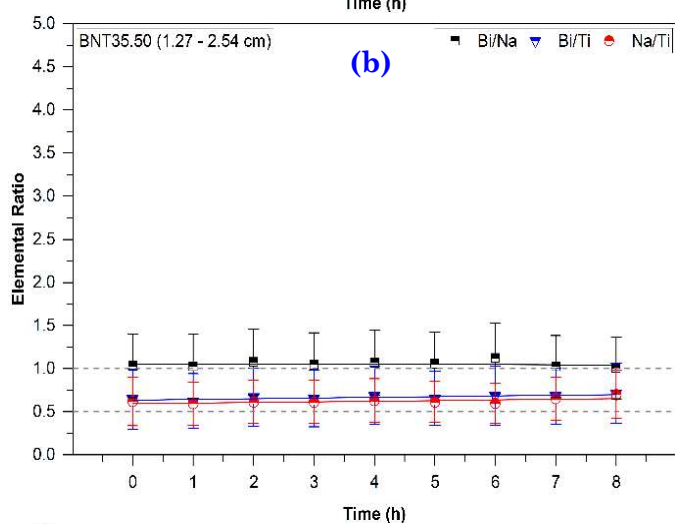
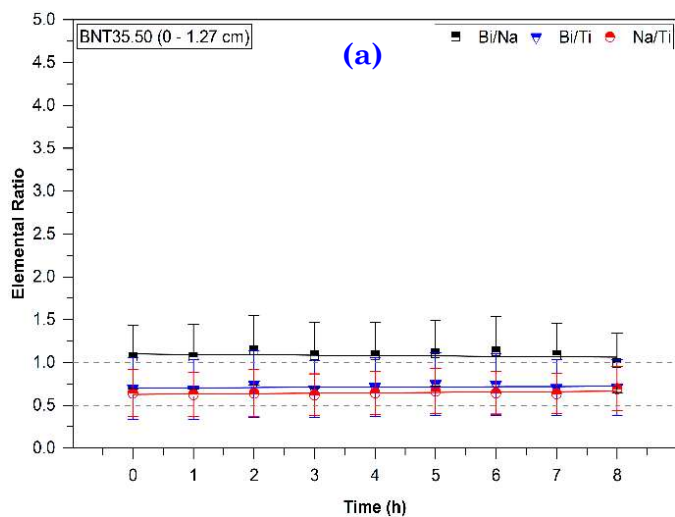
Figure 4-20: Mass spectrometry-based time-resolved elemental ion ratios in the plasma of a conditioned BNT35.50 target during ~8 h of continuous sputtering.

The elemental ion ratios suggest that the Na and Ti ions intensities are decreasing during the first two hours which stabilizes onwards as indicated by the $\frac{\text{Bi}}{\text{Ti}}$ and $\frac{\text{Na}}{\text{Ti}}$ ratios. This tendency of Na ions could partially be linked to the decreased population of sublimated Na

atoms in BNT35.50 plasma, as described earlier. However, the Bi ions intensity is gradually increasing overtime, as demonstrated by the evolving $\frac{Bi}{Na}$ ratio. In summary, the plasma ion chemistry of conditioned BNT35.50 targets remains largely stable during ~8 h of continuous sputtering and closely resembles that of BNT50.50, except for the Na¹⁺ (23 m/z) IEDF. The low-energy fraction of Na¹⁺ ions is strongly reduced (~1% vs ~8%), indicating a lower population of sublimated Na neutrals due to reduced target surface temperature, consistent with the lower Bi₂O₃ content. Consequently, Na₂O sublimation as Na neutrals and their charge-exchange reactions with Ar¹⁺ ions are suppressed, which is expected to limit NaO_x surface defects formation during film growth.

Composition and morphology of as-deposited films

To monitor the evolution of film composition during ~8 h of continuous deposition using conditioned BNT35.50 targets, films were deposited at hourly intervals under the same conditions as previously. The final space and time resolved, EDX-derived composition of films deposited at hourly intervals, along with their spatially averaged composition, is shown in Figure 4-21.



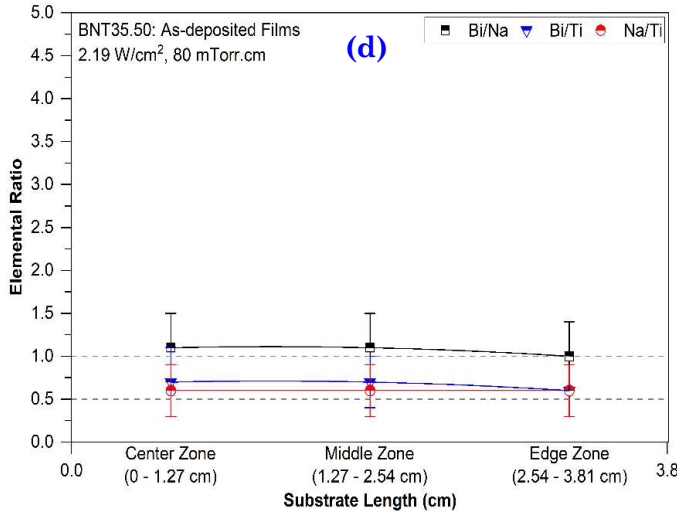


Figure 4-21: (a–c) Time-resolved composition of films deposited at hourly intervals, and (d) spatially averaged composition of these films, using a conditioned BNT35.50 target.

The time-resolved compositional analysis shows that the elemental ratios remain relatively stable throughout the ~8 h of deposition, highlighting the effective stabilization of BNT35.50 target surface in response to the ~10 h conditioning. In contrast, the BNT50.50 target surface continued to evolve for up to ~4 h under similar conditions. The spatially averaged composition shows that the $\frac{Bi}{Na}$ ratio in BNT35.50 films is 1.1 ± 0.4 in the center and middle zones while 1.0 ± 0.4 at the substrate edge, remaining close to the desired value of 1. In contrast, BNT50.50 films exhibited higher $\frac{Bi}{Na}$ ratios of 1.5 ± 0.5 in the center and middle regions and 1.4 ± 0.5 at the edge zone. A similar trend is observed for the $\frac{Bi}{Ti}$ ratio of BNT35.50 films, showing mean values of 0.7 ± 0.4 in the center and middle and 0.6 ± 0.3 at the edge, which are closer to the desired value of 0.5, whereas BNT50.50 films displayed significantly higher ratios of 1.0 ± 0.5 and 0.9 ± 0.4 , respectively. The reduced Bi incorporation in BNT35.50 films is qualitatively consistent with simulations predicting an overall ~4 at.% lower Bi flux toward the substrate from the conditioned

BNT35.50 target compared to the BNT50.50 target. The quantitative discrepancy between the film composition and the simulations arises from the fact that SiMTRA code only models the deposition fluxes arriving at the substrate, while it does not account for the later processes like re-evaporation of atoms after landing on a surface, which seems to be playing a more significant role than the amount of deposition fluxes in the current case. Finally, the average $\frac{Na}{Ti}$ ratio in BNT35.50 films remains approximately 0.6 ± 0.3 across the substrate, comparable to that in the BNT50.50 films and close to the desired value of 0.5. The GIXRD technique was used to analyze the crystalline structure of as-deposited films, as shown in Figure 4-22.

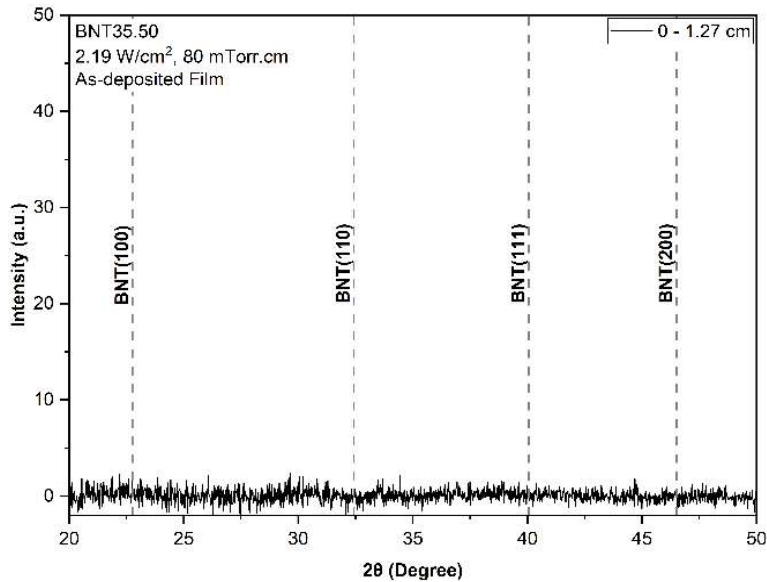


Figure 4-22: GIXRD pattern of the as-deposited film from the center zone of substrate.

Films are predominantly amorphous, consistent with the known crystallization onset of the BNT phase at $\sim 450^\circ\text{C}$ ^{63, 64}. The GIXRD measurements were performed at the substrate center, where maximum film thickness maximizes the probability of detecting the diffracted x-

rays. In BNT50.50 films, a very weak bismuth titanate secondary phase is observed (Figure 4-8, p. 105), potentially due to localized heating associated with the higher-energy, Bi-rich flux arriving at the substrate center. This phase is absent in BNT35.50 films, consistent with the lower Bi content of the target. The time-resolved target bias voltage and film thickness profiles across the substrate, are shown in Figure 4-23.

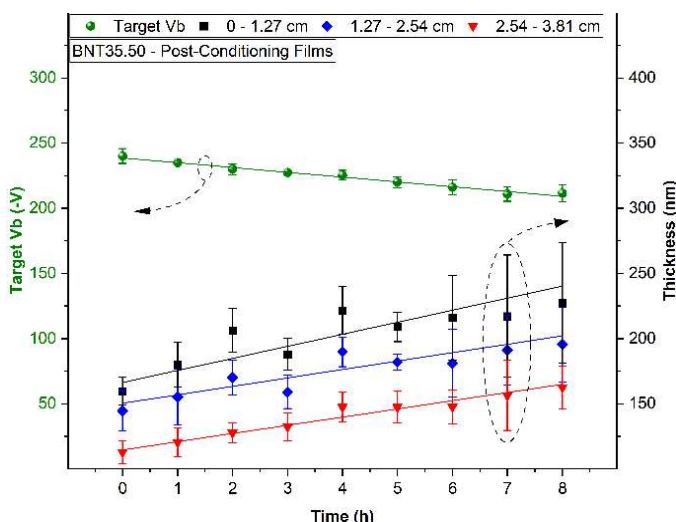


Figure 4-23: Self-bias voltage of the conditioned BNT35.50 targets and the corresponding film thickness profiles across the different zones of substrate.

The target self-bias voltage decreases with target aging, while the film thickness increases over time. Spatially, the thickness profile follows that of a typical sputtered film, consistent with transport simulations. The average deposition rates at the center, middle, and edge zones of substrate are 4.0 ± 0.4 , 3.5 ± 0.4 , and 2.8 ± 0.3 nm/min, respectively. These values correspond to relative reductions of $\sim 13\%$, 15% , and 18% compared to BNT50.50 films, consistent with simulations predicting a ~ 4 at.% lower Bi flux at the substrate. The morphology of as-deposited films in all three zones of the substrate is shown in Figure 4-24.

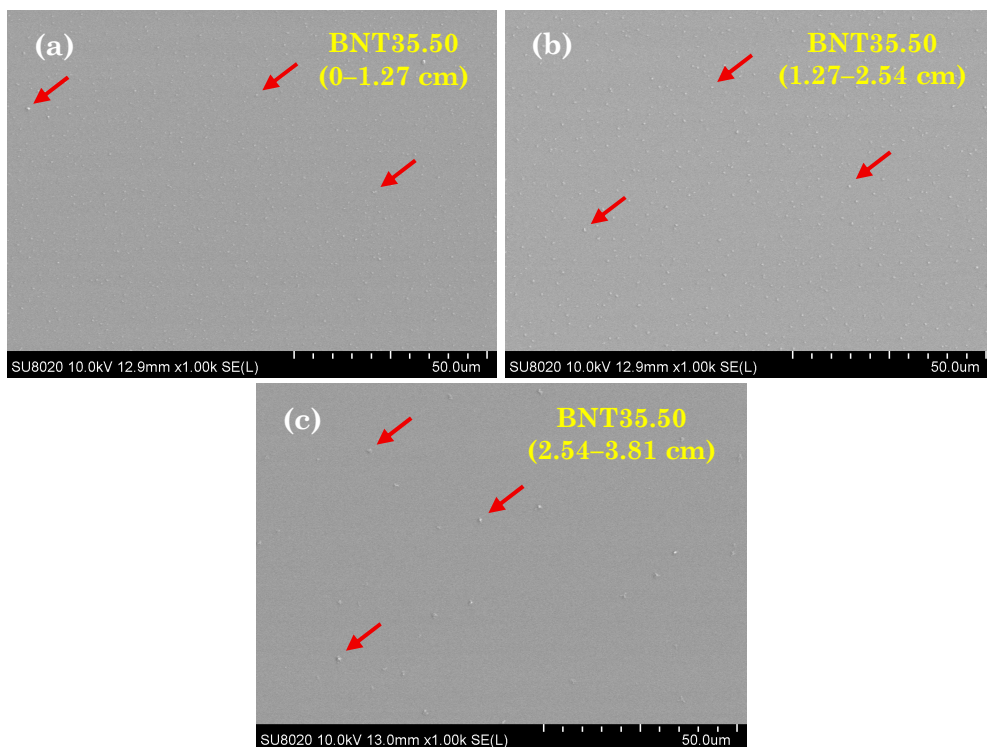


Figure 4-24: Surface morphology of the as-deposited films, having numerous but tiny NaO_x surface defects.

There were relatively small ($\sim 1 \mu\text{m}$) but numerous NaO_x surface defects in the films, in contrast to the fewer but much larger defects ($\sim 5 \mu\text{m}$) in BNT50.50 films (Figure 4-10, p. 107). Similar to the BNT50.50 films, the global defect density is higher in the substrate center and middle zones, and decreases toward the edge; comparable zone-resolved data are not available in the literature. The reduced defect size is attributed to a lower population of sublimated Na atoms, as indicated by the significantly smaller low-energy fraction of Na^+ ions ($\sim 1\%$) in BNT35.50 plasma compared to $\sim 8\%$ in BNT50.50. In summary, the composition of the as-deposited films remains stable, indicating effective stabilization of the BNT35.50 target surface after ~ 10 h of conditioning. The relative contents of Bi, Ti, and Na are close to the desired $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ stoichiometry, consistent with simulations predicting a ~ 4

at.% lower Bi flux from BNT35.50 compared to BNT50.50. The NaO_x surface defects are also smaller (~1 μm vs ~5 μm), which is attributed to a reduced population of sublimated Na species, as evidenced by the lower fraction of low-energy Na¹⁺ ions (~1% vs ~8%). This reduction is expected to improve the film morphology upon annealing.

Composition and morphology of annealed films

The average composition of BNT35.50 films after annealing (700°C for 1 h in ambient air) is shown in Figure 4-25.

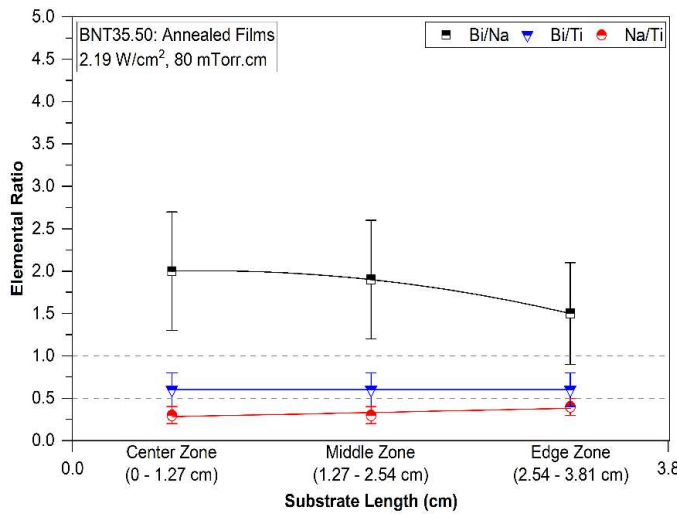


Figure 4-25: Compositional analysis of films deposited from a conditioned BNT35.50 target and annealed at 700°C for 1 h in ambient air.

Overall, ~40–50% of Na was lost from the BNT35.50 films ($\pm 30\%$ uncertainty), similar to that of the BNT50.50 films. The average $\frac{Bi}{Na}$ ratio increased from 1.1 ± 0.4 to 2.0 ± 0.7 in the center, 1.1 ± 0.4 to 1.9 ± 0.7 in the middle, and 1.0 ± 0.4 to 1.5 ± 0.6 in the edge zone during annealing. Similarly, the average $\frac{Na}{Ti}$ ratio dropped from 0.6 ± 0.3 to 0.3 ± 0.1 in the center and middle, and 0.6 ± 0.3 to 0.4 ± 0.1 in the edge zone. The $\frac{Bi}{Ti}$ ratio remains largely unaffected in the range of 0.6–0.7 across the substrate,

similar to the BNT50.50 films. As anticipated, GIXRD analysis shows the coexistence of bismuth titanate phases alongside polycrystalline BNT, with a dominant (110) reflection, as shown in Figure 4-26.

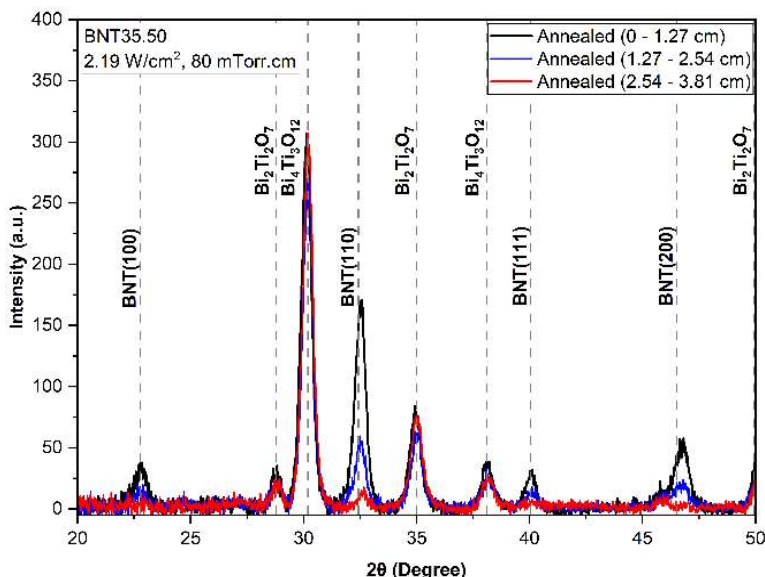


Figure 4-26: GIXRD analysis of films deposited from a conditioned BNT35.50 target and annealed at 700°C for 1 h in ambient air.

Overall, BNT35.50 films contain ~78% bismuth titanate phase fraction across the substrate, compared to ~50% in BNT50.50 films. Spatially, the bismuth titanate fraction in BNT35.50 decreases from edge to center (94% > 78% > 63%), whereas BNT50.50 shows the opposite trend, peaking at the center (73% > 51% > 26%). The Na loss is commonly observed in low-density (e.g., solution-processed) films, where solvent evaporation during annealing creates pathways for Na sublimation^{43, 44}. Increasing the film density during growth can potentially limit this loss from happening later during annealing¹⁰⁵. The SEM based surface morphology and cross-sectional view of a blister in the annealed BNT35.50 films is shown in Figure 4-27.

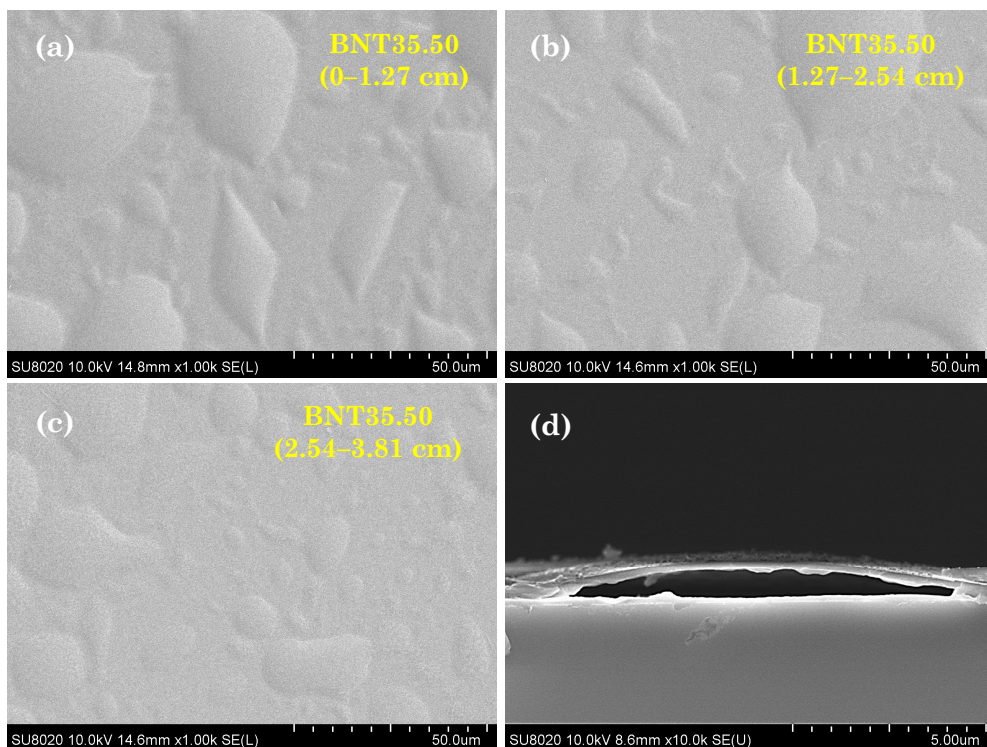


Figure 4-27: (a–c) SEM morphology of annealed BNT35.50 films showing the blister formation and (d) cross-sectional view of a blister revealing the film delamination.

The relatively small ($\sim 1\mu\text{m}$) but numerous NaO_x surface defects on BNT35.50 as-deposited films (Figure 4-24) sublimated during annealing without causing eruptions or film degradation. In contrast, the BNT50.50 as deposited films contain fewer but larger defects ($\sim 5\mu\text{m}$), which rupture under the same annealing conditions and severely degrade the films (Figure 4-14, p. 112). Although no defect rupture is observed in BNT35.50 films, blister formation occurs during annealing, likely due to the release of residual stresses introduced during film growth¹³⁸. In summary, BNT35.50 films lose $\sim 40\text{--}50\%$ Na during annealing at 700°C ($\pm 30\%$ uncertainty). This leads to a significant bismuth titanate phase fraction, averaging $\sim 78\%$ across the substrate. The BNT35.50 films show no defect

eruption or crater formation, but exhibit blistering and partial delamination.

Conclusion

In the hourly grown as-deposited films' composition, the elemental ratios ($\frac{Bi}{Na}$, $\frac{Bi}{Ti}$, $\frac{Na}{Ti}$) remained steady throughout the ~8 h sputtering, indicating an effective stabilization of the BNT35.50 target surface in response to the previous ~10 h conditioning. In contrast, the surface composition of BNT50.50 targets stabilized in around 14–15 h. The simulations indicated that conditioned BNT35.50 targets should transfer ~4 at.% lower flux of atomic Bi to the substrate in comparison to the BNT50.50. This was confirmed experimentally because the as-deposited BNT35.50 films showed nearly equal Bi and Na concentrations, thereby compensating for the previously observed Bi excess in BNT50.50 films. After annealing, the films composition showed an average 40–50% loss of Na through sublimation during post-annealing, similar to the BNT50.50 films. Consequently, the undesired bismuth titanate secondary phases still formed with an average ~78% fraction across the substrate compared to the ~50% in BNT50.50, which will significantly lower the piezoelectric performance of BNT films. Besides the surface, lower film density provides additional pathways for Na sublimation during annealing. It is therefore decided to enhance the energy flux towards substrate which is expected to increase the film density during growth and thereby limit the subsequent Na loss during annealing. This can be achieved by decreasing the target–substrate distance and/or by increasing the applied power density.

In the presumed surface temperature range of ~800°C during sputtering, Bi₂O₃ and TiO₂ likely react to form Bi₄Ti₃O₁₂ on the target surface. This exothermic reaction provides additional heat, further

increasing the surface temperature. As the BNT35.50 composition contains 25% less Bi_2O_3 , its surface temperature is expected to be lower than that of BNT50.50. This moderately decreases the decomposition of $\text{Na}_2\text{Ti}_3\text{O}_7$ but more significantly suppresses the sublimation of Na neutrals. Indeed, the vapor pressure of Na_2O decreases more than fivefold (from 2.13 to 0.4 mTorr) when the temperature drops from 783 to 710°C. The decreased population of Na atoms further weakens the charge-exchange reactions with Ar^{1+} ions in the sheath, reflected by the lower fraction of Na^{1+} ions observed in its IEDF (i.e., ~1% fraction in BNT35.50 Vs ~8% in BNT50.50). Consequently, smaller (~1 μm) and insignificant NaO_x surface defects form, which fully sublimated during annealing. The annealed films remain largely intact; however, blistering occurs, leading to partial delamination from the substrate.

4.2 Influence of the target–substrate distance on film properties

In this section, the conditioned BNT35.50 targets are used to deposit films at a decreased target–substrate distance, and the resulting impact on film properties is examined.

4.2.1 Sputtering of cond. BNT35.50 Target at 2.52 W/cm² and 40 mTorr.cm

To limit the sublimation-driven Na loss from BNT35.50 films, it is decided to enhance the energy flux towards substrate which is expected to increase the film density during growth and thereby limit the subsequent sodium loss during annealing^{75, 139-141}. Specifically, the target–substrate distance is reduced from 8 to 4 cm while maintaining the Ar pressure at 10 mTorr ($P \times D = 40$ mTorr.cm). In addition, the power density is also increased from 2.19 to 2.52 W/cm² in order to maintain a constant Ar^{1+} ion

energy of 250 eV, which also contributes to the increased energy flux at substrate.

Simulations of target sputtering and transport processes

Once again, the Monte Carlo codes TRIM and SiMTRA were used to simulate the target sputtering and species transport processes, respectively. The top-surface composition of conditioned BNT35.50 target's racetrack (Figure 3-13b, p. 83–84) was taken as the representative overall target composition. The target density and the Ar^{1+} ion energy were fixed at 2.3 g/cm^3 and 250 eV. The sputtering yields stay the same as previously shown in Figure 4-16 (p. 115), due to the unchanged target composition, density, and Ar^{1+} ions energy. The corresponding elemental flux ratios at the substrate are shown below in Figure 4-28.

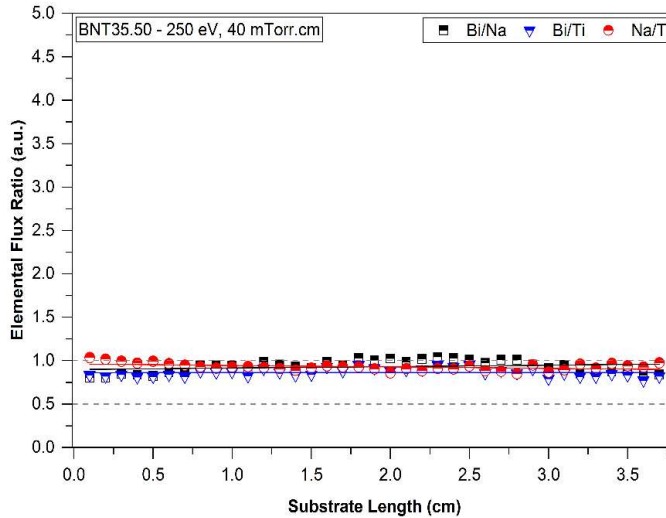


Figure 4-28: SiMTRA-simulated transport of sputtered species from the conditioned BNT35.50 target toward a 3.81 cm long substrate at a target–substrate distance of 4 cm, under 250 eV Ar^{1+} ion bombardment.

Overall, the average elemental flux ratios fall within the range of 0.9–1, which is in good agreement with desired film stoichiometric ratio of $\frac{\text{Bi}}{\text{Na}}$ (i.e., 1). At present, the Na flux is ~8 at.% higher than Bi, whereas

the Bi flux was ~25 at.% higher than Na at 80 mTorr.cm, highlighting the significance of gas-phase scattering and its dependence on the mass of a sputtered specie. The $\frac{Bi}{Ti}$ and $\frac{Na}{Ti}$ ratios markedly deviate from their required value (i.e., 0.5), indicating a substantially lower Ti flux reaching the substrate. However, its impact on film composition during growth will likely be limited, as ~38 at.% Ti deficiency previously showed no significant deviation in the films composition. At the reduced target–substrate distance of 4 cm, the total deposition flux and its average K.E. increase significantly compared to 8 cm. Due to the fewer collisions, the arriving fluxes of Bi, Ti, Na, and O increase by ~91, 123, 157, and 158 at.%, respectively. Simultaneously, the average K.E. of Bi, Ti, Na, and O species nearly doubles, reaching 11.4 ± 1.7 , 5.9 ± 1.7 , 2.2 ± 0.6 , and 3.8 ± 0.9 eV, respectively, compared to 5.2 ± 1.4 , 2.7 ± 1.1 , 1.3 ± 0.7 , and 2.4 ± 1.0 eV at 8 cm. Overall, this corresponds to an approximately fourfold increase in the energy delivered by the sputtered elemental species, contributing to a likely higher total energy flux at the substrate during growth which can lead to the densification of films ^{75, 139-141}. Besides, the overall deposition flux is maximum at the substrate center which decreases by ~10% in the middle and ~35% at the edge zone. The transport simulations were extended to target–substrate distances of 4–16 cm to assess the impact of gas-phase collisions on the composition of the arriving flux, as shown below in Figure 4-29.

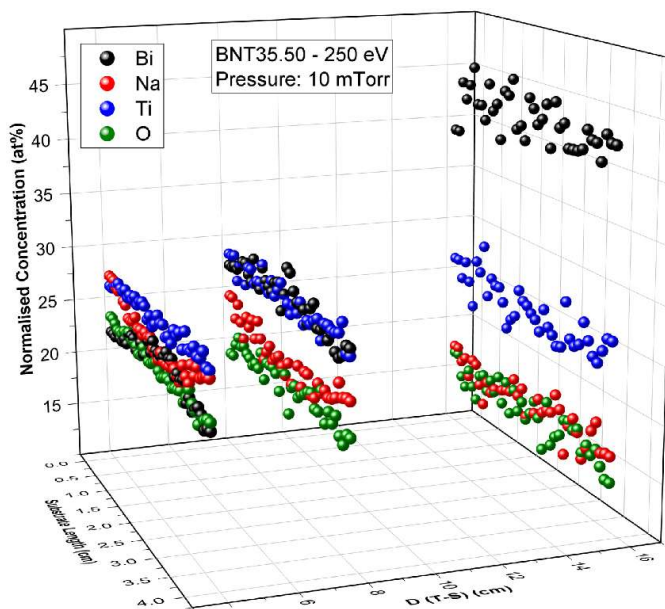


Figure 4-29: SiMTRA-simulated normalized transport of sputtered atoms from the conditioned BNT35.50 target toward a 3.81 cm long substrate for target-substrate distances of 4–16 cm, under 250 eV Ar¹⁺ ion bombardment.

As the distance (or equivalently the $P \times D$ product) increases, lighter species such as O (16 u) and Na (23 u) undergo stronger gas-phase scattering in Ar, leading to progressive attenuation of their flux at the substrate. In summary, the simulations predict that substrate receives ~8 at.% more Na than Bi at 2.52 W/cm² and 40 mTorr.cm. In addition, the energy delivered by elemental sputtered species increase by around fourfold, contributing to a likely higher total energy flux at the substrate during growth which can lead to the densification of films.

Composition and morphology of as-deposited films

The films were deposited for ~3h on Si (100) substrates placed 4 cm away from the target surface while the Ar pressure was maintained at 10 mTorr. The space-resolved compositional analysis of as-deposited films across the substrate is shown in Figure 4-30.

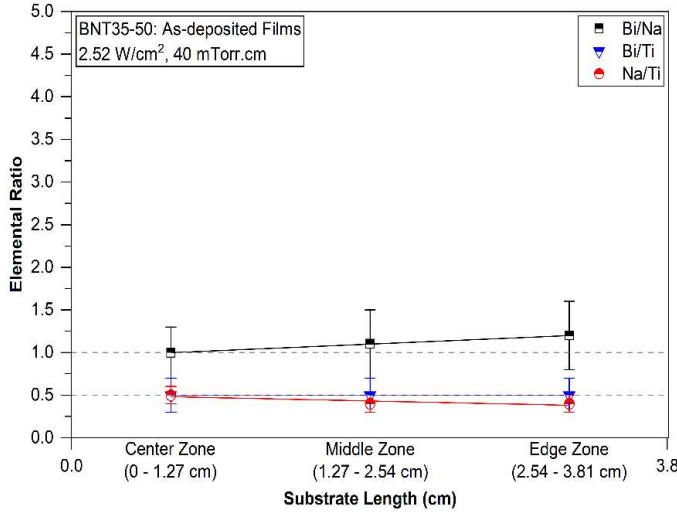


Figure 4-30: Average composition of films deposited from a conditioned BNT35.50 target at 2.52 W/cm² and 40 mTorr.cm.

On average, the $\frac{Bi}{Na}$ ratio is 1.0 ± 0.3 at the center, 1.1 ± 0.4 at the middle regions, and 1.2 ± 0.4 at the substrate edge, remaining close to the desired value of 1. In contrast, the 80 mTorr.cm films exhibited 1.1 ± 0.4 at the center and middle and 1.0 ± 0.4 at the edge zone. The mean $\frac{Bi}{Ti}$ ratio (0.5 ± 0.2) also remains very close to the nominal value of 0.5 across the substrate, having nearly ideal spatial distribution. In comparison, the 80 mTorr.cm films showed mean values of 0.7 ± 0.4 in the center and middle while 0.6 ± 0.3 at the edge zone. Finally, the average $\frac{Na}{Ti}$ ratio is 0.5 ± 0.1 at the center and 0.4 ± 0.1 in the middle and edge zones, which is close to the nominal value of 0.5 and markedly improved compared to the 0.6 ± 0.3 of 80 mTorr.cm films. Overall, both the $\frac{Bi}{Ti}$ and $\frac{Na}{Ti}$ ratios show a more uniform spatial distribution than in the 80 mTorr.cm films. Although the transport simulations predicted a substantially lower Ti flux at the substrate, the as-deposited film composition suggests a limited impact on stoichiometry, while re-evaporation of Bi and Na likely plays a more dominant role in regulating the final composition. The spatially-resolved

thickness profile of films follows that of a typical sputter-deposited film on a static substrate, with greater thickness at the center that decreases toward the edges, in agreement with the transport simulations. Overall, the average deposition rates at the center, middle, and edge zones of substrate are 4.4 ± 0.3 , 3.5 ± 0.4 , and 2.8 ± 0.3 nm/min, respectively. The surface morphology of as-deposited films across the substrate (Figure 4-31), along with the EDX elemental maps of a deposited micron-sized particulate (Figure 4-32), are shown below.

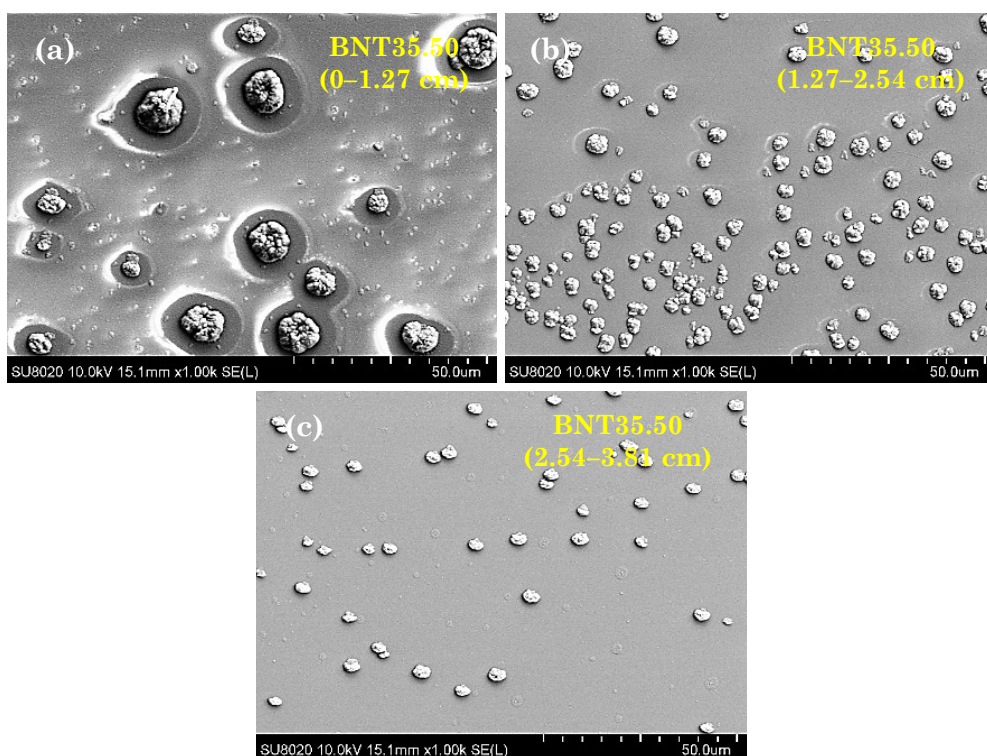


Figure 4-31: SEM surface morphology of films deposited from a conditioned BNT35.50 target at 2.52 W/cm^2 and 40 mTorr.cm, revealing the deposition of micron-sized particulates that were ejected from the target surface.

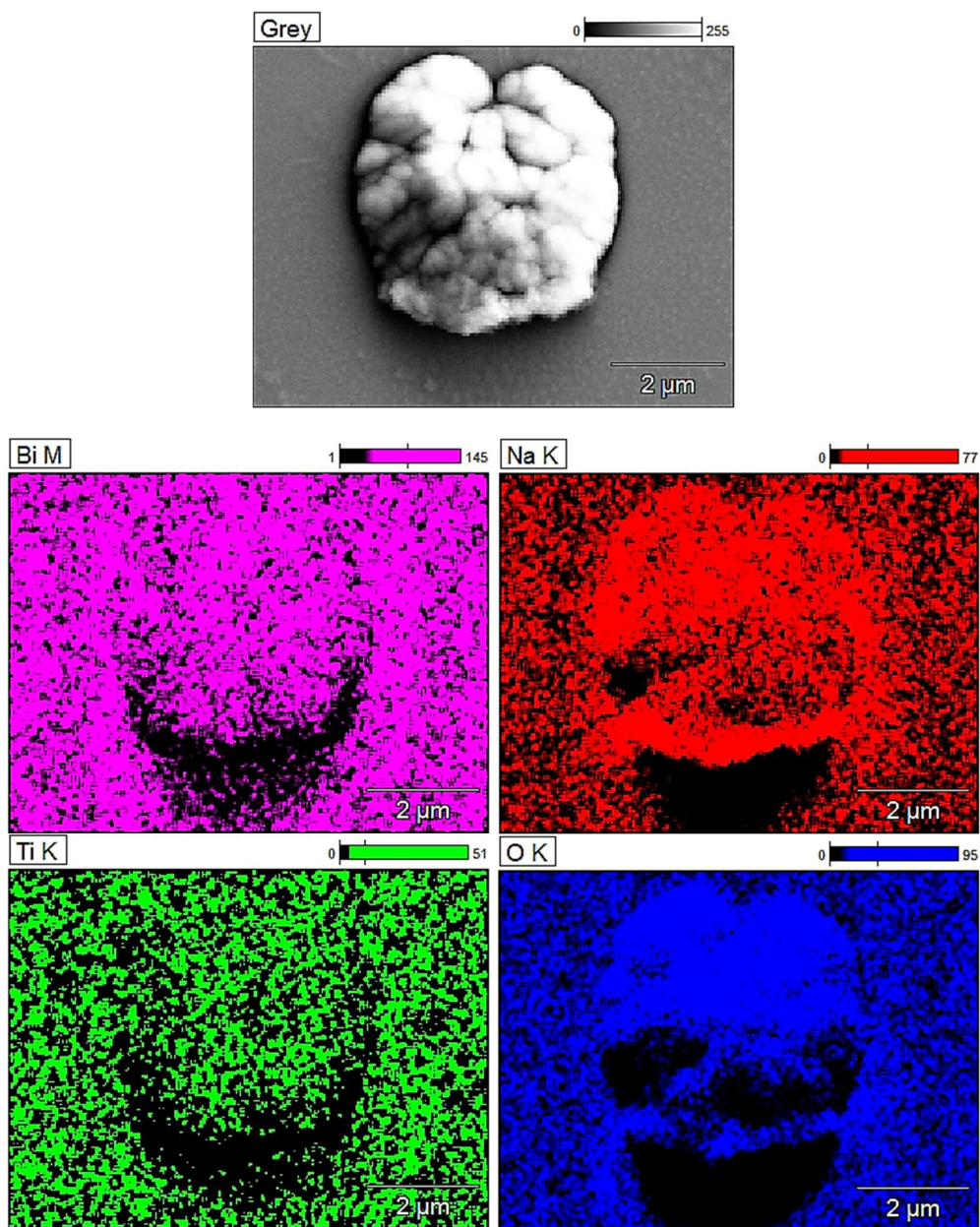


Figure 4-32: EDX elemental maps of a deposited particulate on BNT film, likely ejected from the target surface due to aging.

Numerous $\sim 1\ \mu\text{m}$ -sized NaO_x surface defects are observed across the substrate (Figure 4-31). In addition, $\sim 5\text{--}10\ \mu\text{m}$ particulates are deposited on the films, producing visible shadowing and localized thickness reduction around them. Their size matches that of the BNT

precursor powders (Figure 3-1, p. 57), while EDX elemental mapping (Figure 4-32) confirms the presence of Bi, Na, Ti, and O. Such particulates were not observed previously and are likely associated with target ageing, as the compressed powder targets had already undergone ~20 h of sputtering at this stage. In summary, the as-deposited films grown at 2.52 W/cm² and 40 mTorr.cm exhibit improved stoichiometry, consistent with the simulations predicting an ~8 at.% excess of Na over Bi at the substrate. The usual NaO_x surface defects were present in the films, along with micron-sized particulates likely originating from target ageing after ~20 h of sputtering.

Composition and morphology of annealed films

As usual, the as-deposited films were annealed in ambient air at 700°C for 1 h inside a lab furnace. The spatially-resolved compositional analysis of films is shown in Figure 4-33.

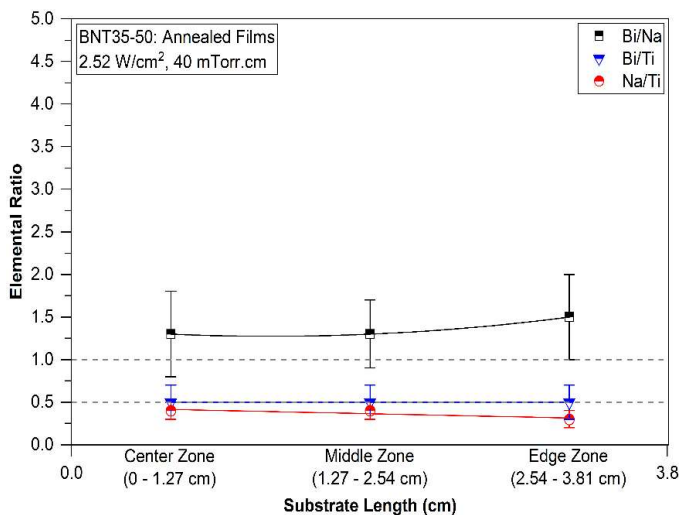


Figure 4-33: Average composition of BNT35.50 annealed films, deposited at 2.52 W/cm² and 40 mTorr.cm.

Overall, approximately 15–25% of Na was lost from the 40 mTorr.cm films, with an associated uncertainty of ±20%, compared to the

40–50% loss in the 80 mTorr.cm films. Indeed, the average $\frac{Bi}{Na}$ ratio has increased from 1.0 ± 0.3 to 1.3 ± 0.5 in the center, 1.1 ± 0.4 to 1.3 ± 0.4 in the middle, and 1.2 ± 0.4 to 1.5 ± 0.3 in the edge zone of substrate. Similarly, the average $\frac{Na}{Ti}$ ratio has dropped from 0.5 ± 0.1 to 0.4 ± 0.1 in the center and 0.4 ± 0.1 to 0.3 ± 0.1 in the edge, while it remained steady at 0.4 ± 0.1 in the middle zone of substrate. Finally, the $\frac{Bi}{Ti}$ ratio remained fixed at 0.5 ± 0.2 across the substrate, which is very close to its nominal value of 0.5 compared to the 80 mTorr.cm films, which had it in the range of 0.6–0.7. The decreased Na loss is likely associated with an increased film density resulting from the higher energy flux during growth⁸⁷. This is consistent with the transport simulations, which predicted around fourfold increase in the energy delivered by the sputtered elemental species, contributing to a likely higher total energy flux at the substrate during growth at 2.52 W/cm² and 40 mTorr.cm. Rossnagel *et al.* described that frequent collisions between sputtered atoms and the background gas reduce both the energy and directionality of the deposition flux reaching the substrate¹⁴⁰, while Depla *et al.* showed that reducing pressure or target–substrate distance preserves higher-energy flux during transport⁷⁵. Thomann *et al.* further demonstrated that the energy delivered to the substrate surface increases with increasing sputtering power and decreasing pressure¹⁴¹. The resulting increase in film density likely reduces the diffusion pathways available for Na during annealing, thereby limiting its sublimation loss, consistent with the lower Na loss observed in the current annealed films, grown at 2.52 W/cm² and 40 mTorr.cm. The GIXRD analysis of the annealed films (Figure 4-34) reveals the coexistence of a weaker bismuth titanate phase alongside the dominant polycrystalline BNT phase, characterized by an intense (110) reflection.

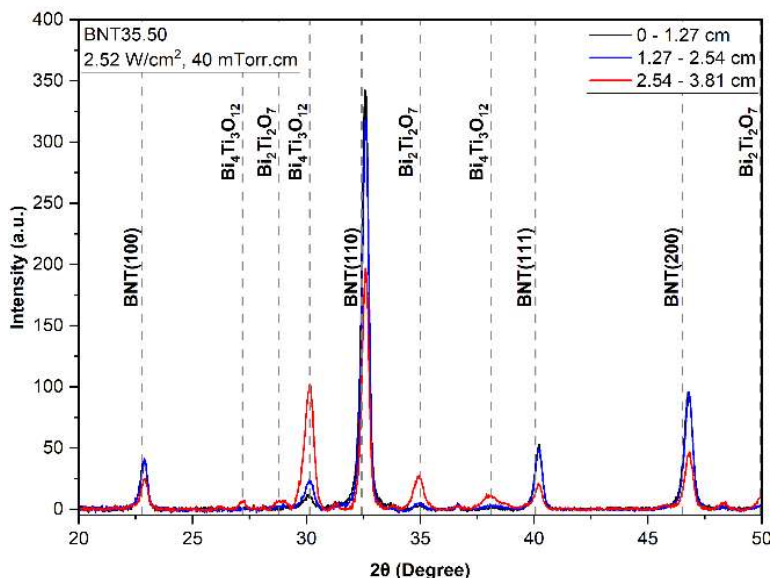


Figure 4-34: GIXRD scans of BNT35.50 annealed films, deposited at 2.52 W/cm² power density and 40 mTorr.cm.

The overall fraction of the bismuth titanate secondary phase in the current films decreased significantly to ~15%, compared with ~78% at 80 mTorr.cm. Spatially, the bismuth titanate fraction at 40 mTorr.cm follows the same zonal trend observed at 80 mTorr.cm, namely edge > middle > center, with respective fractions of 37%, 6%, and 3%, compared with 94%, 78%, and 63% at 80 mTorr.cm. This is in good agreement with the compositional analysis, indicating reduced Na loss from the 40 mTorr.cm annealed films, likely due to their enhanced density, which improved the stoichiometric balance between Bi and Na. Consequently, the BNT phase fraction improved significantly, representing a step toward the realization of stoichiometric Bi_{0.5}Na_{0.5}TiO₃ films. The surface morphology of annealed BNT35.50 films is shown in Figure 4-35.

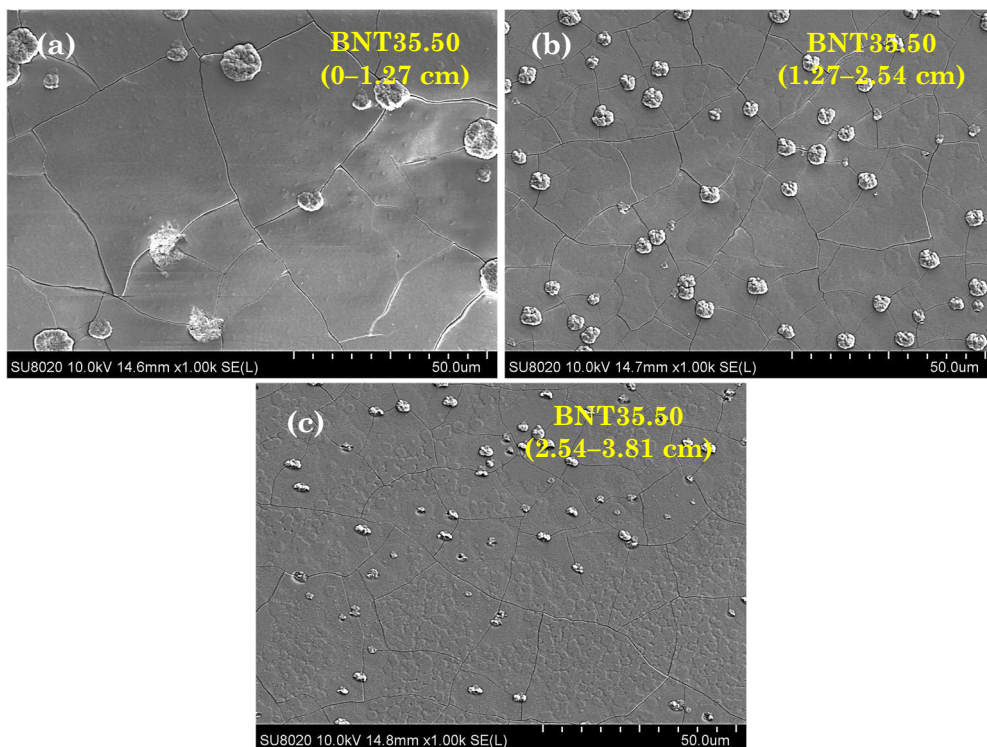


Figure 4-35: Surface morphology presenting the vanishing of tiny NaO_x surface defects, while micron-sized particulates are still present alongside the cracks formation.

The NaO_x surface defects have completely vanished due to the sublimation similar to the annealed films of 80 mTorr.cm (Figure 4-27, p. 128), however, the deposited micron-sized particulates are still present. The current films exhibit cracking, unlike the blister formation observed in the annealed films at 80 mTorr.cm. In summary, the 40 mTorr.cm films lost approximately 15–25% Na during annealing at 700°C ($\pm 20\%$ uncertainty). The reduced Na loss is likely associated with an increased film density resulting from the higher energy flux during growth, which decreases the diffusion pathways available for Na sublimation. This is consistent with the transport simulations, which predicted an approximately fourfold increase in the energy delivered by the sputtered elemental species at 40 mTorr.cm. Most likely, the overall plasma–surface

interaction is intensified, contributing to a higher total energy and heat flux at the growing film surface. Consequently, the fraction of bismuth titanate secondary phase decreased significantly to ~15% across the substrate, compared with ~78% in the 80 mTorr.cm films. The usual NaO_x surface defects vanished during post-deposition annealing, while the deposited particulates decreased were still present and cracks formed due to increased thermal stresses.

Conclusion

By reducing the target–substrate distance by half at 40 mTorr.cm and increasing the power density to 2.52 W/cm², the gas-phase transport of sputtered flux and the growth conditions of BNT35.50 films were significantly modified. The transport simulations predicted an ~8 at.% excess of Na over Bi at the substrate together with an approximately fourfold increase in the energy delivered by the sputtered elemental species, implying a substantially intensified plasma–surface interaction and higher total energy flux during growth. Consequently, the as-deposited films exhibited improved stoichiometry compared to the 80 mTorr.cm films. Following annealing at 700°C, the films showed a substantially reduced Na loss of ~15–25% in comparison to the ~40–50% observed in the 80 mTor.cm films, which is likely associated with increased film density and the resulting reduction in diffusion pathways for Na sublimation. This led to a major suppression of the bismuth titanate secondary phase, decreasing its overall fraction from ~78% at 80 mTorr.cm to ~15% at 40 mTorr.cm. Therefore, it was decided to further increase the energy flux towards the substrate during film growth by increasing the applied power density in order to further suppress Na loss and to promote the formation of a stoichiometric BNT phase across the substrate. Furthermore, the usual NaO_x surface defects disappeared

during annealing, while the deposited particulates remained present and cracks developed due to increased thermal stresses.

4.3 Influence of the sputtering power density on film properties

In this section, the conditioned BNT35.50 targets are used to deposit films at increased applied power densities and the resulting impact on film properties is examined.

4.3.1 Sputtering of cond. BNT35.50 Target at 2.96 W/cm² and 40 mTorr.cm

To compensate for the remaining sublimation-driven loss of Na during annealing and to improve the remaining imbalance of Bi/Na stoichiometry, it was decided to increase the density of as-deposited films by boosting the energy flux towards the substrate via increasing the applied power density from 2.52 to 2.96 W/cm².

Simulations of target sputtering and transport processes

Identical simulation conditions were implemented as previous, except the Ar¹⁺ ion energy, which was increased to 260 eV in contrast to 250 eV at 2.52 W/cm², due to the 10 V increase in target's self-bias at 2.96 W/cm². Consequently, the sputtering yields of Na and O slightly increased by ~5% (from 0.21 to 0.22 atoms/ion) and 2.5% (from 0.40 to 0.41 atoms/ion), respectively. However, the Bi and Ti sputtering yields remained fixed at 0.03 atoms/ion and 0.05 atoms/ion, respectively. These smaller yield changes do not produce any significant variations in the elemental fluxes reaching the substrate (Figure 4-36), indicating little potential for compositional changes in the as-deposited films. However, the average K.E. of Bi and Ti elemental fluxes have modestly increased by 7% (from 11.4 ± 1.7 to 12.2 ± 1.6 eV) and 12% (from 5.9 ± 1.3 to 6.6 ±

1.4 eV), respectively, which may slightly enhance the film densification during growth.

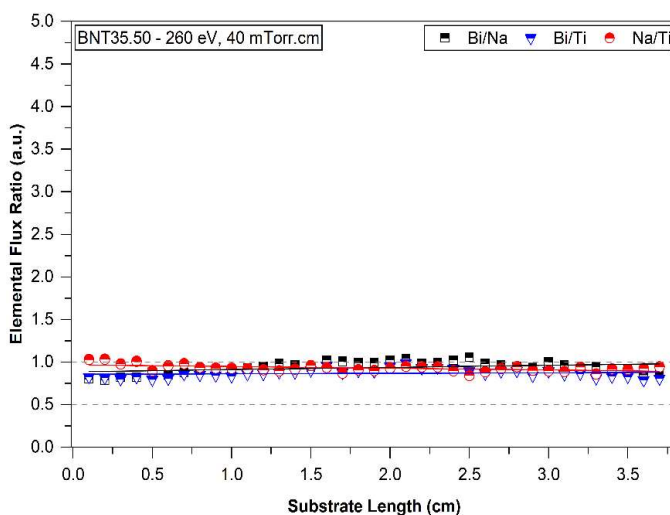


Figure 4-36: SiMTRA-simulated transport of sputtered species from the conditioned BNT35.50 target toward a 3.81 cm long substrate at 40 mTorr.cm and 2.96 W/cm².

Composition and morphology of as-deposited films

Similar deposition, characterization, and data-analysis conditions were employed as previously, except for the increased power density of 2.96 W/cm² and the target ageing of ~25 h, including ~10 h conditioning followed by ~15 h sputtering. The spatially resolved compositional analysis of the as-deposited films is presented in Figure 4-37.

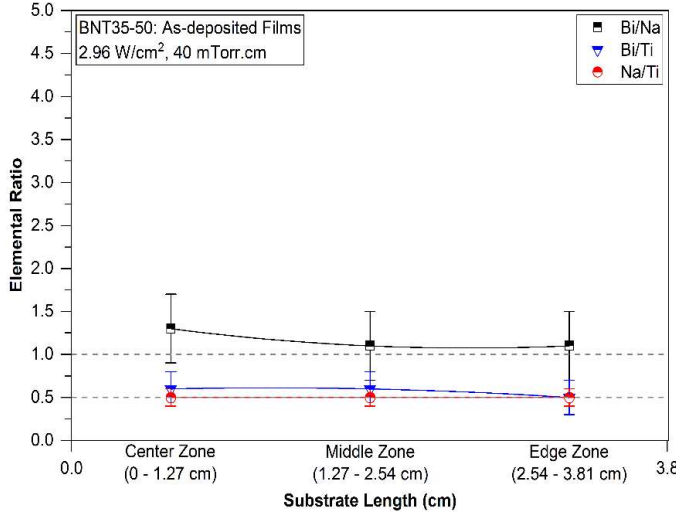


Figure 4-37: Average composition of BNT35.50 as-deposited films, deposited at 40 mTorr.cm and 2.96 W/cm².

On average, the $\frac{Bi}{Na}$ ratio in the 2.96 W/cm² films is 1.3 ± 0.4 at the center and 1.1 ± 0.4 in the middle and edge zones of the substrate, remaining close to the desired value of 1. In comparison, the 2.52 W/cm² films exhibited $\frac{Bi}{Na}$ ratios of 1.0 ± 0.3 at the center, 1.1 ± 0.4 in the middle, and 1.2 ± 0.4 at the edge zone. A similar trend is observed for the $\frac{Bi}{Ti}$ ratio, with the 2.96 W/cm² films showing 0.6 ± 0.2 at the center and middle while 0.5 ± 0.2 at the edge zone, remaining close to the nominal value of 0.5, whereas the 2.52 W/cm² films exhibited 0.5 ± 0.2 across the substrate. Finally, the average $\frac{Na}{Ti}$ ratio in the 2.96 W/cm² films is 0.5 ± 0.1 across the substrate, matching the nominal value of 0.5. In contrast, the 2.52 W/cm² films showed 0.5 ± 0.1 at the center and 0.4 ± 0.1 in the middle and edge zones. Overall, these elemental ratios are consistent with the transport simulations, indicating no significant change in the composition of the as-deposited films. The spatially-resolved thickness profile of as-deposited film follows that of a typical sputter-deposited film on a static substrate, with a greater thickness at the center that decreases toward the edges.

Overall, the average deposition rates on the center, middle, and edge zones of substrate were 5.0 ± 0.2 nm/min, 3.4 ± 0.3 nm/min, and 2.9 ± 0.3 nm/min, respectively, showing only a minor increase in the deposition rates with the increased applied power density. The surface morphology of as-deposited films in all three zones of the substrate is presented in Figure 4-38. As usual, NaO_x surface defects alongside micron-sized deposited particulates are evident across the substrate in the as-deposited films.

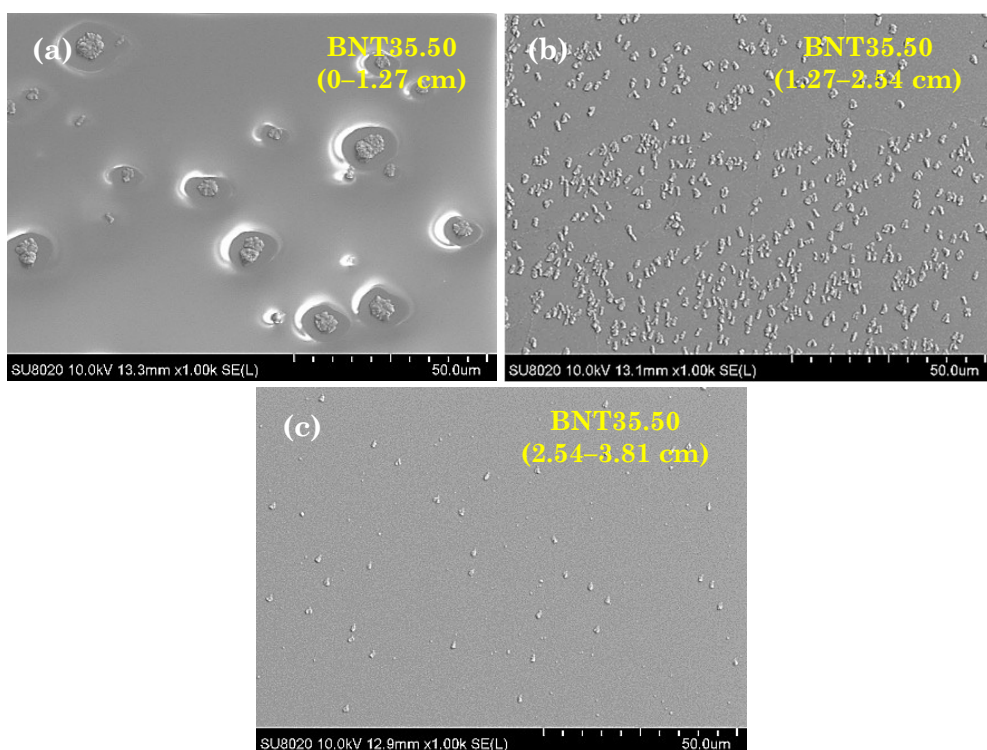


Figure 4-38: SEM surface morphology of films deposited from a conditioned BNT35.50 target at 2.96 W/cm^2 and 40 mTorr.cm, revealing the deposition of micron-sized particulates that were ejected from the target surface.

In summary, no major compositional evolution was observed in the as-deposited films at 2.96 W/cm^2 power density, compared to that at 2.52 W/cm^2 ; which show a good agreement with the transport simulations. The

formation of usual NaO_x surface defects happened everywhere alongside the micron-sized particulate deposition.

Composition and morphology of annealed films

As usual, the as-deposited films were annealed in ambient air at 700°C for 1 h inside a lab furnace. The spatially resolved compositional analysis of the films is shown in Figure 4-39.

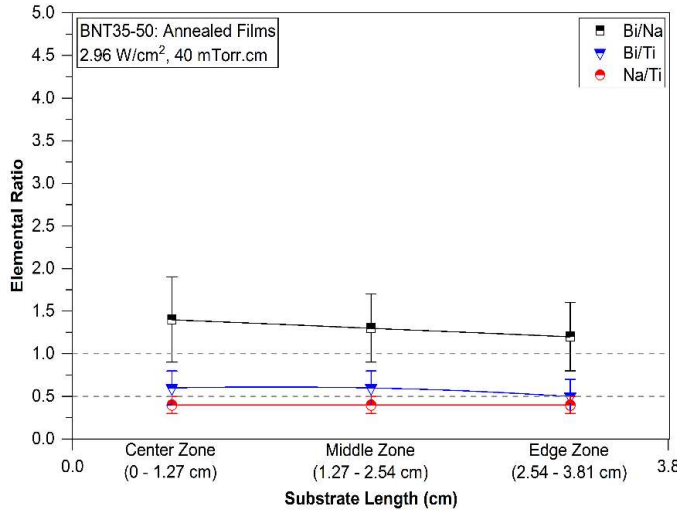


Figure 4-39: Average composition of BNT35.50 annealed films, deposited at 2.96 W/cm^2 and 40 mTorr.cm.

Overall, insignificant amount of Na was lost from the 2.96 W/cm^2 films ($\sim 20 \pm 25\%$), compared with $\sim 15\text{--}25\%$ loss in the 2.52 W/cm^2 films. The average $\frac{\text{Bi}}{\text{Na}}$ ratio increased from 1.3 ± 0.4 to 1.4 ± 0.5 at the center, 1.1 ± 0.4 to 1.3 ± 0.4 in the middle, and 1.1 ± 0.4 to 1.2 ± 0.4 at the edge zone of substrate. Similarly, the average $\frac{\text{Na}}{\text{Ti}}$ ratio dropped from 0.5 ± 0.1 to 0.4 ± 0.1 across the substrate. Finally, the $\frac{\text{Bi}}{\text{Ti}}$ ratio remained nearly unchanged at 0.6 ± 0.2 at center and middle while 0.5 ± 0.2 at the edge zone of substrate. The additional decrease in Na loss during annealing of the 2.96 W/cm^2 films is likely associated with the increased energy flux towards the substrate during growth, which enhanced the film density and

consequently reduced the diffusion pathways available for Na sublimation 75, 87, 139-141. This is partially consistent with the transport simulations, which showed a modest increase in the energy of sputtered Bi and Ti elemental fluxes arriving at the substrate. Indeed, hybrid ERD–RBS measurements performed in the middle zone of the substrate revealed a significant increase in the film mass density, from 3.7 g/cm³ at 2.19 W/cm² and 80 mTorr.cm to 4.6 g/cm³ at 2.96 W/cm² and 40 mTorr.cm. However, comprehensive systematic measurements of film density under all the investigated conditions were not feasible due to time and resource limitations. The GIXRD analysis of annealed films is shown in Figure 4-40, where the substrate's center and middle zones have a pure polycrystalline BNT phase exhibiting an prominent (110) reflection. The BNT-related diffraction peaks are slightly shifted towards the higher angles, suggesting the presence of mechanical stress build up during the growth process.

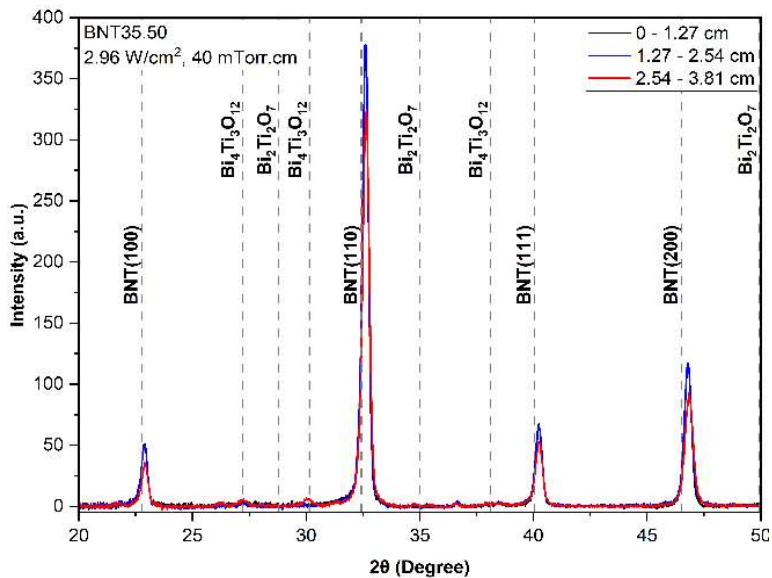


Figure 4-40: GIXRD scans of BNT35.50 annealed films, deposited at 2.96 W/cm² power density and 40 mTorr.cm.

The overall fraction of BNT phase in the current films is $\sim 99\%$ compared to the $\sim 85\%$ in films of 2.52 W/cm^2 . Only the edge zone of substrate shows a weaker bismuth titanate secondary phase of about 3% intensity compared to the BNT phase. This suppression is consistent with the films composition, which suggested almost negligible loss of Na during the annealing step. The surface morphology of annealed films is presented in Figure 4-41, where the NaO_x surface defects have mostly vanished and cracks were formed, as previously observed in the 2.52 W/cm^2 films.

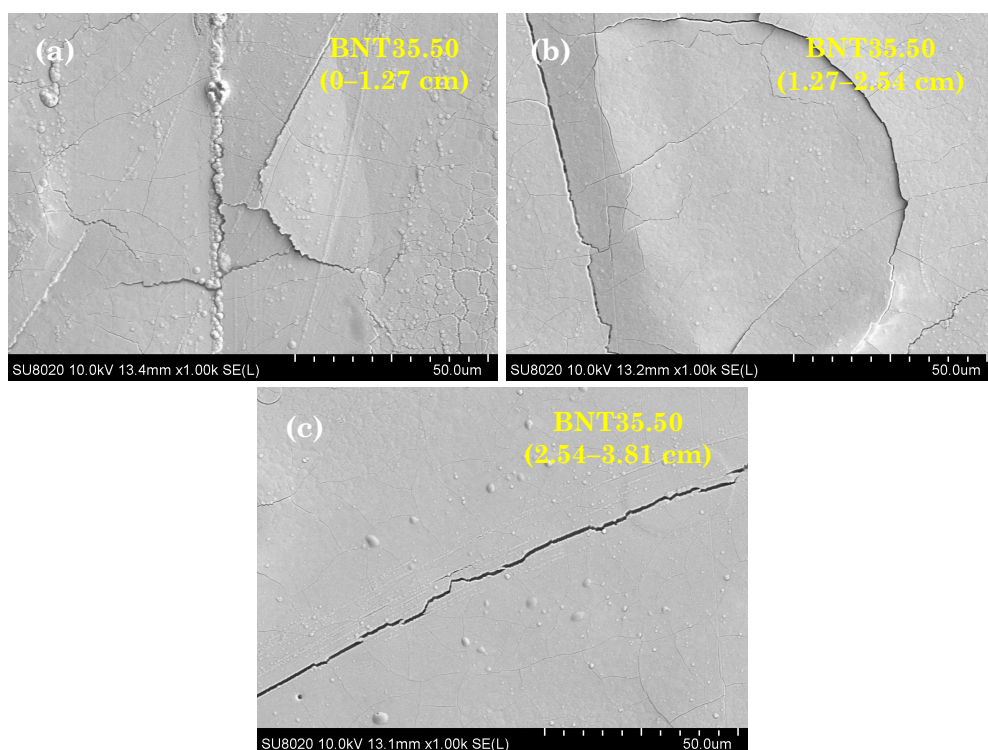


Figure 4-41: SEM surface morphology of annealed films, deposited at 2.96 W/cm^2 and 40 mTorr.cm , highlighting the cracks formation due to stress build up during growth.

In summary, negligible Na loss was observed due to the further improved density of 4.6 g/cm^3 at 2.96 W/cm^2 and 40 mTorr.cm , resulting in an average BNT phase fraction of $\sim 99\%$ across the substrate. Spatially, only $\sim 3\%$ bismuth titanate phase remained at the edge zone of substrate.

The usual NaO_x surface defects disappeared during annealing, while cracks formed across the films.

Conclusion

The simulations predicted no major change in the elemental deposition fluxes at 2.96 W/cm^2 , which was consistent with the composition of as-deposited films. However, a modest increase in the average K.E. of the Bi and Ti elemental fluxes was predicted, suggesting a potentially higher energy flux towards the substrate and a further increase in film density. This is consistent with the negligible Na loss observed during annealing, resulting in an average BNT phase fraction of $\sim 99\%$ across the substrate, compared with $\sim 85\%$ at 2.52 W/cm^2 . Therefore, it was decided to further increase the energy flux towards the substrate during film growth by increasing the applied power density beyond 2.96 W/cm^2 . The aim is to further enhance film densification, suppress Na loss, promote the formation of a stoichiometric BNT phase across the substrate, and eliminate the residual $\sim 1\%$ bismuth titanate phase fraction at the edge zone. Furthermore, the usual NaO_x surface defects were still present on the as-deposited films, which vanished due to the sublimation during post-deposition annealing. The micron-sized particulates deposition was also observed, potentially due to the aging of the sputtering targets. During post-deposition annealing, the films got cracked as previously observed at 2.52 W/cm^2 .

The improvements in film properties achieved across all three zones of substrate are particularly significant, as Hamieh *et al.* controlled the composition only within the middle zone of substrate. They sputtered a conditioned BNT50.50 target at 2.19 W/cm^2 and 80 mTorr.cm while maintaining the film growth temperature at 200°C , producing c-axis oriented BNT films on a rotating substrate^{63, 64}. Their c-axis orientation

was attributed to the LaNiO_3 base layer, which is itself c-axis oriented, perovskite structured, and closely lattice-matched to BNT. Cracks also formed in their films, but at a lower scale, likely because the LaNiO_3 base layer reduced lattice-mismatch strain during growth, thereby limiting the cracks formation.

4.3.2 Sputtering of cond. BNT35.50 Target at 3.51 W/cm² and 40 mTorr.cm

To compensate for the remaining Na loss and eliminate the residual ~1% bismuth titanate phase fraction from the edge zone, it was decided to further enhance film densification by increasing the overall energy/heat flux delivered to the substrate through further increasing the applied power density from 2.96 to 3.51 W/cm².

Simulations of target sputtering and transport processes

Identical simulation conditions were implemented as usual, except for the Ar^{1+} ion energy, which was increased to 280 eV at 3.51 W/cm². Consequently, the sputtering yields of Na and O increased slightly by ~5% (from 0.22 to 0.23 atoms/ion) and 7% (from 0.41 to 0.44 atoms/ion), respectively. In contrast, the sputtering yields of Bi and Ti remained nearly unchanged at 0.03 and 0.05 atoms/ion, respectively. These modest yield variations do not produce any significant changes in the elemental fluxes reaching the substrate (Figure 4-42), indicating limited potential for compositional changes in the as-deposited films. However, mixed trends were observed for the average K.E. of elemental deposition fluxes. For instance, the average K.E. of Bi decreased slightly from 12.2 ± 1.6 to 11.9 ± 1.6 eV, whereas that of Ti increased modestly from 6.6 ± 1.4 to 6.9 ± 1.5 eV, while no significant changes were noticed for that of the Na and O fluxes. Nonetheless, Thomann *et al.* reported that increasing the

applied electrical power enhances the energy delivered by the plasma to the growing film, which may still promote further film densification ¹⁴¹.

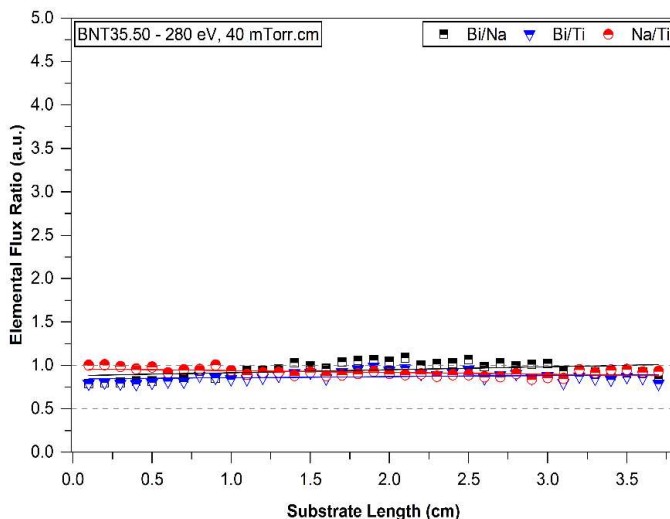


Figure 4-42: SiMTRA-simulated transport of sputtered species from the conditioned BNT35.50 target toward a 3.81 cm long substrate at 40 mTorr.cm and 3.51 W/cm².

Composition and morphology of as-deposited films

Similar conditions were implemented during film deposition, characterization, and data analysis as usual, except for the increased power density of 3.51 W/cm² and the further usage of the targets up to ~30 h, including ~10 h of conditioning followed by ~20 h of sputtering. The spatially resolved composition profile across the substrate is shown in Figure 4-43.

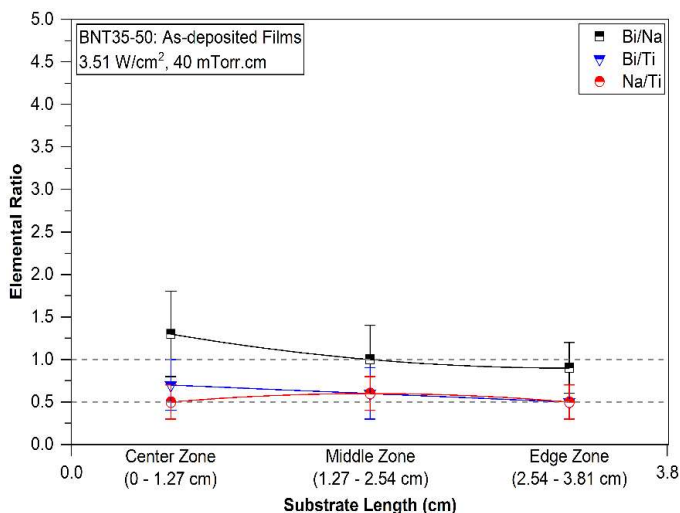


Figure 4-43: Average composition of BNT35.50 as-deposited films, deposited at 40 mTorr.cm and 3.51 W/cm².

Overall, the elemental ratios show no significant deviation from the targeted film stoichiometry. On average, the $\frac{Bi}{Na}$ ratio in 3.51 W/cm² films is 1.3 ± 0.5 at the center, 1.0 ± 0.4 in the middle, and 0.9 ± 0.3 at the edge zones of the substrate. In comparison, the 2.96 W/cm² films exhibited $\frac{Bi}{Na}$ ratio of 1.3 ± 0.4 at the center and 1.1 ± 0.4 at the middle and edge zones of substrate. A similar trend is observed for the mean $\frac{Bi}{Ti}$ ratio, with the 3.51 W/cm² films showing 0.7 ± 0.3 at the center, 0.6 ± 0.3 in the middle, and 0.5 ± 0.2 at the edge zone of substrate. In contrast, the 2.96 W/cm² films exhibited 0.6 ± 0.2 at the center and middle, and 0.5 ± 0.2 at the edge zone. Finally, the average $\frac{Na}{Ti}$ ratio in 3.51 W/cm² films is 0.5 ± 0.2 at the center and edge zones, and 0.6 ± 0.2 at the middle zone of substrate, compared with 0.5 ± 0.1 across the substrate in the 2.96 W/cm² films. These compositional trends are consistent with the transport simulations, which predicted no major change in the deposition fluxes reaching the substrate. The spatially resolved thickness profile of films follows the typical trend of sputter-deposited films on static substrates, with

maximum thickness at the center that decreases toward the edges. The average deposition rates in the center, middle, and edge zones of the substrate are 5.7 ± 0.3 , 3.3 ± 0.4 , and 3.0 ± 0.3 nm/min, respectively, indicating a slight increase with applied power density. The surface morphology of the as-deposited films across the substrate is shown in Figure 4-44. As usual, NaO_x surface defects alongside micron-sized deposited particulates are evident across the substrate in the as-deposited films.

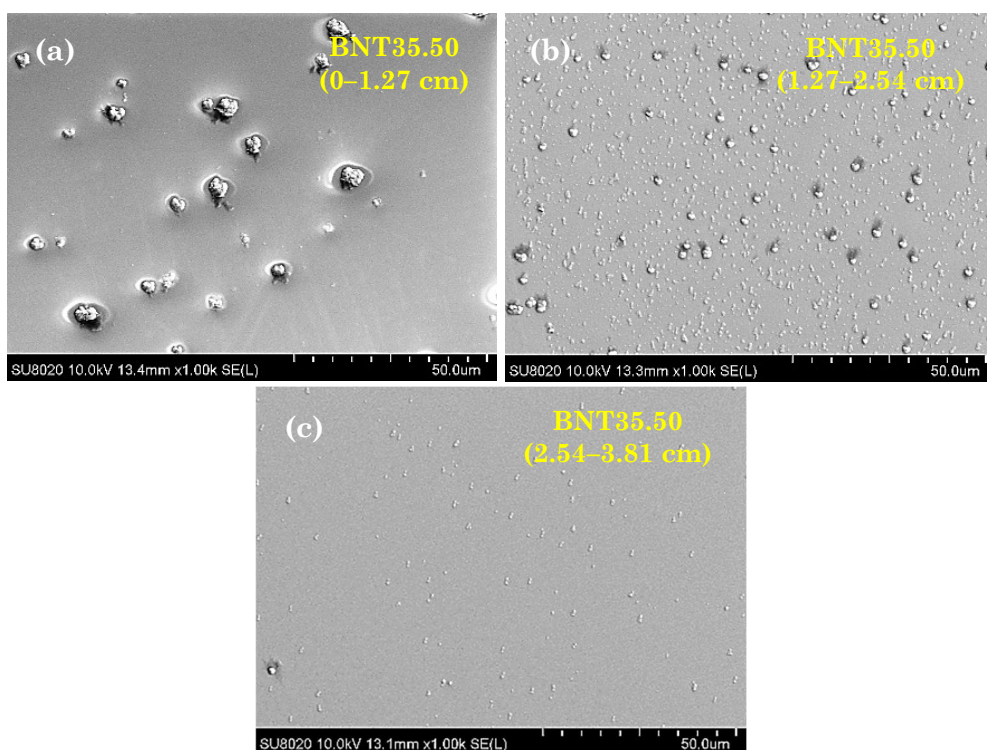


Figure 4-44: SEM surface morphology of films deposited from a conditioned BNT35.50 target at 3.51 W/cm^2 and 40 mTorr.cm, revealing the deposition of micron-sized particulates that were ejected from the target surface.

In summary, the as-deposited films at 3.51 W/cm^2 show no significant compositional deviation, consistent with the simulations.

Similar to the previous films, widespread NaO_x surface defects and deposited micron-sized particulates are also observed.

Composition and morphology of annealed films

As usual, the as-deposited films were annealed in ambient air at 700°C for 1 h inside a lab furnace. The spatially resolved compositional analysis of the films is shown in Figure 4-45.

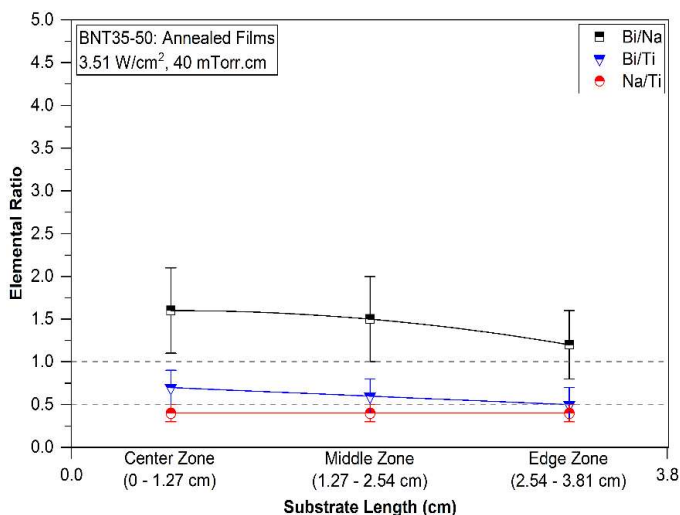


Figure 4-45: Average composition of BNT35.50 annealed films, deposited at 3.51 W/cm^2 and 40 mTorr.cm.

Overall, insignificant amount of Na was lost from the 3.51 W/cm^2 films during annealing ($\sim 25 \pm 30\%$), similar to the trend previously observed in the 2.96 W/cm^2 films. The average $\frac{\text{Bi}}{\text{Na}}$ ratio increases from 1.3 ± 0.5 to 1.6 ± 0.5 in the center, 1.0 ± 0.4 to 1.5 ± 0.5 in the middle, and 0.9 ± 0.3 to 1.2 ± 0.4 at the edge zone of the substrate. Similarly, the average $\frac{\text{Na}}{\text{Ti}}$ ratio decreases from 0.5 ± 0.2 to 0.4 ± 0.1 at the center and edge while 0.6 ± 0.2 to 0.4 ± 0.1 at the middle zone of substrate. Finally, the $\frac{\text{Bi}}{\text{Ti}}$ ratio remains unchanged in the range of 0.5–0.7 across the substrate. The GIXRD analysis of annealed films is shown in Figure 4-46, where not only

have the bismuth titanate phases re-emerged, but the intensity of BNT phase has also significantly lowered compared to the 2.96 W/cm² films.

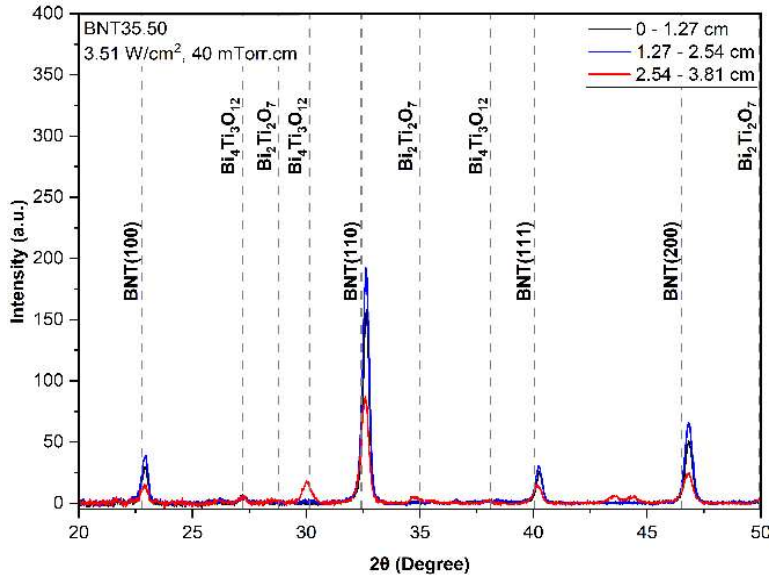


Figure 4-46: GIXRD scans of BNT35.50 annealed films, deposited at 3.51 W/cm² power density and 40 mTorr.cm.

Spatially, the bismuth titanate phase fraction is ~3% at the center, ~2% in the middle, and ~19% at the edge, whereas the 2.96 W/cm² films showed only ~3% at the edge zone of substrate. This corresponds to an overall bismuth titanate phase fraction of ~8%, compared to the only ~1% in the 2.96 W/cm² films. In addition, the BNT-related peaks show nearly 50% reduction in intensity and a slight shift toward higher diffraction angles. Since the composition of the 3.51 W/cm² films remains close to the desired stoichiometry, the altered crystalline phase formation likely originate from the residual stress developed during film growth, which may have affected the films crystallinity and diffraction behavior ¹³⁸. Birkholz *et al.* observed similar stress-induced changes in the sputter-deposited Ti films, where increased energy flux toward the substrate during film growth generated large compressive stress and altered the X-ray diffraction pattern and preferred crystal orientation ¹⁴². Similarly,

Castrup *et al.* showed that energetic bombardment during sputter-deposition of Pd and PdAu films strongly modified the XRD pattern, where low-pressure atomic peening generated compressive stress with strong (111) texture, while higher Ar pressure promoted different preferred orientations ¹⁴³. Furthermore, Panda *et al.* reported that increasing substrate temperature during magnetron sputtering altered the residual stress state and crystalline orientation of AlN films, while excessive adatom mobility reduced the crystallite size and the intensity of XRD peaks ¹⁴⁴. The surface morphology of annealed films is presented in Figure 4-47, where the NaO_x surface defects have mostly vanished and cracks were formed, as previously observed in the 2.96 W/cm² films.

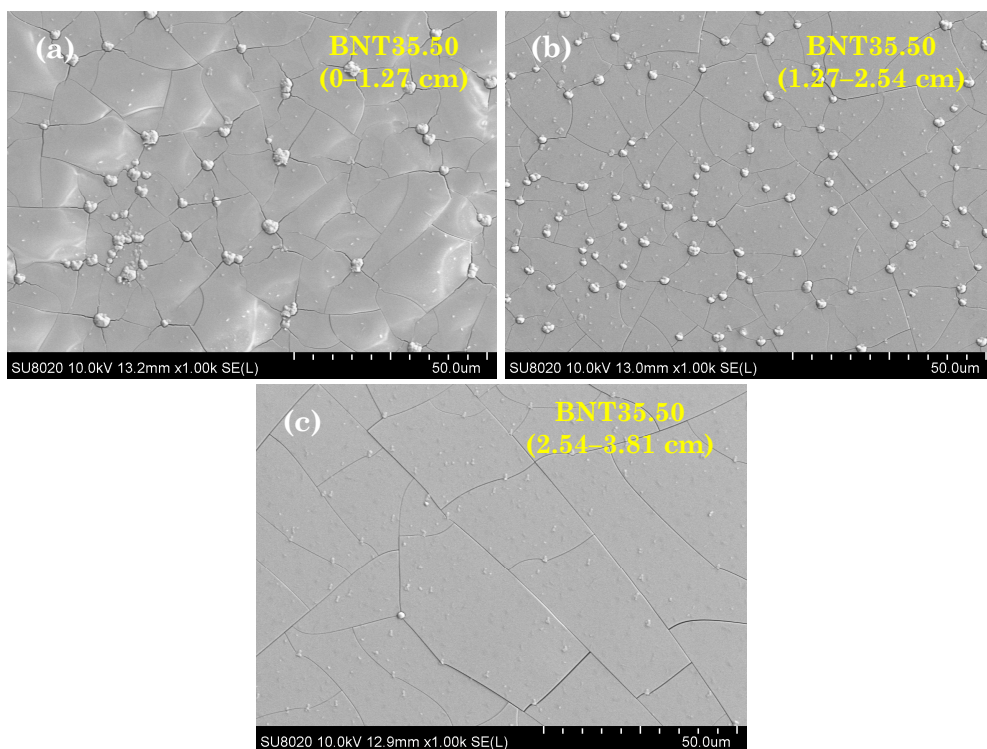


Figure 4-47: SEM surface morphology of annealed films, deposited at 3.51 W/cm² and 40 mTorr.cm, highlighting the cracks formation due to stress build up during growth.

In summary, despite a negligible Na loss during annealing ($\sim 25 \pm 30\%$), the 3.51 W/cm^2 films still developed an average bismuth titanate phase fraction of $\sim 8\%$. Spatially, this resulted in the bismuth titanate phase fractions of 3% in center, 2% in middle, and 19% in edge zone. Besides, the X-ray diffraction peaks of BNT phase showed nearly 50% reduction in intensity along with a slight shift toward higher angles, likely due to the increased stress build-up during film growth. The usual NaO_x surface defects disappeared during annealing, while cracks formed across the films.

Conclusion

The simulations predicted no significant evolution in the elemental deposition fluxes or their average K.E. at 3.51 W/cm^2 , consistent with the composition of the as-deposited films. During annealing, only negligible Na loss was observed ($\sim 25 \pm 30\%$), comparable to that of the 2.96 W/cm^2 films ($\sim 20 \pm 25\%$). However, the films still developed an average bismuth titanate phase fraction of $\sim 8\%$, compared with only $\sim 1\%$ at 2.96 W/cm^2 . Spatially, the bismuth titanate phase fraction reached $\sim 3\%$ at the center, $\sim 2\%$ in the middle, and $\sim 19\%$ at the edge, whereas the 2.96 W/cm^2 films showed only $\sim 3\%$ at the substrate edge. In addition, the X-ray diffraction peaks of the BNT phase exhibited nearly 50% reduction in intensity together with a slight shift toward higher angles at 3.51 W/cm^2 . This likely originated from the excessive stress buildup during film growth caused by the enhanced energy flux toward the substrate and the resulting stronger plasma-surface interactions. Furthermore, the usual NaO_x surface defects were still present on the as-deposited films, which vanished due to the sublimation during post-deposition annealing. The micron-sized particulates deposition was also observed, potentially due to the aging of the sputtering targets. Finally, the films developed cracks during post-deposition annealing, similar to those previously observed at 2.96 W/cm^2 .

Taken all together, these results strongly suggest that the film deposition from conditioned BNT35.50 targets at 40 mTorr.cm and 2.96 W/cm² results in the optimal Bi_{0.5}Na_{0.5}TiO₃ stoichiometric films on a 3.81 x 2 cm² substrate. However, the optimization of surface morphology in terms of cracks formation and micron-sized particulates deposition is still an open question to explore.

4.4 Summary

This chapter investigated the influence of sputtering conditions on the stoichiometry, crystalline composition, and microstructure of BNT thin films deposited from conditioned BNT50.50 and BNT35.50 powder targets. The study combined plasma diagnostics based on energy-resolved mass spectrometry, Monte Carlo simulations of sputtering and gas-phase transport, and detailed characterization of the deposited films. The central challenge was the Bi/Na imbalance in the films: excess Bi deposition happens during the film growth and sublimation-driven Na loss during post-annealing. The *in-situ* NaO_x surface defects formation also happened which may rupture during the post-annealing. The influence of three main deposition parameters was examined on the resulting film properties: target composition, target–substrate distance, and sputtering power density.

The composition of as-deposited films at 2.19 W/cm² and 80 mTorr.cm indicates that BNT50.50 targets require a conditioning period of ~14–15 h rather than the originally proposed 10 h. Afterwards, the as-deposited films still exhibited a significant Bi excess, with a $\frac{Bi}{Na}$ ratio of 1.4–1.5 ± 0.5 instead of the desired value of 1. During post-deposition annealing for 1 h at 700°C, a substantial loss of Na ~40–50% occurred, leading to the formation of an undesired bismuth titanate secondary phase fraction of ~50%. In addition, rupture of the NaO_x surface defects

caused severe surface degradation, rendering the BNT50.50 targets unsuitable for further investigation. In contrast, the as-deposited films of BNT35.50 targets showed no significant Bi excess and their composition remained close to the desired stoichiometry, which was attributed to the 30% lower Bi content in the pristine BNT35.50 target compared with BNT50.50. However, a similar Na loss of ~40–50% still happened during annealing, resulting in an even higher bismuth titanate secondary phase fraction of ~78%.

The substantial Na loss during annealing is likely facilitated by the lower density of the as-deposited films, providing additional diffusion pathways for Na sublimation. At 2.52 W/cm² and 40 mTorr.cm, the Na loss during annealing decreased to ~15–25% compared with the previously observed ~40–50%. Consequently, the bismuth titanate phase fraction was reduced to only ~15%, compared with ~78% at 2.52 W/cm² and 80 mTorr.cm. This was ascribed to likely densification of films, as the decreased target–substrate distance and increased power density deliver higher energy flux during growth. At the further increased power density of 2.96 W/cm², the Na loss became nearly negligible and the bismuth titanate phase fraction decreased to only ~1%. Correspondingly, the mass density of the films increased significantly, reaching 4.6 g/cm³ compared with 3.7 g/cm³ at 2.19 W/cm² and 80 mTorr.cm. However, further increasing the power density to 3.51 W/cm² likely promoted excessive stress buildup during film growth. This was reflected by nearly 50% reduction in the intensity of the BNT X-ray diffraction peaks together with a slight shift toward higher diffraction angles, likely caused by the enhanced energy flux toward the substrate and the resulting stronger plasma-surface interactions.

The *in-situ* formation of NaO_x surface defects in BNT films is likely linked to a substantial population of low-energy Na neutrals in the plasma phase. Sputtering-induced heating can raise the target surface temperature to $\sim 800^\circ\text{C}$, where Bi_2O_3 and TiO_2 react exothermically to form $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. In this temperature range, $\text{Na}_2\text{Ti}_3\text{O}_7$ can decompose into Na_2O , followed by the sublimation of Na. A fraction of these Na neutrals subsequently undergoes charge-exchange collisions with Ar^{1+} ions in the sheath near the MS orifice or substrate, producing the low-energy component observed in the Na^{1+} IEDF. The BNT50.50 target contains 25% more Bi_2O_3 content than BNT35.50, which likely enhances $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ formation and increases the local heat release at the target surface. This can promote Na_2O sublimation, whose vapor pressure increases more than fivefold (from 0.4 to 2.13 mTorr) when the temperature rises from 710 to 783°C . Accordingly, the fraction of low-energy Na^{1+} ions is much larger in BNT50.50 plasma ($\sim 8\%$ of the IEDF) than in the BNT35.50 ($\sim 1\%$). This explains why NaO_x surface defects are larger and rupture during annealing in BNT50.50 films, whereas they remain smaller and sublime without film degradation in BNT35.50 films.

Taken all together, deposition from conditioned BNT35.50 targets at 2.96 W/cm^2 and 40 mTorr.cm appears to be the most promising route for obtaining near-stoichiometric $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ films across the entire substrate. However, reducing the stress buildup during growth and the formation of cracks during annealing still remain open challenges. Micron-scale particulates deposition is witnessed, which is plausibly associated with target aging, and can be avoided by using freshly conditioned targets. For the context, Hamieh *et al.* obtained c-axis oriented BNT films on a rotating ‘c-axis oriented’ LaNiO_3/Si substrate at 200°C , by sputtering conditioned BNT50.50 targets in Ar at 2.19 W/cm^2 and 80 mTorr.cm. The use of the lattice-matched LaNiO_3 base layer likely

reduced lattice mismatch, stress development, and crack formation during BNT film growth. However, the composition control remained limited to the middle zone of the substrate. In addition, NaO_x surface defects were initially absent in their films, but reappeared once the film thickness exceeded ~ 400 nm during the 4th hour of continued deposition.

Chapter 5 Conclusion and Perspective

5.1 General conclusion

This research work aimed to investigate the deposition of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT) thin films via RF magnetron sputtering, which presents significant challenges, particularly in controlling the stoichiometry, crystalline composition, and surface morphology. During the deposition, sodium oxide surface defects form and excess Bi is incorporated, while Na loss becomes prominent during post-deposition annealing.

Our research strategy involved the usage of two target compositions, namely a stoichiometric powder-based $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT50.50) and a 2.5 at.% Bi-deficient powder-based $\text{Bi}_{0.35}\text{Na}_{0.5}\text{TiO}_{2.8}$ (BNT35.50). Process parameters such as the applied RF power and the target–substrate distance were also varied in order to modify the deposition flux and the plasma–film interaction during growth, thereby influencing the film properties. Overall, our goal was to better understand the process–plasma–film properties relationship and to contribute to the knowledge-based optimization of BNT film deposition for ferroelectric and piezoelectric applications, with an emphasis on the challenges discussed above. Our conclusions are summarized below.

5.1.1 NaO_x surface defects

Growing BNT thin films on unheated substrates using the BNT50.50 target at 2.19 W/cm² power density and 10 mTorr Ar pressure resulted in the formation of NaO_x surface defects. During the 1 h post-deposition annealing at 700°C, these defects ruptured due to the likely expedited sublimation of Na and O atoms, rendering the films unsuitable for device applications. Mass spectrometry analysis of the BNT50.50 plasma revealed that among all detected ions in the deposition flux, only

the Na^{1+} IEDF exhibited a secondary low-energy peak (≤ 10 eV), while its main peak remained centered around ~ 25 eV (like all the other ions). The low-energy component represented $\sim 8\%$ of the total Na^{1+} IEDF. Under identical conditions, the BNT35.50 plasma exhibited nearly an order of magnitude decreased low-energy Na^{1+} ion population ($\sim 1\%$), together with the formation of relatively smaller NaO_x defects that did not rupture during post-deposition annealing.

During sputtering, the surface temperature of the BNT targets is expected to rise to $\sim 800^\circ\text{C}$, likely promoting the exothermic reaction between Bi_2O_3 and TiO_2 to form $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. Within this temperature range, $\text{Na}_2\text{Ti}_3\text{O}_7$ at the target surface can decompose into Na_2O , which possesses a relatively high vapor pressure and readily sublimates, releasing low-energy (≤ 0.1 eV) Na and O neutrals. Even small temperature variations are significant in this regime, as the vapor pressure of Na_2O increases more than fivefold from ~ 0.4 mTorr at 710°C to 2.13 mTorr at 783°C . Since the BNT35.50 composition contains 25% less Bi_2O_3 than BNT50.50, the extent of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ formation and the associated heat release are expected to be lower, leading to a relatively decreased target surface temperature. Consequently, the population of sublimated low-energy Na neutrals in BNT35.50 plasma is also expected to be lower than in BNT50.50 plasma. A small fraction of these Na neutrals subsequently undergoes charge-exchange collisions with Ar^{1+} ions in the sheath near the MS orifice or substrate, followed by re-acceleration through only partial plasma-surface potential drop, thereby producing the low-energy component observed in the Na^{1+} IEDF. However, the charge exchange reactions between Na (23 u) and Ar^{1+} (40 u) are expected to remain relatively inefficient because of the mass mismatch and the large difference in ionization potential (Na = 5.14 eV, Ar = 15.76 eV). As a result, majority of the sublimated Na atoms are expected to remain neutral and therefore

remain undetected during mass spectrometry analysis. These low-energy Na neutrals can subsequently incorporate into the growing films and contribute to the formation of NaO_x surface defects.

5.1.2 Excess of Bi deposition

Film growth on unheated substrates using BNT50.50 target at 2.19 W/cm² power density, 10 mTorr Ar pressure, and 8 cm target–substrate distance resulted in a $\frac{Bi}{Na}$ ratio of $1.4\text{--}1.5 \pm 0.5$, leading to the formation of undesired bismuth titanate secondary phase fraction of ~50% relative to BNT. Simulations suggested that this behavior originates from the lower gas-phase scattering of heavy Bi (209 u) atoms during their transport through Ar (40 u). Under identical conditions, the as-deposited films from the 2.5 at.% Bi-deficient BNT35.50 target showed no significant Bi excess and exhibited nearly equal concentrations of Bi and Na.

5.1.3 Sublimation-driven loss of Na during annealing

When provided with sufficient kinetic energy, for instance during thermal annealing, the relatively smaller Na atoms can diffuse through amorphous, semi-crystalline, and low-density matrices, eventually reaching the film surface and sublimating. Consequently, the poorly crystallized and low-density as-deposited BNT films exhibited substantial Na loss during the 1 h post-deposition annealing at 700°C. Films deposited on unheated substrates from the conditioned BNT35.50 targets at 2.19 W/cm² and 80 mTorr.cm, despite showing no significant Bi excess in the as-deposited state, still lost ~40–50% of Na during annealing. This subsequent Bi excess promoted the formation of only ~22% crystalline BNT phase. Transport simulations suggested that reducing the target–substrate distance from 8 to 4 cm significantly decreases the number of gas-phase collisions. This not only doubles the sputtered elemental fluxes

but also provides them twice as much average kinetic energy, resulting in an approximately fourfold increase in the energy delivered to substrate by the sputtered elemental species. Under these conditions, films deposited at 2.52 W/cm² and 40 mTorr.cm showed a substantially lower Na loss of ~15–25% during annealing, which corresponded to an increase of the crystalline BNT phase fraction to ~85%. This improvement was attributed to the likely densification of the films caused by the enhanced energy flux delivered during growth through the reduced target–substrate distance and increased power density. Keeping the remaining deposition parameters unchanged and increasing only the applied power density to 2.96 W/cm² further suppressed the Na loss through additional film densification, resulting in nearly phase-pure Bi_{0.5}Na_{0.5}TiO₃ films with ~99% crystalline BNT phase fraction across the substrate, except for only ~1% bismuth titanate phase at the substrate edge. Consistently, the mass density of the films increased significantly, reaching 4.6 g/cm³ compared with 3.7 g/cm³ at 2.19 W/cm² and 80 mTorr.cm. However, further increasing the power density to 3.51 W/cm² likely promoted excessive stress buildup during film growth. This was reflected by nearly 50% reduction in the intensity of the BNT X-ray diffraction peaks together with a slight shift toward higher diffraction angles, likely caused by the enhanced energy flux toward the substrate and the resulting stronger plasma-surface interactions.

5.2 Perspectives and outlook

5.2.1 Addressing the NaO_x surface defects formation

Findings of this thesis suggest that the NaO_x surface defects grow on BNT films due to the presence of a relatively large population of sublimated Na atoms in the deposition flux. These sublimated Na atoms originate from the thermal decomposition of Na₂Ti₃O₇ in ~700–800°C temperature range on target surface. The temperature rise on BNT

targets surface occurs due to the applied sputtering power (i.e., Ar ions energy), insulating nature of the precursor powders inside the target, and the exothermic reaction between Bi_2O_3 and TiO_2 which forms $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. Therefore, it would be interesting to sputter the mixture-powder BNT35.50 at lower power densities like $\leq 1 \text{ W/cm}^2$ and analyze the plasma and the surface morphology of as-deposited films. Decreased sputtering power could lead to the lower target surface temperatures, reducing the decomposition of $\text{Na}_2\text{Ti}_3\text{O}_7$ and the subsequent sublimation of Na atoms, likely resulting in the NaO_x defects-free BNT films deposition on unheated substrates. For implementing this strategy, plasma should be ignited either at a higher power density and/or a higher Ar pressure followed by the scaling down of power to $\leq 1 \text{ W/cm}^2$ and pressure to 10 mTorr. According to some of our experiments, powder BNT targets-based plasma remained stable for extended periods of time at $\sim 0.9 \text{ W/cm}^2$ and 10 mTorr argon pressure; once ignited at 2.19 W/cm^2 . Another promising approach would be to use $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{Na}_2\text{Ti}_3\text{O}_7$ powders for target fabrication instead of the existing Bi_2O_3 , TiO_2 , and $\text{Na}_2\text{Ti}_3\text{O}_7$ mixture. This could lower the target surface temperature by eliminating the exothermic Bi_2O_3 – TiO_2 reaction, thereby moderately limiting $\text{Na}_2\text{Ti}_3\text{O}_7$ decomposition and, more importantly, decreasing Na sublimation from Na_2O . This may reduce the formation of NaO_x surface defects during BNT growth on unheated substrates. It would also be interesting to sputter ceramic BNT powder targets instead of compressed mixed-powder targets. The crystalline BNT phase is expected to be more thermally stable ¹⁴⁵ than $\text{Na}_2\text{Ti}_3\text{O}_7$, which could suppress the release of low-energy Na neutrals from the target surface. This improved thermal stability may also permit higher sputtering powers and higher deposition rates without significant target decomposition. Finally, the substrate-heating strategy proposed by Hamieh *et al.* ^{63, 64} could be further explored to re-evaporate the arriving

low-energy Na atoms before they accumulate on the growing film. A possible approach would be to preheat the substrate to 200°C, followed by a slow temperature ramp of 5–10°C/h during deposition. In this way, the film surface would remain sufficiently energetic to promote re-evaporation of low-energy Na neutrals, potentially preventing the renewed formation of NaO_x surface defects and enabling the growth of micron-thick BNT films.

5.2.2 Addressing the film cracking and micron-sized particulate deposition

The surface cracks formation on BNT films, deposited on Si substrate, occurred during the post-annealing at 700°C. Its potential reasons are the stress buildup during film growth (caused by the increased deposition rates and the increased K.E. of the film-forming species) and the lattice miss-match between the film and substrate. The cracks formation can be reduced by growing BNT films at lower deposition rates, so lower power densities like $\leq 1 \text{ W/cm}^2$ is also interesting in this regard. Another useful method is the BNT film's growth on a base layer like LaNiO₃/Si, having closely similar crystalline structure and lattice parameters as BNT^{63, 64}.

The micron-sized particulates deposition on film's surface primarily occurs due to the target-aging, while low-density targets like ours are even more prone to particulates ejection. Moderately heating the pristine mixture-powder BNT targets at ~300–400°C can increase its density and address the particulates ejection problem. At atmospheric pressure, Na₂Ti₃O₇ starts decomposition around 710°C, so the proposed temperature range is within the safety zone.

Appendix A Hybrid ERDA-RBS Analysis of Films

A.1 Analysis Report

The hybrid ERDA-RBS analysis of seven films was performed by IMEC, Belgium, and the original analysis report is reproduced here. In this batch, two samples were the as-deposited films while the other five were annealed films ('A' in the nomenclature represents the annealing). Notably, the detected C and H atoms are likely originated from the IPA inside our powder targets, which is also in agreement with the mass spectrometry analysis of BNT plasmas. The films washing with IPA right after the deposition can also leave residues behind. However, the number of C and H atoms drops sharply once the films were annealed at 700°C, suggesting the efficient evaporation of residual IPA during films annealing.

Request ID:	ERD24_125A
Title:	Analyze BiNaTiOx for Zikriya
Requester:	Johan Meersschaut
Related requests:	

Report date	2025.01.07
Author(s)	Karim-Alexandros Kantre
Reviewer(s)	Johan Meersschaut

RQM-input

Analyze BiNaTiOx for Zikriya
~ 100 nm BiTiNaOx

Sample description

Sample ID	Description	Comments	Substrate
PTV-H2-R	BiTiNaOx		Silicium
PTII-H2A-R	BiTiNaOx		Silicium
PT2-H2-R	BiTiNaOx		Silicium
PT1-H2A-R	BiTiNaOx		Silicium
PT4-3HA-C	BiTiNaOx		Silicium
PT4-3HA-R	BiTiNaOx		Silicium
PT4-3HA-E	BiTiNaOx		Silicium

Basic info about ERD

Some basic information on ERD and the analysis request procedure can be found at:

[https://imecinternational.sharepoint.com/teams/t0004/MCA-ANALYSIS-TECHNIQUES/SitePages/ERD%20\(Elastic%20Recoil%20Detection\).aspx](https://imecinternational.sharepoint.com/teams/t0004/MCA-ANALYSIS-TECHNIQUES/SitePages/ERD%20(Elastic%20Recoil%20Detection).aspx)

http://imecwww.imec.be/ImecUser/services/qa/pdf/E_16050_01_00.pdf

Retrieval of samples after analysis

After the completion of the analysis and the report, the samples are available to be retrieved by the user. Directions to collect your samples are described here: <\\winbe\mcaiba\Public\USER-Sample-retrieval.pdf>

Access to the results

Tables with results are included as '*embedded Microsoft excel*' objects. Double-click the objects to launch Excel and access the results. The plots are included as '*.png*' files. Contact the authors if you need access to the underlying data.

Limit of Detection

For the compositional analysis (based on the slab regions), the limit of detection for the various elements is 0.1 at.% i.e., 0.001 atomic fractions.

If the areal density is reported, then we report the number of events (detections) in the excel file. Based on the number of events, one calculates the statistical uncertainty. A signal of less than 10 events is comparable to the background and is below the limit of detection.

Unit of thickness or depth

Ion beam analysis techniques probe the atomic areal densities. Therefore, the results are reported in units of $1 \cdot E+15$ atoms/cm². If the mass density of the material is known, then the corresponding physical thickness can be estimated. To convert a reported thickness to a physical thickness, go to the directory <\\winbe\mcaiba\Public> and open '*TFU_to_nm.hta*'.

In a depth-profile graph, the horizontal axis (depth) is derived from the energy loss. The vertical axis (atomic fraction) is the areal density of an element detected in a depth interval divided by the total areal density expected in the same interval. The depth interval used in the analysis is $20 E+15$ at/cm².

Publication policy

If the results contribute significantly to the research which is considered for a publication, then the scientists who generated the data should be given the opportunity to get insight in their usage and presentation in the draft manuscript. Please consult the imec procedure on Author guidelines [doc. 54031](#).

ERD experimental conditions

Data acquisition: 2025.01.05

Primary ion beam: $^{79}\text{Br}^{6+}$ (12.601 MeV)

Scattering angle: 40°

Sample tilt: 15°

Calibration check: ERDcc25_001.pdf

Data-analysis

Hydrogen efficiency: 1H_2023.11.29.eff

Selected signals: Scattered Br was used for Bi. Recoil signals were used for the other elements.

Compositions: The compositions are based on the slab regions as indicated with vertical lines in the depth-profile spectrum.

Concentrations: The concentrations (F) refer to atomic fractions: i.e., at.%, not weight %. The uncertainty D(F) is the estimated uncertainty with coverage factor 1.

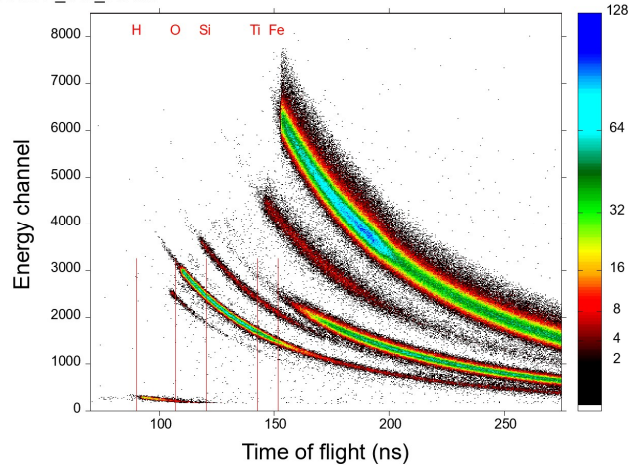
Results

ERD24_125_01A			ERD24_125_02A			ERD24_125_03A			ERD24_125_04A		
PTV-H2-R			PTII-H2A-R			PT2-H2-R			PT1-H2A-R		
	F	D(F)		F	D(F)		F	D(F)		F	D(F)
H :	0.078	±0.011	H :	0.004	±0.001	H :	0.086	±0.012	H :	0.006	±0.001
C :	0.026	±0.002	C :	0.001	±0.001	C :	0.029	±0.002	C :	0.003	±0.001
O :	0.584	±0.021	O :	0.634	±0.019	O :	0.552	±0.023	O :	0.607	±0.020
Na :	0.055	±0.003	Na :	0.046	±0.003	Na :	0.070	±0.004	Na :	0.029	±0.002
Ti :	0.136	±0.007	Ti :	0.166	±0.009	Ti :	0.163	±0.009	Ti :	0.224	±0.012
Bi :	0.121	±0.007	Bi :	0.149	±0.008	Bi :	0.100	±0.005	Bi :	0.130	±0.007

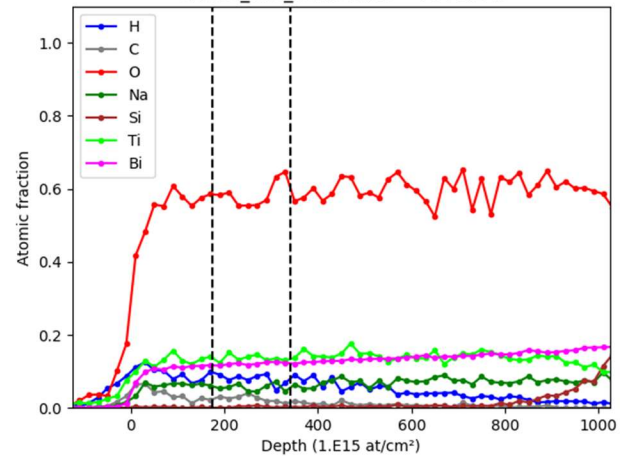
ERD24_125_05A			ERD24_125_06A			ERD24_125_07A		
PT4-3HA-C			PT4-3HA-R			PT4-3HA-E		
	F	D(F)		F	D(F)		F	D(F)
H :	0.003	±0.001	H :	0.004	±0.001	H :	0.006	±0.001
C :	0.008	±0.001	C :	0.004	±0.001	C :	0.003	±0.001
O :	0.592	±0.021	O :	0.593	±0.021	O :	0.608	±0.020
Na :	0.090	±0.005	Na :	0.088	±0.005	Na :	0.092	±0.005
Ti :	0.189	±0.010	Ti :	0.202	±0.011	Ti :	0.199	±0.010
Bi :	0.119	±0.006	Bi :	0.110	±0.006	Bi :	0.092	±0.005

Experimental data – spectra

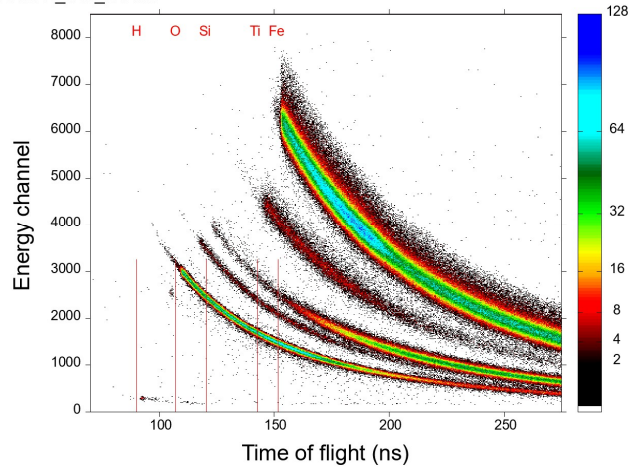
ERD24_125_01A.flt



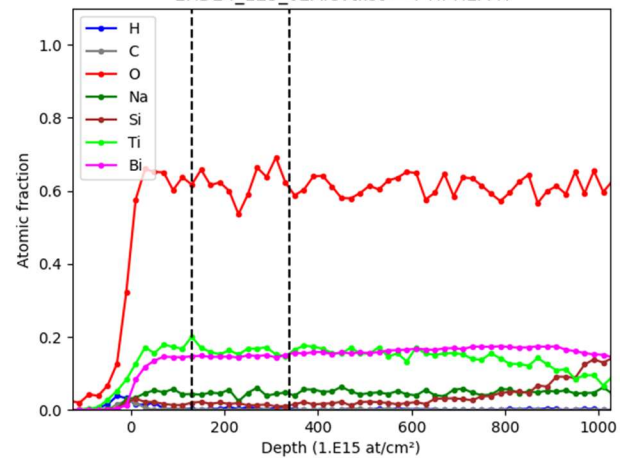
ERD24_125_01A.evt.lst — PTV-H2-R



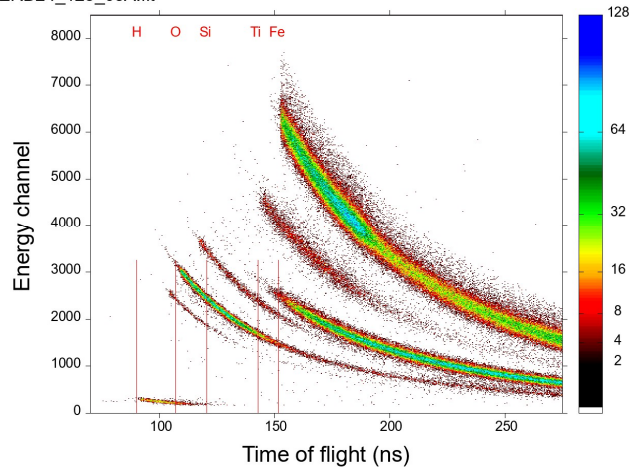
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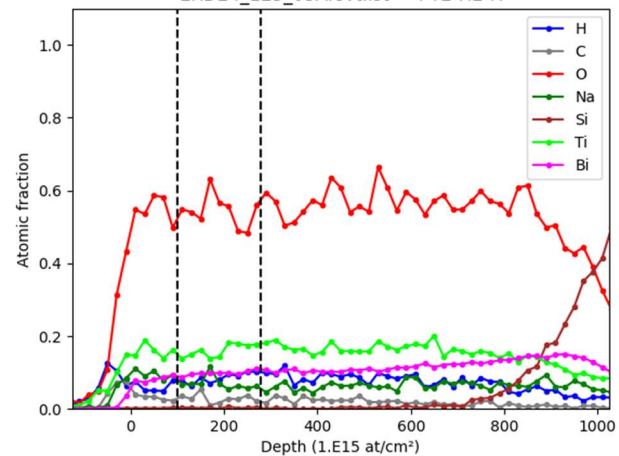
ERD24_125_02A.evt.lst — PTII-H2A-R



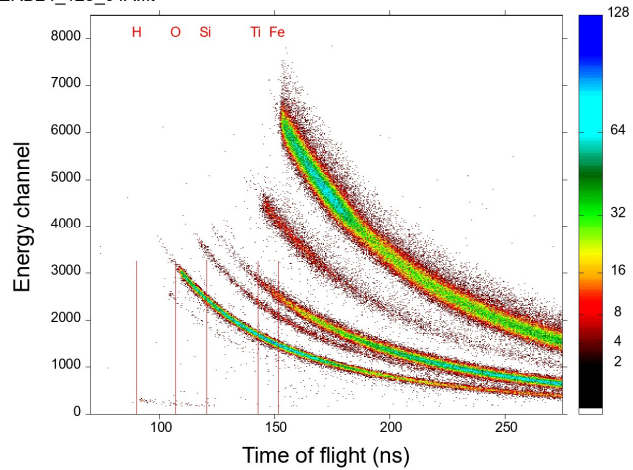
ERD24_125_03A.flt



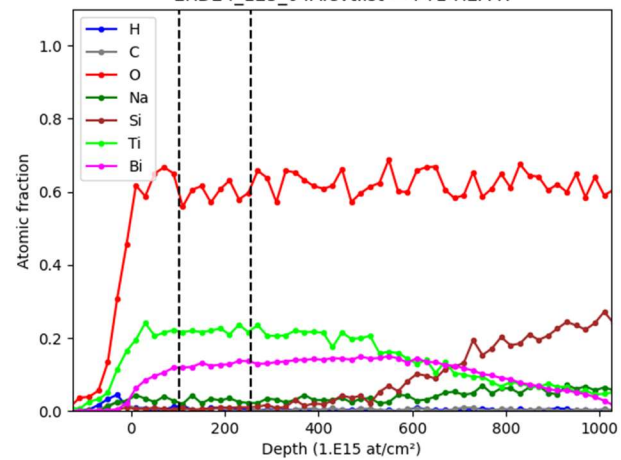
ERD24_125_03A.evt.lst — PT2-H2-R



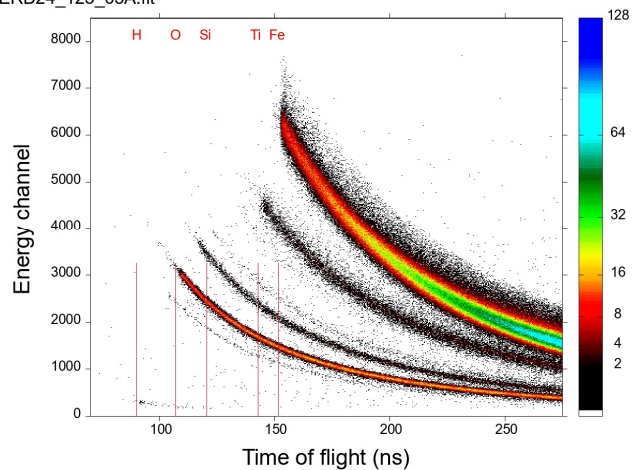
ERD24_125_04A.flt



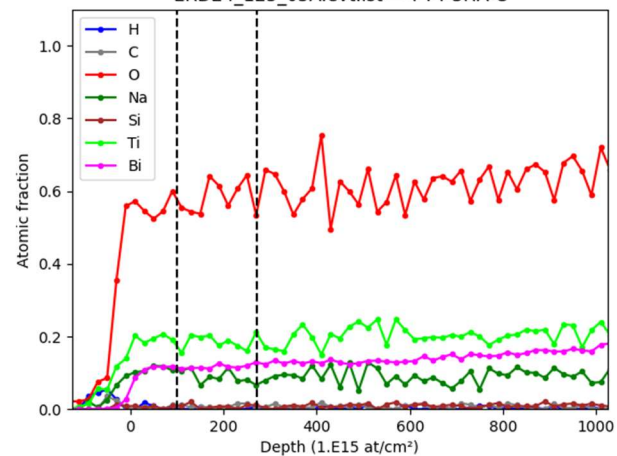
ERD24_125_04A.evt.lst — PT1-H2A-R



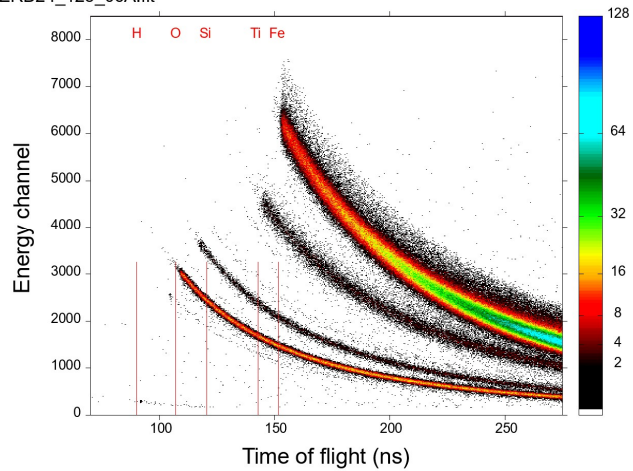
ERD24_125_05A.flt



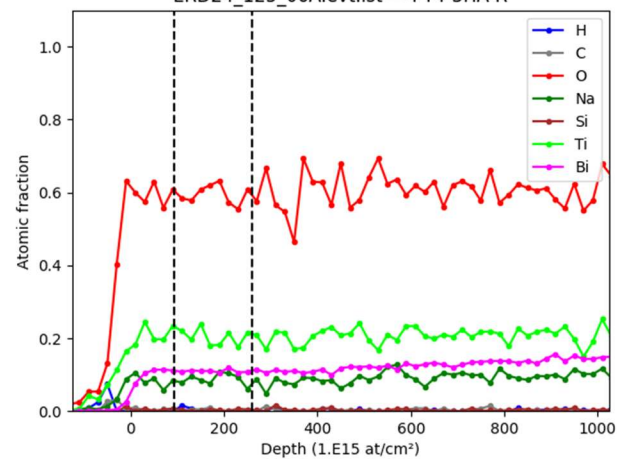
ERD24_125_05A.evt.lst — PT4-3HA-C

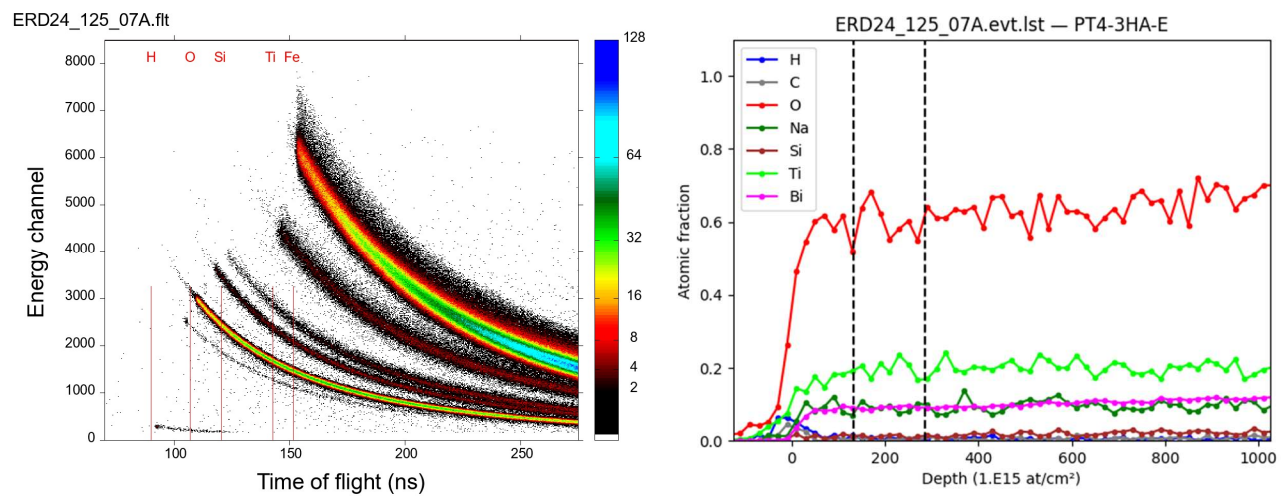


ERD24_125_06A.flt



ERD24_125_06A.evt.lst — PT4-3HA-R

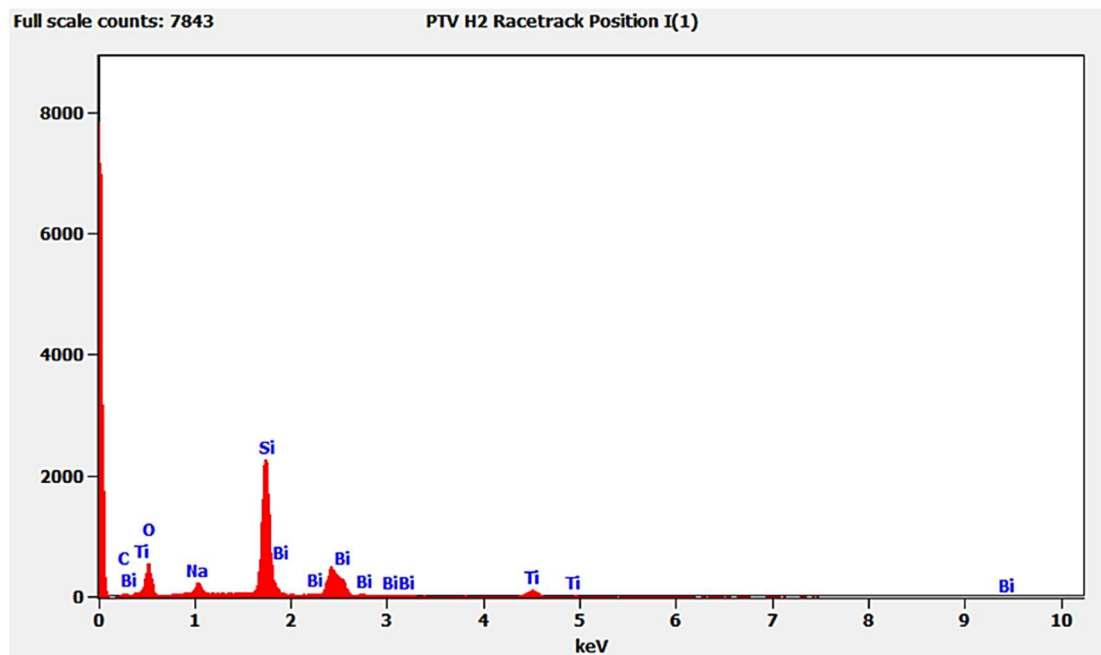




Appendix B EDX Analysis of Films

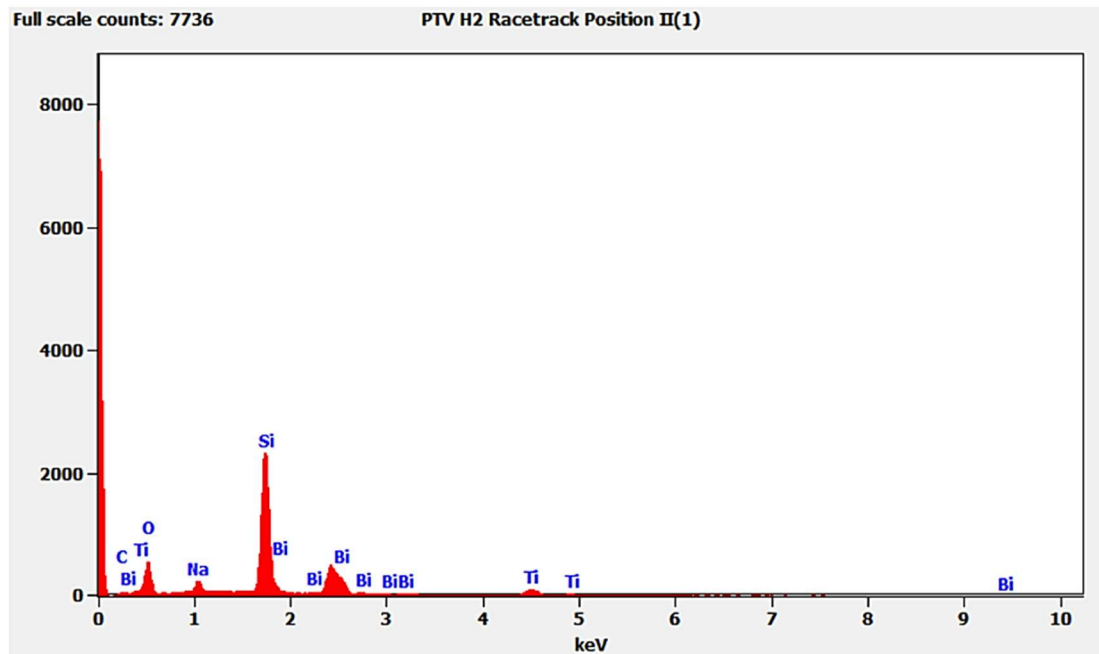
B.1 Analysis Report

The EDX analysis of those seven films is also reproduced here as a reference. Total three measurements were performed on each film, one at the film's geometric center and the other two at the positions offset by ± 0.5 cm over the substrate length and the average value was used for reporting purpose (see appendix C for details on calculations, p. 181).



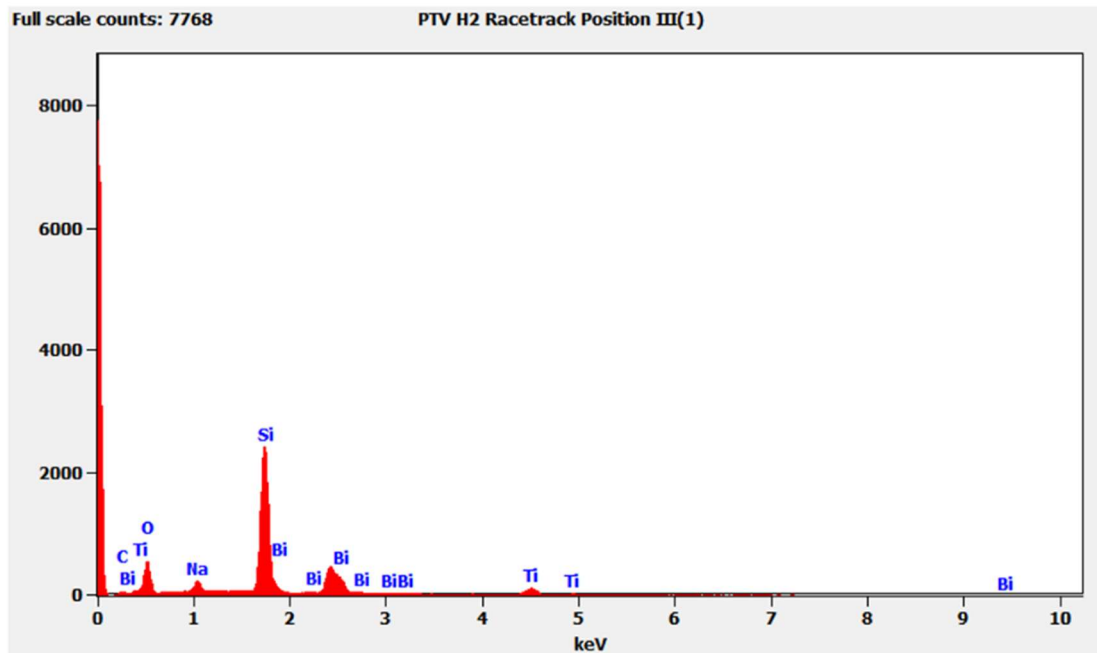
Quantitative Results for: PTV H2 Racetrack Position I(1) 10kv, x1k, 50 microns

Element Line	Weight %	Weight % Error	Atom %	Atom % Error
O K	21.5	± 0.4	61.2	± 2.3
Na K	4.3	± 0.2	8.5	± 0.7
Ti L	19.4	± 2.7	18.4	± 5.2
Bi M	54.7	± 1.2	11.9	± 0.5
Total	100.0		100.0	



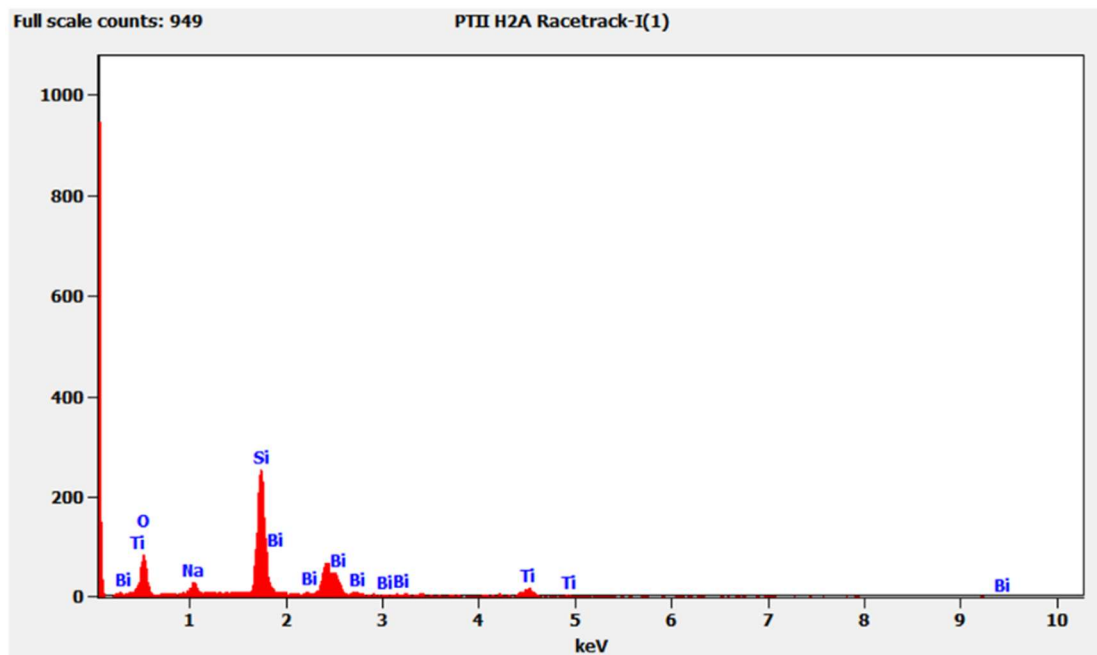
Quantitative Results for: PTV H2 Racetrack Position II(1) 10kv, x1k, 50 microns

Element Line	Weight %	Weight % Error	Atom %	Atom % Error
O K	21.7	± 0.4	61.8	± 2.4
Na K	4.2	± 0.2	8.4	± 0.8
Ti L	18.6	± 2.9	17.7	± 5.6
Bi M	55.5	± 1.3	12.1	± 0.6
Total	100.0		100.0	



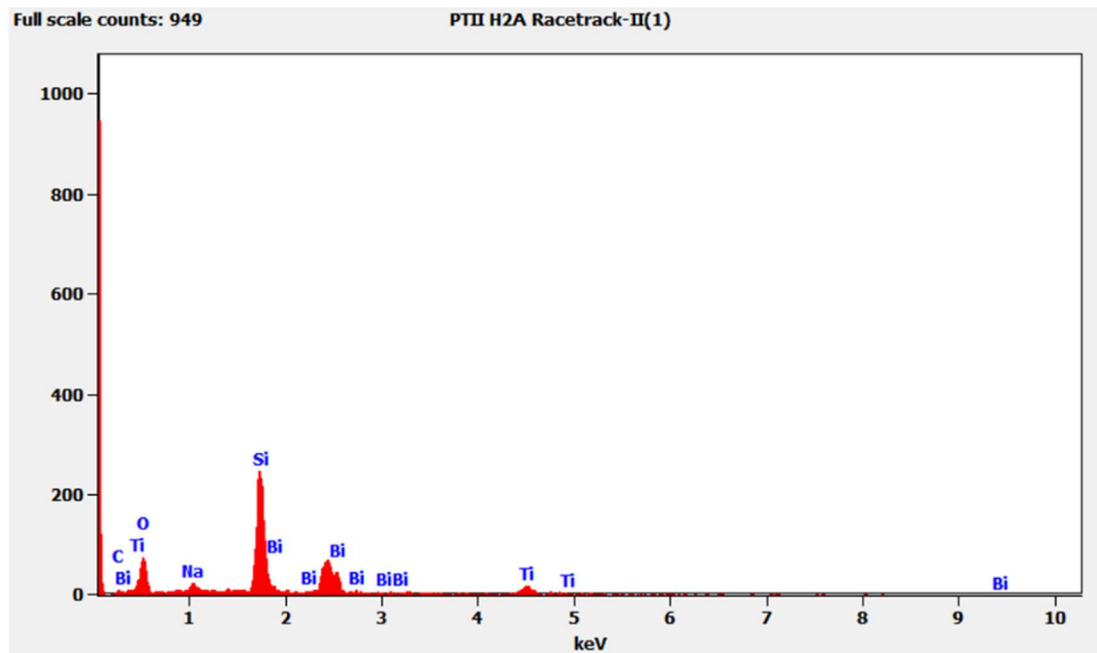
Quantitative Results for: PTV H2 Racetrack Position III(1) 10kv, x1k, 50 microns

Element Line	Weight %	Weight % Error	Atom %	Atom % Error
O K	22.2	± 0.4	61.7	± 2.3
Na K	4.2	± 0.2	8.2	± 0.8
Ti L	20.3	± 2.8	18.8	± 5.2
Bi M	53.3	± 1.3	11.3	± 0.5
Total	100.0		100.0	



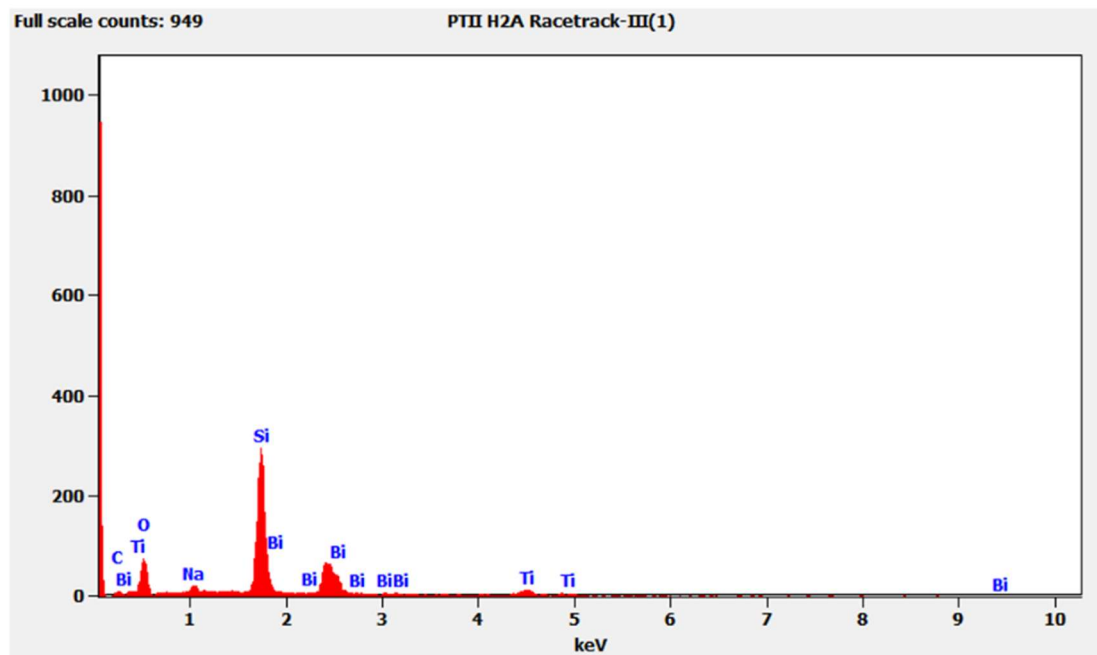
Quantitative Results for: PTII H2A Racetrack-I(1)

Element Line	Weight %	Weight % Error	Atom %	Atom % Error
O K	26.2	± 0.9	74.9	± 5.3
Na K	5.0	± 0.4	10.0	± 1.8
Ti L	0.0	---	0.0	± 0.0
Bi M	68.8	± 3.5	15.1	± 1.5
Total	100.0		100.0	



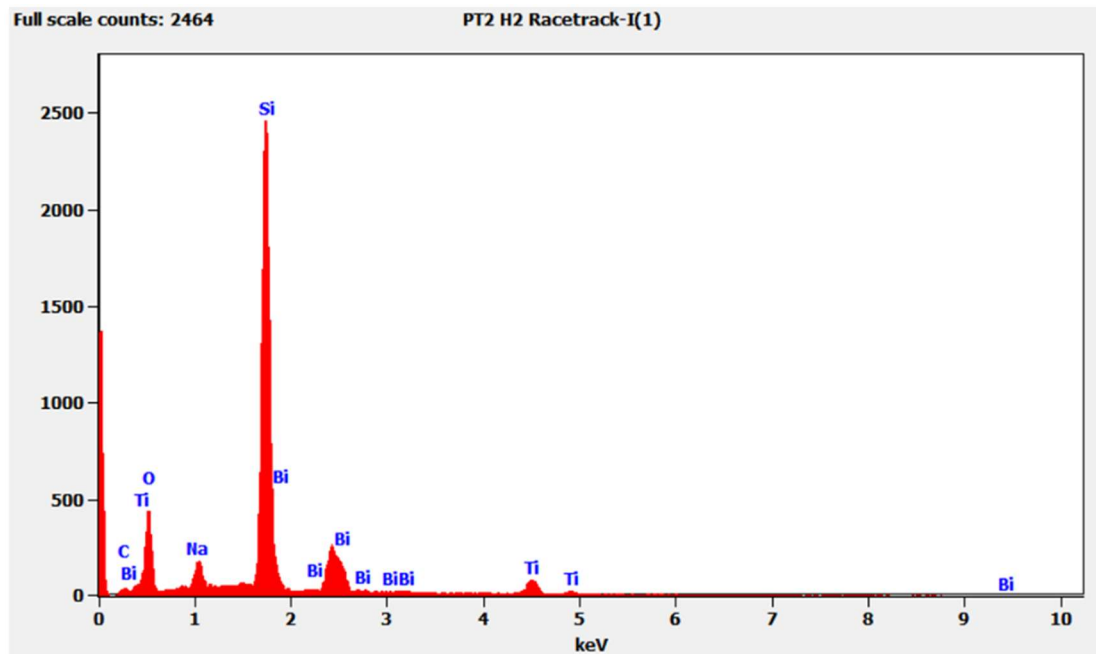
Quantitative Results for: PTII H2A Racetrack-II(1)

Element Line	Weight %	Weight % Error	Atom %	Atom % Error
O K	22.6	± 1.1	66.4	± 6.5
Na K	2.6	± 0.4	5.2	± 1.4
Ti L	15.2	± 8.4	14.9	± 16.5
Bi M	59.6	± 2.8	13.4	± 1.3
Total	100.0		100.0	



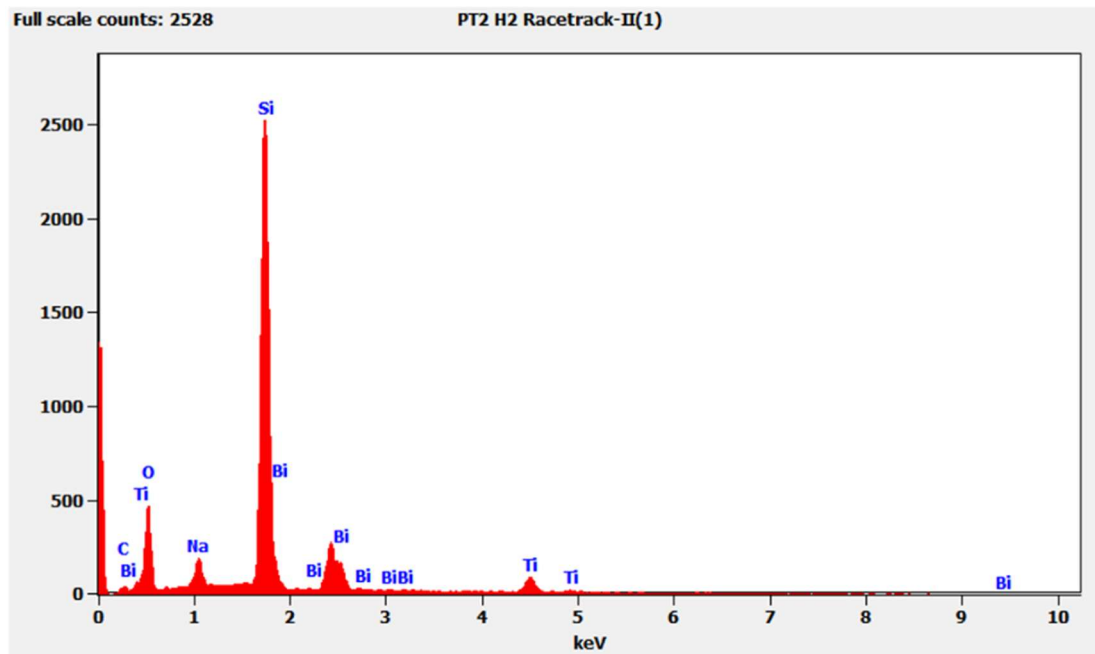
Quantitative Results for: PTII H2A Racetrack-III(1)

Element Line	Weight %	Weight % Error	Atom %	Atom % Error
O K	21.8	± 0.8	67.4	± 5.1
Na K	2.2	± 0.4	4.7	± 1.6
Ti L	12.5	± 9.7	12.9	± 20.0
Bi M	63.4	± 3.7	15.0	± 1.7
Total	100.0		100.0	



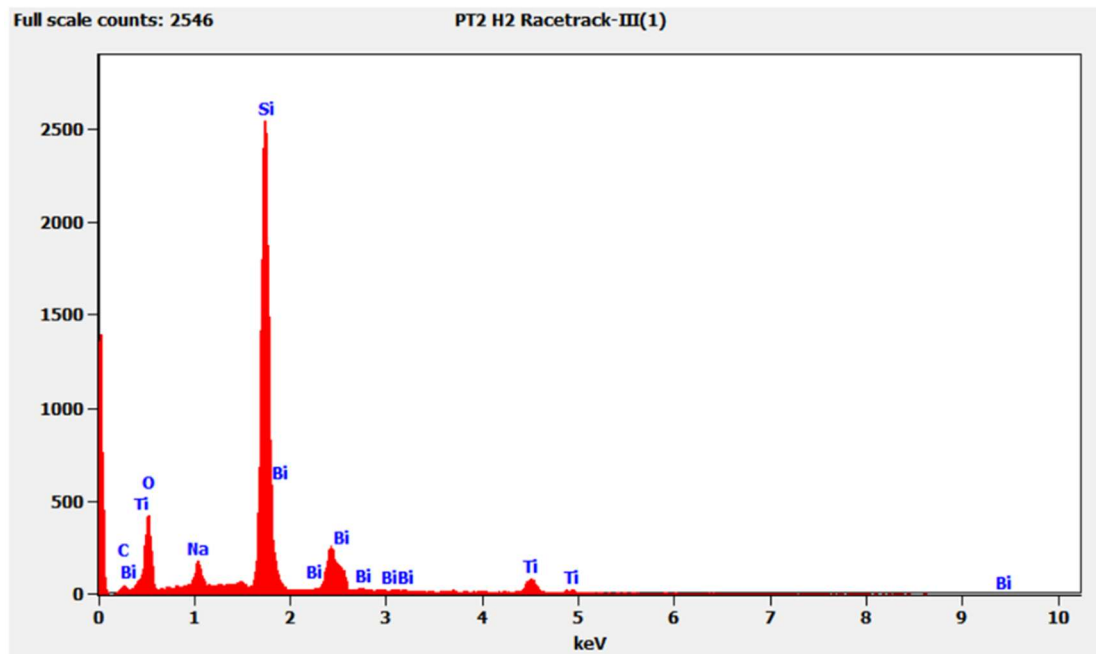
Quantitative Results for: PT2 H2 Racetrack-I(1)

Element Line	Weight %	Weight % Error	Atom %	Atom % Error
O K	26.8	± 0.6	64.8	± 2.8
Na K	5.6	± 0.3	9.5	± 0.9
Ti L	21.2	± 3.7	17.1	± 6.0
Bi M	46.4	± 1.5	8.6	± 0.6
Total	100.0		100.0	



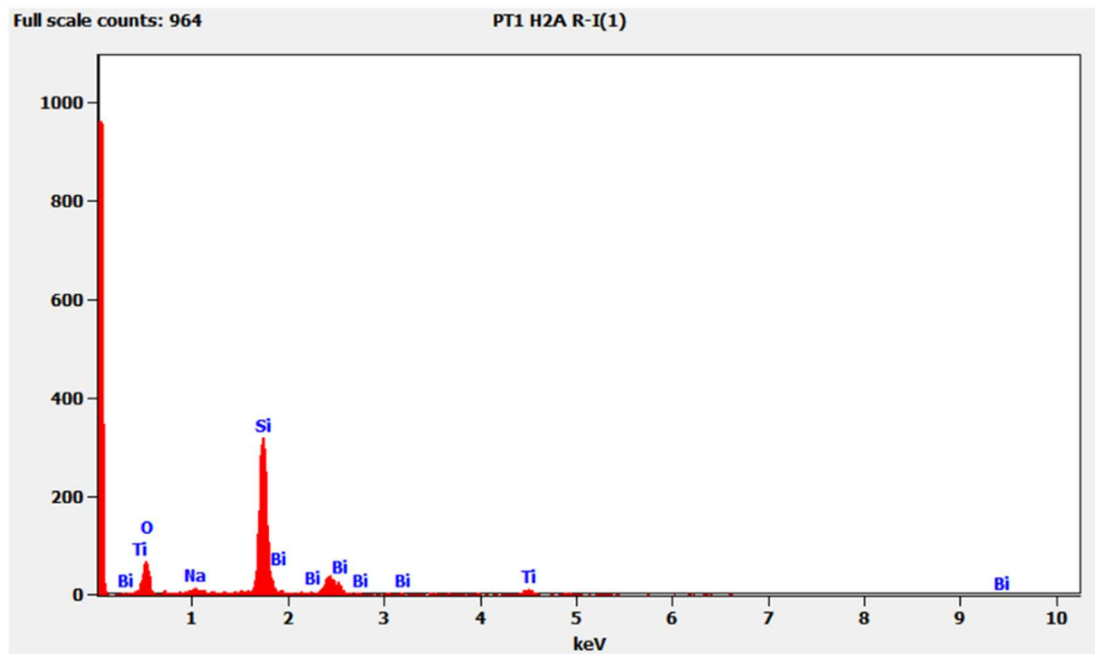
Quantitative Results for: PT2 H2 Racetrack-II(1)

Element Line	Weight %	Weight % Error	Atom %	Atom % Error
O K	27.7	± 0.4	65.4	± 2.0
Na K	6.1	± 0.3	10.0	± 0.9
Ti L	20.8	± 3.5	16.4	± 5.5
Bi M	45.4	± 1.2	8.2	± 0.4
Total	100.0		100.0	



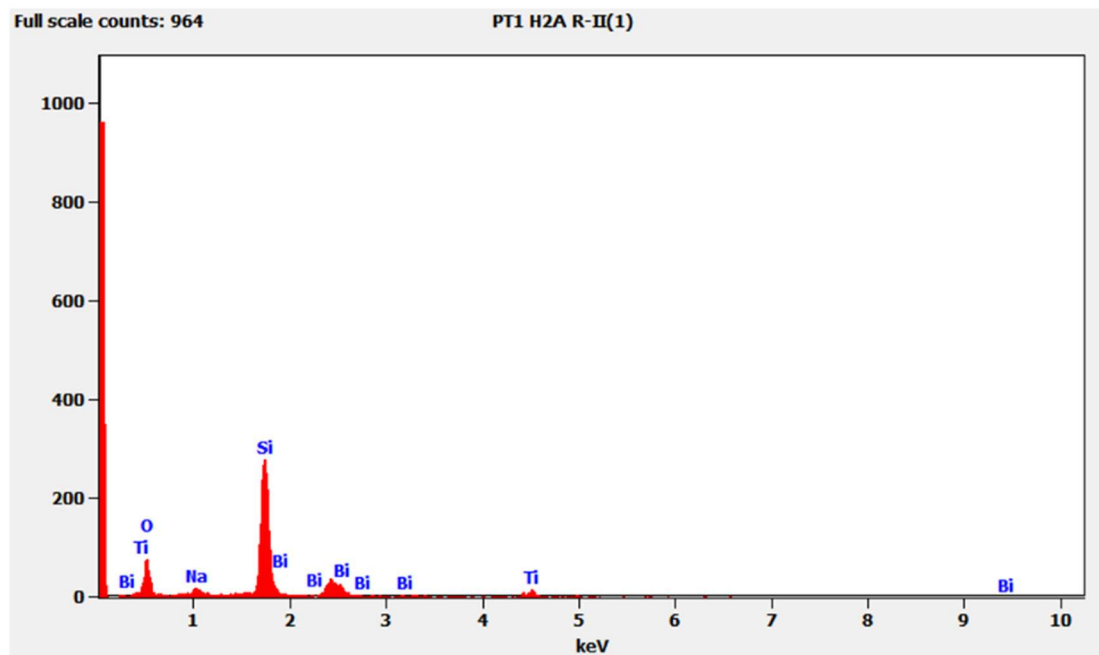
Quantitative Results for: PT2 H2 Racetrack-III(1)

Element Line	Weight %	Weight % Error	Atom %	Atom % Error
O K	27.9	± 0.6	65.5	± 2.8
Na K	5.4	± 0.3	8.8	± 0.9
Ti L	22.7	± 3.8	17.8	± 6.0
Bi M	44.0	± 1.2	7.9	± 0.4
Total	100.0		100.0	



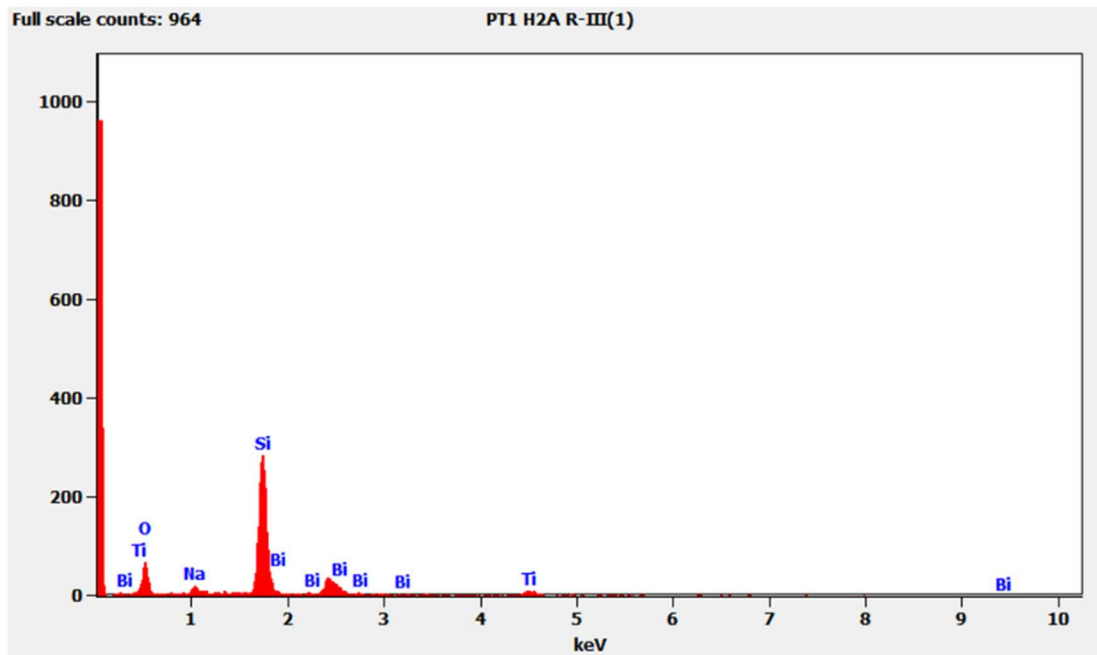
Quantitative Results for: PT1 H2A R-I(1)

Element Line	Weight %	Weight % Error	Atom %	Atom % Error
O K	32.5	± 1.2	78.3	± 5.7
Na K	4.6	± 0.8	7.7	± 2.7
Ti L	3.9	± 10.4	3.1	± 16.7
Bi M	59.0	± 3.9	10.9	± 1.4
Total	100.0		100.0	



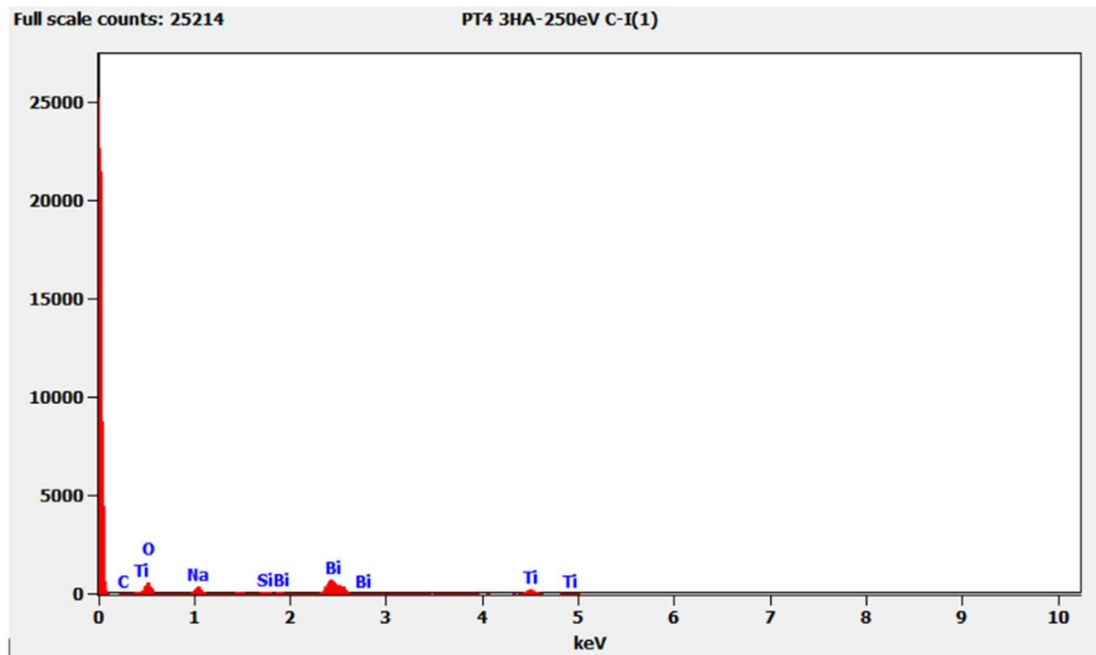
Quantitative Results for: PT1 H2A R-II(1)

Element Line	Weight %	Weight % Error	Atom %	Atom % Error
O K	30.8	± 1.2	74.7	± 5.6
Na K	4.3	± 0.8	7.3	± 2.6
Ti L	9.6	± 8.9	7.8	± 14.5
Bi M	55.3	± 4.7	10.3	± 1.7
Total	100.0		100.0	



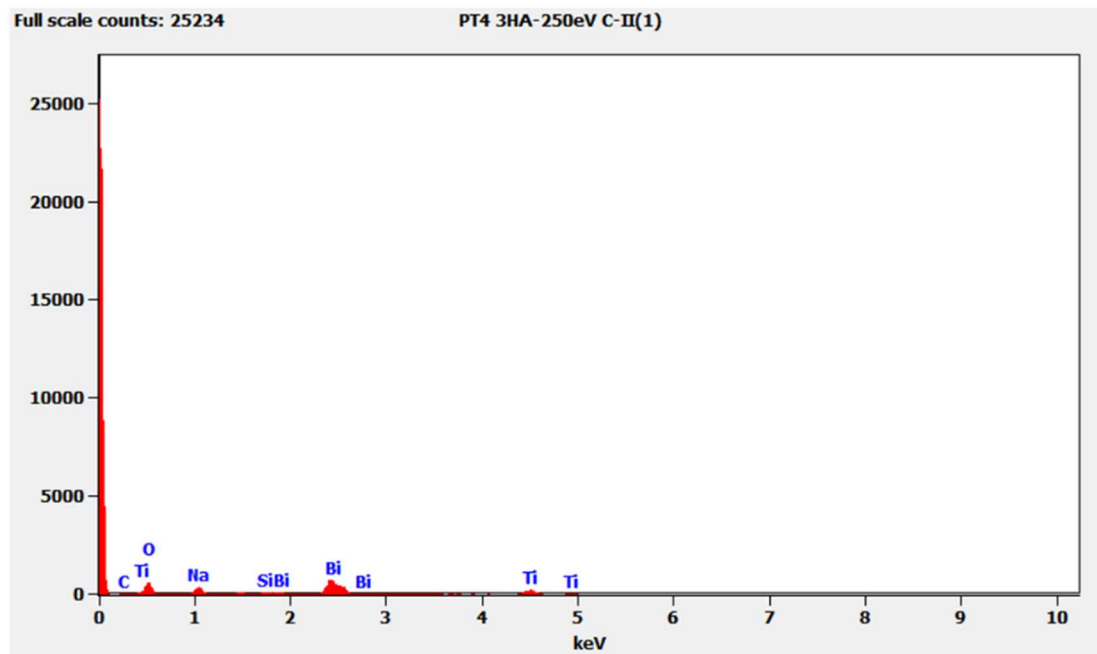
Quantitative Results for: PT1 H2A R-III(1)

Element Line	Weight %	Weight % Error	Atom %	Atom % Error
O K	31.2	± 1.2	78.2	± 6.0
Na K	5.6	± 0.9	9.8	± 3.1
Ti L	0.0	---	0.0	± 0.0
Bi M	63.1	± 4.3	12.1	± 1.6
Total	100.0		100.0	



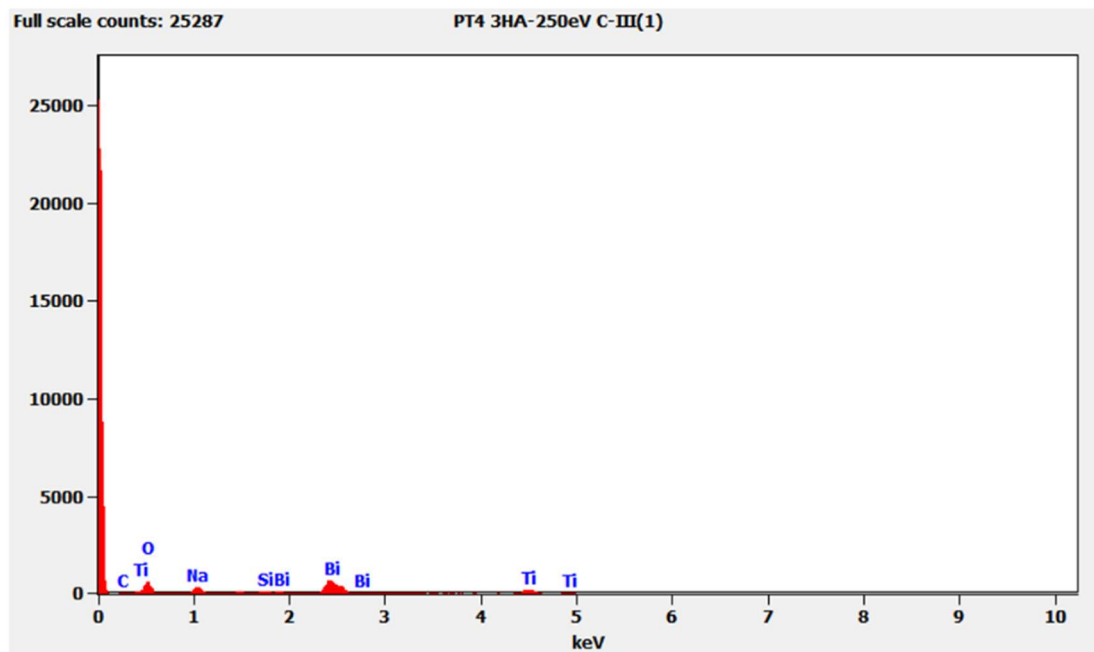
Quantitative Results for: PT4 3HA-250eV C-I(1)

<i>Element Line</i>	<i>Weight %</i>	<i>Weight % Error</i>	<i>Atom %</i>	<i>Atom % Error</i>
<i>O K</i>	17.1	± 0.3	53.6	± 1.9
<i>Na K</i>	4.8	± 0.1	10.5	± 0.6
<i>Ti K</i>	21.1	± 0.7	22.1	± 1.5
<i>Bi M</i>	57.1	± 1.0	13.8	± 0.5
<i>Total</i>	100.0		100.0	



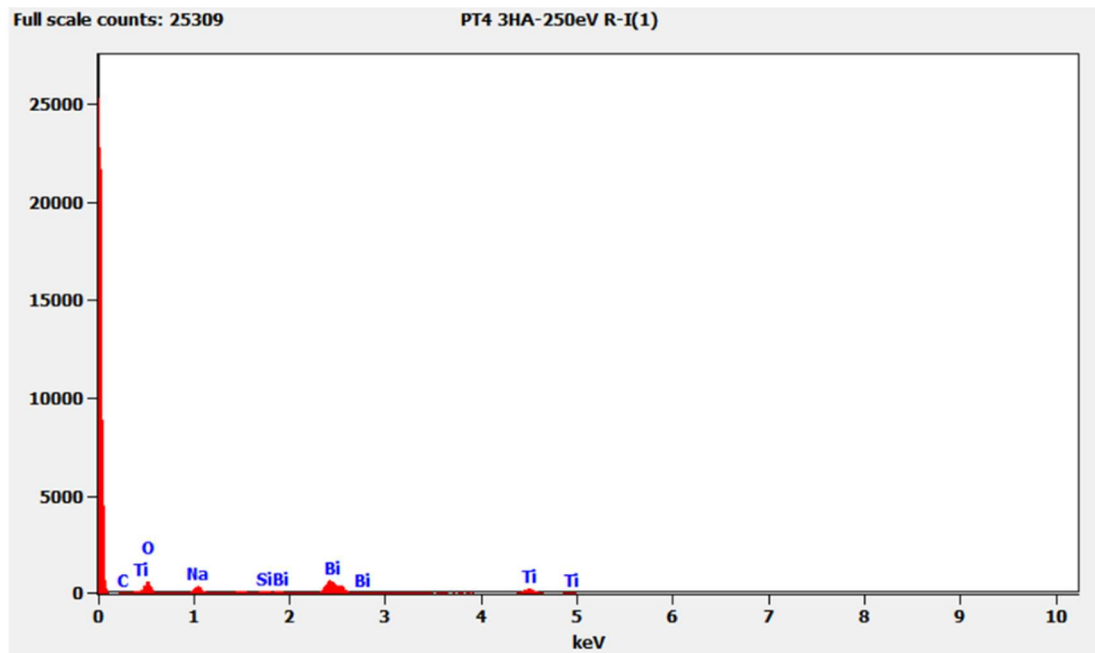
Quantitative Results for: PT4 3HA-250eV C-II(1)

Element Line	Weight %	Weight % Error	Atom %	Atom % Error
O K	17.0	± 0.2	53.6	± 1.5
Na K	4.7	± 0.1	10.2	± 0.6
Ti K	21.3	± 0.7	22.4	± 1.5
Bi M	57.1	± 1.0	13.8	± 0.5
Total	100.0		100.0	



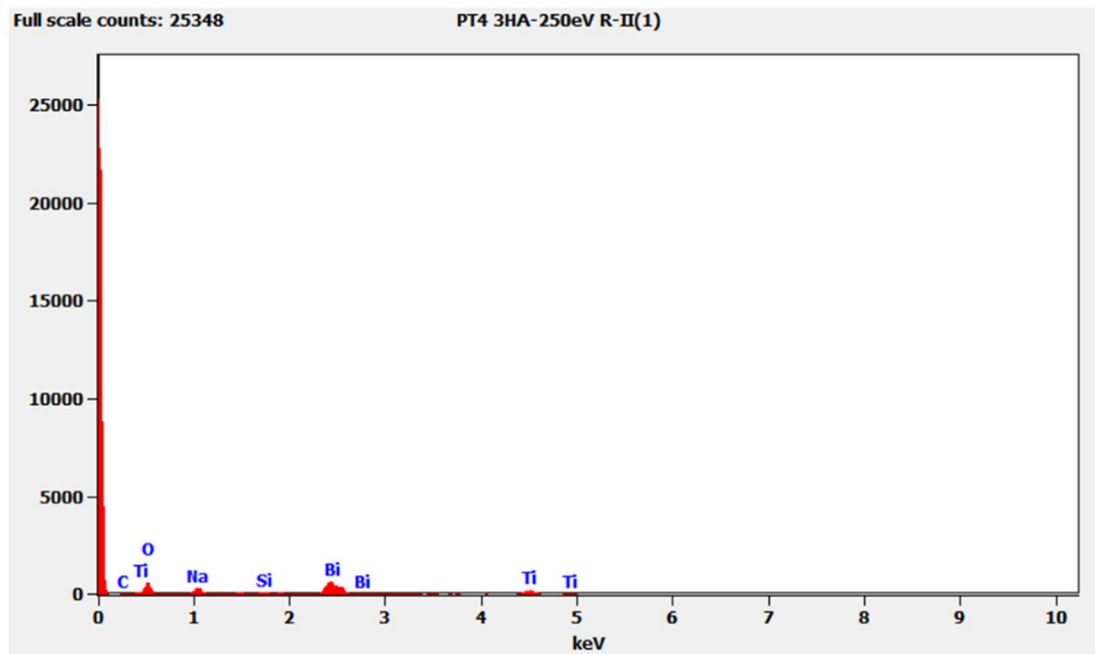
Quantitative Results for: PT4 3HA-250eV C-III(1)

Element Line	Weight %	Weight % Error	Atom %	Atom % Error
O K	17.9	± 0.3	54.5	± 1.9
Na K	4.9	± 0.1	10.4	± 0.6
Ti K	21.9	± 0.7	22.3	± 1.5
Bi M	55.3	± 1.0	12.9	± 0.5
Total	100.0		100.0	



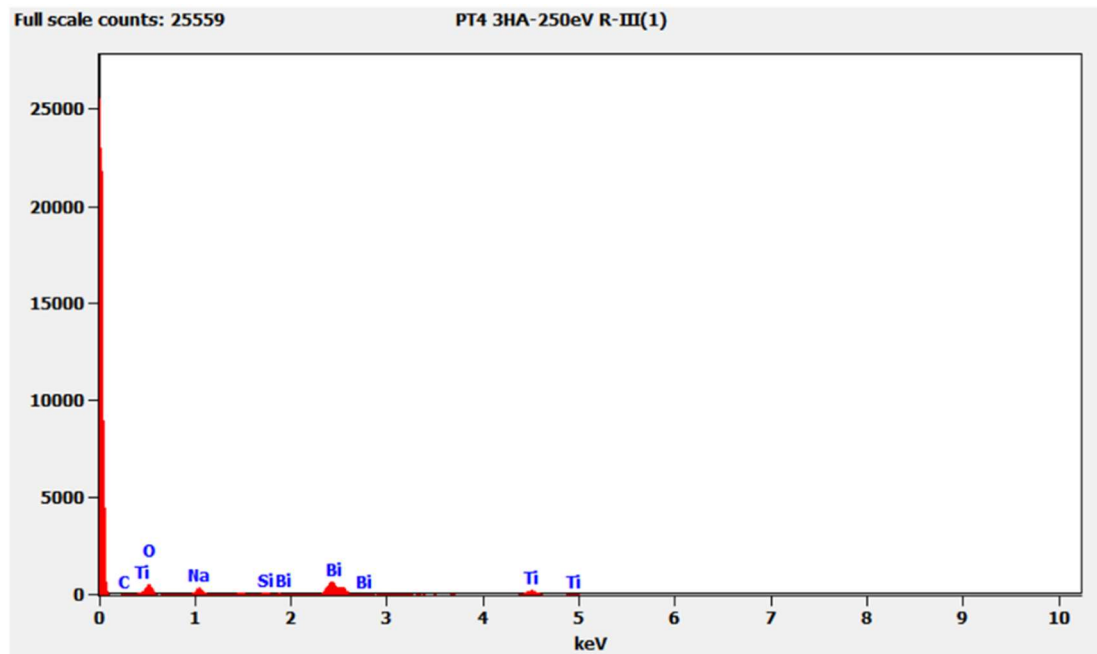
Quantitative Results for: PT4 3HA-250eV R-I(1)

Element Line	Weight %	Weight % Error	Atom %	Atom % Error
O K	17.4	± 0.3	52.7	± 1.9
Na K	4.9	± 0.1	10.5	± 0.6
Ti K	24.0	± 0.8	24.3	± 1.6
Bi M	53.7	± 1.0	12.5	± 0.5
Total	100.0		100.0	



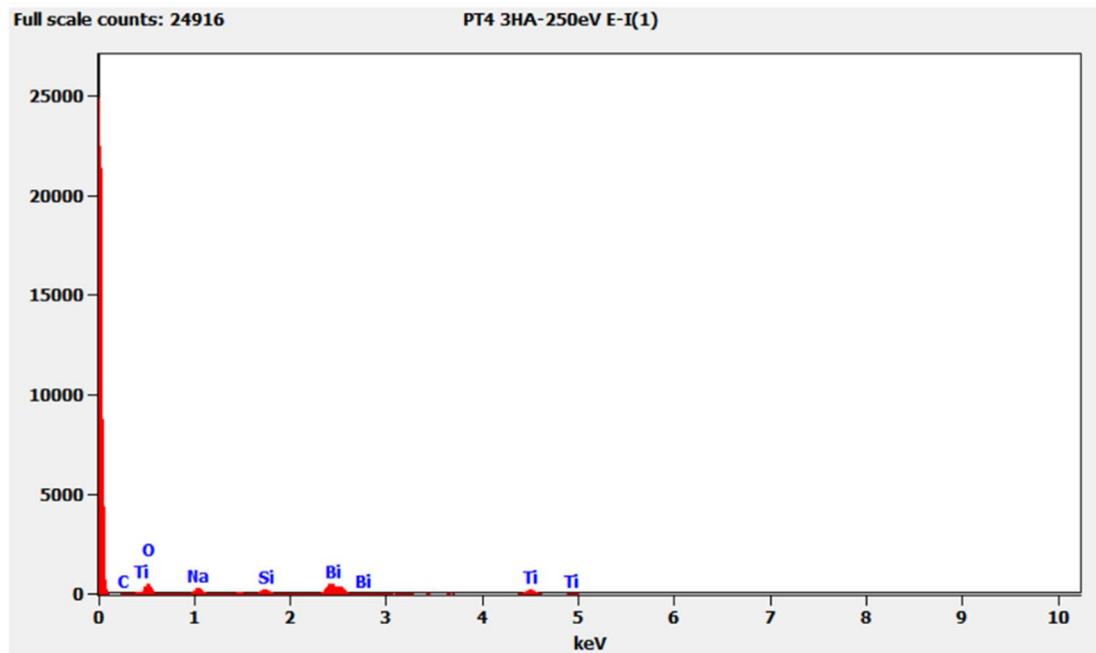
Quantitative Results for: PT4 3HA-250eV R-II(1)

Element Line	Weight %	Weight % Error	Atom %	Atom % Error
O K	17.1	± 0.2	52.5	± 1.5
Na K	5.0	± 0.1	10.8	± 0.6
Ti K	23.2	± 0.8	23.9	± 1.6
Bi M	54.6	± 1.0	12.8	± 0.5
Total	100.0		100.0	



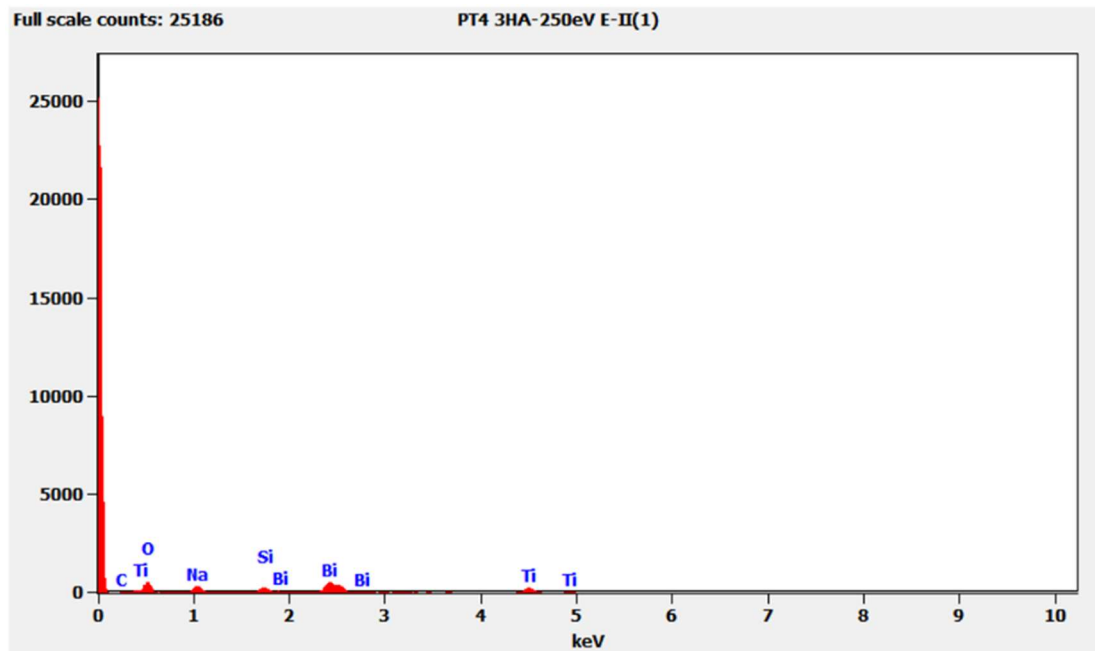
Quantitative Results for: PT4 3HA-250eV R-III(1)

Element Line	Weight %	Weight % Error	Atom %	Atom % Error
O K	17.3	± 0.3	52.9	± 2.0
Na K	4.7	± 0.1	10.1	± 0.4
Ti K	23.8	± 0.8	24.3	± 1.6
Bi M	54.1	± 1.0	12.7	± 0.5
Total	100.0		100.0	



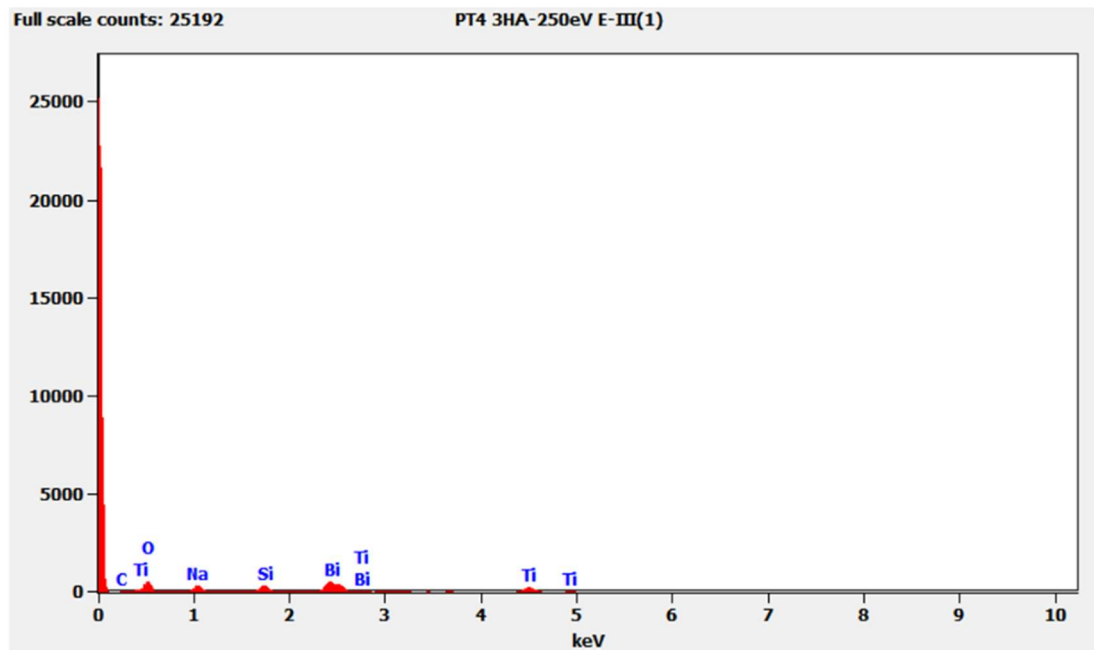
Quantitative Results for: PT4 3HA-250eV E-I(1)

Element Line	Weight %	Weight % Error	Atom %	Atom % Error
O K	18.9	± 0.4	54.7	± 2.1
Na K	5.3	± 0.2	10.7	± 0.6
Ti K	23.9	± 0.8	23.1	± 1.6
Bi M	51.9	± 1.1	11.5	± 0.5
Total	100.0		100.0	



Quantitative Results for: PT4 3HA-250eV E-II(1)

Element Line	Weight %	Weight % Error	Atom %	Atom % Error
O K	19.2	± 0.4	54.3	± 2.0
Na K	5.5	± 0.2	10.8	± 0.6
Ti K	25.7	± 0.8	24.3	± 1.6
Bi M	49.6	± 1.1	10.7	± 0.5
Total	100.0		100.0	



Quantitative Results for: PT4 3HA-250eV E-III(1)

Element Line	Weight %	Weight % Error	Atom %	Atom % Error
O K	19.5	± 0.4	54.6	± 2.0
Na K	5.4	± 0.2	10.6	± 0.6
Ti K	26.1	± 0.8	24.4	± 1.6
Bi M	49.0	± 1.1	10.5	± 0.5
Total	100.0		100.0	

Appendix C EDX Results Calibration By Hybrid ERDA-RBS

C.1 Calculations Report

The EDX-based elemental quantification of as-deposited films was mainly performed using the following lines: Ti La at 0.455, O Ka at 0.525, Na Ka at 1.041, and Bi Ma at 2.42. However, the Ti La signal dropped significantly after the annealing of films, potentially due to the change of its chemical state and the matrix effects. The EDX results demonstrated this outcome which can be witnessed for the two annealed films: PTII-H2A-R (BNT50.50, pp. 172–173) and PT1-H2A-R (BNT35.50, pp. 175–176). This renders the EDX results of those two films unreliable for the calibration through their hybrid ERDA-RBS analysis. Therefore, Ti Ka line at 4.508 keV was used for the quantification of titanium in other annealed films by EDX analysis (see pp. 176–180), while keeping everything else constant. Finally, the EDX results of two as-deposited (PTV-H2-R and PT2-H2-R) and three annealed (PT4-3HA-C, PT4-3HA-R and PT4-3HA-E) films were used; for the calibration purpose using their hybrid ERDA-RBS analysis. The entire calibration procedure is described stepwise as under:

- First, the mean value of three EDX at.% results ($x_1 \pm \sigma_1, x_2 \pm \sigma_2, x_3 \pm \sigma_3$) for each film was calculated (Eqs. C.1 and C.2).

$$\bar{x} = \frac{x_1 + x_2 + x_3}{3} \quad (C.1)$$

$$SD_{means} = \sqrt{\frac{(x_1 - \bar{x})^2 + (x_2 - \bar{x})^2 + (x_3 - \bar{x})^2}{n - 1}}, \quad n = 3$$

$$\sigma_{EDX} = \sqrt{\frac{\sigma_1^2 + \sigma_2^2 + \sigma_3^2}{3}}$$

$$\Delta x = \sqrt{SD_{means}^2 + \sigma_{EDX}^2} \quad (C.2)$$

- Second, the hybrid ERDA-RBS atomic percentages ($at\% \pm \sigma(at\%_i)$) of Bi, Ti, Na, and O were calculated by excluding the C and H for those five films (Eqs. C.3, C.4).

$$S = \sum_i F_i \quad \therefore i \in \{Bi, Ti, Na, O\}$$

$$at\%_i = 100 \cdot \frac{F_i}{S} \quad (C.3)$$

$$\frac{\partial p_i}{\partial F_i} = \frac{S - F_i}{S^2}, \frac{\partial p_i}{\partial F_k} = \frac{-F_i}{S^2} \quad (k \neq i) \quad \therefore p_i = \frac{F_i}{S}$$

$$\sigma(p_i) = \sqrt{\left(\frac{\partial p_i}{\partial F_i}\right)^2 \sigma^2(F_i) + \sum_{k \neq i} \left(\frac{\partial p_i}{\partial F_k}\right)^2 \sigma^2(F_k)}$$

$$\sigma(at\%_i) = 100 \cdot \sigma(p_i) \quad (C.4)$$

- Third, the calibration factors ($k \pm \sigma_k, l \pm \sigma_l, m \pm \sigma_m$) for each film were determined using the equations C.5–C.7.

$$\left(\frac{Bi \text{ at}\%}{Na \text{ at}\%}\right)_{Hybrid \text{ ERD-RBS}} = k \left(\frac{Bi \text{ at}\%}{Na \text{ at}\%}\right)_{EDX} \quad (C.5)$$

$$\left(\frac{Bi \text{ at}\%}{Ti \text{ at}\%}\right)_{Hybrid \text{ ERD-R}} = l \left(\frac{Bi \text{ at}\%}{Ti \text{ at}\%}\right)_{EDX} \quad (C.6)$$

$$\left(\frac{Na \text{ at}\%}{Ti \text{ at}\%}\right)_{Hybrid \text{ ERD-RBS}} = m \left(\frac{Na \text{ at}\%}{Ti \text{ at}\%}\right)_{EDX} \quad (C.7)$$

$$\left(\frac{A}{D}\right)_{Hybrid \text{ ERDA-RBS}} = Q \cdot \left(\frac{C}{B}\right)_{EDX} \quad \therefore Q \in \{k, l, m\}$$

$$Q = \frac{A \cdot B}{C \cdot D}$$

$$\left(\frac{\sigma_Q}{Q}\right)^2 = \left(\frac{\sigma_A}{A}\right)^2 + \left(\frac{\sigma_B}{B}\right)^2 + \left(\frac{\sigma_C}{C}\right)^2 + \left(\frac{\sigma_D}{D}\right)^2$$

$$\sigma_Q = Q \cdot \sqrt{\left(\frac{\sigma_A}{A}\right)^2 + \left(\frac{\sigma_B}{B}\right)^2 + \left(\frac{\sigma_C}{C}\right)^2 + \left(\frac{\sigma_D}{D}\right)^2}$$

- Finally, the average calibration factors and their error margins ($k = 1.2 \pm 0.4$, $l = 1.1 \pm 0.4$, and $m = 0.9 \pm 0.2$) were calculated using the individual calibration factors (and their error margins) of all the five films, according to the equations C.1 and C.2.

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Résumé

Ce travail est consacré à la synthèse et à la caractérisation de couches minces ferroélectriques et piézoélectriques de $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT). Les films ont été déposés sur des substrats de silicium (Si) à l'aide de cibles élaborées à partir de poudres synthétisées au laboratoire, par pulvérisation cathodique magnétron radiofréquence (RF) dans une décharge d'argon (Ar). L'analyse de la surface des cibles, les diagnostics plasma et la caractérisation des films ont été réalisés, conjointement à la modélisation des processus de pulvérisation et du transport en phase gazeuse, afin de comprendre les corrélations entre la chimie cible-plasma-film. Afin d'optimiser la composition des couches minces de BNT, l'influence de paramètres tels que la composition des cibles, la densité de puissance de pulvérisation et la distance cible-substrat a été étudiée, notamment pour surmonter des difficultés telles que le dépôt excessif de bismuth (Bi) durant la croissance des films et la perte de sodium (Na) induite par sublimation lors des traitements thermiques. Ces investigations ont conduit à l'élaboration d'un protocole de dépôt permettant l'obtention de films de BNT stœchiométriques et hautement cristallisés, déposés sur des substrats non chauffés. Dans le but d'identifier les mécanismes à l'origine de la formation de défauts de surface de type NaO_x sur les films de BNT, l'effet de la composition des cibles sur la fraction ionisée du flux de dépôt a été examiné. Un processus de sublimation des atomes de sodium a été mis en évidence à la surface de la cible, se produisant simultanément à la pulvérisation cathodique, et susceptible d'être à l'origine de la formation des défauts de surface NaO_x observés sur les films de BNT.

Abstract

This work is dedicated to the synthesis and characterization of ferroelectric piezoelectric $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT) thin films. The films were deposited on Si substrates using homemade powder targets by RF magnetron sputtering in an Ar discharge. The target surface analysis, plasma diagnostics, and film characterization were performed, alongside modelling of sputtering and gas-phase transport processes, to understand the correlation between the target-plasma-film chemistry. To optimize the composition of BNT films, the influence of parameters like the target composition, sputtering power density, and target–substrate distance were investigated for addressing the challenges such as excess deposition of Bi during film growth and sublimation-driven Na loss during the annealing of films. This lead to the realization of deposition protocol for stoichiometric and highly crystallized BNT films, grown on unheated substrates. To study the root-causes of NaO_x surface defects formation on BNT films, the effects of target composition on the ionized part of deposition flux was investigated. A sublimation process for Na atoms was identified, concurrently occurring on the target surface alongside the sputtering, which is likely linked to the growth of NaO_x surface defects on BNT films.