

# Supplementary Materials: Preparation and Characterization of $Nb_xO_y$ Thin Films: A Review

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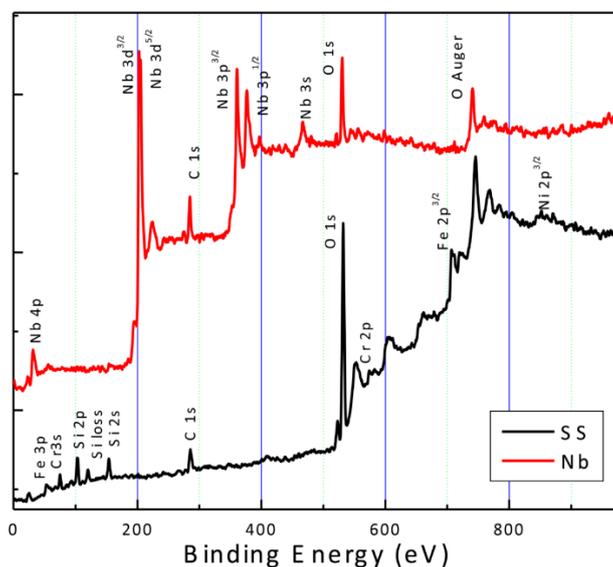
## 1. Biocompatibility

Biomaterials are an essential factor in the production of biomedical components and implants. The biomaterial surface makes contact first with the living tissue once the material is inserted within the body. Consequently, the initial response from the living tissue given to the biomaterial relies on the surface properties. At present, it is unusual that biomaterials with strong bulk features also have surface qualities appropriate for certain clinical applications [1]. For this reason, the production of surface enhancement methods for biomaterials has been in rapid expansion over the last few years. With this, suitable biomaterials with surface characteristics decoupled from the bulk properties can be generated. For example, an ideal surface, physical properties, as well as chemical properties may be achieved by modification of the surface functionality through the deposition of a thin film. The aspect of corrosion resistance remains one of the most significant surface features for orthopaedic or dental implants that can be modified. The resistance to corrosion of metallic materials determines the durability of the device. This is very critical due to the harmfulness of corrosive products [2].

René et al. [1] in one of his works, carried out a study on the Biocompatibility of Niobium Oxide Coatings. He stated that niobium oxide coatings prepared via the magnetron sputtering process were analysed to be a feasible surface improvement for substrates of stainless steel (SS) in biomedical implants. The Niobium coatings which were prepared on a stainless-steel substrate diameter of 15 mm possessed a surface roughness averaging 2  $\mu\text{m}$ . The authors reported that three distinct in vitro tests consisting of cellular adhesion, proliferation and viability were performed with the use of human alveolar bone derived cells to ascertain the coatings biocompatibility. The substrates of stainless steel together with tissue culture plastic were studied as well, and this was with the intention of giving a comparative information. René and Co. however reported that there was zero toxic response recorded on the surfaces, which thus indicated the Nb coatings operation as a biocompatible, bioinert material. They also studied the cell morphology through the use of immune fluorescence, with the outcome confirming the cells' healthy state on the Nb surface. René et al. identified that the XRD coating characterization revealed the film to be of polycrystalline form, with a cubic structured body centre. They reported that the binding energy of the Nb peaks (Figure 1), corresponded to metallic Nb and not any  $NbO_x$  phases. They also conducted a water contact angled measurement test which disclosed the surface of the Nb to more hydrophobic than that of the SS substrate [1].

In another study, Yuncang Li, et al. [3] in one of his works performed a study on Titanium-niobium pentoxide composites for biomedical applications. They reported the strength of the titanium scaffolds to have significantly decreased after the introduction of high porosity. This drastic decrease may result in incapability of load tolerance in biomedical applications. However, to concurrently meet the demands for biocompatibility, reduced elastic modulus, and required potency for orthopaedic implant materials, it was greatly desiring to develop fresh biocompatible titanium-based materials with improved strength. Hence, they opted to this study which developed a  $Nb_2O_5$  strengthened composite of titanium through powder metallurgy for use in biomedical applications. The authors moreover discovered the strength of the bolstered  $Nb_2O_5$  titanium composites ( $Ti-Nb_2O_5$ ) to be remarkably larger than that of only titanium, with results from the cell culture illustrating the

Ti-Nb<sub>2</sub>O<sub>5</sub> composite, showcasing exceptional biocompatibility alongside cell adhesion. Yuncang Li, et al. also, uncovered humanlike osteoblast cells growing and dispersing healthily across the surface of the Ti-Nb<sub>2</sub>O<sub>5</sub> composite, thus demonstrating the Nb<sub>2</sub>O<sub>5</sub> reinforced titanium composite to be a favourable implant material because of its outstanding biocompatibility and increased mechanical strength.



**Figure S1.** XPS spectra showing the empty substrate together with the Niobium-coated steel. The binding energy of the Niobium peaks was visible at: Nb 3d<sup>3/2</sup> (202 eV), Nb 3d<sup>5/2</sup> (205 eV), Nb 3p<sup>3/2</sup> (360.6 eV) and Nb 3p<sup>1/2</sup> (376.5 eV) [1].

## 2. Deposition Methods

### 2.1. Sol Gel

In recent times, the sol-gel method of film deposition has become a favourable process for synthesizing materials in the form of nanoscale powders, coatings, as well as porous systems. This procedure is predominantly applied at the laboratory scale and has thus involved with the production of various novel nanomaterials. The sol-gel technique, which is a low temperature process has been broadly studied in different fields of technical and engineering applications to produce metal oxide nanostructures. This is presumably as a result of the precision of the products obtained from the process [4]. Since after Ebelman synthesized silica gel in 1846, this method has continually been improved and the materials synthesized from this process have been utilized in numerous applications possessing good magnetic, optical, thermal, mechanical, and electrical properties. Many different forms of materials can be obtained in a commercial way through the application of the sol-gel technique, such as, nanoparticles, ceramics, thin films and glass. Remarkable achievement was attained in high-level fine-grain ceramics with good piezoelectric, dielectric, ferroelectric, electro-optical or optical properties. This achievement was as a result of the ability to fabricate the superior ultrafine ceramic powders.

Sol-gel coating technique is a process in which small molecules are used to produce solid materials. This approach is utilized for manufacturing metal oxides of various kinds. The method consists of the translation of monomers to colloidal solutions (sol) which serves as the precursor for a combined system (gel) of distinct particles. It comprises of the precursor being dissolved in the required amount of solvent and stirred for hours. After which, solvent evaporation is carried out in a muffle furnace. The dried thin film obtained are then calcined at high temperatures depending on the application of the film. The as-deposited films possess amorphous structure and only show crystallinity at extreme temperatures. The sol-gel approach makes use of various kinds of precursors

provided a solvent is readily accessible for their dissolution. During the sol-gel procedure, the sol can be obtained either through hydrolysis or through polymerization reactions by introducing suitable reagents in the solution of the precursor. The precursor sol is then deposited either on a substrate to create a film by either of dip coating or spin coating procedure, after which it is put in a container of the needed shape or, it is used for the synthesis of powders [4]. The gelation procedure performed by the sol condensation or through the inclusion of polymers transforms the sol into a gel. The gel could then be employed for the production of materials of assorted types which include, xerogel, nanoparticles, ceramics or glass depending on the additional production procedures included. Vaporization of the solvent brings about the production of nanoparticles and xerogels, and the achieved xerogel produced as ceramics via heat treatment. Hence, this sol-gel technique could be used to achieve materials of different kinds, with a controlled shape, phase, and size of the obtained materials.

### 2.2. Chemical Spray Pyrolysis

The chemical spray pyrolysis method of film production is an economical deposition process, which requires no vacuum for the synthesis of materials into powder or film forms. For films, they tend to be deposited over a wide range of substrates easily adaptable to large area depositions and industrial manufacturing processes [5]. This is a process whereby a nanostructure is derived when the precursor already dissolved in a solution of the solvent is either sprayed or injected at ambient atmosphere, into extremely fine droplets of 1–2  $\mu\text{m}$  by making use of high air pressure stream with the aid of a nanoporous nebulizer on the heated substrate in the furnace. This thus, brings about pyrolysis/decomposing of the precursor for the formation of the desired end product on the substrate. The film and substrate are afterwards subjected to heat treatment at high temperatures. The films are of amorphous structure when deposited but change to a twisted hexagonal crystal phase after heating to temperatures above 500 °C. Before this deposition process, the substrates have already been exposed to conventional cleaning and degreasing procedures. The nanostructured parameters which include the particle size, shape, and thickness, can be controlled with the regulation of the spray pressure, the size of the precursors' droplet, the spray duration, the distance of the substrate from the spray gun, in addition to the furnace and substrate temperatures with the use of either manual or automated control systems. Also, Porous films with a moderate to very high temperature quality may be obtained by changing the deposition parameters [5]. Contrary to other deposition methods, the spray pyrolysis process possesses various unique benefits. For example, its film microstructure (compact or porous) can be altered based on the condition of spray, repeatability, adhesive depositions and its easy doping nature. However, this method is a commercial one that prohibits utilization of top-quality reagents and compositions due to its basic equipment and experimental set up. The spray pyrolysis approach has been implemented for depositing a vast range of niobium oxide thin films which have applications in many areas.

### 2.3. Sputtering

The method of sputtering is a physical vapour deposition (PVD) vacuum method which is used for the deposition of extremely thin films on a substrate for a broad range of industrial and scientific purposes. Sputter deposition thus far presents itself as the favourable deposition method for thin film applications in which stoichiometry, purity, and density are crucial to the performance of the film, particularly for metals. The method includes the ejection of a material from a target source onto a "substrate" for instance, a silicon wafer. During the sputter deposition process, the cathode surface (the target) is the source of the material which forms the film. The material then travels via low-pressure gaseous environment, prior to its condensation on a substrate for the formation of a film. In other words, the sputtering process occurs when an ionized molecule of a gas is used for the displacement of atoms of a target material. The displaced atoms subsequently condense on the substrate at an atomic level, thus creating a thin film [6]. This deposited thin film is then annealed at extreme temperatures based on its application. The as-deposited film of the sputtering deposition process is usually of amorphous nature and barely evolve to crystalline structure at high

temperatures. Often than not, the gas which is utilized for sputtering is an inert argon gas. However, for more effective momentum transport, there should be a close relation between the atomic weight possessed by the sputtering gas and the atomic weight of that of the target. Thus, neon favours sputtering of weightless elements, whereas krypton or xenon can be applied for weighty elements [7]. A significant advantage of the sputter deposition process over the evaporation deposition technique is that materials, which have excessive melting points can simply be sputtered, in contrast, there is a doubt of these same materials vaporizing inside the resistance evaporator. Also, sputtered films generally possess a superior adhesion on the substrate in contrast to evaporated films. Furthermore, sputtering sources which are well suited with reactive gases like oxygen, have no hot spots since they quickly cooled down again to prevent overheating. However, the various parameters which are in control of the sputter deposition process, contributes in making it a complex one, nevertheless, this gives experts a large amount of control over the growth, and microstructure of the film as well. Among the earliest worldwide commercial utilizations of sputtering which yet exist as one of the major key application areas is in the manufacture of hard disks for computer.

#### 2.4. Pulsed Laser Deposition (PLD)

The PLD process is also a PVD process whereby a laser carrying high-power pulse as well as a small frequency bandwidth, is applied at the source for melting, evaporating and ionizing the required material from the target surface. This disintegrating process creates a temporary, extremely luminous beam of radiation that quickly extends from the target surface [8]. The disintegrated material then deposits on a suitably positioned substrate where it condenses, followed by the subsequent growth occurrence of the thin film. To prevent disturbance from ambient atmosphere, the target material together with the substrate are kept in a vacuum chamber, with the directed pulsed laser beam entering the chamber through a fitting opening. The morphology of the niobium oxide thin film in a PLD process is of amorphous structure and remain amorphous even at higher temperatures [9]. This method of PLD has been employed for fabricating high-quality films of metals, oxides, polymers, biocompatible materials for over ten years, and it is particularly used when the other deposition methods have been challenging [10]. Contrary to the thermal process of evaporation that generates a vapour composition based on the vapour pressure of the elements within the target material, the laser-induced emission creates a material plume that possesses a stoichiometry comparable to the one of the targets. The required stoichiometry of the film for multi-element materials is relatively simpler to achieve with the use of PLD than with the use of other deposition processes [11]. The flexibility of the PLD process is that there are virtually no limitations to the target material that can be used. Since the initial study on high  $T_c$  superconductors, the PLD approach has been steadily implemented in a vast variety of materials. It is currently used for the growth of ultra-thin epitaxial amorphous, polycrystalline, and single-crystalline films, heterostructures, superlattices, and also sharp interfaces which include materials with quite complex stoichiometry [12]. PLD which is a straightforward application process is commonly applied in research laboratories, moreover, PLD's niobium oxide thin films is encouraging for many industrial applications.

#### 2.5. Biased Target Ion Beam Deposition (BTIBD)

The reactive BTIBD method was established as an improvement for the traditional IBD, with the main advantage of being able to use a low energy ion source which generates inert gas ions of excessively high-density that possess extremely low energy. These low-energy inert ions prevent the issue of spillage pollution previously encountered in the IBD process due to sputtering occur only on the biased target. This low energy sputtering causes a reduced kinetic energy possessed by the sputtered species from the target, and this is favourable for obtaining interfacial smoothness together with the decrease of diffusion mixing of interlayers. The energy dispensation of atoms sputtered from a target relies on the mass and energy of the sputtering ion, target material, and geometry of the system. The process has the concept of an ion source of low energy being focussed on a sputtering target with negative bias. At low-energy molecular ion beams are intact after deposition, while

fragments of molecular ions and atomic ions reach deeper into the material at high deposition energy, a process identified as ion implantation [13]. The maximum energy possessed by the ions is less than the sputter limit of the vacuum system materials, hence, solely the ions which make it to the target gain enough energy to produce the sputtering effect. No attempt has been made to secure the entire ions at the target, since ions which overshoot the target do not result in undesirable sputtering. Practically, the ion beam could be significantly wider than the target so as to optimize uniformity of illumination to enhance the production of the film. Moreover, the application of a broad ion beam enhances the efficiency of the target material utilization as well as the conformity of deposition thickness. The manufactured films via the BTIBD process are observed to majorly consist of tetragonal phase at both high and low temperatures. The BTIBD process is appropriately fitting for applications which require atomically engineered thin films as well as interfaces since it provides a wide variety of adatom energy, control, process pressures, and superior uniformity and repeatability [13].

#### 2.6. Electron Beam Evaporation (E-beam)

The E-beam evaporation method is a PVD process, which at relatively low substrate temperatures produces a high rate of deposition between 0.1  $\mu\text{m}/\text{min}$  and 100  $\mu\text{m}/\text{min}$ . The evaporation process occurs in a vacuum, typically at a pressure of  $10^{-5}$  torr. A current of 5 to 10 kV is passed via a tungsten filament which heats it up to the moment where thermionic emission of the electrons occurs. It is believed that whenever electron beams possess energies of 5–10 kV, there is the certainty of thermionic emission taking place. The electron beam's electric density is huge, and it is capable of evaporating different materials, inclusive of metals of high melting points, in conjunction with compounds of oxides, and sublimating substances [14]. Production of the E-beam could result from electron guns using thermionic emission, field electron emission or alternatively, the anodic arc process [15]. The E-beam evaporation which accelerates at a high kinetic energy, makes use of a directed electron beam for heating and evaporation of metals. Evaporation takes place on the target surface at a position close to the area of beam concentration. Hence there is little or no occurrence of contamination from the crucible. When the heated electrons reach the source material, they very easily lose their energy [16]. The kinetic energy of the electrons is changed to thermal energy which increases the materials' surface temperature, thus resulting in vaporization and subsequent deposition on the substrate. The resultant deposition can afterwards be used for coating surfaces. The rate of deposition is dependent on the start material along with the power of the E-beam and the thickness of the deposited film can originally be measured using a quartz crystal monitor. Notwithstanding temperature, the as-prepared film of the E-beam deposition process comprise of amorphous structure. The E-beam method presents comprehensive advantages towards the control of the film structure along with its morphology, having desirable qualities like; dense coating, low contamination, high thermal performance, high productivity, and high reliability. Hence, it possesses possible industrial applications such as, in the aerospace industries for wear-resistance together with thermal barrier coatings, within the cutting and tool industries it is used for hard coatings, and in the semiconductor industries it is used for electronic and optical films as well as for thin-film solar applications.

#### 2.7. Electrochemical Deposition Process (ECD)

This is a synthesizing procedure whereby a film of solid metal can be prepared through a solution of ions (electrolyte) on an electrical conducting surface called an electrode [17] in an electrochemical cell [18]. The process of electrochemical deposition is basically utilized for depositing, or plating, a material on another. Hence, the reason why it is sometimes also referred to as electroplating. The electrochemical deposition process functions based on certain basic electrochemical characteristics [19]. Anode and cathode electrodes are submerged in an electrolytic solution already consisting of liquefied metal salts, in addition to some other ions that allow sufficient current flow. The flow of electricity through the electrolytic solution, results in oxidation of the metal ions at the anode causing their dissolution in the solution [20], while the melted metal ions contained

in the electrolytic solution are being reduced at the cathode at the boundary between the solution and cathode in a way that coating is performed on the cathode. The rate at which the anode dissolves is directly proportional to the deposition rate on the cathode, given that the ions of the electrolyte solution are being continually restored by the anode [21]. Good material selection for the electrode and electrolyte for this process cannot be over emphasized, as a wrong material selection will result in unwanted or no deposition at all. Moreover, emphasis on the right polarities must be ensured for the required reaction to occur to form the film [19]. The thin film derived via this Electrochemical process is analysed to be of amorphous structure irrespective of the temperature applied.

The Electrochemical Deposition process is also employed in the electrical oxidation of anions over a solid substrate just like when preparing silver chloride on silver wire for the production of electrodes of silver/silver-chloride [22]. Electroplating can mainly be used for altering the surface features of an object, for example, abrasion and wear resistance, lubricity, protection from corrosion etc., however, it may further be utilized for increasing the thickness of small parts or for the formation of objects by the process of electroforming. Comparison of different deposition parameters with the use of the electrochemical process have been carried out, this was in order to fabricate films of uniform thickness as well as to lower the expenses of the electrochemical process [23]. The electrochemical deposition technique is also among the most functional methods for producing nanostructured electrocatalysts. By the adoption of this approach, electrocatalyst sizes, shapes, and structures could be put under control at the surface of the conductive materials through the alteration of the electrochemical conditions of deposition. The process further possesses some efficiencies such as, being economical, possessing a better interfacial bonding between coating material and substrate, and the absence of a capping reagent or a surfactant, or any other dispersing agent included during the electrodeposition method.

### 2.8. Chemical Vapour Deposition Process (CVD)

The process of CVD is a gas phase vacuum deposition technology which makes use of thermally induced chemical reactions for the deposition of thin films on hot substrate surfaces with the use of precursors. If need be, the temperature of the reaction could be lower with the use of the plasma-enhanced CVD (PECVD) [24]. This CVD process is frequently applied in the semiconductor industry for manufacturing solid materials of high quality and high-performance. CVD is generally used for depositing conformal films and enhance substrate surfaces in methods that even better traditional surface modification processes are not able to achieve [25]. The traditional CVD process comprises of a combination of gaseous reactant precursors transported simultaneously to a reactor chamber. The reactant precursors consequently undergo reaction with the heated substrate material resulting in thin solid films on the surface of the substrate. This, however, is in contrast to the ALD process which allows the alternating exposure of precursors for reactions to occur with the substrate material for the achievement of universally acceptable deposition rates. Initially, most of the precursors are usually solids or liquids under normal conditions before being vaporized by a bubbler for use in CVD. By the variation of experimental conditions, which include substrate material, temperature of substrate, composition of the reaction gas mixture, the total pressure of the gas flow, etc., films having a broad variety of tribological, chemical, as well as physical properties could be developed [26]. The deposited film's structure can be of monocrystalline, polycrystalline, or amorphous forms. The lattice structure is based mainly on the reaction rate, the substrate, as well as the process temperature. Thanks to the flexibility, the speed of deposition, and the excellent step coverage of the CVD process, as all these qualities have made the process a very famous one throughout the years. A significant characteristic of the CVD approach is its outstanding throwing power which allows the manufacturing of coatings that possess uniform thickness and low porosity features on even complex shapes of substrates. An additional essential quality is its ability to perform selective deposition on patterned substrates. This works by selecting species of precursors that reacts best with the particular surfaces. CVD is utilized in various applications of thin film. It also has applications in the development of materials of high temperature viz, tungsten, ceramics, etc. It is also used in the manufacture of high-temperature composites of fibre, solar cells, as well as particles of accurate

dimensions. High Tc superconductors, and carbon nanotubes have recently been also produced via this method.

### 2.9. Atomic Layer Deposition (ALD)

ALD is an advanced CVD process that permits the deposition of ultra-thin films of some nanometres onto a substrate in an entirely controlled manner. ALD does just allow excellent thickness control and uniformity but it also enables the conformal coating of 3D structures for high-aspect-ratio structures [27]. Most ALD reactions make use of two chemicals, designated as precursors or reactants. Thus, the ALD technique comprises of a substrate surface being subjected to alternating precursors, which are not introduced simultaneously but rather infused successively with an inert purge gas sequence in between the precursors' doses. The purging sequence is compulsory so as to avoid coalescence and unwanted gas phase reactions, and also, for the removal of residual precursors and by-products from the reactor chamber. Nevertheless, the alternate introduction of the precursors results in self-limiting surface reactions, which specifies that there is only an end to the reaction when the entire substrate reactive sites have been exhausted. The reactants' sequential, self-limiting surface reactions permits growth control of the required thin film. The total quantity of material which is deposited on the substrate surface following one complete ALD cycle, can be defined by the kind of reaction between the precursor and substrate surface. The ALD cycle generally constitutes a cycle of four steps, performed based on the number of times required, in order to attain the needed deposition film thickness. These four steps are dependent on time measured in seconds via the ensuing procedures [28];

- exposing the first precursor to the substrate surface inside the reactor chamber for  $t_{1s}$  to create a monolayer upon the substrate.
- Purging the reactor of surplus and undesirable products (excess precursor reactants and reaction by-products) for  $t_{2s}$  with the use of an inert purge gas in order to produce a high-performance niobium oxide thin film.
- Introducing the second precursor into the reactor chamber for  $t_{3s}$ , to react with the absorbed species on the reaction site in order to deposit the expected thin film following the self-limiting surface reaction between the already formed reaction site and the second reactant species; and
- A second purging of the reactor to get rid of the excess unreacted precursor and reaction by-products for  $t_{4s}$ , while still making use of the inert purge gas.

The thin film thickness and film uniformity can be perfectly controlled accurately by a number of cycles. The exceptional self-limiting growth technique even on complex 3D structures which brings about excellent conformality in conjunction with thickness uniformity of the film contributes in making ALD a unique deposition process. The film level and interface control along with the high standard of the ALD fabricated film are desirable for various applications. The thin film produced are of amorphous phase and become polycrystalline at temperatures higher than 300 °C.

ALD is a technology, which enables the development of novel and better products. ALD offers coatings and material properties that are either cost-effective with existing methods or impossible to achieve at all [29]. Thanks to the ALD's ability to develop superior conformal, uniform thin films at the atomic level at low temperatures, as this is one of the advantages that makes it very attractive over other methods of deposition. These benefits have also resulted in a major progress of the system in diverse applications in present-day technology. The method unlike other techniques typically produces pinhole-free films, which are of benefits to a broad range of applications. The potential seen in ALD with regards to the miniaturization of microelectronic devices according to Moore's law, is a key driving factor for the current attention it is getting worldwide [30].

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